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Selected problems of materials science

Vol. 2

Nano-dielectrics metals in electronics. Metamaterials. Multiferroics. Nano-magnetics

Textbook

*Recommended by the Methodological Council
of the Igor Sikorsky Kyiv Polytechnic Institute
as a study aid for master’s applicants
on the specialty 105 “Applied Physics and Nanomaterials”*

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The textbook examines physical foundations and practical application of current electronics materials. Modern theories are presented, more important experimental data and specifications of basic materials necessary for practical application are given. Contemporary research in the field of microelectronics and nanophysics is taken into account, while special attention is paid to the influence of the internal structure on the physical properties of materials and the prospects for their use. English-language lectures and other classes on the subject of the book are held at Igor Sikorsky Kyiv Polytechnic Institute at the departments of “Applied Physics” and “Microelectronics” on the subject of materials science, which is necessary for students of higher educational institutions when performing scientific works.

For master’s degree applicants in specialty 105 “Applied physics and nanomaterials”.

Розглянуто фізичні основи та практичне застосування актуальних матеріалів електроніки. Подано сучасні теорії, наведено найважливіші експериментальні дані та специфікації основних матеріалів, які потрібні для практичного застосування. Враховано сучасні дослідження у галузі мікроелектроніки та нанофізики, при цьому особливу увагу приділено впливу внутрішньої структури на фізичні властивості матеріалів і на перспективи їх використання. Англомовні лекції та інші види занять за тематикою книги проводяться в КПІ ім. Ігоря Сікорського на кафедрах «Прикладна фізика» та «Мікро-електроніка» за напрямом матеріалознавство, що необхідно студентам вищих навчальних закладів при виконанні наукових робіт.

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Preface

The need to work with scientific and technical English-language literature imposes new requirements on students of Technical university: to study special courses in English. This is important already at the first level of bachelor's training, but it especially applies to the second and third levels - master's students and postgraduate students. However, at present, only a part of students are able to actively use technical English, and, therefore, the textbooks written in English are relevant. The importance of this tutorial publication is due to the fact that Materials Science is a very demanding training course for specialists in the applied physics and electronics.

The book examines both well-known physical theories of applied electronics and correspondent development based on new ideas. The modern theoretical and experimental data are presented, as well as specifications of functional materials necessary for practical use in electronics. Special attention is paid to the influence of internal structure on the physical properties of materials and the prospects of their use. The writing style of this book is similar to a textbook: it considers new developments, some methods of parameter calculation and practical application of functional dielectrics. Modern theoretical ideas, new experimental data, main characteristics of basic materials are considered. Main focus is on explaining the physical mechanisms of many effects used in modern electronics. Book provides significantly new in-depth knowledge, which is useful especially for master's and postgraduate theses, and can also be used by bachelors in diploma theses.

Key features:

(1) Provides students with scientifically based understanding of micro- and nanomaterials and their practical applications.

(2) Takes simplified mathematical approach to theories, essential to understand of micro- and nano-materials, and summarizes at end of each chapters.

(3) Interweaves modern experiments and theories in topics such as micro- and nanomaterials.

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Introduction

Further progress in the creation of materials with new properties prepared real opportunities for subsmall elements appearance in the electronics (nano-electronics). This progress is caused by such changes in the structure of a matter that affect its fundamental properties. Until now, these properties have been determined mostly for the macroscopic objects. However, dimensional effects observed in the thin films, in the surface properties of crystals, and in the ultra-small particles of matter have long been noticed (and used in technology).

At the present time, it becomes possible to "manage" the properties of a substance by the changing its fragmentation. In connection with the needs of technology, great progress has been achieved in the field of nanophysics – a new scientific direction of physical materials science related to the creation and study of structure and properties of materials condensed from very small crystals, clusters, fragments (containing only 10^3–10^6 atoms). In scientific terminology, "nano" means 10^{-9}: one nanometer (nm) is equal to one thousandth of a micrometer (micron), or one millionth of a millimeter, or one billionth of a meter. The ultrafine microstructure having an average the size of phases or granules (clusters), layers or threads of the order of (or less) 100 nm is considered as nanostructured. Due to the small size of the blocks (particles, granules, phases) from which they are built, nanomaterials demonstrate unique mechanical, optical, electrical, and magnetic properties.

Polycrystalline fine-grained materials with an average grain size of 50–150 nm are sometimes called *microcrystalline*; and if the average grain size is less than 50 nm – *nanocrystalline*. It is known that even in a *polycrystalline* substance, a decrease in the size of crystallite grains can lead to a significant change in its properties. Such changes become particularly noticeable when the average crystal grain size decreases to 100 nm, but the properties change greatly if the grain size becomes smaller than 10 nm.

Nanotechnology in some aspects is a logical continuation and development of microtechnology. Microtechnology, operating with objects of the order of a micrometer, became the basis for creation of modern microelectronics. Cell phones, computers, the Internet, various household, industrial and consumer electronics – all this has changed the information space beyond recognition. It is assumed that nanotechnology – technology of technical application of nanometer objects, which are millionths of a millimeter, which is comparable to the size of individual molecules and atoms – will change the world just as significantly.

Nanotechnology requires highly precise electrical and mechanical devices to arrange the atoms and molecules of various materials in a new order. For research in nanophysics, it is necessary to apply very large computing power to simulate the behavior of atoms in nanostructures. As a result, new materials are created, mostly with special properties required for technology. For example, these are thin and flexible solar cells; flexible plastic screens as thick as a sheet of paper and with the brightness of a modern monitor; compact electronic devices, the size and energy consumption of which are hundreds of times smaller than the size and energy consumption of modern devices. In addition, nanotechnology enables the creation of transparent and flexible materials as light as plastic and as hard as steel, light and flexible construction and building materials, highly efficient filters for air and water, medicines that act at a deeper level, and much more.

Therefore, nanophysics and nanotechnology are a set of methods of manufacturing and processing structures with a size of 1–100 nm (at least in one of the dimensions). It is generally recognized that nanotechnology is the most promising direction of the modern electronic industry. It is believed that the country that masters nanotechnology earlier will take a leading place in the techno-sphere of the XXI century. That is why, the economically developed countries of the world allocate billions of dollars to the development of nanotechnology.

This book consists of **5 chapters** that are not related to each other by topic, but they are united by presentations of cutting-edge trends in electronic materials science.

Chapter 1 is dedicated to nanodielectrics. The modern successes of materials science were largely determined by the long-term and detailed study of the structure and properties of new macroscopic mono- or polycrystalline materials containing about 10^{22} atoms/cm^3. Both single crystals and polycrystals (in crystallite grains) have a long-range arrangement of atoms: in the case of polycrystals, disordered grain boundaries occupy only 10^{-9}–10^{-4} atoms of a total volume of the material. The technical properties of such bulk materials (electrical, mechanical, thermal, magnetic, semiconductor, corrosion, etc.) have now approached their maximum achievable values. Therefore, it is considered that it is unlikely to achieve a significant improvement in the characteristics of bulk materials only by improving the technology or changing the concentration of constituent elements.

It is assumed that further progress in the creation of materials with new properties should be associated with such changes in the structure of matter that will affect its fundamental properties, defined mostly for macroscopic objects. One of the most promising scientific directions in the field of physical materials science is the creation and study of the structure and properties of materials condensed from very small crystals, clusters, fragments, which consist of only 10^3–10^6 atoms. Materials of this structure are called nanostructured or nanocrystalline.

Nanocrystalline materials represent a special state of condensed matter - macroscopic ensembles of ultra-small particles with sizes up to several nanometers. The unusual properties of these materials are determined both by the characteristics of individual particles (crystallites) and by their collective behavior, which depends on the nature of the interaction between nanoparticles. If the dimensions of a solid body in one, two or three directions are comparable to some characteristic physical parameters that have the dimension of length (the size of magnetic domains, the length of the free path of electrons, the Debrouglie wavelength, etc.), then dimensional effects will be observed in the corresponding properties. For example, the diameter of an exciton in semiconductors ranges from tens to hundreds of nanometers, the distance between domain walls in magnetic materials reaches several hundred nanometers. This enables the transition to a new generation of materials whose properties change by adjusting the size and shape of their constituent structural elements (particles, grains, crystallites). Thus, dimensional effects should be understood as a set of phenomena associated with a change in the properties of a substance as a result of a direct change in particle size; the contribution of separation boundaries to the properties of the system; proportionality of the size of particles with physical parameters having the dimension of length.

Chapter 2 describes special electronic properties of metals. Main task is to discuss the highly unusual properties of some metals and alloys that extend application possibilities of electronic energy band theory. Considerable attention is paid to the special electronic states in metals, such as the intermediate valence, heavy-fermions, valence instability, and so on. Superconductivity in metals and alloys are also briefly discussed in connection of this effect use in electronics. Zero resistance nature of superconductors, magnetic field influence on them and mechanism of electron-phonon interaction are discussed as well. The high-temperature superconductivity is considered as a basis for new components of electronic equipment.

Nanometals are metallic particles a few nanometers in size or thin films of the same thickness. These objects are of interest not only in connection with their special mechanical properties, but also due to unusual physical and chemical characteristics, sometimes significantly different from those of coarse-grained metals. Metal materials with magnetic properties are extremely interesting from the point of view of creating data storage facilities. Metals enclosed, for example, in a carbon matrix, acquire resistance to oxidation without losing their magnetic properties. Encapsulated or anchored nanometals are less susceptible to sintering at elevated temperatures. Thin metal films can be used in the electronics industry as compounds or as magnetic and electrical layers. Nanometals are used, including in energy sector, in manufacture of rocket engines, pyrotechnic materials, microelectronic films and coatings, the production of superconducting alloys and powder metals and alloys of increased strength. Any metal capable of forming extended flexible filament can be processed into nano-metal spheres using modern technology.

In recent years, an important class of solids with anomalous properties is discovered: they are compounds of rare-earth metals, characterized by incomplete 4*f*-shell. Their electronic properties are difficult to explain within existing concepts. These substances are intermediate between magnetic and nonmagnetic materials, as well as between metals and dielectrics, because most of their electrons are found amongst localized and free states. Studies of these compounds help to understand many properties of metals and magnetics, to extend conceptions of band theory for metallic and dielectric states, as well as to investigate possible types of electronic states in crystals. Some compounds and metals are known, in which electrons have the binary, ambivalent nature: keeping largely localized (atomic) nature, they also can show intention to collectivization. To systems with unstable valence (or intermediate valence) belong compounds of rare-earth metals and actinides, i.e., the elements that have incomplete 4*f*- or 5*f*-shells. These compounds have unique physical properties and anomalous characteristics that explain formation of heavy fermions – peculiar electrons, that have effective mass in 10^2-10^3 times greater than mass of free electron.

Heavy fermions arise in such system, where the proximity of valence instability exists. Such fermions have record large effective mass; heaviest fermions are observed primarily in compounds of cerium and uranium – the elements, located in beginning of 4*f*- and 5*f*-periods. Among compounds with heavy fermions there are magnetic materials, disordered in their normal state crystals, as well as superconductors. Superconductivity is one of "cooperative" effects in the ensemble of conduction electrons, and it cannot be explained by simple models of "independent electrons". In the technique superconductivity is interesting in sense that superconductors have no skin effect and can significantly reduce energy loss. In superconductors two effects are found by Josephson: the current, which flows indefinitely long time without any voltage applied across a junction that consists of two superconductors, parted by weak link; when external voltage is applied, Josephson junction demonstrates effect of microwave generation. With these effects a variety of sensitive electronics devices are elaborated.

Chapter 3 is devoted to metamaterials. They are artificial created media elaborated for controlling of electromagnetic or acoustic waves propagation. Periodic structure of metamaterial includes the active (resonant) subwave-scale elements. Due to their special structure, metamaterials have such electromagnetic, optical, acoustic or other properties, which can not be reproduced by known in nature homogeneous materials. Further, only metamaterials with special *electromagnetic* properties are considered (although *acoustic* metamaterials are also studied and are widely used). As the special structure of electromagnetic metamaterials design, so the properties of actually received materials used in the structural elements, have a specific effect on the propagation of the electromagnetic radiation. This applies especially to such properties of metamaterials, which are not observed in the known bulk materials (at that, the especially impressive property of some metamaterials is the demonstration of negative refractive index in a certain frequency range.

The electromagnetic *metamaterials* are artificially structured in special way mediums that electrical and magnetic properties are significantly different from original structural materials. For example, metamaterial can have *negative refractive index* that is never observed in natural materials. Internal structure of metamaterials plays important role in the formation of characteristics and parameters. Metamaterials are constructed from the *discrete* resonant micro- and nano- elements: a sort of “meta-atoms", which *mimic* electromagnetic reaction of real atoms and molecules in the natural substances. The "meta-atoms" are grouped in the form of single or multilayered lattices, while their small size (less than wavelength of radiation) makes it possible to treat the created lattice as *homogeneous* for given wavelength (by analogy with natural crystals), and use the concept of "effective medium" for characteristics calculating.

The ε-*negative* (ENG) materials are characterized by negative value of $\varepsilon < 0$ but positive $\mu > 0$, so they have virtual (imaginary) refractive index that promotes the EM waves reflection. ENG phenomenon is possible both in natural materials and in artificially created media. First, the plasma has such characteristics including plasma in solid state matirials and second *ε-negative* materials can be created artificially. The μ-*negative* (MNG) materials possess negative value of $\mu < 0$ in some frequency range but the positive $\varepsilon > 0$, so they have virtual value of refractive index that contributes EM waves reflection. First, *natural materials,* in which at certain frequency parameter $\mu < 0$ can be obtained, are the ferrites, in which the ferromagnetic resonance at the beginning of microwave frequency range is seen.

Second, MNG can be created artificially as metamaterial. Artificially created the *double negative* (DNG) metamaterial possess both the negative $\varepsilon < 0$ and $\mu < 0$ in some frequency range, and they have *negative value* of refractive index: $n = -(\varepsilon\mu)^{1/2} < 0$.

Chapter 4. Multiferroics. There are the class of crystalline solids, in which at least two of three ordering parameters coexist: magnetic, electrical, or mechanical. Some classes of structurally ordered solids, whose properties are widely used in *functional electronics*, namely: the ferromagnetics, ferroelectrics and ferroelastics, despite completely different nature of structural orderings arising in them, demonstrate a number of *similar* properties: the anomalies in physical properties in vicinity of phase transition to the ordered state, the appearance of domains, the presence of hysteresis, etc. They are combined into one common group of substances with common name *ferroics*, according to common prefix "ferro" in English terminology (ferromagnetics, ferroelastics, ferroelectrics). Substances, in which functional magnetic, electrical, and elastic properties coexist, can have remarkable properties for electronics applications.

Previously, magnetoelectrics and multiferroics were of interest to relatively narrow circle of specialists, since very small magnitudes of magnetoelectric effects, as well as rather low temperatures, at which they manifested themselves did not allow to talk about their practical application. One of reasons was low temperature at which magnetoelectric effects were manifested, and another reason was the need to apply very high controlling fields. But in recent years, there has been a surge in research activity in this area, which has found expression in numerous reviews and special issues of journals devoted to multiferroics. The reason for this interest is due, on the one hand, to significant progress in understanding of physical mechanisms of magnetoelectric interaction in the multiferroics, and, on the other hand, to discovery of materials, which under normal conditions and moderate values of magnetic and electric fields, exhibit such magnetoelectric properties that allow magnetoelectrics specific practical applications in spin electronics, magnetic memory and sensor technology. Perhaps, the earliest studies of multiferroics were discovery of large ferroelectric polarization in epitaxial films of $BiFeO_3$ ferromagnetic and ferroelectricity with magnetic ordering in $TbMnO_3$, which proved their *compatibility*.

Before electric and magnetic ordering in solids are considered separately: the point is that electric charges of electrons and ions are responsible for the *charge* effects, whereas magnetic charges are absent, so only electron *spins* govern magnetic properties. The field of multiferroics has greatly expanded in last years, particularly with discovery of many different types of multiferroic materials. Next, we consider, in particular, such materials, which have both magnetic and electric ordering - the magneto-ferroelectrics, which are now more often called by the name of wider class of multiferroics. The connection between magnetic and electric subsystems in the multiferroics, which manifests itself in form of magnetoelectric effects, makes it possible to control the *magnetic properties* of a material by using the *electric field*, and vice versa, to modulate electrical properties by magnetic field. In addition to scientific interest in their physical properties, the multiferroics have potential for applications as actuators, switches, magnetic field sensors, and new types of electronic memory devices.

Chapter 5 describes magnetic nanostructures. The nanostructuring of bulk magnetic materials allows controlling their characteristics within wide limits. Nanotechnology can be used primarily to create materials with a given type of magnetization type – both for very soft magnetic materials and for extremely magnetically hard materials. Apparently, the possibilities of volumetric materials used by engineers already reached their maximum. It is believed that it is hardly possible to get any significant improvement in their performance only through a more thorough technology or by changing in components. Therefore, it might be assumed that a subsequent creation of materials with *new properties* should be associated with fundamental changes in the *structure* of substances, affecting such properties that are necessary for contemporary applications. It is considered that one of most promising is new research area in field of material science is creation of materials which are condensed from *very small* crystals, clusters, fragments that consist of around 10^2–10^5 atoms.

Main reason of nanomaterials difference from conventional materials is that the *ratio of surface to volume* in nanomaterials is rather big. The smaller size of nanocluster, the greater is influence of its surface properties as compared to bulk properties. In a certain sense, the nanostructure transforms properties of crystal surface into the volumetric properties of condensed nano-material. In other words, properties of nano-formed substance depends on the ratio of number of atoms located on surface of nanocluster to number of atoms located in its volume, and this ratio might be quite different. Therefore, by controlling the size and the shape of clusters, the properties of nano-material can be purposefully changed.

Nano-structurization of *magnetic materials* enables to operate in a wide range of their characteristics. Nanotechnology can be used, primarily, to create material with adjusted type of magnetization curve: both for extremely magnetically-soft materials and for extremely magnetically-hard materials. Fundamental magnetic properties of a matter in their nano-state vary considerably due to correlation in the interaction of spin and orbital moments in lattice cells, located on the surface of nano-particle. The properties of ferromarnetics and ferrimagnetics in their nano-state can be changed especially strongly. In the magnetics formed from nano-clusters the nature of short-range ordering becomes different, that is why new properties appear (sometimes, very important for technical application).

Currently, many different technologies for obtaining an image of the internal structure of the body are used in medicine, including magnetic resonance imaging (MRI). This technology allows medicine to make significant progress in the field of diagnostics and therapy. In a magnetic field, magnetic nanoparticles are magnetized and create an induced magnetic field, which disturbs the process of magnetic relaxation of protons in the water molecules surrounding the magnetic nanoparticles. In turn, this leads to a reduction in the spin-spin relaxation time of protons, and, as a result, is registered as contrast in MRI. Nanoparticles are used for controlled drug delivery, which is of great importance for improving the effectiveness of drugs, as well as for the convenience of patients. Protecting drugs before they reach the target organ increases the convenience of using drugs that have a short half-life in the body. Treatment with heat is called hyperthermia. The use of magnetic nanoparticles in hyperthermia is due to the fact that magnetic nanoparticles more effectively absorb the energy of an external magnetic field.

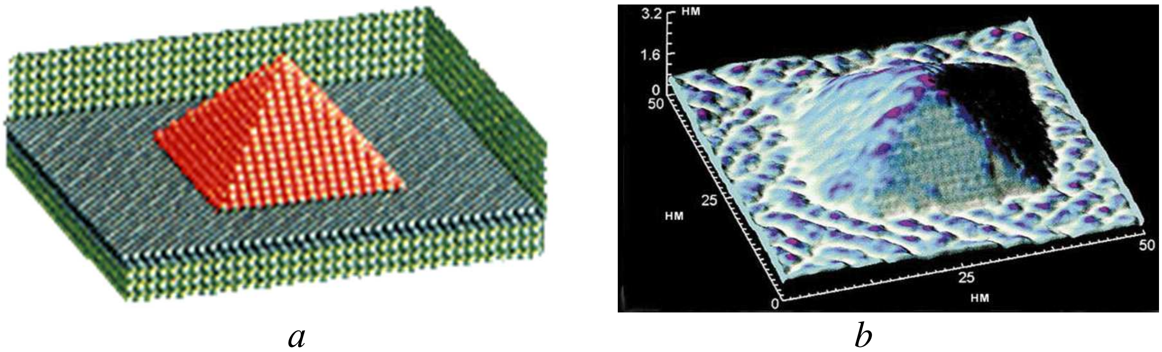
Chapter 1. Nanodielectrics

Contents

New concepts: nanoelectronics, nanotechnologies, nanoparticles, nanowires, nanostructures, nanocomposites, nanoprobe microscopy and others have become widely used now. At that, nanomaterials and nanodevices start to play a particularly important role in the electronics.

Nanoelectronics is rapidly developing field of electronics, which is engaged in development of technological and physical foundations for construction of integrated electronic circuits with element sizes less than 100 nanometers.

Term "nanoelectronics" itself reflects a transition from the microelectronics of modern semiconductors, where the dimensions of elements are measured in the units of micrometers, to the much smaller elements: with dimensions of tens of nanometers. With transition to the nano-size elements, the *quantum effects* begin to dominate in circuits, opening up many new properties, and, accordingly, signifying the prospects for their useful use.



a *b*

Fig. 1.1. Three-dimensional images of quantum dot: a - computer model of quantum dot which is pyramid with germanium atoms spontaneously formed on silicon substrate; b - quantum dot image by scanning electron microscope

The enormous possibilities of nanotechnology are shown by two examples. Figure I.1 demonstrates germanium quantum dot grown on the silicon substrate. On the area of one square micron over a thousand of these quantum dots can be accommodated. Historically, first studied quantum dots were the microcrystals of cadmium selenide (CdSe). Electrons in such microcrystal are in three-dimensional potential well so that they have several stationary levels of energy with a characteristic distance between them (exact expression for energy levels depends on shape of quantum dot). While electrons make transitions between the energy levels of a quantum dot, the photons can emit, similarly to transition of electron between the energy levels of an atom. It is possible also to arouse ("throw") the electron into the highest energy level and obtain the radiation from transition between levels (luminescence). In this case, unlike actual atoms, the frequencies of transitions are easy to control, changing size of a microcrystal. Once again note that observations of cadmium selenide nanoclusters ("microcrystals") luminescence served as the first opening of quantum dots. For example, in nanophysics, one of the first nanoclusters observed were CdSe clusters of different colors. The length of the optical wave (and the color of fluorescence) depends on the size of these clusters (Fig. 1.2). In the most studied semiconductor CdSe, the blue (blue) shift of the absorption band begins with nanoparticles 10-12 nm in size.

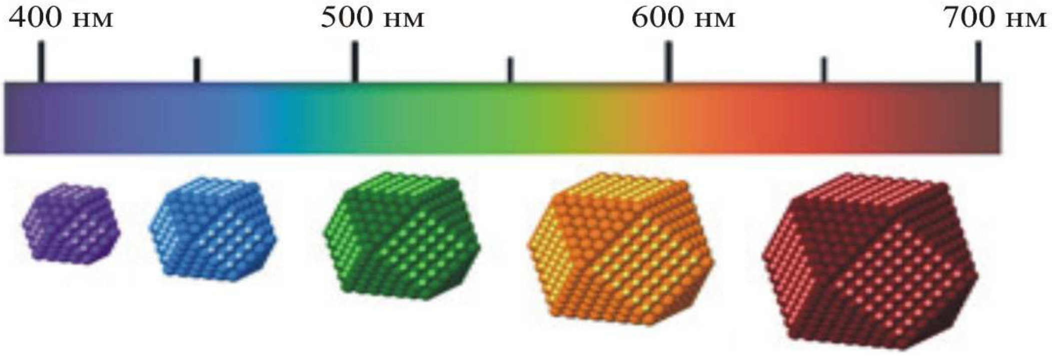


Fig. 1.2. Fluorescence of cadmium selenide nanoclusters: 400 nm – violet color; 450 nm – blue; 500 nm – green; 600 nm – yellow; 700 nm is red

In CdSe clusters, the fluorescence covers almost the entire range of visible light (wavelengths 400–700 nm). The length of optical wave in CdSe clusters (and fluorescence color) depends on the size of these clusters. It is determined that fluorescence of cadmium selenide nanoclusters corresponds: for size of ~ 400 nm – purple; ~450 nm – blue; ~500 nm – green; ~600 nm – yellow; ~700 nm – red. Observed blue shift of absorption band begins with nanoparticles of 10^{-12} nm in size. In semiconductor clusters, absorption of photons generates electron-hole pairs while their recombination is accompanied by fluorescence. In other words, decrease in the size of semiconductor nanoparticles is accompanied by a shift in absorption band in the high-frequency region. At present, many experiments are devoted to quantum dots formed in two-dimensional electronic gas. In two-dimensional electronic gas electrons motion perpendicularly to the plane is limited, so region on plane can be isolated by means of gate metallic electrodes superimposed on heterostructure. Quantum dots in the two-dimensional electronic gas can be connected by the tunnel contacts to other regions of the two-dimensional gas, and electrical conductivity through a quantum dot can be studied. And there are many such examples.

Thus, we can conclude that *Nanoelectronics is the field of science and technology engaged in the creation, research and application of electronic devices with nanometer-sized elements, the functioning of which is based on the quantum effects.*

1.1 Introduction

Electronics is defined as an important branch of science and technology. The scientific aspects of electronics consist in the research of *electrons interaction with electromagnetic fields* in a material. The practical aspects of electronics are the methods of new materials and technology creating, in which this interaction is applied, i.e., the development of different electronic devices, which perform various functions in information converting and transmission systems, as well as in the controlling systems, computer technology and power devices.

In its development, the electronics has gone through several stages:

- tube electronics;
- semiconductor electronics;
- *microelectronics* – integrated electronics;
- ***nanoelectronics*** – the modern, fourth stage of electronics development;
- molecular electronics (?) – possible future direction.

Each of these types of electronics is originated in the depths of physics, mathematics and chemistry, while for nanoelectronics and molecular electronics the advances in biology are also important.

The present time can be called as the time of the triumph of microelectronics. Indeed, microelectronics began with the integrated circuits which housed about 10 transistors per square centimeter (1960). A decade later (in (1970), their density was already 2000 per cm^2, then, in 1980, this density reached 1 million transistors and now it is already more than 40.10^6 transistors per cm^2. The *nanoelectronics* is designed to eliminate significant difficulties that arose during further development of microelectronics. The point is that scaling down of semiconductor devices dimensions may have following consequences:

- The decrease of insulating layers thickness leads to the increase of electric field on the gate of transistor that leads to tunneling of electrons and gate breakdown.
- In low dimensional systems some quantum phenomena begin to affect the devices properties, when material dimensions are less than 10 nm. The point is that structure of electrons energy bands in low dimensional solids changes in comparison to three-dimensional bulk materials.
- The heat dissipation due to higher density of devices becomes mane problem of microelectronics. that is wny, it is necessary to significantly reduce devices energy consumption, which can be provided by the nanoelectronics.

Currently rapidly developing nanotechnology represents the further progress in the obtaining materials with new properties: they prepare real opportunities for the emergence of electronics of small elements. This progress is due to such changes in structure of matter that affect its *fundamental properties*. Until now, main properties of materials have been determined mainly for the macroscopic objects. However, dimensional effects observed in thin films, in properties of crystal surface and in very small particles of matter have long been known, and now start to be used in engineering.

The definition of nanoelectronics can be viewed from different angles.

There is no clear boundary between "nanoelectronics" and "microelectronics", since the specific micro-or-nano sizes are not decisive but are conditional. However, unlike the classical laws used in electronics and microelectronics, the basis for the operation of the nanoelectronic devices is the *quantum effects*: quantum capacity, kinetic inductance, quantum conductivity, plasmons, two-dimensional electron gas, and others. Due to this, not only a specific nomenclature of properties appears, but also new prospects for their use. In particular, if in micro-size devices quantum effects are largely undesirable (for example, in the operation of a classical transistor, when its size decreases, there is a size limitation due to the tunneling of charge carriers), then in nano-electronics the quantum effects are already the basis for the operation of some devices.

In this case, the main point is that it is possible to control the properties of matter by the changing its fragmentation. Due to the needs of technology, great progress has been made in the field of *nanophysics,* which is a new scientific field of physical materials science, associated with the creation and study of the structure and properties of materials condensed from very small crystals, clusters, fragments having a total volume of 10^3–10^6 atoms. In scientific terminology, term "nano" means 10^{-9}: one nanometer (nm) is equal to one thousandth of a micrometer ("micron"), or one millionth of a millimeter, or one billionth of a meter. An ultrathin microstructure having an average size of phases or granules (clusters), layers or filaments of the order of (or less) per 100 nm is considered nanostructured. Due to the small size of the blocks (particles, granules, phases), from which they are constructed, the nanomaterials demonstrate unique mechanical, optical, electrical and magnetic properties.

Polycrystalline fine-grained materials with an average grain size of 40 to 150 nm are sometimes called *microcrystalline*; and if the average grain size is less than 40 nm – *nanocrystalline*. It is known that in a polycrystalline substance, a decrease in the size of the "grains" of crystallites can lead to a significant change in its properties. Such changes become especially noticeable, when the average crystal grain size decreases to 100 nm, but the properties change greatly, when the grain size becomes less than 10 nm. In recent years, a new scientific and technical field is developing – magnetoelectronics, or, as it is now called – "spintronics", engaged in the study and practical implementation of devices that use electron spins. Spintronics studies magnetic and magneto-optical interactions in metal and semiconductor structures, as well as quantum magnetic effects in nanometer-sized structures. Of particular importance for magnetoelectronics are modern nanotechnologies that allow the implementation of new advances in the field of nanophysics.

Thus, nanotechnology is a set of methods for the manufacture and processing of structures having a length of 1–100 nm (at least in one of the dimensions). It is generally accepted that nanotechnology is the most promising area of modern technology. It is believed that those who previously mastered nanotechnology will take a leading place in the technosphere of the XXI century. That is why economically developed countries allocate billions of dollars for the development of nanotechnology. Currently, the world market already sells more than 3,000 products manufactured using nanotechnology. In the next 10 years, the global need for certified nanotechnology professionals will be in the millions; the value of the world market for nanotechnology products will be about 1 trillion US dollars. In recent years, more than tens of thousands of nanotechnology companies have been established, and their number is doubling every two years.

Nanosize materials in modern technologies. As the size of object decreases to micro- and, especially, nano-scale, the influence of the surface and shape on all its physical properties increases significantly in comparison with the influence of the bulk material of the object. From a thermodynamic point of view, this fact is explained by an increase and subsequent dominance of the *free surface energy*, which is determined by the shape of the object and its surface area ~ R^2, in comparison with the free volumetric energy of the sample, proportional to *R3*, with a decrease in its characteristic size *R*. Moreover, with a decrease sizes and shape factors below the "critical" ones, the physical properties of objects themselves can fundamentally change: the nano-objects and low-dimensional structures are characterized by the *size-induced* structural and phase transitions such as metal ⇒ semiconductor ⇒ dielectric or paramagnetic ⇒ ferromagnetic ⇒ antiferromagnetic ferroelectric ⇒ paraelectric, elasticity ⇒ plasticity and many others. These effects, predicted within the framework of phenomenological theories, have numerous experimental confirmations and are consistent with the modern quantum-mechanical microscopic calculations, proving fundamental changes in the band structure and symmetry of the unit cells, induced by the nanoscaling of the object. In this case, researchers are faced with nanomaterials, the physical properties of which may differ significantly from the "generating" bulk materials.

For a number of properties of nano-scale objects, the nature of their material can play a secondary role in comparison with the primary role of shape (for example, a quantum dot, ellipsoid, sphere, tube, wire, or mono-layers), topological dimension (for example, ID, 2D, 3D confinement or fractal) and quantum size effect (in particular, the dimensions of the object are below or above the characteristic or critical dimensions).

The most technologically, advanced and promising nano-objects for the applications are the nanotubes, nanowires, graphene and clathrates, which clearly demonstrate the leading role of the *nanoscale* for the use of their physical characteristics in the modern submicronics and nanoelectronics, optoelectronics, data storage devices and computer memory, environmental energy and medicine.

Turning to specific examples, we note that, first of all, those nanoscale affects: electronic emission, electromechanical and thermoelectric properties of objects. Single-wall nanotubes, synthesized from the semiconductors with different band gaps (carbon, silicon, boron nitride or zinc oxide) can have both low (up to the dielectric) and very high (up to the metallic) electrical conductivity, which can be easily controlled, even electrically.

They are the objects with an almost ideal surface, since the existing defects, as a rule, affect only the structure of several nearby cells, but do not violate the structure of the tube of other nano-particle as a whole. Therefore, for the use of nanotubes as channels for field-effect transistors, their easily controllable electrical conductivity and extremely low wall roughness in comparison with conventional silicon channels play a decisive role. The result is the advanced scaling of gate and channel lengths down to a few nm, reduced channel scattering and, as a result, improved transistor performance.

Many already implemented applications of nanoelectrnis are known:

Memory storage. Electronic memory designs in the past have largely relied on the formation of transistors. However, research into crossbar switch based electronics have offered an alternative using reconfigurable interconnections between vertical and horizontal wiring arrays to create ultra high density memories. Some companies has proposed the use of *memristor* material as a future replacement of Flash memory. An example of such novel devices is based on *spintronics*. The dependence of the resistance of a material (due to the spin of the electrons) on the magnetic external field is called magneto-resistance. This effect can be significantly amplified (giant magneto-resistance) for the nanosized objects, for example when two ferromagnetic layers are separated by a nonmagnetic layer, which is several nanometers thick. This effect has led to a strong increase in the data storage density of hard disks and made the gigabyte range possible. Besides, the so-called tunneling magnetoresistance is very similar to giant magneto-resistance but is based on the spin-dependent tunneling of electrons through the adjacent ferromagnetic layers. Both effects are used to create the non-volatile main memory for computers, such as the so-called magnetic random access memory or MRAM.

Nano-modifications of carbon, especially graphene and similar 2D (layered), 1D (tubes) and 0D (fullenes) materials are one of the main directions of nanophysics and nanoelectronics. Such materials as one atom thick, have remarkable properties that can be combined to create various electronic circuits. For example, the technologies associated with probe microscopy make it possible to build various structures of individual atoms on the surface of semiconductor in ultrahigh vacuum, simply by rearranging them that is basis for creating monatomic electronic devices.

Optoelectronic devices. In the modern communication technology, the traditional analog electrical devices are increasingly replaced by the optical or optoelectronic devices due to their enormous bandwidth, capacity and respectively. Two promising examples are the photonic crystals and quantum dots. The photonic crystals are materials with a periodic variation in the refractive index with a lattice constant that is half the wavelength of the light used. They offer a selectable band gap for the propagation of a certain wavelength, thus they resemble a semiconductor, but using light or photons instead of electrons. Quantum dots are the nanoscaled objects, which can be used, among many other things, for the construction of lasers. The advantage of a quantum dot laser over the traditional semiconductor laser is that their emitted wavelength depends on the *diameter* of the dot. Quantum dot lasers are cheaper and offer a higher beam quality than conventional laser diodes.

Displays. The production of displays with low energy consumption might be accomplished using carbon nanotubes (CNT) and/or silicon nanowires. Such nanostructures are electrically conductive and due to their small diameter of several nanometers, they can be used as field emitters with extremely high efficiency for field emission displays (FED). The principle of operation resembles that of the cathode ray tube, but on a much smaller length scale.

Quantum computers. Entirely new approaches for computing exploit the laws of quantum mechanics for novel quantum computers, which enable the use of fast quantum algorithms. The quantum computer has quantum bit memory space termed "Qubit" for several computations at the same time. This facility may improve the performance of the older systems.

Plasmatronics. Collective oscillations of free electrons inside a metal have the characteristic plasmon resonance with a wavelength of the order of hundreds of nanometers. Thus, it is possible to transmit the electromagnetic wave along a chain of metal nanoparticles, exciting the plasmon oscillations in them. This technology will allow the logical chains introducing into computer technology that can work much faster and transmit more information than traditional optical systems, and the size of such systems will be much smaller than the accepted optical ones.

Medical diagnostics. There is great interest in constructing nanoelectronic devices that could detect the concentrations of biomolecules in real time for use as medical diagnostics, thus falling into the category of nanomedicine. A parallel line of research seeks to create nanoelectronic devices which could interact with single cells for use in basic biological research. These devices are called nanosensors. Such miniaturization on nanoelectronics towards in vivo proteomic sensing should enable new approaches for health monitoring, surveillance, and defense technology

Another example is emitters from nanowires, multi-walled or single-walled nanotubes and their arrays, made of a wide variety of materials (carbon, silicon, gallium arsenide or boron nitride, coated with silver, titanium, platinum or gold, which are used in vacuum electronics as a new type of field cathodes. The main advantage of such emitters is the nanometer curvature of their tip. Due to the strong field concentration near the tops of the nanotubes or nanowires, the nanoscale provides the ultra-high field gains and ultra-low threshold voltages of the cathode.

The use of empty nanotubes, inside which it is possible to move the metal nanoparticles and fix their position using electrical or magnetic pulses, will make it possible to achieve the ultra-high density of data recording. In this case, the material of the tube and the method of its manufacture do not play a noticeable role (which means that you can choose the cheapest one). The ultra-high density is achieved due to the fact that one nanotube is capable of fixing not only two positions of the nanoparticle (presence or absence), but much more positions of the particle (in fact, the coordinate of particle in tube).

Thermoelectric and electrocaloric properties of fullerenes and clathrates (their high electrical conductivity combined with low thermal conductivity due to the dominant contribution of the ballistic mechanism of heat transfer) determine the high efficiency of fullerenes in the thermoelectric converters of a future. Due to the unique possibilities of storing and releasing other atoms and molecules (in particular hydrogen), fullerenes and clathrates may be of fundamental importance for the energy of the future. It turned out that the formation of fullerenes, clathrates and other very diverse supra-molecular ensembles is primarily determined not by the chemical nature of their constituent substances, but by their topological, geometric and charge correspondence.

This list of examples of unique properties that are "universal" for various nanomaterials and their use for the applications in various fields of science and technology is far from complete. It should be noted, however, that for successful application of nanomaterials properties it is necessary to develop new technologies, such as the self-assembly; if possible, to use also the biochemical nano-assemblers and the "intelligent" molecular micro- and nano-machines, which will make it possible to synthesize sufficient quantities of identical units of nanomaterial and integrate them directly into circuits.

In conclusion, we note that the words "nanotechnology" and nanodevices have become commonplace these days. For example, these are words containing "nano", such as "nanoscale", "nanoparticle", "nanophase", "nanocrystal" or "nanomachine". The field of nanotechnology and nanophysics owes its origin to the study of active particles; free atoms, clusters, reactive particles. Nanotechnology also means the application of new methods and tools: pulsed cluster beams, innovations in mass spectrometry, vacuum technologies, microscopes and much more. Nanophysics and nanotechnology will expand into various fields, including chemistry, physics, materials science, engineering, and biology. This progress is justified because nanoscale materials represent a new field of matter, as well as new opportunities for fundamental science.

Next, we discuss the most promising for applications in the electronics of such nanoobjects, in which, in order to use their physical characteristics, the leading role is nanodimension. Known but important for understanding sections of nanophysics are given in smaller print.

1.2 Size effects

The fundamental physical, chemical, and biological properties of substances change significantly when their constituent elements are reduced to nanometer sizes (due to their size, shape, surface chemical properties, and topology). For example, six-nanometer copper granules shows five times the hardness of ordinary copper; the semiconductor cadmium selenide (CdSe) can take on any color depending on its size-controlled granules. It is obvious that in CdSe the value of the band gap changes in the spectrum of electronic states. Therefore, the properties of small particles of a substance are significantly different from the properties of a massive material. For these reasons, there has been a great scientific and technical interest in nanomaterials, and nanophysics has become an arena of active research. New molecular technologies have been developed and further major "breakthroughs" in material technology are expected, which will allow creating their structure atom by atom (atom by atom) [1].

Nanophysics covers a large section of physical science, where different sections of physics, chemistry and even biology collide. This branch of physics is developing rapidly, as nanostructures have great prospects for use in military, space, and commercial information and biological technologies. From the point of view of thermodynamics, the peculiarity of nanomaterials is determined by the *growth of their free surface energy*, which is determined by the shape of object and its surface area R^2, compared to the free *volume* energy of sample, which is proportional to R^3. With the reduction of sizes and form factors below some critical ones, the very physical properties of objects can fundamentally change: nano-objects and low-dimensional structures are characterized by *size-induced* structural and phase transitions: dielectric–metal, paramagnetic–ferromagnetic, ferroelectric–paraelectric, etc. Fundamental changes in the band structure and symmetry of elementary cells of nanoscale objects are also proven by microscopic calculations. At the same time, the physical properties of nanomaterial may have significant differences from the properties of original bulk material.

To have idea of the real dimensions of the elements and structures with which nanophysics operates, in Fig. 1.3 compares the sizes of atom, molecule, quantum dot, colloidal gold particle, bacterium, and living cell in the logarithmic scale. Nanoclusters, to which quantum dot belongs, are larger than atoms and molecules, but smaller than bacteria and living cells. Objects of nanophysics have characteristic sizes from 10 to 300 nm. Nano-objects can be compared to crystals, since the atoms are arranged in such and such. In terms of size, microcrystals are placed between ordinary crystals and nanocrystals. The "characteristic size" of 40-50 μm can be considered a conventional boundary between microcrystals and crystals.

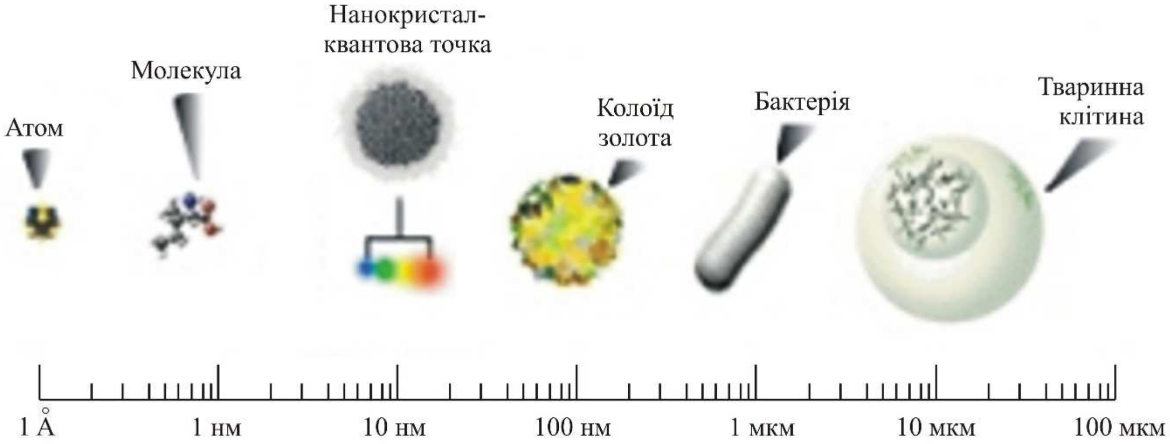


Fig. 1.3. Comparison of the sizes of various microscopic objects

For some properties of nanoscale objects, the nature of their material may be secondary to the shape: quantum dot, spherical cluster, tube, wire, or monolayers, and depends on the topological dimension (e.g., 1*D*, 2*D*, 3*D*, or fractal). Reducing the size of crystal blocks in a substance (primarily in ferromagnetics and ferroelectrics) can lead to significant changes in their properties. Such changes occur when the average size of crystal grains decreases to 100 nm.

The change in physical properties of materials is most noticeable if grain size is smaller than 10 nm. Polycrystalline fine-grained materials with an average grain size of 50 to 150 nm are sometimes called ***submicrocrystalline***, and if the average grain size becomes smaller than 50 nm, then ***nanocrystalline.*** In this case, the concept of "long-range order" in the arrangement of atoms of a substance can no longer be applied.

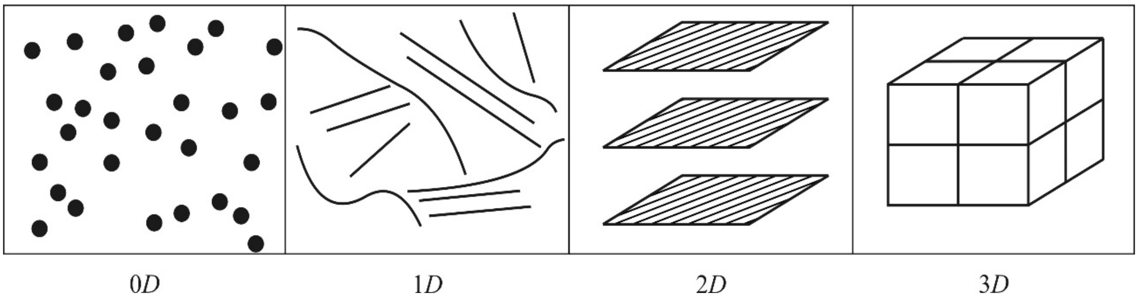


Fig. 1.4. Types of nanocrystalline materials: 0D - zero-dimensional clusters (quantum dots); 1D - one-dimensional clusters (nanotubes and quantum threads); 2D - two-dimensional nanomaterials (films and layers); 3D – three-dimensional structures (nanocomposites)

The term "nano" comes from the Greek word "nannos" - a dwarf. The main types of nanocrystalline structures are shown in Fig. 1.4. Their characteristic sizes are 5-300 nm.

Historically, crystals were first identified by the correct shape of their faces, which is characteristic of each type of crystal. But in very small particles, this specific feature of crystals is broken. On the example of a cubic crystal of magnesium oxide (MgO) in Fig. 1.5 shows a significant discrepancy in the faceting of crystals, microcrystals and nanoparticles. Using this example, you can make sure that the change in size leads to a change in the shape of the crystal. If the dimensions exceed 100×100 nm, the crystal long-range order prevails in the arrangement of atoms, and the MgO crystal has a regular cubic shape. But microcrystals of MgO already have a tendency to the hexagonal shape, while nanosized "crystal" takes on shape of dodecahedron [2].

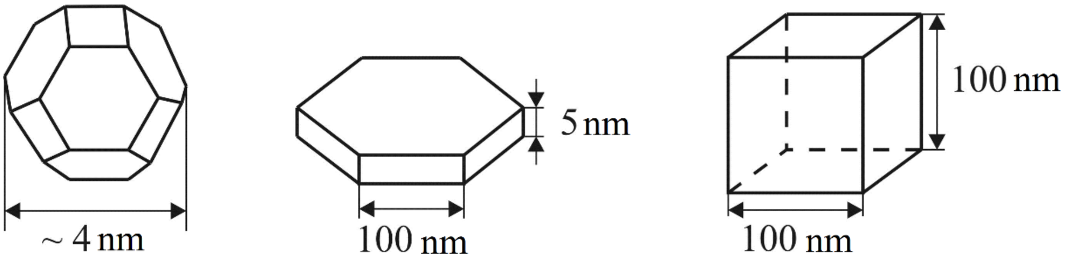


Fig. 1.5. Different forms of magnesium oxide: 4 nm – nanoparticle, 5×100 nm – microcrystal, 100×100 nm – crystal

Some of the nanomaterials always have a close arrangement of atoms. Such are the well-studied amorphous metal alloys (metallic glasses). The technical characteristics of these substances have been significantly changed, which makes it possible to create, for example, ferromagnetics with such magnetic properties that cannot be achieved in materials with a long-range arrangement of atoms. The surface properties of a solid differ significantly from its bulk properties. The fact is that on the surface of a crystal, the regular electronic bonds of atoms are "broken", as a result of which the equilibrium structure of the surface is arranged in a different way than the structure of volume. Studies have shown that the number of atoms in the unit cell changes on the surface of the crystal, a different symmetry of the structure is created, and the frequencies of oscillations of crystal lattices (phonon frequencies) also change.

As a result, the *Debye temperature* of the crystal changes (usually decreases) on the surface of a crystal and, accordingly, its *melting temperature decreases*. Lowering the melting temperature of near-surface layer is widely used in microelectronic technology, for example, during production of epitaxial layers. The *unit cell* of crystals also changes on the surface. These properties are fundamental because they are determined by the particularity of the bonds of atoms in solids. The decrease in the melting temperature of nanomaterials can be quite large. The experimental dependence of the melting temperature of nanoparticles of two different substances - gold (which has a metallic bond) and the semiconductor cadmium sulfide (which has an ionic-covalent bond) is shown in Fig. 1.4. It can be seen that the lowering of the melting temperature for nanoparticles can reach 1000 K, which is used in nanotechnology.

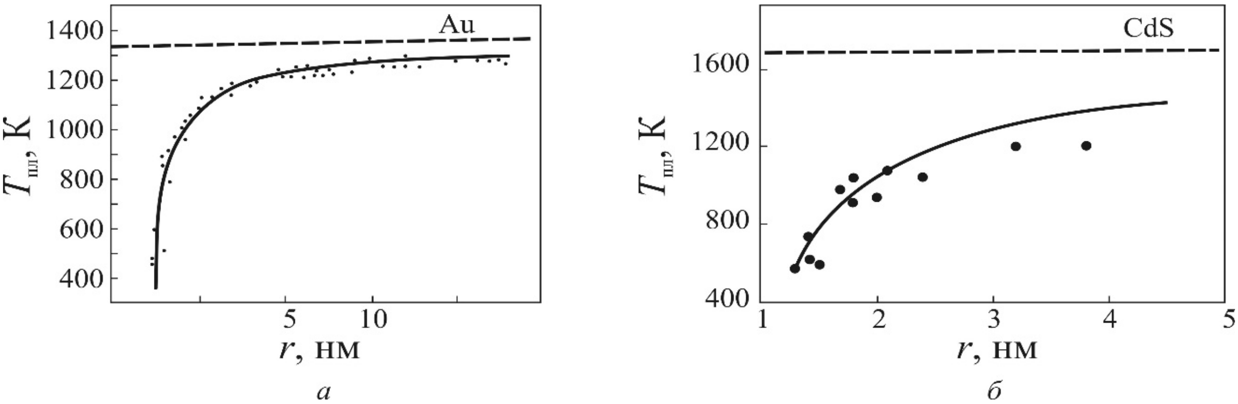


Fig. 1.6. Experimental data on the melting temperature: a – typical metal (gold); b – typical semiconductor (CdS) depending on the particle size (horizontal lines show the melting point of macroscopic samples)

The main reason for the difference between nanomaterials and ordinary materials is that in such substances the ratio of the number of atoms on the surface to the number of atoms in the volume is very large. The smaller the size of the nanocluster, the more the influence of the surface properties prevails over the bulk properties [1].

In a certain sense, nanostructures allow you to *"transform" surface properties of crystal into bulk properties*. Depending on the ratio of the surface of the clusters to their volume, the properties of this or that substance in the nanostructured form are quite different. Therefore, by changing the size and shape of nanoclusters, these properties can be purposefully changed. In addition, the structural state of the nanocluster grain itself changes significantly. Defects in the crystal structure typical of single crystals and large (over 100 μm) crystallites in polycrystals, such as dislocations (which typically have a density of about 10^4 cm^{-2}), as well as vacancies and packing defects (with a density of 10^6–10^{10} cm^{-3}) in nanomaterials often cannot be contained inside the grain and come to the surface, turning the structure of the grain into an almost defect-free one. However, in an array of nanoclusters – nanocomposites – intergranular boundaries are characterized by structural instability, and therefore nanocrystalline bulk materials are characterized by a high diffusion mobility of atoms, which is 5-6 orders of magnitude higher than that of ordinary polycrystalline materials.

The theoretical model of different sizes nanoclusters formation is shown in Fig. 1.5. It is assumed that all interatomic bonds are spherically symmetric (the model of densely packed elastic spheres). In the simplest case, in this model, one atom is surrounded by 12 atoms, since 12 is the maximum coordination number. It is obvious that only 13 atoms are contained in the first cluster. Then percentage ratio of number of atoms on surface (12) to number of atoms in volume (1) is 92%. In the second cluster in Fig. 1.7, another layer of atoms is added to the surface, so their total number is 55, and the ratio of the number of surface atoms to volume atoms is 76%. As the number of atoms in the clusters increases, about half of them are contained within the cluster volume.

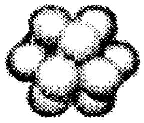
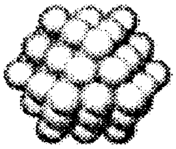
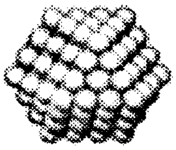
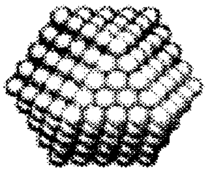
Cluster	*Atoms number*	*Ratio, %*
	13	92
	55	76
	147	63
	309	52

Fig. 1.7. Percentage ratio of the number of atoms inside a cluster to the number of atoms placed on surface

If the size of the particles is 4 nm, then about 50% of them are on the surface.

The "dimensional" effect affects not only the properties of the crystal lattice, but also the energy spectrum of electrons in the cluster (for example, the energy spectrum of electrons in semiconductors changes). There are new opportunities for creating semiconductor devices using the nanostate of electrons in a semiconductor. The magnetic properties of substances, especially those that are ferro-, antiferro-, and ferrimagnetic, also change significantly due to the violation of the correlation of the interaction of spin and orbital moments of electrons on the surface of crystals. Magnetic materials compacted from close-order clusters acquire new properties useful for technical applications. Reducing the size of grain clusters is assumed to be an effective method of controlling many properties of solids. There are good reasons for such predictions. Small size of grain causes large changes in the structure of solid body. If the thickness of boundary is three to four atomic monolayers (0.5 to 1.5 nm), then the surface layer accounts for about 50% of the entire substance. In ordinary crystals and polycrystalline substances, this ratio is equal to 10^{-9}–10^{-6}, respectively.

The intergranular boundary of nanocomposite itself is characterized by structural instability, which is why nanocrystalline compacted materials are characterized by high diffusion mobility of atoms, which is five to six orders of magnitude higher than in ordinary polycrystalline materials. The growth of diffusion in nanocrystalline materials can be due to the following reasons [3]:

- lower concentration of impurities in intercrystalline boundaries compared to boundaries of usual type, characteristic of polycrystals;
- possibility of accelerated diffusion along intercrystallite boundaries, which are interconnected and form an almost continuous network.

We can assume that the structures of intercrystalline boundaries in nano- and ordinary polycrystals are quite different due to the porosity of nanocrystalline materials, which also accelerates diffusion. Studies of various nanomaterials (Pd, Ag, TiO_2, MgO, WO_3, ZnS) and nanocomposites (Ag–Mg, Ag–WO_3) showed that compacted nanocrystalline material has almost uniform structure. Coherent double boundaries are very often observed, but the grains themselves are characterized by a periodic atomic structure.

1.3 Nanoclusters

The highly developed surface of isolated nanoparticles makes a major contribution to their properties. A distinctive feature of clusters is the non-monotonic dependence of their properties on the number of atoms in the cluster.

Structure of nanoclusters. A cluster is a group of a small and, in general, a variable number of interacting atoms, ions, or molecules. Clusters should be energetically stable. Theoretically, the minimum number of atoms in a cluster is two. The upper limit of the cluster corresponds to the number of atoms when the addition of one more atom no longer changes the properties of the cluster. From a physico-chemical point of view, this change ends when the number of atoms in the group reaches 1-2 thousand. It is assumed that clusters should have a dense and regular packing of atoms and be built from the simplest stable atomic configurations. For this, the structure of the cluster should contain as large a proportion of tetrahedra as possible - the smallest in terms of volume of stable atomic configurations [2].

For relatively large clusters, the usual cubic or hexagonal packing of atoms is observed for crystals. But small clusters can have a different symmetry, which is characterized by the symmetry axis of the fifth order (which is "forbidden" in macroscopic crystals). Many clusters are different groupings of three atoms, in which the atoms are placed at equal distances from each other and form an equilateral triangle, Fig. 1.8. Tetrahedron, octahedron, cube, pentagonal pyramid, icosahedron, etc. are usually considered structural elements of clusters. The smallest stable cluster with a fifth-order symmetry axis contains seven atoms and is shaped like a pentagonal bipyramid, which is a stable configuration with fifth-order symmetry axes. The most complex of those shown in fig. 1.8 configurations is an icosahedron containing a central atom surrounded by 12 atoms arranged in 20 equilateral triangles and having six fifth-order symmetry axes. This icosahedron can also be presented as a figure composed of 20 identical tetrahedra that have a common vertex and are connected to each other by common faces.

Symmetry of nanomaterials. Nanomaterials exhibit the short-range ordering of their atoms. Their relatives are, for instance, well-studied amorphous metal alloys (metal glasses). In such substances their structure is changed quite significantly, allowing create, for example, ferromagnetics with such magnetic properties that in principle can not be obtained in the materials with long-range ordering of atoms.

Topological models of ***amorphous materials*** are well developed, they based on a combination of hard and soft areas random dense packing: this is close to the nanostructures. With regard to inorganic glasses with covalent bonds and random packing of atoms, these structures correspond to the model of random and continuous grid of atoms. All said models are characterized by a set of different size spheres, randomly packed to largest density.

They differ in the rules of packaging, in the interaction potentials, in the relaxation modes, etc. In many configurations of random dense packing the crystallographic structural elements are allocated, as well as the non-crystalline packing of clusters that illustrated by Bernal polyhedra, Fig.1.8.

As known, coordination number (CN) in crystals might be 4, 6, 8 and 12. In the amorphous metallic alloys coordination number for alloys of transition metals with copper remains only close to CN = 12 regardless of compound (in ideal model CN = 12). In reality, for example, in Ni-Li and Cu-Ti alloys average coordination number is 12.8. In the alloys of rare earth metals and transition metals, as usual, CN = 12, but in the amorphous alloys CN generally decreases. For example, in $DyFe_2$

alloy CN = 7.1 ± 1, while in the alloy $TbFe_2$ CN = 8.4 ± 1.8; at that, the environment of iron atoms is approximately same as in crystal. Thus, the short-range ordering in amorphous and in crystalline states of metallic alloys is different [2].

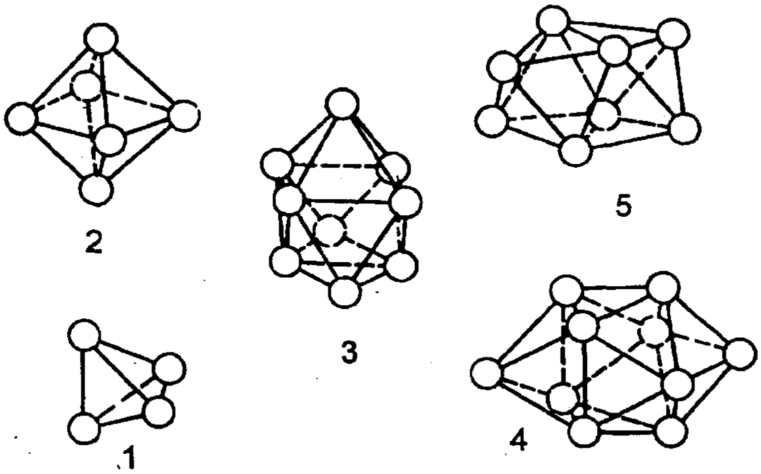
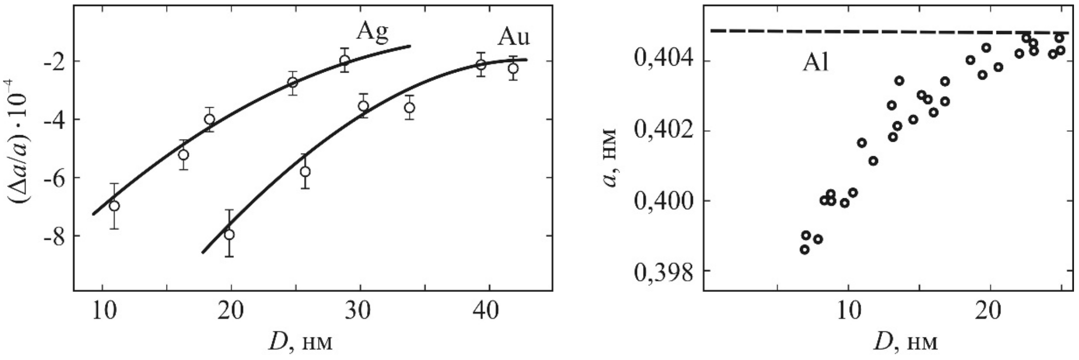


Fig. 1.8. Models of amorphous structures clusters: 1 – tetrahedron; 2 – octahedron; 3 – trigonal prism with three semi-octahedrons; 4 – Archimedes' antiprism with two semi-octahedrons; 5 – tetragonal dodecahedron

Consideration of the relative stability of various structural modifications showed that for clusters containing less than 150–300 atoms, icosahedral forms should be the most stable. Indeed, the existence of stable icosahedral metal particles smaller than 10 nm has been confirmed by numerous experiments. An increase in the number of atoms in the cluster leads to a rapid increase in the energy of elastic deformation, proportional to the volume; as a result, in a large-sized cluster, the increase in elastic energy exceeds the decrease in surface energy, which results in the destabilization of the icosahedral structure. Thus, there is some critical size above which icosahedral structures become less stable than the cubic or hexagonal structures characteristic of nanoparticles larger than 10 nm.

Lattice parametre of nanoclusters. The transition from massive crystals to nanoparticles is accompanied by the change in interatomic distances and periods of crystal lattices. It is important to find out whether crystal lattice periods decrease or increase with decreasing particle size and at what nanoparticle size this change becomes noticeable. The available experimental data are contradictory, and theoretical analysis does not make it possible to unequivocally state how the parameter of crystal lattice of a nanoparticle will change depending on its size. The fact is that both an increase and a decrease in the crystal lattice parameter are possible in the case of a decrease in the size of nanoparticles.

For both gold (Au) and silver (Ag), the distance between lattice atoms in nanoparticles decreases with decreasing particle size, Fig. 1.9a. This was established by the method of electron diffraction.



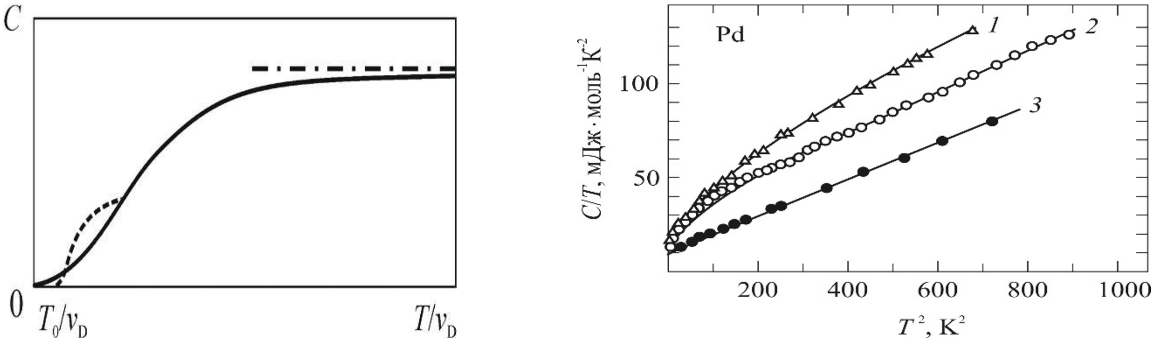
а *б*

Fig. 1.9. Relative change in lattice period δa/a from nanoparticles diameter D: a – gold and silver; b – aluminum

The effect of nanoparticle size on crystal lattice parameter was noted not only for metals, but also for compounds (for example, a decrease in the lattice period of sub-microcrystalline nitrides of titanium, zirconium, and niobium depending on the size of the particles). The most likely reason for the decrease in lattice period of small particles compared to massive substance is non-compensation of interatomic bonds of the surface atoms, in contrast to the atoms located inside the particle, and, as a result, the reduction of distances between atomic planes near the surface of a particle, that is, surface relaxation. Indeed, an atom in surface layer has fewer neighboring atoms than in bulk, and they are all located on one side of it. This disrupts the balance and symmetry in the distribution of forces and masses and leads to change in equilibrium interatomic distances, shear deformations, and smoothing of vertices and edges. However, sometimes there is not a decrease, but an increase in the nanoparticle lattice parameter. For example, a decrease in the size of Si particles from 10 to 3 nm is accompanied by the increase in lattice parameter by 1%. An increase in the CeO_2 lattice period was also found when the particle size decreased from 25 to 5 nm. However, it is possible that this increase in the lattice period is due to the adsorption of water.

Thus, experimental data on the influence of size effect on parameters of crystal lattice of nanoparticles are ambiguous. This ambiguity can be caused primarily by the adsorption of impurities or the different chemical composition of particles; another possible reason for the ambiguity of results is the structural transformations caused by the decrease in particle size.

Phonon spectrum and heat capacity of nanoclusters. The main reason for the change in the thermodynamic characteristics of a nanocrystal compared to the massive substance is a change in the form and boundaries of phonon spectrum, i.e. the change in function of frequency distribution of atomic vibrations. This is confirmed by the results of studying massive monocrystalline Si and nanopowder of the same Si by the inelastic scattering of slow neutrons. According to these studies, in the phonon spectrum of small particles, low-frequency modes of oscillations occur, which are not present in the spectra of massive crystals. In nanoparticles, only such waves can occur, the length of which does not exceed twice the largest size of the particle d, and therefore, from the side of low-frequency oscillations, the phonon spectrum is limited by some minimum frequency: $\omega_w \sim \upsilon_s/2d$, where υ_s is the speed of sound (in massive samples, there is no such limitation). The value of ω_w depends on the properties of substance, the shape and size of a particle. It can be expected that decreasing the particle size will shift the phonon spectrum towards high frequencies.



a *b*

Fig. 1.10. Temperature dependence of heat capacity C: a – solid line corresponds to Debye theory; the dash-dotted line is Dulong-Piti limit; the dashed curve shows deviation of heat capacity from Debye theory caused by quantum size effect of heat capacity of nanoparticles; b – heat capacities of palladium with diameter of 3 nm (1), 7 nm (2) and massive palladium (3)

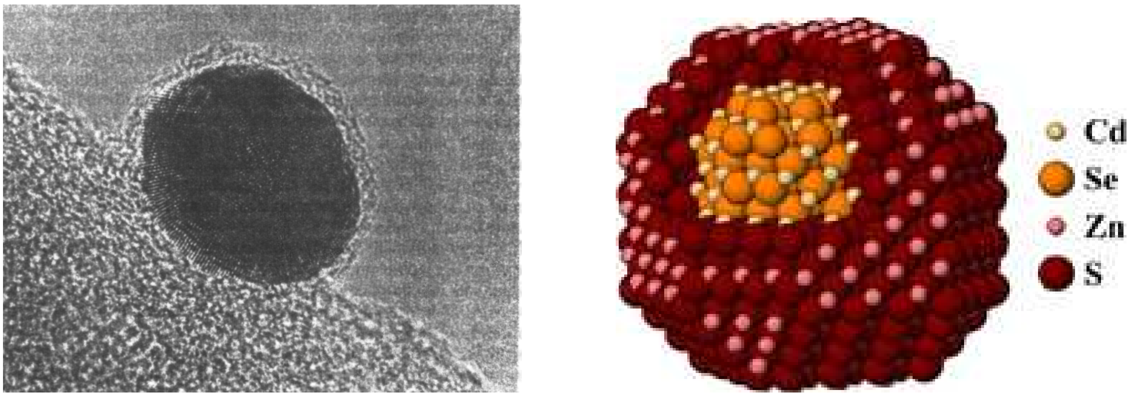
Features of vibrational spectrum of nanoparticles should primarily be affected by the heat capacity, Fig. 1.10. Experimental data on the heat capacity of nanopalladium are shown in Fig. 1.10*b*. The increase in the heat capacity of Pd nanoparticles compared to massive palladium in the interval $1.4\ \text{K} < T < 300\ \text{K}$ is entirely determined by the additional lattice contribution, since the electronic heat capacity, regardless of the size of particles, is described by usual linear law, and the value of coefficient of electronic heat capacity of nanoparticles is the same as that of massive palladium. It is also shown that the heat capacity of Cu nanoparticles is ~ 2 times greater than the heat capacity of massive copper up to temperature of 450 K. But during further temperature increase, Cu nanoparticles grow intensively and, accordingly, the heat capacity decreases to the value of the heat capacity of massive copper [2].

Optical properties of nanoclusters. In massive crystals, quanta of light falling on the crystal are partly reflected and partly passed through the crystal or absorbed. Light is almost completely reflected from metal samples, and light propagates almost without loss in dielectrics. Special optical properties are observed in semiconductors - in the frequency band in which the energy of light quanta becomes commensurate with or exceeds the width of the band gap.

In nanoclusters of metals and semiconductors, unlike their crystals, the properties of electrons cannot be described on the basis of the idea of a "gas of free electrons". In the small cluster, there can be no free movement of electrons, and therefore all changes that occur in the state of cluster electrons under the influence of external disturbances (for example, optical radiation) are not reduced to their movement inside the cluster, but to energy transitions between different quantum energy levels electrons

Thus, the scattering and absorption of light by nanoparticles compared to a macroscopic solid has a number of features. Size effects of optical properties are significant for such nanoparticles, the size of which is significantly smaller than the length of an optical wave, but does not exceed 10-15 nm.

Experimentally, these features are most clearly revealed in the case of large number of particles study. For this, nanoparticles must be placed in the transparent "matrix" - for example, in glass or in polymer, in the volume or film. Due to the specific optical properties of nanoparticles, such "solutions" (as well as granular films with nanoparticles) can have an intense color. The classic object of studying the optical properties of nanostructured metals in dispersed media is gold, Fig. 1.11*a*. Dispersed gold has been used for high-quality glass coloring for hundreds of years. Colloidal gold, capable of coloring the environment, has been studied since Faraday.



a *b*

Fig. 1.11. Optical properties: a – colloidal gold particle about 12 nm in size: b – model of heterostructural cluster composed of a CdSe core with an epitaxial coating with a ZnS shell.

Both in dispersed media and during light absorption by fine-grained metal films, absorption peaks appear in the visible part of a spectrum that are absent in massive metals. For example, granular films of gold particles with a diameter of 4 nm have a clearly defined absorption maximum in the range of 560 – 600 nm.

Absorption spectra of metal nanoparticles Ag, Cu, Mg, In, Li, Na, K also have maxima in the optical range.

The study of size effects on the optical and luminescent properties of semiconductor substances is of great interest, since optical absorption is one of the main methods of studying the band structure of semiconductors. Semiconductors are characterized by interband absorption of light. This absorption is due to the transition of electrons from the valence band to the conduction band. The absorption coefficient α for a massive semiconductor crystal depends on the difference between the light energy $h\nu$ and the width of the energy gap E_g (forbidden zone): $\alpha \sim (h\nu - E_g)^{1/2}$.

Characteristic features of the behavior of nanoscale structures are clearly revealed in their optical absorption and emission spectra. Due to peculiarities of energy structure of clusters, it can be expected that peculiarities of their optical properties will be manifested in selective absorption of light of certain frequencies. This absorption is caused by transitions of electrons from lower to higher energy levels, or in the discrete emission of light of certain frequencies, caused by reverse transitions of electrons from higher to lower energy levels. Therefore, electronic processes in low-dimensional systems are primarily studied using light absorption and emission methods. It is the optical and luminescent properties of nanocluster arrays that enable their practical use. For example, in nanophysics, one of the first nanoclusters observed were CdSe clusters of different colors. The optical wavelength (and fluorescence color) depends on the size of these clusters, Fig. 1.11b. In the most studied semiconductor CdSe, the blue shift of the absorption band begins with nanoparticles 10-12 nm in size.

Absorption of photons generates electron-hole pairs in semiconductor clusters, and their recombination is accompanied by fluorescence. In other words, a decrease in the size of semiconductor nanoparticles is accompanied by a shift of the absorption band to the high-frequency region. A manifestation of this effect is a blue (blue) shift of the absorption band of semiconductor nanoparticles when their size decreases. Thus, in CdSe clusters, fluorescence covers almost the entire range of visible light (wavelengths 400–700 nm). But in other chalcogenides, depending on the size and chemical composition of the clusters, fluorescence is observed both in the ultraviolet and in the infrared band of the spectrum. The ZnS, CdS and ZnSe clusters fluoresce in the ultraviolet band of the spectrum, CdSe and CdTe clusters - in the visible band, and PbS, PbSe and PbTe clusters - in the infrared band (700–3000 nm). In addition, cluster heterostructures with exceptional optical properties can be created from chalcogenides. Modern technologies make it possible to build a shell from a wider bandgap semiconductor on the cluster core, which consists of a narrowband semiconductor, for example, a ZnS shell is built on a CdSe core (Fig. 1.11b). This makes it possible to obtain materials with a continuous absorption spectrum (fluorescence excitation) in a wide range of wavelengths, which depends on the size of the nanoclusters. Such clusters are characterized by increased brightness and greater photostability compared to traditional fluorophores.

Peculiarities of the behavior of light-generated charge carriers (electrons and holes) in semiconductors are caused by the emergence of their bound states - excitons - as a result of the Coulomb attraction between an electron and a hole. Recall that an exciton is such a bound state of an electron and a hole that arises as a result of the Coulomb attraction between them and exists in the crystal as a single entity. It follows from this that interband absorption processes in nanoclusters at the temperatures at which their quantum properties are revealed must have an excitonic character. Intense absorption of light caused by the formation of excitons is observed at lower energies (ie, lower frequencies of light) than interband absorption, because the binding energy of the exciton is small compared to E_g. Therefore, on the energy scale, exciton absorption is placed close to the intrinsic absorption of light by a semiconductor, but differs from it by a lower absorption onset frequency. Interband absorption in a semiconductor is described by a smooth dependence of the absorption coefficient on the energy of a light quantum, while exciton absorption begins with a sharp peak-like growth at energies lower than the threshold value of the interband absorption energy. Intrinsic absorption of light is accompanied by the appearance and sharp increase of photoconductivity, while no photoconductivity is observed during exciton absorption of light [2].

Thus, electronic excitation of semiconductor crystals leads to the formation of a weakly bound electron-hole pair (exciton). The exciton delocalization radius can be considered analogous to the Bohr radius of atoms. But the Bohr radius of the exciton is much larger, it can significantly exceed the period of the semiconductor crystal lattice. Reducing a semiconductor crystal to the size of a nanocluster, comparable to the size of an exciton, significantly affects its optical properties. In other words, the specific properties of semiconductor nanoparticles are due to the fact that the size of nanoparticles can be compared with the size of the Bohr radius of excitons in a macroscopic crystal. In semiconductors, the Bohr radius of an exciton can vary widely – from 0.7 nm for a CuCl crystal to 10 nm for a GaAs crystal. From theoretical calculations, it follows that with a decrease in the size of nanoparticles, the lines of the optical spectrum should shift to the high-frequency region. The energy of electronic excitation of an isolated molecule is usually significantly greater than the energy of the interband transition (gap width) in a macroscopic semiconductor. Therefore, in the case of the transition from a crystal to a molecule, that is, in the case of a particle reduction, there must be a range of such sizes in which the energy of electronic excitation will smoothly change from a smaller value to a larger one. This size range corresponds to the size of nanoclusters, which can be considered as one example of quantum dots.

The unique optical properties of semiconductor nanoclusters, like other quantum dots, are promising for use in medicine as optical sensors, fluorescent markers, photosensitizers, and in optoelectronics for the production of photodetectors operating in the infrared frequency band, efficient solar cells, superminiature LEDs, light emitters and nonlinear optical devices

1.4 Quantum-dimensional effects

Strong dependence of properties of a solid on its size is observed in many cases. For example, in piezoelectrics the frequency of piezoelectric resonance and magnitude of dielectric constant depend on the size of a sample. Just like that, the magnetic permeability of ferromagnetic films and the dielectric permittivity of ferroelectric films strongly dependent on their thickness, etc.

As for the electrical conductivity of low dimensional nanosized materials, in addition to quantization effect of electronic energy spectrum, the wave properties of particles begin to affect. The coherence length of electronic wave in a solid at normal temperature has a magnitude of several nanometers. Therefore, at distances of 1–10 nm the wave properties of electrons begin to be detected. This is expressed by the fact that when a substance is taken in small quantities, it can not always be clearly attributed to isolators, conductors, or semiconductors. For example, some chemical elements taken in an amount of, say, 20, 50 and 100 atoms will consistently pass the stages of isolator, semiconductor and conductor, respectively [3].

Dimensional effect occurs if the length of a body at least in one dimension becomes comparable with some critical magnitude l_{cr}. For classical dimensional effects l_{cr} is the classical value, such as the diffusion length, the length of the free run of electrons, etc. During charge carriers movement or oscillation in the semiconductor nanostructures the wave nature of electrons and the discreteness of energy spectrum vividly manifest itself. There is a quantum mode of transfer of charge carriers, in contrast to the classical regime when free path of electrons is much smaller than the size of a system and electrons are regarded as classical charged particles.

This Section deals with the basic fundamental physical phenomena that determine transfer of charge carriers in the nanosized structures. Since the size of nanostructures is comparable to free path of electrons, charge carriers can freely pass through nanostructure without scattering on defects, impurities, phonons, etc. In such structures the phase of non-interacting electron waves is maintained throughout the path and therefore effects of phase interference are observed.

Recall that the basis of quantum mechanics is based on the fact that there is light under the (corpuscular-hvil) nature. Photon momentum modulus $p = |\mathrm{p}|$ you can see through $p = h/\lambda$, where $\lambda = c/\nu$, c is the light velocity, ν is the frequency, found for a given quantum of light with energy E from Planck's formula: $E = h\nu$. The physical dimension of Planck's constant h means "moment of motion" = energy×time = length×momentum; i.e.. the action is the moment of amount of movement - a physical quantity that has the dimension of the product of energy by time ($E \times t$). It is one of the most important dynamic characteristics of the movement of particles and their systems - both in classical and quantum mechanics. That is why, the Planck's constant h (or $\hbar = h/2\pi$) belongs to the fundamental physical constants in the same way as Boltzmann's constant k_B, like the electron charge e and the electron mass m_e. Planck's constant was accepted by physics in the conditions of rejection of classical ideas - together with quantum (wave) mechanics. Note that a formal transition from quantum mechanics to the classical Newtonian mechanics can always be made if $h = 0$. Planck's constant is associated with a wide range of physical phenomena in the microcosm, for which the quantization of quantities with the dimension of action is essential.

In quantum mechanics, the formula $p = h/\lambda$ is usually written in vector form: $\boldsymbol{p} = \hbar\boldsymbol{k}$, where $|k| = 2\pi/\lambda$. The quantity k, called the wave vector, is widely used in quantum mechanics. The direction of the wave vector coincides with the direction of the momentum vector p of the photon, that is, the wave vector is directed in the direction of the propagation of the light wave. The modulus of the wave vector $|k|$ is called the wave number.

De Broglie established that wave properties are inherent not only to photons, but also to any particles of matter. It is very important for nanoelectronics that the electron has a wave nature. The wavelength corresponding to any moving particle is called the de Broglie wave and is determined by the formula: $\lambda = h/p = h/(mv)$, where

m is the mass of the particle and υ is its speed. The wave properties of *microparticle* make it impossible to describe its movement by simultaneously specifying precise values of coordinates and velocities. This fact is mathematically described by the Heisenberg uncertainty ratio:

$$\Delta p_x \Delta x \geq \hbar/2; \quad \Delta p_y \Delta y \geq \hbar/2; \quad \Delta p_z \Delta z \geq \hbar/2,$$

where Δp_x, Δp_y, and Δp_z are the uncertainty of the particle momentum components along the x, y, and z axes, respectively; Δx, Δy and Δz – uncertainty of particle coordinate values at the same moment in time. It should be noted that for combinations of the type $\Delta p_x \Delta y$, $\Delta p_y \Delta x$, $\Delta p_z \Delta y$, etc. the ratio of uncertainties does not apply - the uncertainties of the values of coordinates and components of momentum that are not conjugated to each other can independently have any values. This feature of the uncertainty ratio *acquires considerable significance* for the analysis of the behavior of electrons in nanoscale structures.

The ratio of uncertainties is also valid for energy and time variables: $\Delta E \Delta t \geq \hbar/2$, where ΔE is the uncertainty of the energy of the system in the quantum state; Δt is the time the system stays in this state. The ratio of uncertainties belongs to the fundamental provisions of physics; it has comprehensive experimental confirmation. The de Broglie wavelength □ for an electron with an effective mass m* and moving in a crystal at a speed υ is:

$$\lambda = h/p = h/m^*\upsilon = h\,(2m^*E_{\text{к}})^{-1/2}$$

where $p = m^*\upsilon$ – impulse; E_k is kinetic energy. Thus, *the shorter the effective mass of the electron, the greater the de Broglie wavelength* [1]

In most ***metals***, the effective mass of electrons is almost the same as in a vacuum: $m^* \sim m_e$, therefore, for metals, the de Broglie wavelength of an electron is small: $\lambda \leq 1$ nm. This value is close to the crystal lattice parameter. Therefore, it is almost impossible to observe quantum nanoscale effects in metals under normal conditions (at temperature of about 300 K), but it is quite possible at a very low temperature, when the de Broglie wavelength becomes about 10 times longer.

In *semiconductors*, the effective mass of an electron is smaller than in metals. So, at a temperature of 4 K, for silicon $m^* = 0{,}2m_e$ and $\lambda \approx 500$ nm, and for gallium arsenide $m^* = 0{,}07m_e$ and $\lambda \approx 5000$ nm. At room temperature (about 300 K) for silicon $m^* = 0{,}9m_e$ and, accordingly, $\lambda = 8$ nm; for gallium arsenide $m^* = 0{,}07m_e$ and λ=30 nm.

Thus, since the de Broglie wavelength in semiconductors is nanoscale, it is technologically easier to create conditions for the manifestation of quantum-dimensional effects in them.

Potential wells, barriers and tunneling. To analyze the properties of quantum systems, their energy models should be used. Nanoparticles in their discrete spectrum can be compared with atoms. Based on known energy distribution, the method of potential curves allows determine dynamic parameters of moving particle.

According to classical mechanics, the particle can overcome the potential barrier only if its energy exceeds the potential energy on the top of a barrier. Quantum particle behaves completely differently: the different from zero probability exists to penetrate the barrier, even if energy of quantum particle is less than the height of potential barrier. Such quantum-mechanical effect is the isoenergetic tunneling.

From the point of view of classical physics, in case of a tunneling effect, the law of energy conservation is violated. But for quantum physics of tunneling effect, it is possible to overcome the "deficit" of particle energy over a short time $\Delta t = \hbar/(2\Delta E)$ in accordance with the uncertainty relation. Therefore, in terms of quantum physics, if during this time the particle can tunnel through the barrier, then law of conservation of energy is not violated. The thing is that after the tunneling the particle retains its energy. The tunneling effect lies at the basis of tunnel diodes operation and is widely used in other nanoelectronic devices.

Another feature of a quantum particle behavior in the potential well of nano- and atomic size is the discreteness of energy spectrum. Exactly a discreteness of energy spectrum of electrons is the basis of functioning of many nanoelectronic structures. The configurations of real potential wells and barriers in the “micro-world” depend on the geometric features of fields that form of these wells. Behavior of micro-particle in potential well can be determined by Schrödinger equation solving under corresponding initial conditions. This is differential equation: for its solution it is necessary to know how potential energy U of micro-particles depends on coordinates, that is, need to set the function U(x, y, z). Here and thereafter it will be assumed that this function does not depend on time (since micro-particle is in the stationary state).

To find out main features of micro-particle behavior in the potential well, it is enough to consider the one-dimensional case $U(x)$ and the potential well of rectangular shape (Fig. 8.40, a). The width of potential well is denoted by l, and its depth is U^0. In this model the width of barriers that limits potential well to the right and to the left is infinite. The depth of well U^0 can vary from a finite value to infinity (if the well would be considered as indefinitely deep).

The solution of Schrödinger equation (result of which is graphically illustrates in Fig. 1,12) enables to determine the energy spectrum of micro-particle, that is, a complete set of its energy values E and the wave function $\Psi(x)$, whose module square $|\Psi(x)|^2$ is the probability density of finding micro-particle at point x.

It can also be shown that on the width of well l it is possible to put the integer number of de Broglie half-waves: $l \approx n(\lambda/2)$. For the infinitely deep well the wave function is expressed in the terms of trigonometric functions: through cosines in case of odd n ($n = 1$, 3, 5) and sinus in case of even n (these solutions in Fig. 1.12*b* are shown by the dashed curves). It can be seen from the figure that in this case the amplitude of de Broglie wave at points $x = \pm 1/2$ vanishes. So, when $U^0 \to \infty$, the micro-particle can neither penetrate inside the barrier nor go beyond the boundary of the well.

However, if the depth of well is finite, then the amplitude of de Broglie wave at the points $x = \pm 1/2$ does not vanish for any n and has continuation beyond the boundary of barrier.

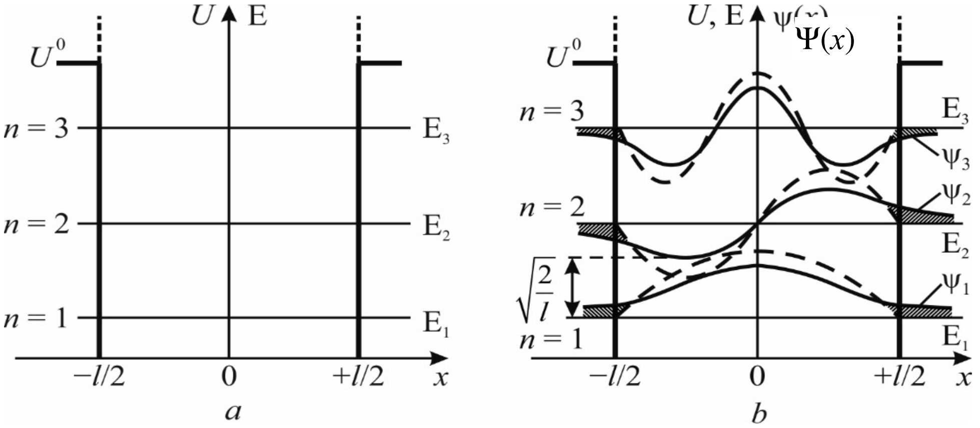


Fig. 1.12. One-dimensional potential well: a – energy spectrum of micro-particle in potential well; b – wave functions $\Psi(x)$ for three states of micro-particles ($n = 1, 2, 3$) in potential well (dotted line shows distribution function in case of infinitely deep of well)

This important result is shown in Fig. 1.12*b* by solid curves in the shaded areas. That is, micro-particle in the potential well of ultimate depth U^0 can penetrate beyond the boundary of barrier for energies E less than U^0, which contradicts the law of energy conservation of classical physics and never observed in the “macro-world”. In addition, from Fig. 1.12*b*, which shows the probability density for three different values of n, implies that the energy spectrum of quantum particle is discrete, with its minimal energy not equal to zero ($E_1 > 0$). This energy is called zero energy and usually is denoted as E_0. Zero energy is peculiar to any quantum systems: physical vacuum, quarks in hadrons, nucleons in atomic nuclei, electrons in atoms, atoms in molecules and crystals. The probability to find micro-particle at different points inside the well, as seen from Fig. 1.13, greatly varies. There are some points, where probability of "visiting" by particle shows the maximum: they are called the parochial (x_p). There are also points in which the particle never seen, these are nodes (x_p). Such behavior is not a characteristic of macro-particles. It should be noted that the probability of penetration by micro-particle beyond boundary of barrier ($x = \pm 1/2$) is not equal zero, but it only gradually decreases with the increasing distance from boundaries of barrier (shaded areas in Fig. 1.13).

The most important result is that if the barrier width is not infinite, then probability of its penetration by microparticle beyond boundary of barrier (tunneling effect) is different from zero.

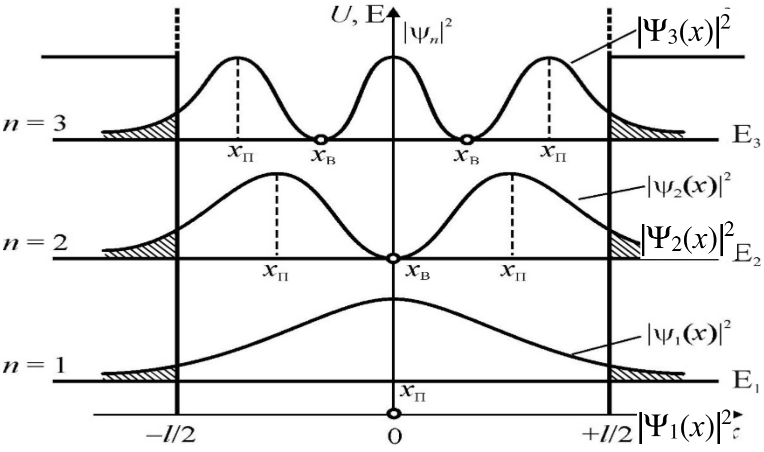


Fig. 1.13. Probability density $|\Psi(x)|^2$ to find micro-particle at different points x of potential well of ultimate depth

Quantum dimensional effects in the electronic structures are observed when the role of critical length l_{cr} is played by electron de Broglie wavelength (λ_e) when the size of a structure at least in one dimension has the order of λ_e. Thus, the quantum-dimensional effects are conditioned by wave nature of electrons. In the nanosized regions behavior of electrons is determined by the reflection of electronic waves from the boundaries of such areas, as well as the interference of electronic waves or the passage of waves through potential barriers. The quantization of the energy of electrons might be spatially limited in their displacements, or the passage of electrons through nanometer dielectric layers is quantized, or the electrical resistance of nanowires has quantum peculiarities, and others.

De Broglie wavelength for electron that has effective mass m^* and moves in crystal with velocity υ has following meanings: $\lambda_e = \hbar/p = \hbar/m^*\upsilon$, where $p = m^*\upsilon$ is the impulse. Thus, de Broglie wavelength the greater the less effective electron mass. In most metals it is almost same as in vacuum:$m_{ef} \sim m_e$ so that de Broglie wavelength is relatively small. However, in some semiconductors the effective mass of electron can vary widely. At room temperatures (~ 300 K) in silicon $m_{ef} = 0.9\ \mathrm{m_e}$ and $\lambda_e = 8$ nm, in gallium arsenide $m_{ef} = 0.07m_e$ and $\lambda_e = 30$ nm. Thus, in semiconductors the size of de Broglie wave has a nanoscale, and hence the quantum-dimensional effects are technologically easier to implement just in semiconductors.

Density of states g(E) determines the number of quantum states of electrons per unit of volume (or area, or length, depending on dimension of object) referenced to single energy interval. According to this definition, the density of states is equal to d*n*(*E*), i.e., number of states in the energy range from *E* to *E* + d*E*:

$$g(E) = \mathrm{d}n(E)/\mathrm{d}E.$$

The knowledge of density of states $g(E)$ and probability of their filling by electrons w(E) allows determine the distribution of electrons of a system in quantum states and to describe many electrical, optical and some other properties of a system. The electrons are characterized by a half-integer spin, therefore the probability of their filling quantum states is determined by statistics of Fermi-Dirac, which is based on Pauli principle.

Energy spectrum of electrons E(k) as the density of their quantum states are most important characteristics of a quantum object, which determine its electronic properties and the response to external influences.

The energy spectrum characterizes the dependence of energy of a particle on its impulse: E(p) or, equivalently, the energy dependence on wave vector E(k), since the impulse and wave vector are bound by simple relation $p = \hbar k$ (module of wave vector is determined by inverse wavelength: $k = 2\pi/\lambda$). The energy spectrum represents a set of possible values of particle's energy in given conditions. If energy is quantized, then energy spectrum is called the discrete (quantum), but if energy can accept continuous series of values, then the spectrum is called the continuous.

"Infinite" crystal quantum properties are characterized by three-dimensional (3D) long-range ordering of atoms. From the point of view of nanophysics, even a crystal having one micron sizes already looks "infinite", since in all directions its regular crystalline lattice consists of thousands of atoms being many times larger than the de Broglie wave

Metals and semiconductors crystals are filled with three-dimensional 3D-electronic gas, in which electrons can move freely in any direction. The energy of electron in the 3D gas:

$$\mathrm{E} = \frac{\left(m_{ef}\upsilon\right)^2}{2} = \frac{p^2}{2m_{ef}} = \frac{\left(p_x^2 + p_y^2 + p_z^2\right)}{2m_{ef}} = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m_{ef}}$$

where p and k are quasi-impulse and quasi-vector of electron, respectively, and m_{ef} is electron's effective mass (for simplicity it is considered as isotropic). The spectral dependence of E(k) looks like quasi-continuous, since the energy levels are as much as electrons are held in the 3D crystal ($10^{14}…10^{22}$ cm^{-3}).

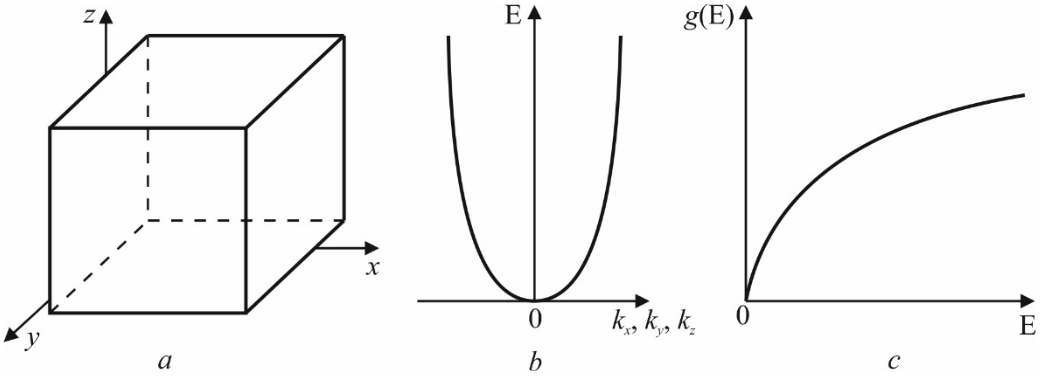


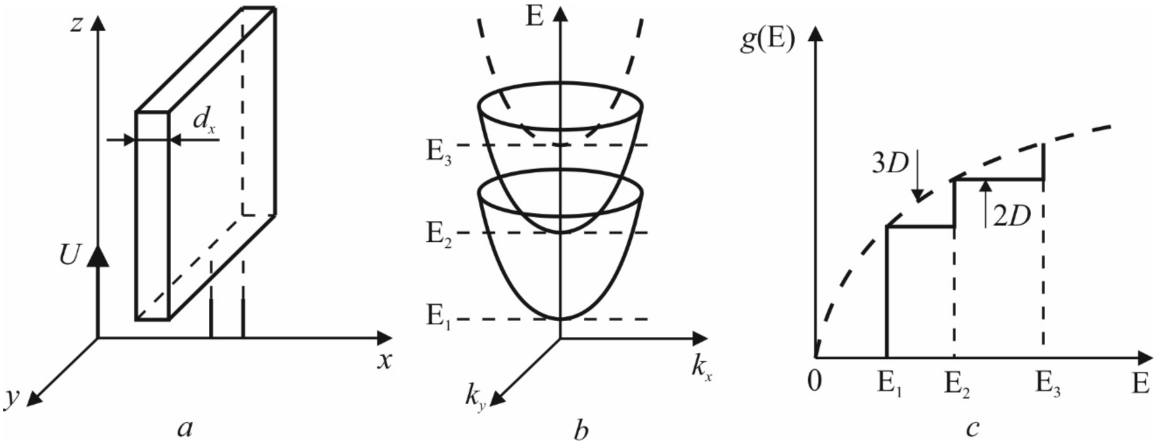
Fig. 1.14. Electronic spectrum of unlimited size crystal: a – model of sample; b – dependence of electron energy on quasi-vector components; c – dependence of quantum states density g(E) on electrons energy

In Fig. 1.14*b* the dependence of energy on wave vector components near the bottom of conduction band is given, and in Fig. 1.14*c* the density of quantum states of electrons $g(E)$ for unbounded (3D) crystal is described by parabola: $g(E) \sim E^{1/2}$.

Near the bottom of conduction band the density of states is small, but it gradually increases with the growth of E, reaching saturation. From Fig. 1.14*b,* it is evident that in limits of same band the functions $E(k)$ and $g(E)$ are quasi-continuous, and therefore properties of 3D crystals under the influence of fields change continuously.

Quantum well corresponds to two-dimensional (2D) object. Usually this is a thin layer of crystal which thickness d is commensurate with de Broglie wavelength ($d \sim \lambda$). The system of electrons in such a layer is called the two-dimensional (or 2D) electronic gas. Fragment of such a layer is presented in Fig. 1.15*a*. The motion of electrons in this layer is limited by the segment d_x in the direction x but is not limited in the directions y and z.

Moving in the x direction, the electron is not able to leave thin layer, since its output work (equal, for example, in aluminum arsenide ~ 4.5 eV) is much greater than thermal energy (0.026 eV at room temperature). Therefore, the motion in x direction is legitimately regarded as a movement in the one-dimensional deep enough rectangular potential well with the width d_x, Fig. 1.15*a*. The energy of such motion is quantized and characterized by quantum number $n = 1, 2, 3,…$



a *b* *c*

Fig. 1.15. Two-dimensional (2D) nano-object (thin layer): a – schematic representation of thin layer limited along; x-axis; b – potential holes for electrons in this layer; c – dependence of state density on energy in case of infinitely deep quantum well

If the quantum well would be infinitely deep, then on its width d_x the integer quantity of half-wave $\lambda_n/2$ will be spaced. This means that only those states of electrons motion would be stationary, which will correspond to standing wave formed by de Broglie waves falling and reflected from the walls of a well (dotted curves in Fig. 1.15). The values of E_n are called quantum-dimensional levels [3].

The motion energy along the *y* and *z* is not quantized and is determined by same expressions as for free particle (or for volume). Therefore, the total electron energy, taking into account that effective mass of electron m_{ef} is the same for movements in all directions, can be represented as

$$\mathrm{E} = \frac{\hbar^2\left(k_y^2 + k_z^2\right)}{2m_{ef}} + \mathrm{E}_n = \frac{\hbar^2\left(k_y^2 + k_z^2\right)}{2m_{ef}} + \frac{\hbar^2\pi^2 n^2}{2m_{ef} d_x^2}$$

where the quantum number $n = 1, 2, 3, \ldots.$

Consequently, the energy spectrum of electron in a quantum well of two-dimensional nano-object will be discrete-continuous. Each dimensional level of E_n corresponds to a set of possible energy values due to free motion of electron along the axes *y* and *z*. This set of energies *E* is the two-dimensional subbands of dimensional quantization. The dependences $E(k_y,k_z)$ and $g(E)$ are shown in Fig. 1.15, *b, c*.

The graph of $E(k_y,k_z)$ dependences is the paraboloids system; the bottom of *n*-th paraboloid corresponds to the level $E = E_n$. The dependence of $g(E)$ is straightforward. Each dimensional subband makes equal contribution $m_{ef}/\pi\hbar^2$ to the density of states. Strictly speaking, the model of infinitely deep rectangular potential well is valid only for the motion of electron in the "isolated" thin film with nanosized thickness *d*. Such separate model – flat-parallel film of nanometer thickness – is difficult to implement. In practice, in the nano-sized structures such nano-layers are formed inside the crystal, so that charge carriers movement is limited in one dimension; therefore, it is possible to assume that these carriers are in the one-dimensional potential well. An example is the electrons in the nanometer layer of narrow-band semiconductor between two layers of broadband semiconductor.

Practical examples of quantum wells with 2D electronic gas may be conductive channels in the unipolar transistors (metallic oxide-semiconductor structures on silicon) and narrow-band layers in heterostructures from compounds $A^{III}B^{V}$ (required for injection lasers). Systems of closely spaced equilibrium quantum wells, which make electronic tunneling possible, form the superlattices that are the heterostructures made of two or more different materials. In these heterostructures an important role belongs to the transition layer, that is, the boundary between two materials

All elemental materials of which semiconductor heterostructures are made (Zn, Cd, Hg, Al, Ga, In, Si, Ge, P, As, Sb, S, Se, Ti, Ti) are located in the central part of the Periodic Table Elements and belong to II–VI groups. In the middle there is a silicon, which in the technology of electronic materials occupies the same important place as the steel in manufacture of structural materials. In addition to silicon, electronics often deal with semiconductor $A^{III}B^{V}$ compounds and their solid solutions, as well as with $A^{II}B^{VI}$ compounds. Of the compounds of the type $A^{III}B^{V}$ most often used the GaAs (gallium arsenide) that forms solid solutions $Al_xGa_{1-x}As$. The use of such solid solutions allows creation of heterostructures with a continuous (rather than abrupt) change in the relative content of elements of group III. In such heterostructures the width of the bandgap also changes continuously.

For the manufacture of heterostructures, it is very important to reconcile the parameters of crystalline lattices of two contacting materials. If two materials that have different permanent of crystal lattices are grown on one another, then, with increasing thickness of layers, large mechanical stresses and deformations can occur in area of the interface that can cause microcracks occurrence in layers. Mechanical stresses and deformations appear irrespective of whether the transition between two layers is smooth or not. In order to reduce deformations, the permanent gratings of two materials must differ at least. That is why, in the application of heterostructures the solid solutions of AlAs-GaAs system are most often used, since aluminum and gallium arsenides have almost identical lattice parameters. In this case, GaAs in a form of single crystals is the ideal substrate for heterostructures growing. Another natural substrate is the indium phosphide, InP, used in the combination with solid solutions of GaAs-InAs, AlAs-AlSb and other semiconductors of $A^{III}B^{V}$ type.

The progress in the creation of thin-layer heterostructures is due to the emergence of practical technologies for the growth of thin layers by methods of molecular beam epitaxy (MBE), metal-organic vapor phase epitaxy (MOVPE) and liquid phase epitaxy. These methods provide opportunity to grow heterostructures with a very sharp boundary [3].

The quantum wire (quantum thread) is a one-dimensional (1D) nano-object. The motion of the electrons is limited along the axes x and z by sizes d_x and d_z, respectively, but not limited along the axis y (Fig. 1,16). Square cross section of quantum wire is only a comfortable model for calculation but does not violate the generality of reasoning. It is important that potential well for free electrons in a quantum wire (thread) is two-dimensional.

The motion of electron is associated with the axes y but its energy must be quantized in one-dimensional potential wells d_x and d_z. The total electron energy is

$$\mathrm{E} = \frac{\hbar^2 k_y^2}{2m_{ef}} + \mathrm{E}_{mn} = \frac{\hbar^2 k_y^2}{2m_{ef}} + \frac{\hbar^2 \pi^2 n^2}{2m_{ef} d_x^2} + \frac{\hbar^2 \pi^2 m^2}{2m_{ef} d_z^2}$$

where $m, n = 1, 2, 3, \ldots$ and E_{mn} is the energy of dimensional levels. The position of each of them depends on two quantum numbers m and n and on the quantities d_x and d_z while in the direction of wire (y) spectrum is continuous. The conduction band in the quantum wire is divided into one-dimensional subbands, Fig. 1.16*b*. The density of states per unit length g(E) has a series of sharp peaks, Fig. 1.16*c* corresponding to dimensional levels. This means that most electrons in subbands have energy near corresponding dimensional level.

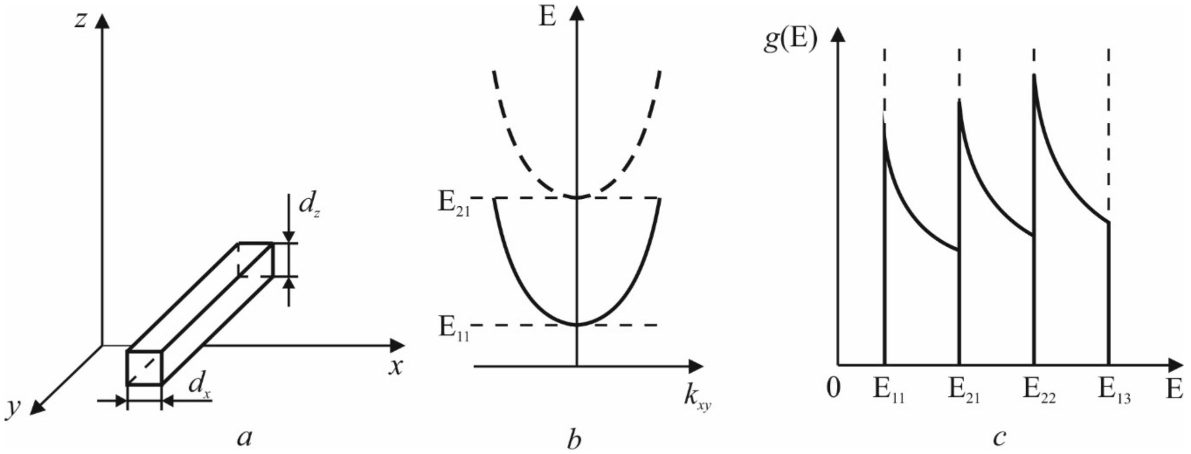


Fig. 1.16 .One-dimensional (1D) nano-object (quantum wire): a – model representation; b – energy dependence on wave vector; c – density of states dependence on energy

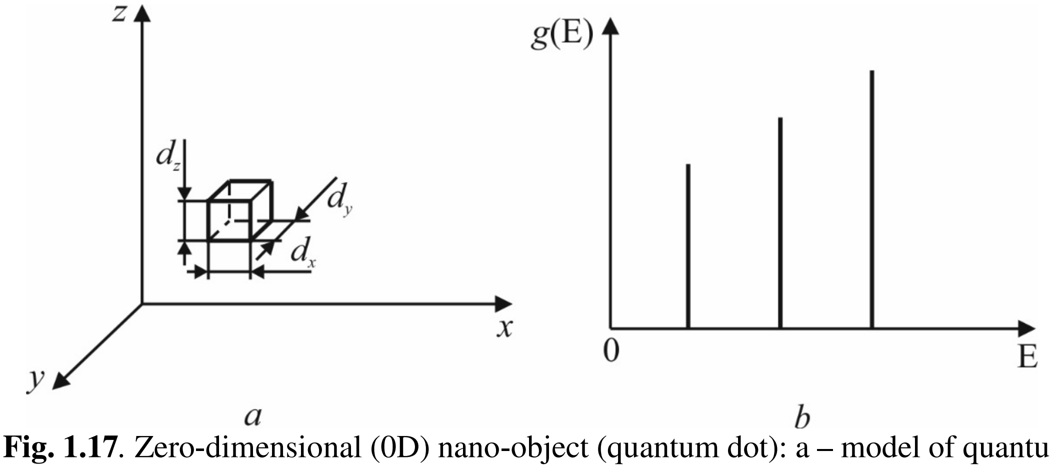
Most methods for producing quantum wires are based on the fact that in a system with two-dimensional electronic gas (usually on basis of heterostructure) by one or another technological way the motion of electrons in one of directions is limited. The conductivity of quantum wires can have important features. The most interesting case is short wire with a length that is less than the length of free run of electrons (the latter is determined by scattering on impurities and defects of wire). In this case, the electron, having flown from one contact of a quantum wire reaches to another contact without collisions, like a projectile released from a cannon. Such analogy has led to the consideration of structures in which there are no collisions of electrons, which are often referred to as ballistic ones.

Quantum dot is zero-dimensional (0D) nano-object, where the motion of electrons is limited in all three dimensions: *x, y, z*. Figure 1,17*a* shows a convenient model for calculations; in fact, the shape of quantum dot is usually different from cubic. Potential well for a quantum dot is a three-dimensional. The energy of free electrons should be quantized for movements in all three dimensions. The energy spectrum of electrons in quantum dot is quite discrete, as in a separate atom. Energy is defined by the expression:

$$E = \frac{\hbar^2 \pi^2 l^2}{2 m_{ef} d_x^2} + \frac{\hbar^2 \pi^2 n^2}{2 m_{ef} d_y^2} + \frac{\hbar^2 \pi^2 m^2}{2 m_{ef} d_z^2}$$

where $l, m, n = 1, 2, 3, \ldots$, while d_x, d_y, d_z are dimensions of the dot in three directions. The energy spectrum of electrons consists of separate dimensional levels of E_{lmn}, which resembles the spectrum of isolated atom. The energy E_{lmn} depends on three quantum numbers l, m, n and sizes d_x, d_y, d_z. The graph of the density of states $g(E)$ for the quantum dot has a type of delta function: $g(E) = \infty$, if $E = E_{lmn}$ (E coincides with dimensional level) and $g(E) = 0$, if $E \neq E_{lmn}$ (i.e., E lies in the gap between dimensional levels).

As example of quantum dots the nanocrystals can serve, grown on the surface of epitaxial layer of another material. In the Introduction to this book one quantum dot is shown (Fig. I.5), the islet from Ge atom is grown on Si surface while its image is obtained by atomic-force microscopy.



a *b*

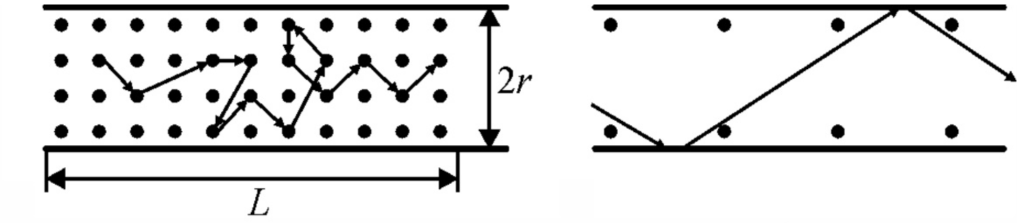
Fig. 1.17. Zero-dimensional (0D) nano-object (quantum dot): a – model of quantum dot; b – density of states dependence on energy

Historically, first studied quantum dots were microcrystals of cadmium selenide (CdSe). Electrons in such microcrystal are in three-dimensional potential well so that they have several stationary levels of energy with a characteristic distance between them (exact expression for energy levels depends on shape of quantum dot). While electrons make transitions between the energy levels of a quantum dot, the photons can emit, similarly to transition of electron between the energy levels of an atom. It is possible also to arouse ("throw") the electron into the highest energy level and obtain the radiation from transition between levels (luminescence). In this case, unlike actual atoms, the frequencies of transitions are easy to control, changing size of a microcrystal. Once again note that observations of cadmium selenide nanoclusters ("microcrystals") luminescence served as the first opening of quantum dots.

The length of optical wave in CdSe clusters (and fluorescence color) depends on the size of these clusters. It is determined that fluorescence of cadmium selenide nanoclusters corresponds: for size of ~ 400 nm – purple; ~450 nm – blue; ~500 nm – green; ~600 nm – yellow; ~700 nm – red. Observed blue shift of absorption band begins with nanoparticles of 10–12 nm in size. In the semiconductor clusters absorption of photons generates electron-hole pairs while their recombination is accompanied by fluorescence. In other words, decrease in size of semiconductor nanoparticles is accompanied by a shift in absorption band in the high-frequency region.

At present, many experiments are devoted to quantum dots formed in two-dimensional electronic gas. In two-dimensional electronic gas electrons motion perpendicularly to the plane is limited, so region on plane can be isolated by means of gate metallic electrodes superimposed on heterostructure. Quantum dots in the two-dimensional electronic gas can be connected by the tunnel contacts to other regions of the two-dimensional gas, and electrical conductivity through a quantum dot can be studied.

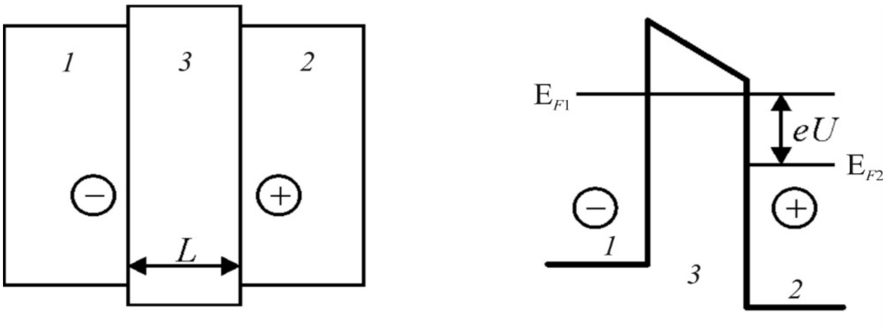
Ballistic conductivity of nanoscale conductors. The conductance (G) of ordinary wire with a circular cross section equals to $G = 1/R = \sigma S/L$, where $S = \pi r^2$ is cross-sectional area, L is length of wire, r is its radius and σ is specific electrical conductivity. This formula is valid, if r and L are much greater than the mean free path of electrons λ_e. In these conditions, the motion of electron in the conductor has a diffusive character, and trajectory of its motion is the broken line, Fig. 1.18*a*.



a *b*

Fig. 1.18. Schematic representation of diffusion type (a) and ballistic type (b) electron motion in conductor

If $\lambda_B > L$ and $\lambda_e > r$, Fig. 1.18*b*), then the electron flies from one contact to another practically without collision with atoms of crystalline lattices. Such a mode of movement is called ballistic. The moving electron does not feel resistance to its motion in conductor's volume [3].



a *b*

Fig. 1.19. Spatial (a) and energy (b) presentation of ballistic conductor (3) and contacts to it

In Fig. 1.19*a* the ballistic conductor 3 with quantum-sized diameter is placed between two metal contacts 1 and 2. Suppose that temperature is of the order of several degrees Kelvin and all electrons in contacts on energy diagram of Fig. 1.19*b* are located below Fermi levels E_{F1} and E_{F2}. If the potential U is applied between the contacts, then energy levels of metal *2* are reduced by a value of eU with respect to levels of metal *1*. In this case $E_{F1} - E_{F2} = eU$. The current can be generated only by electrons that have energy in the range from E_{F1} to E_{F2}. It is just these electrons that from contact 1 that have the ability to move to free levels of contact *2*.

If conductor (or semiconductor) 3 is characterized by N dimensional subzones, and it is a ballistic (that is, it has quantum-dimensional section S) then its electrons are located in the dimensional subzones. Only those electrons of sub-regions can participate in the transfer of a current that are located in the range from E_{F1} to E_{F2},. In this case the conductance is $G = 2e^2N/h$, while the resistance is $R = h/2e^2N$.

Thus, unlike the classical wire, the resistance of ballistic quantum wire does not depend on its length L. The number N is determined by a distance between subzones, and this distance increases when the intersection of wire S decreases. If one gradually reduces the diameter of a wire, then from the interval E_{F1}—E_{F2} will be in turn, one after another, the dimensional subband deviate. With the departure of each of subband the conductance G shows a jump decrease by $2e^2/h$. When there in the interval E_{F1}—E_{F2} there is not a single subband, the conductivity G will vanish.

The quantity $2e^2/h$ is called the *conduction quantum* while reciprocal value $h/2e^2 = 12.9$ kΩ is the quantum of resistance. In fact, the quantization of resistance is conditioned by dimensional quantization of energy. To monitor the effect of quantization of resistance, the sufficiently low temperatures (~ 1 K) are required. At higher temperatures jumps of conductance G becomes blurred or disappear, because of thermal motion in the contacts "throws" electrons at the level where $E > E_F$. It should be noted that resistance measured in these conditions is the resistance in contacts. In the ballistic nanowire there is no scattering of electrons. Consequently, it should not have any electrical resistance.

It should be noted that functioning of many instrumental structures of nanoelectronics is determined by the features described above energy spectra of quantum-dimensional elements. In this case it is important that considered quantization of energy is observed only when the size of objects has the order of de Broglie wave (at least in one dimension).

Resonance tunneling. Usual tunneling effect, as already noted above, is micro-particles passage through a potential barrier, which height U^0 is greater than the energy of moving particle. At the same time, not every time particle with this energy passes through the barrier. There is a certain probability of its passage through the barrier, called the coefficient of transparency.

The magnitude of transparency coefficient is the greater the smaller width of the barrier l and the difference between its height U^0 and energy of particle E, that is, the smaller "deficit" of particle energy inside the barrier; $U^0 - E$. In a nanosized structure this effect can be manifested, for example, in the passage of electrons through thin layers of dielectric.

The tunneling time is very small: $\hbar/(U^0 - E) \approx 10^{-15}$ s, which can be estimated using the uncertainty relation: $\Delta E \cdot \Delta t \geq \hbar/2$. Tunneling effect has essential probability, if the barrier width l is comparable to de Broglie wavelength of electron. It defines the boundaries of functioning elements in the integrated circuits, constructed on a basis of traditional principles. But if tunneling effect would be put in the basis of principle of device, it can increase its speed to hundreds of terahertz. For example, just on this principle some single electron devices work.

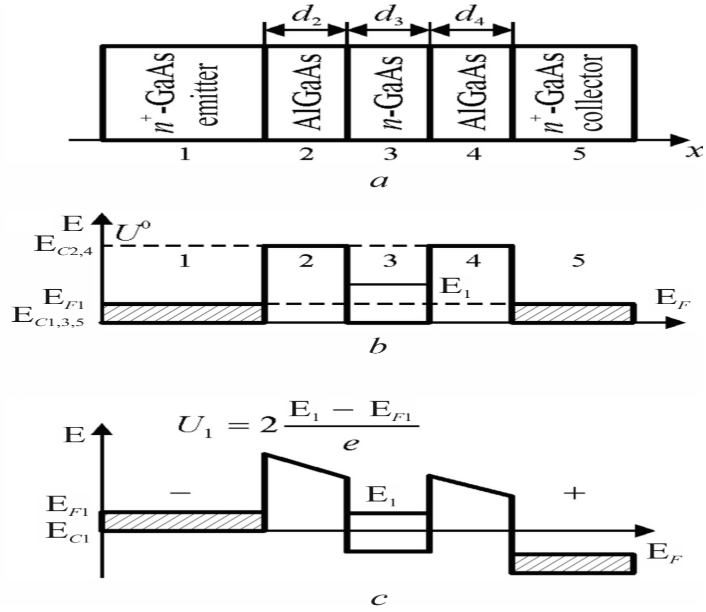


Fig. 1.20. Structure (a) and energy diagrams (b, c) resonance tunnel diode

Important for nanoelectronics features show the so-called resonance tunneling effect. It manifests itself in the two- or multidirectional periodic structure, Fig. 1.20*a*), and looks like the sharp increase in probability of particle passing through barriers, if its energy coincides with any dimensional energy level of potential well that separates barrier, Fig 1.20*c*.

Resonance tunneling through a series of barriers only occurs if the width of wells and barriers is of the order of de Broglie wavelength. In this effect the time of electron passage of structure includes, in addition to time of tunneling, the time of electron life in the well, that is, the time τ of its life on the resonant level. For example, according to estimations, for double heterostructure consisting of layers $Al_{0.3}Ga_{0.7}As$(5nm)–$Ga_{0,7}As$(7nm)–$Al_{0.3}Ga_{0.7}As$(5nm) at the barrier height of 0.2 eV the time is $\tau \sim 10^{-11}$ s. Thus, tunneling time provides the operation of corresponding devices in the terahertz range. It should be noted that the value of τ decreases also with further reduction of structure size [12].

Two-barrier structures are of great interest to electronics, because they can operate at ultrahigh-frequency (microwave) devices in the range of hundreds of gigahertz (GHz) and switches with delay time less than 1 ps (picoseconds). These devices are created on the basis of two-barrier structure – resonant-tunnel diode and transistor. Moreover, multi-barrier structures, called superlattices, are developed and found wide application.

Superlattices. As known, there are various possibilities for creating p-n junction, but they all were implemented in the same semiconductor, doped in different ways – acceptors and donors. In the light of subsequent presentation, such junction can be called the homojunction, for example, the pSi-nSi.

The following heterojunctions occur at the contact of two different chemical components of semiconductors. In this contact not only the band gap changes, but also other fundamental properties change: band structure, effective masses of charge carriers, their mobility, physical-chemical and optical properties.

Heterojunctions can be sharp and smooth. In a sharp heterojunction the change in chemical composition occurs at a distance of the order of lattice constant. In ideal heterojunction there are no defects and boundary states at interface. The possibility of obtaining monocrystalline heterojunctions, that is, the close contacts of various chemical compositions of semiconductors carried out in single crystal is associated with development of technological methods of epitaxial growth of semiconductor crystals, that is, the formation of uniformly oriented layers of crystals of one substance on the surface of another substance.

The heterostructure is the combination of several heterojunctions in a single crystal structure that forms part of semiconductor device. In the case of many layers of alternating crystals, the planar periodic structure is formed, which is called the superlattice. The characteristic dimensions of the layers in heterostructures and superlattices are nanometers, and therefore corresponding semiconductor devices belong to relatively new generation of electronics devices – nanoelectronics.

Superlattices are crystalline structures in which, apart from the periodic potential of crystalline lattices, there is another periodic potential, period of which far exceeds the constant lattice, but corresponds to the nanoscale. The most widely used are the semiconductor superlattices. They consist of layers of two semiconductors, differing in either chemical composition or type of conductivity. Superlattices are made, for example, with the help of molecular-beam epitaxy technology, which allows build up layers of any compound and thickness. Period of repetition of layers lies from several nanometers to tens of nanometers (for comparison, lattice constant of crystals Si and GaAs is about 0.5 nm).

Two types of semiconductor superlattices are widely used: the composite and the doped (it is appropriate to note that there are also superlattices exist made of metals, superconductors and dielectrics). The composite superlattices are heterostructures made of different chemical composition layers having different widths of bandgap, but with the close values in the magnitude of lattice parameters. For example, composite superlattices are $Al_xGa_{1-x}As$–GaAs; $In_xGa_{1-x}As$–GaAs;

$In_xGa_{1-x}As$–InP; ZnS–ZnSe and many others. Additional periodic potential in them is created by the periodical changing the width of bandgaps. The doped superlattice is a periodic sequence of layers of the n- and p-type of same semiconductor. Donor atoms in n-layers supplies electrons, which bind to acceptor atoms in the p-layers. Embedded in the crystal lattice charges of ionized acceptors and ionized donors create obviously need for superlittice additional periodic potential.

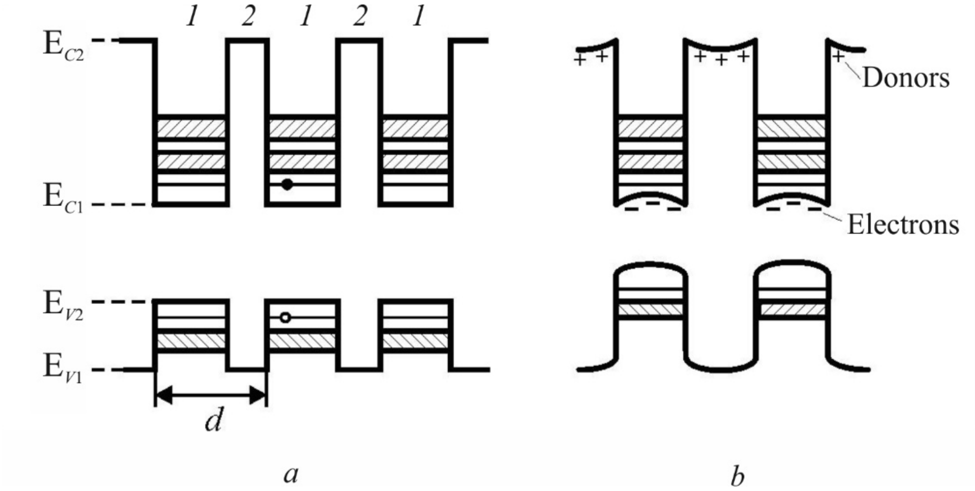


Fig. 1.21. Energy charts of simple composite (a) and modulated-doped (b) superlattices: d – period of superlattice

Exactly this potential crucially changes the band structure of semiconductor on basis of which superlattice created. Therefore, superlattice can be considered as a new, synthesized semiconductor that does not exist in nature and has unusual properties. The choice of composition materials for layers can broadly vary the band structure of the superlattice. The combination of methods for obtaining materials with a modified zone structure is at the basis of the so-called "band engineering".

Energy diagram of superlattice (its potential profile) is given as example in Fig. 1,.21*a* for the composite superconductor $Al_xGa_{1-x}As$–GaAs in the direction perpendicular to layers. Due to periodic change in the bandgap $\Delta E_e = E_{C1.2} - E_{V1.2}$ a sequence of rectangular quantum wells separated by the barriers is created. The wells are formed in a narrow-band semiconductor: for electrons – in the conduction band, for holes – in the valence band. It should be noted that the superlattices with much more complex profile exist, for example, in the structures Ge_xSi_{1-x}–Si or GaAs–Ga.

In Fig. 1.21*b* the potential profile of modulated-doped superlattice is shown. In this case the donor impurity is implemented only in the wide-band material. Electrons from donor levels pass into the quantum wells, spatially separating by ionized donors. The alternation of charges causes periodic bends of the edges of bands. The Fig. 1.21*a,b* shows the mini-bands on which the valence band and the conduction band are divided.

Figure 1.22 shows potential profile of doped superlattice. The charges of ionized donors and acceptors create a sequence of potential wells for electrons and holes. The electrons and holes are spatially separated: the holes are located in the potential wells of valence band of p-layer, while the electrons are in the potential wells of conduction band of n-layer. Bindings show mini-band; E_g is the width of bandgap of output semiconductor, ΔE_{ef} is the effective width of superlattice bandgap. To obtain doped superlattices the GaAs is often used.

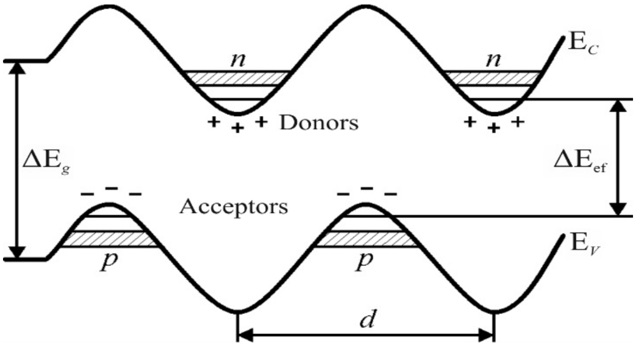


Fig. 1.22. Energy charts of doped superlattice: ΔE_{ef} – effective width of suppressed band gap; d – its period

To construct energy spectrum of electrons in the superlattice, Schrödinger equation can be solved (as in case of a bulk crystal) but taking into account the additional periodic potential. Using results of band structure calculating, it is possible to make qualitative conclusions about energy structure of superlattice. Its potential is periodic, so the dimensional levels are split into bands. Spectrum has band character; in the band as many levels as the wells in structure. Since period of superlattice is much larger than usual lattice constant, the superlattice bands represent a finer splitting of energy band of ordinary semiconductor that are called the mini-bands. The splitting of the conduction band and the valence band into the mini-bands is shown by the hatching in Fig. 1.22.

The smaller the width of well, the greater distance between mini-bands and the more effective band gap ΔE_{ef}; as well the smaller width of barrier the wider mini-band. Thus, one can rebuild the energy spectrum of superlattice by a simple change in the thickness of layers, which is easy to accomplish in the molecular-beam epitaxy method. The graph of states density $g(E)$ has a stepped form, like for a quantum well, but with another form of steps.

Electronic gas in superlattices differs in the fact that electrons and holes are spatially separated. Generated by light electron-hole pairs (equilibrium carriers) becomes also spatially separated, which prevents their recombination and increases their lifetime to ~ 10^{-3} seconds.

In modulated-doped composite superlattice a wide-band semiconductor (e.g., AlGaAs) is doped with donor impurity. The electrons from donor levels of barrier pass into the wells in conduction band of the narrow-band semiconductor. Ionized donors (impurity centers) remain in the barriers while 2D electronic gas with high density and mobility of electrons is formed in the wells. High mobility is due to the fact that density of electrons in the narrow-gap layer is greater than density of centers of dispersion, and donor impurity centers are located in wide-gap layers.

The effect of increasing mobility is especially significant at low temperatures, when main contribution to electrons dissipation makes their scattering on impurities. High mobility electrons allow create high-speed devices on superlattices, such as transistors with high-conductive channels. The switching time of such transistors can be picoseconds.

Thus, semiconductor superclattices are solid-state structures in which, besides to three-dimensional periodic potential of crystalline lattices, there is additional one-dimensional potential, the period of which substantially exceeds lattice constant. The presence of such a potential substantially changes energy spectrum so that superlattices have a number of interesting properties that are absent in ordinary semiconductors.

Superlattices represent a unique opportunity to almost randomly modify their band structure. The features of the superlattices luminescence (possibility of rearranging the emitted wavelengths, the excitonic nature of radiation up to room temperature, the strong limitation of impurity capture, the femtosecond kinetics, etc.) are used to create new generation of light-emitting devices. Acoustic properties of superlattices are characterized by the presence of selective reflection of phonons. Semiconductor superlattices are characterized by essentially nonlinear transport properties due to the presence of very narrow mini-bands in their energy spectrum.

Quantum nanoelectronic devices. The physical limitations of semiconductor microelectronics required new solutions. One of them is molecular electronics, which makes it possible to implement logical devices based on one molecule or a group of molecules and new principles of molecular computing systems. Although most of these ideas have not yet been realized, research in the field of molecular electronics and thin organic films has forced technologies and devices to move into the nanometer zone. As a result, artificial neural networks have become available in modern software packages. Thus, studies of molecular systems stimulated the development of solid-state electronics.

Molecular electronics has moved towards sensors and biosystems, while solid state electronics has prevailed with several ideas of quantum electronic devices.

Three major breakthroughs are worth mentioning here: resonant tunneling devices, single-electron devices, and quantum dots. These devices are based on the phenomenon of electron tunneling through a complex barrier having intermediate electronic states. When the energy level of the electrons in the source coincides with one of the intermediate levels, the probability of tunneling increases dramatically, even if the total barrier thickness is greater than the tunneling distance.

The idea of one-electron devices is due to the discovery of the Coulomb blockade: the transfer of one electron between two particles separated by a tunnel distance will create a potential barrier proportional to their radius. If the particles are relatively large, then this potential barrier is much smaller than kT even at very low temperatures, so that the rest of the electrons can move between these particles almost unhindered, ignoring the potential barrier. However, a decrease in the particle size can lead to another situation where the potential barrier is comparable to or even exceeds kT at a certain temperature. In this case, the potential barrier caused by the transfer of one electron will prevent further electron transfer, and this effect is called Coulomb blockade. Another very attractive idea for future quantum computing systems has to do with quantum dots. These are regularly spaced nano-objects (eg, nanoclusters, nanoislands, nanoparticles, macromolecules) separated by nanometer distances to provide a relay-race charge transfer mechanism.

Resume. Limitation of the substance in terms of size means changes in the conditions of movement of free charge carriers. In a certain range - up to micrometers - these changes can have a purely quantitative nature, without changing the laws of particle motion. In the case of further reduction, they can become significant and take on the features of not only quantitative, but also qualitative laws of particle movement. If we talk about the range of large sizes, then it is natural to expect that the laws of motion will be the laws of classical physics. It is also natural to expect that these laws will be the laws of quantum physics in the range of small sizes.

The transition from "large sizes" to "small" should be sought on the basis of quantum physics, where quantum mechanical laws apply: the main parameters are the de Broglie wavelength of a free electron: $\lambda = h/p$ where p is the momentum of the electron and h is Planck's constant. Let's estimate the length of the Debrougli wave of a free electron in those crystalline materials in which such electrons exist - in metals and semiconductors. It is natural that it will be different in these materials, since the concentrations of free charge carriers are very different in them, and therefore the values of the quasi-momentum of the electrons involved in the transfer of the electric charge are significantly different. In metals, there is one free electron per atom of the crystal lattice, and therefore, in order of magnitude, the concentration of the latter is close to 10^{22} cm^{-3}. In semiconductors, it can be many orders of magnitude smaller, depending on the nature of the semiconductor, the degree and nature of its doping, and temperature.

At high concentrations of free charge carriers, they are in a state of strong degeneracy, and therefore only those of them whose energy is close to the Fermi energy Ef, which is quite large, participate in charge transfer. Correspondingly, the quasi-momentum of the electron is also large, and therefore the length of its de Broglie wave is small. In our semiconductors, especially at low levels of their doping, and therefore low concentrations of free charge carriers, the latter can be in a non-degenerate state, and therefore, the average energy of the carriers participating in charge transfer is a value close to the thermal energy of k_BT. In any case, this value is smaller than the Fermi energy for degenerate charge carriers. Moreover, at low temperatures it will be small in absolute terms. Accordingly, the quasi-momentum of a non-degenerate electron will also be small, and its de Broglie wavelength will be large.

Numerical values of the de Broglie wavelength of a free electron in metals and semiconductors provide an answer to the question: it is the nanometer scale that leads to the appearance of fundamentally new quantum properties in small structures that are not inherent in massive crystals. If, for the sake of simplicity, the crystal structure is considered to be elementary cubic, then the concentration of atoms of 10^{22} cm^{-3} increases the thickness of the crystal lattice by approximately 0.5 nm. This value is of the same order as the de Broglie moment length of a free electron in a metal. At the same time, it is more than two orders of magnitude inferior to the de Broglie wavelength of a free electron in a semiconductor. It follows from this that to form a structure in a metal that would, on the one hand, already be crystalline, that is, if at least a few elementary cells were formed, and on the other hand, have dimensions smaller than the de Broglie wavelength of a free electron, is practically impossible At the same time, for semiconductors, which, unlike metals, allow control of the concentration of free charge carriers within very wide limits, this task is a goal within reach.

The dimensions of a real structure can be limited by the de Broglie wavelength of a free electron in a different number of directions - in one, two or three directions. As a result, later quantum-dimensional structures with many fundamentally different physical properties arise. If the restriction of the system movement occurs in one direction, then a structure called a 2D structure or quantum layer (another common name is a quantum well) arises. The main feature of the energy spectrum of a quantum layer is its dimensional quantization in one direction (the direction of size limitation) and the continuous dependence of the energy of the charge carrier on its quasi-momentum in the other two directions (in the plane of the layer). Physical phenomena characteristic of 2D structures are the quantum Hall effect and quantization of ballistic contact conductivity. The main technological approaches to the controlled production of 2D structures are ecstasy from molecular beams or organometallic compounds and hydrides.

Under the quantum limitation of the size of the system in two directions, 1D structures, or quantum threads (roads, wires), are obtained. The main feature of the energy spectrum of a quantum thread is its dimensional quantization in the plane perpendicular to the oci of the thread, and the continuous dependence of the energy of the charge carrier in its quasi-momentum for the direction along this oci. Physical phenomena characteristic of ID structures are the Peierls phase change "metal - dielectric" in the case of cooling of a 1D crystal below the critical temperature and suppression of the scattering processes of free charge carriers. Innovative technological approaches to the controlled production of 1D structures are a combination of molecular beam epitaxy and electronic lithography or the use of self-organization processes for epitaxial growth of low-density material on surface surfaces. Carbon nanotubes are a special type of 1D structures.

Due to the presence1 of a quantum-dimensional spatial limitation of the system in three directions, structures called 0D structures or quantum dots are obtained. The main feature of the energy spectrum of a quantum dot is its full dimensional quantization in ycix three directions. Physical phenomena characteristic of 0D structures are Coulomb blockade and one-electron processes. The main technological steps to the controlled production of 0D structures are the combination of molecular beam or MOS hydride entaxy with electronic lithography, the use of self-organization processes for the epitaxial growth of low-density material on a crystal-incompatible substrate, as well as the method of colloidal chemistry. Fullerenes are a special type of 0D structures [3].

The combination of a large number of quantum shapes into ordered systems with one-dimensional quantum potential wells and tunnel-transparent potential barriers, in which, in addition to the natural three-dimensional periodic potential of crystal lattice layers, an artificial one-dimensional periodic potential arises, which leads to the formation of a new class of low- dimensional structures, which are called superlattices. The main feature of the energy spectrum of the superlattice is its interband nature. Physical phenomena characteristic of superlattices are the presence of complex structures with negative differential resistance on the current-current characteristics, resonant tunneling of electrons, amplification and generation of electromagnetic interference. The main technological approaches to the controlled production of superlattices are epitaxy from molecular beams or organometallic compounds and hydrides.

1.5 Carbon nanostructures

Another important example, that demonstrates how internal bonding and symmetry influence on the properties of materials, is various forms of carbon. In Periodic Table of Elements carbon relates to subgroup 4; electronic shell of carbon atom has four valence electrons with configuration s^2p^2, allowing carbon to have valences –4, +2, +4. In addition to amorphous carbon black, only two crystalline (three-dimensional) allotropic modifications of carbon were previously known: graphite and diamond. Recently, fullerite was added to them - a new bulky form of carbon, which is a crystalline structure consisting of C_{60} molecules.

Classification of carbon structures is shown in Fig. 1.23. The classic (*three-dimensional*) structures of solid carbon comes in different forms known as allotropes depending on the type of chemical bond. The two most common allotropes of pure carbon are diamond and graphite

Diamond is one of 3*D* form of a carbon; its structure is formed from electronic state of sp^3-hybridization, Fig. 1.24*a*. In diamond crystal each carbon atom is surrounded by four others that are in the tetrahedral sites; neighbouring atoms are combined together by a strong covalent bond. In diamond the atoms form tetrahedra with each bound to four nearest neighbors. These tetrahedra are rigid, the bonds are strong, and of all known substances diamond has the greatest number of atoms per unit volume, which is why it is both the hardest and the least compressible (distance between atoms in diamond is 0.154 nm). Diamonds have been adopted for many uses because of the material's exceptional physical characteristics. It has the highest thermal conductivity and the highest sound velocity. It has low adhesion and friction, and its coefficient of thermal expansion is extremely low. Its optical transparency extends from the far infrared to the deep ultraviolet and it has high optical dispersion. It also has high electrical resistance. It is chemically inert, not reacting with most corrosive substances, and has excellent biological compatibility.

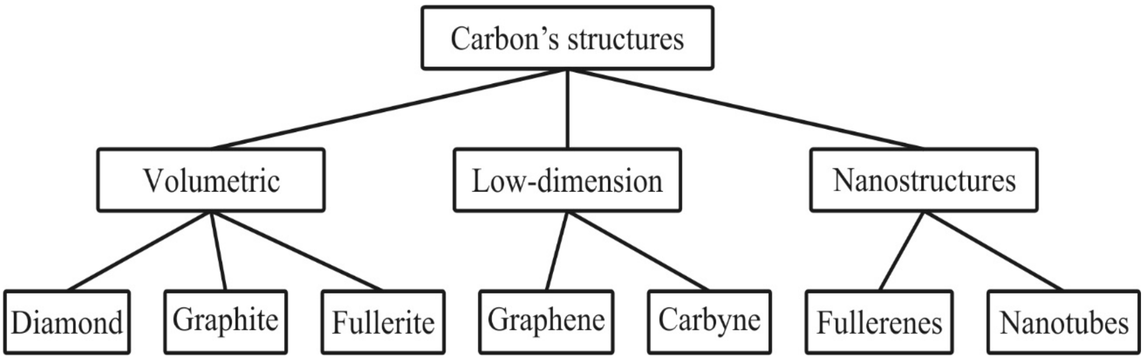


Fig. 1.23. Classification of different forms of carbon

Graphite is a substance where carbon atoms are connected with each other forming the *hexagonal netting*, in which each atom has three neighbours, Fig. 1.24*b*. In such quasi-two dimensional (plane) form of carbon its structure is originated from the state of sp^2-hybridization, The layers of plane nettings of graphite are accommodated one above another. In covalent chemical bonds formation the three electrons from each atom take part in creating σ-bonding. Distance between atoms, arranged in hexagonal mesh nodes of graphite, is 0.142 nm – less than in diamond. That is why neighbouring atoms within each layer of graphite are linked by *more strong* covalent bonds. However, these layers fit together by the *weak* Van der Waals forces, in which four electrons are involved. The hexagonal graphite netting is located at distance of 0.335 nm from each other, i.e., the distance between atoms is bigger more than twice than in layers. This bonding between layers is the π-bond. Large distance between layers determines the weakness of forces that combine layers. This structure – strong segments, poorly linked – makes specific properties of graphite, particularly, its flexibility that explains a slight sliding of layers relative to each other, as well as low hardness of graphite and large anisotropy of its properties. Thus, in graphite, the bonds between nearest neighbors are even stronger thtn in diamond, but the bonds between parallel adjacent planes are weak, so the planes easily slip past each other. That is why graphite is much softer than diamond. However, the stronger bonds make graphite less flammable [3].

Carbine is linear polymer of carbon that can be obtained in vitro in form of long chains of carbon atoms, parallel to each other, Fig. 1.24*c*. String (linear) structure of carbine is formed by the *sp*-hybridized carbon atoms. In the very long molecule of carbine the carbon atoms are strongly linked in chains by the *triple* bond, as well as by the *double* bonds between them. Carbyne can be obtained in forms of fiber, powder and films of different structure: disordered long chains, amorphous and quasi-amorphous material with microcrystalline inclusions, by-layer oriented chains. Crystalline-type samples of carbine have a shape of plate-form crystals, as well as samples in a form of fiber up to 10 mm lenth. Thus carbyne is a modification of carbon, known as an allotrope. It is manufactured synthetically, comprises one single and very long chain of carbon atoms, and is regarded as material with extremely interesting electronic and mechanical properties.

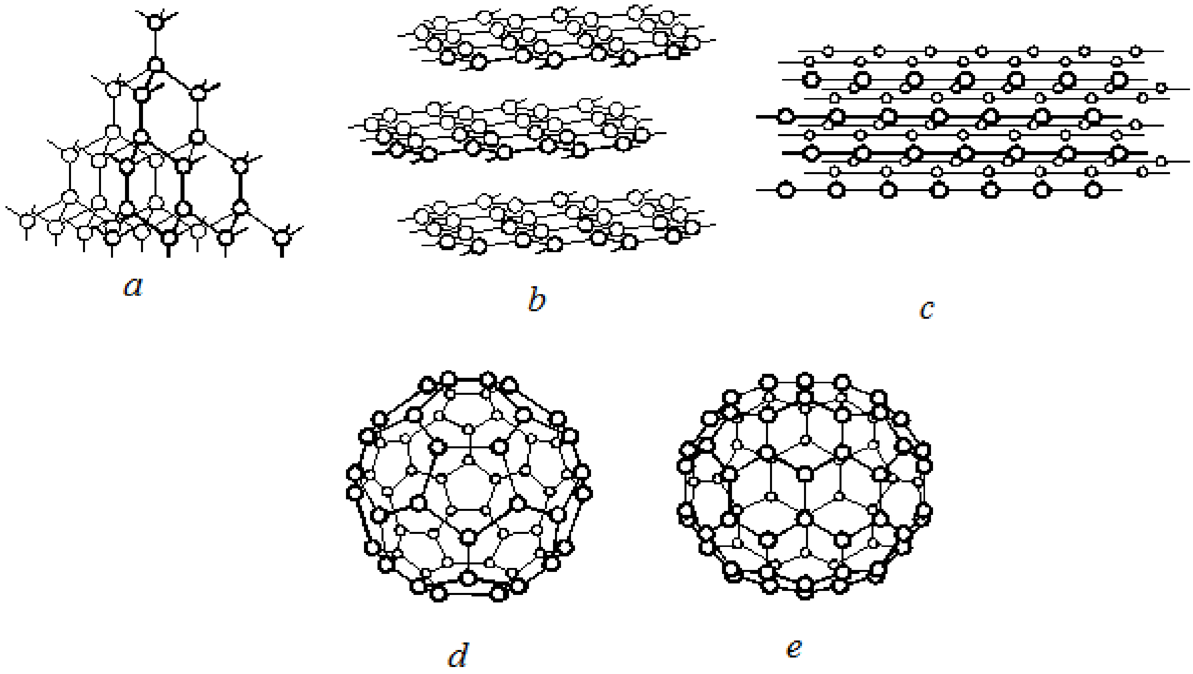


Fig. 1.24. Carbon atoms location in various structures: a – diamond, b – graphite, c – carbine, d – fullerene C_{60}, e – fullerene C_{70}

Graphene is the plane polymer of carbon: the layer of carbon atoms with thickness only one atom is connected by the sp^2-bonds in the two-dimensional hexagonal crystal lattice. Graphene can be represented as a single plane of graphite, separated from bulk crystal, Fig. 1.25*a*. The graphene is characterized by big mechanical stiffness and large thermal conductivity. The high mobility of charge carriers in the graphene at room temperature makes it promising material for use in various electronic devices. In particular, graphene can be regarded as important material for nanoelectronics that allows in some cases replace silicon in integrated circuits. One of the areas of application is the use of graphene as a very sensitive sensor for detecting individual molecules of chemical substances on the surface of the film. Such substances as NH_3, CO, H_2O, NO_2 were studied. Sensors with a size of 1×1 μm2 were used to detect the attachment of individual NO_2 molecules to graphene. The principle of operation of this sensor consists in the ability of various molecules in graphene to play the role of donors or acceptors, which, in turn, changes the electrical resistance of graphene.

The study of graphene has shown that, due to its high strength and electrical conductivity, it is not only a valuable material for a number of industries, but can also be used to conduct experiments to test the provisions of the theory of relativity. The fact is that in graphene electric charges behave like relativistic particles with zero rest mass. As is known, near the Dirac points, quasiparticles (in this case, they are electrons and holes) are characterized by a linear dispersion law. These particles, known as massless Dirac fermions, were previously predicted by Einstein's theory of relativity and described by the Dirac equation.

Thus, graphene - two-dimensional carbon - has electronic properties that are completely unlike the properties of other electronic materials. Graphene is a semiconductor, but its unusual property is that its band gap is exactly zero. The unique band structure of graphene causes exotic effects that can improve the characteristics of electronic devices. Unlike most materials, the rate of charge carriers in graphene does not decrease either near the top of the valence band or near the bottom of the conduction band. It became in all zones, including the point where the conduction zone and the valence zone meet. In addition to the fact that graphene does not have a band gap of finite width (other semiconductor materials are characterized by a band gap of 1–2 eV), the energy of an electron in graphene is a linear function of its momentum in a two-dimensional layer (in all other quasi-two-dimensional materials, the electron energy is proportional to the square of the momentum).

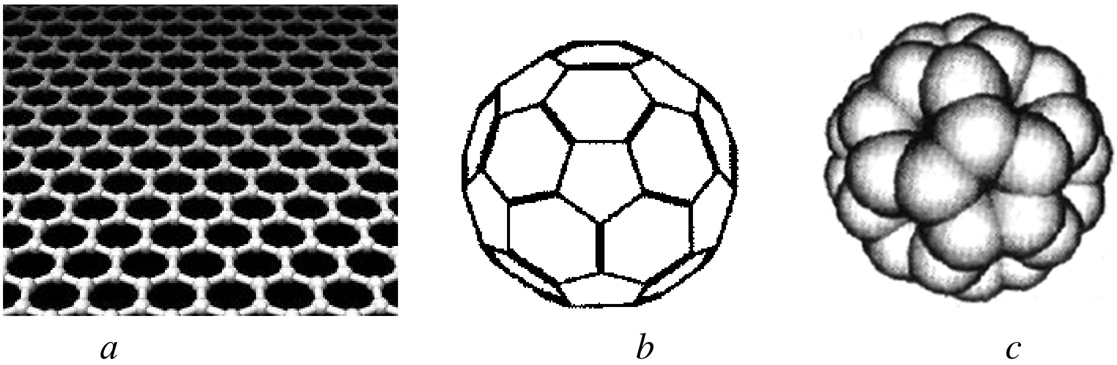

a *b* *c*

Fig. 1.25. Graphene (a) and lower models of C_{60} fullerene: b – hexagons and pentahedra of a truncated icosahedron; c – electron cloud on the fullerene surface

Such a linear dispersion dependence of energy on momentum is similar to the law of dispersion of photons in free space, which is described by the Dirac equation. This means that electrons in graphene move at a constant speed regardless of the direction of their momentum, that is, they behave like photons. This is also true in the limiting case - at the Dirac point, where the density of states vanishes. This feature of graphene determines the existence of an integer quantum Hall effect in it.

Among the new physical results of experiments with graphene, it is worth noting some relativistic effects. In particular, massless fermions (predicted by Dirac) in a magnetic field acquire dynamic mass described by the well-known equation E = mc2, just as photons (Bose particles that have no rest mass) acquire it under the influence of the Sun's gravity. Electronic field devices on graphene exploit the fact that a curtain voltage modulates the density of states in graphene and switches it between the Dirac point and highly conductive states. This switching mechanism is the basis of the principle of operation of the field-effect transistor. Unlike two-dimensional electronic layers in semiconductors, where charge carriers become immobile at low density of states, the mobility of charge carriers in graphene remains high even when the density of states becomes zero at the Dirac point. Therefore, there is a significant difference between semiconductor nanotubes with a bandgap of the order of 1 eV, which effectively blocks current in the "off" (reverse) mode, while the low-conductivity state in graphene has a finite current density even at temperatures close to absolute zero. The minimum conductivity of graphene is determined by defects, edge effects, impurities, and the substrate on which it is deposited.

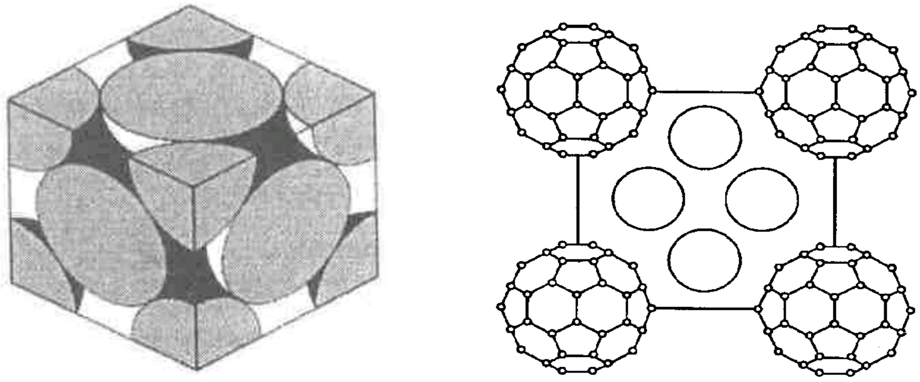
However, if graphene is deposited on a dielectric substrate (such as SiO2), fluctuations in the electrical potential of the substrate blur the physical picture at the Dirac point because the substrate partially binds electrical charges, inducing an "image charge" in the graphene. As a result, an electron-hole disordered background is created in graphene, and the conductivity is determined by the level of this disorder (in contrast to other materials, where the conductivity approaches zero as the disorder of the structure increases).

Fullerenes are molecular compounds belonging to one of relatively new forms of carbon. They are closed polyhedra composed of carbon atoms that are located on a surface of convex polyhedron, Fig. 1.25*b,c*. Discovery of fullerenes is also awarded by Nobel Prize. Most stable form of fullerenes is the molecule C_{60} – polyhedron made of hexagon and pentagon faces. Fullerenes are a new form of carbon - molecular. It was found that pure carbon molecules can have a closed surface in the form of a sphere or spheroid. The s^2p^2 outer electron shell provides fairly stable bonds when neighboring atoms form pentagons and hexagons, from which carbon clusters are formed. The same structure is optimal for the most stable carbon clusters. For example, the C_{60} structure contains 12 regular pentagons (pentagons) and 20 irregular hexagons (hexagons), and two types of bonds should be distinguished in it. One of them is double and is the common side of two hexagons, and the second - single - is the common side of a pentagon and a hexagon. It was experimentally determined that the length of the C–C sides connecting two hexagons is 0.139 nm, while the length of the C–C sides connecting a hexagon to a pentagon is about 0.144 nm. Long sides in the lattice of C60 bonds correspond to single bonds, and shorter sides to double bonds. Thus, the hexagons that make up the structure of the C60 molecule differ little from regular hexagons, which are the basis of graphite, in which the side of a regular hexagon is 0.142 nm.

During the study of the properties of fullerenes, extremely high mechanical and chemical stability of the C_{60} molecule was revealed. For an individual C_{60} molecule, this property is characterized by the bulk compression modulus: C_{60} molecule is less compressible than a diamond crystal. This fact corresponds to the fact that the carbon atoms in the hexagonal lattice are bound together by covalent bonds, which are stronger than in diamond.

Endofullerenes are those fullerenes in which one or more non-carbon atoms are placed inside the fullerene molecule. This formation is one example of nanoclathrates. The fact that the fullerenes are empty inside is used (for C_{60}, the cavity diameter is 0.4 nm). Such a cavity can accommodate any atom; the foreign atom is closed by a continuous shell consisting of carbon atoms. If metal atoms are introduced into the fullerene molecule, then such endohedral complexes are called metalfullerenes. These are unique nanocontainers, which are considered quite promising for use in nanotechnology and nanochemistry.

Fullerites are condensed systems consisting of fullerene molecules. In addition, topical compounds are the *fullerides* – fullerite crystals doped with alkali metal atoms. Some of fullerides exhibit high-temperature superconductivity, for example, in fulleride-superconductor $RbCs_2C_{60}$ critical temperature is 33 K. It turned out that fullerenes can form various compounds and complexes both with simple elements and with their compounds. Such materials came to be called fullerides. The study of properties and applications of fullerites and fullerides concerns physics, chemistry, mathematics, biology, materials science, medicine and architecture. Interest in them is supported by the prospects of their application in nanoelectronics, energy, and in the creation of new polymers. Fullerite crystals can have a different structure, but most often it is a close-packed hexagonal centered crystal (HCC) structure with a crystal lattice constant of 1.417 nm (Fig. 2.13). The distance between two neighboring fullerene molecules is 1.002 nm. The coordination number of fullerene molecules is 12. Given that the radius of the C_{60} molecule is 0.353 nm, the distance between the nearest neighboring carbon atoms is 0.294 nm, which is much smaller than the distance between the hexagonal lattices in graphite (0.335 nm). It was established that the intermolecular forces in fullerite are van der Waals.



a *b*

Fig. 1.26. Unit cell of fullerite lattice (a) Schematic representation of a face of cube perpendicular to Z axis for M_6C_{60}, M = K, Rb, Cs

The unit cell of fullerite contains eight tetrahedral voids and four octahedral voids, each of which is surrounded by four and six C60 molecules, respectively. This circumstance contributes to the formation of more complex crystals based on fullerenes - fullerides where C_{60} molecules contained in the nodes of the crystal lattice of fullerite rotate rapidly. According to nuclear magnetic resonance, the frequency of such rotation at a temperature of $T = 300$ K is about 10^{12} Hz. Molecules in of fullerite lattice occupy four non-equivalent positions. Each of the four molecules of such cube rotates near one of the crystal axes. The rotation is localized due to the C=C bond, which is adjacent to the center of the pentagon of the neighboring molecule, which has a lower electron density.

In the process of cooling solid fullerite to a temperature of 250 K, a phase transition of the first kind was revealed, when its lattice is rearranged into a simple cubic lattice. The phase transformation almost does not change the stable crystal lattice of fullerite, but the frequency of rotation of fullerene molecules decreases millions of times. The nature of such a phase transition is associated with the fact that at the temperature $T = T_{min}$ in the fullerite crystals, individual C_{60} clusters are fixed, while at room temperature the rotation of the molecules does not allow determining their orientation. During heating, there is a "defrosting" of the rotational motion of individual C60 molecules, and therefore the phase transition occurring in the temperature range of 250-260 K is classified as a transition of orientational ordering of the first kind.

Fullerides are compounds of fullerenes, usually with the metals. Fullerides of alkali metals A_3C_{60} (A = K, Rb, Cs) have face-centered lattices. In fullerides, there is no low-temperature phase transition and rotation of C_{60} molecules under conditions of high temperatures, since the connection of fullerene molecules with the metal atom is almost purely *ionic*, that is, the alkali metal donates one valence electron to the C_{60}– molecule. The ionic bond is much stronger than the van der Waals bond, and therefore the possible types of motion of the fullerene molecules are limited. The unit cell of the face-centered lattice of fulleride (that is, smallest part of crystal lattice, the repetition of which can reproduce entire crystal) contains eight tetrahedral and four octahedral voids (interstices). In the first case, the center of the internode is surrounded by four C_{60} molecules at the vertices of the tetrahedron; in the second case, six C_{60} molecules on the vertices of the octahedron [3].

According to their electrical properties, fullerides are semiconductors with a band gap of 1.5–1.95 eV for C_{60} (approximately 1.91 eV for C_{70}) and have a rather hollow structure. In this regard, a significant change in specific electrical resistance under pressure is observed in them. Samples of fulleride measuring 0.3×0.7×0.04 mm were placed in a cell with a diameter of 1 mm, and then subjected to pressure at different temperatures. The results showed that the value of electrical resistance ρ in the case of an increase in pressure to 10^5 atm. decreases almost 10 times. Significant advances in molecular and solid-state chemistry made it possible to synthesize various C_{60} compounds with other elements, including intercalated compounds (with atoms introduced into the fullerite crystal lattice). Thanks to the introduction of monovalent ions of alkali metals into all three planes of solid C_{60}, its properties acquire electrical conductivity of a metallic nature. Large tetrahedral and octahedral cavities in a crystal with an fcc lattice form layered galleries. While the basic structure remains unchanged, metallic properties are achieved when half of the conduction band is filled due to the addition of three electrons per molecule.

Obtaining such compounds based on fullerenes of the M_xC_{60} type (M = K, Rb) contributed to the discovery of the first superconductors of the fullerite type, Fig. 1.26*b*. Analysis of the properties of fullerite doped to saturation with potassium (K) and cesium (Cs) showed that under extreme conditions the composition M_6C_{60} (M is an alkali metal) is formed. In the case of sufficient impurity concentrations ($x > 3$), the fullerite lattice takes on a form different from the fcc lattice. For example, fullerite doping with K, Rb, Cs to saturation is accompanied by the rearrangement of the fcc lattice into bcc with loose packing. One of the faces of such a cube is schematically shown in Fig. 1.26*b*. The cell has the form of four atoms placed in equivalent positions, as in the crystal lattice of a diamond. Each C_{60} molecule is surrounded by 24 metal atoms, and each of these atoms determines the tetragonality of four C_{60} molecules.

Clathrates are nanocellular materials that should be placed alongside graphene and fullerene. The frameworks of well-studied common (for example, water) clathrates are formed by molecules of water or some organic substances, for example, hydroquinone, and the introduced particles ("guests") are various gases and liquids. But for submicroelectronics and nanoelectronics, other clathrates are of interest, which are based on crystals, the lattices of which represent an ordered system consisting of atoms of semiconductor elements, for example, Si, Ge, Sn, etc. Such clathrates can be very strong materials like graphene and fullerenes. Nanoclathrates are molecular ensembles in which the substructures of the "guest" and "host" are connected by weak bonds, while the lattice of the "host" is built from strong covalent bonds, and mobile atoms or molecules of the "guest" are placed in its cavities ", able to oscillate or rotate within the volume intended for them. This feature of clathrates determined their special thermoelectric properties: high electronic conductivity with low thermal conductivity, which determines the high efficiency of clathrates in thermoelectric converters. Fullerenes and clathrates can be fundamentally important for the energy industry of the future due to the ability to store and release other atoms and molecules (in particular, hydrogen). The existence of clathrates, like other types of submolecular ensembles, is determined not so much by the chemical nature of their substance, but by the topological, geometric, and charge correspondence of the "guest" and "host" substructures, which is called complementarity.

Carbon nanotubes, shown in Fig. 1.27, are the lingering cylindrical structures with diameter from one to several tens of nanometers and lengths up to several micrometers. They consist of one or more rolled into a tube hexagonal graphite planes (graphene) and usually are ended with hemispherical head. There are both metallic and semiconducting carbon nanotubes. *Metallic* nanotubes well conduct electricity even near absolute zero temperatures, while in the *semiconductor* type of nanotubes at temperature of absolute zero electrical conductivity is nearly zero but increases with temperature rise. The tubes have a very small diameter and are the micro-capillaries.

Therefore, they are used as capsules for active molecules, for the preservation of metals and gases, etc. High mechanical strength allows the use of carbon materials based on nanotubes as super-strong threads, cords woven from tubes, and composite materials. The applications of nanotubes in microelectronics are widely known: transistors, nanoconductors, transparent conductive surfaces, miniature sensors with ultrahigh sensitivity for detecting molecules in a gaseous medium or in solutions, optical displays and LEDs.

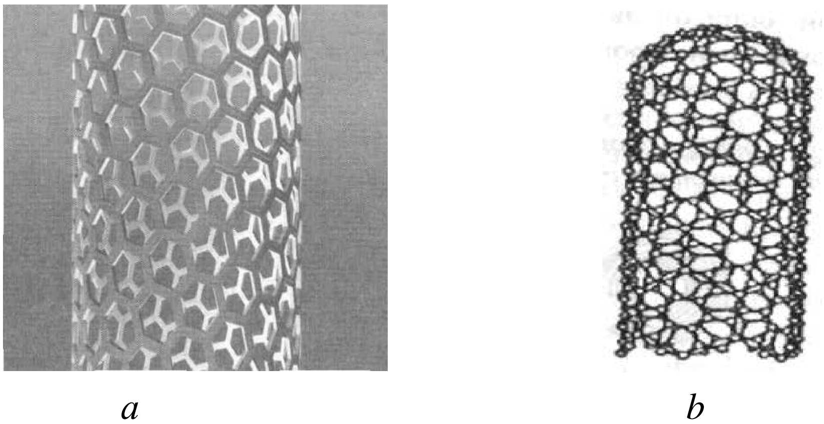


Fig. 1.27. Single-walled carbon nanotubes: *a* – schematic representation; *b* – fullerene-like closed end of nanotube

Single-wall nanotubes, synthesized from the semiconductors with different band gaps (carbon, silicon, boron nitride or zinc oxide) can have both low (up to the dielectric) and very high (up to the metallic) electrical conductivity, which can be easily controlled, even electrically. They are the objects with an almost ideal surface, since the existing defects, as a rule, affect only the structure of several nearby cells, but do not violate the structure of the tube of other nano-particle as a whole. Therefore, for the use of nanotubes as channels for field-effect transistors, their easily controllable electrical conductivity and extremely low wall roughness in comparison with conventional silicon channels play a decisive role. The result is the advanced scaling of gate and channel lengths down to a few nm, reduced channel scattering and, as a result, improved transistor performance.

Another example is emitters from nanowires, multi-walled or single-walled nanotubes and their arrays, made of a wide variety of materials (carbon, silicon, gallium arsenide or boron nitride, coated with silver, titanium, platinum or gold, which are used in vacuum electronics as a new type of field cathodes. The main advantage of such emitters is the nanometer curvature of their tip. Due to the strong field concentration near the tops of the nanotubes or nanowires, the nanoscale provides the ultra-high field gains and ultra-low threshold voltages of the cathode. The use of empty nanotubes, inside which it is possible to move the metal nanoparticles and fix their position using electrical or magnetic pulses, will make it possible to achieve the ultra-high density of data recording. In this case, the material of the tube and the method of its manufacture do not play a noticeable role (which means that you can choose the cheapest one). The ultra-high density is achieved due to the fact that one nanotube is capable of fixing not only two positions of the nanoparticle (presence or absence), but much more positions of particle (in fact, coordinate of a particle in the tube).

The use of oriented arrays of nanoparticles (nanotubes or nanowires) as the nanogenerators of electrical current, operating on the mechanical bending or thermoelectric principle, will make it possible to use the random vibrations or the temperature fluctuations to power supply of various ultra-small devices. For these applications, one must expect various matorials, since the flexoelectric and tertiary pyroelectric effects are inherent in all substances, and when going to the nanosize and mono-layers, strong surface piezoelectric and pyroelectric effects should appear, induced by the loss of the inversion center due to the dominant contribution from the surface. Thermoelectric and electrocaloric properties of the fullerenes and clathrates (their high electrical conductivity combined with low thermal conductivity due to the dominant contribution of the ballistic mechanism of heat transfer) determine the high efficiency of fullerenes in epy thermoelectric converters of a future. Due to the unique possibilities of storing and releasing other atoms and molecules (in particular hydrogen), fullerenes and clathrates may be of fundamental importance for the energy of the future. It turned out that the formation of fullerenes, clathrates and other very diverse supra-molecular ensembles is primarily determined not by the chemical nature of their constituent substances, but by their topological, geometric and charge correspondence.

The list of examples of unique properties that are "universal" for various nanomaterials and their use for the applications in various fields of science and technology is far from complete. It should be noted, however, that for the successful application of nanomaterials properties, it is necessary to develop new technologies such as the self-assembly; if possible, to use also the biochemical nano-assemblers and the "intelligent" molecular micro- and nano-machines, which will make it possible to synthesize sufficient quantities of identical units of nanomaterial and integrate them directly into circuits.

Therefore, as the size of object decreases to micro- and, especially, nano-scale, the influence of the surface and shape on all its physical properties increases significantly in comparison with the influence of the bulk material of the object.

From a thermodynamic point of view, this fact is explained by an increase and subsequent dominance of the *free surface energy*, which is determined by the shape of the object and its surface area ~ R^2, in comparison with the free volumetric energy of the sample, proportional to R^3, with a decrease in its characteristic size R. Moreover, with a decrease sizes and shape factors below the "critical" ones, the physical properties of objects themselves can fundamentally change: the nano-objects and low-dimensional structures are characterized by the *size-induced* structural and phase transitions such as metal ⇒ semiconductor ⇒ dielectric or paramagnetic ⇒ ferromagnetic ⇒ antiferromagnetic ferroelectric ⇒ paraelectric, elasticity ⇒ plasticity and many others.

These effects, predicted within the framework of phenomenological theories, have numerous experimental confirmations and are consistent with the modern quantum-mechanical microscopic calculations, proving fundamental changes in the band structure and symmetry of the unit cells, induced by the nanoscaling of the object. In this case, researchers are faced with nanomaterials, the physical properties of which may differ significantly from the "generating" bulk materials. For a number of properties of nano-scale objects, the nature of their material can play a secondary role in comparison with the primary role of shape (for example, a quantum dot, ellipsoid, sphere, tube, wire, or mono-layers), topological dimension (for example, ID, 2D, 3D confinement or fractal) and quantum size effect (in particular, the dimensions of the object are below or above the characteristic or critical dimensions).

The most technologically, advanced and promising nano-objects for the applications are the nanotubes, nanowires, graphene and clathrates, which clearly demonstrate the leading role of the *nanoscale* for the use of their physical characteristics in the modern submicronics and nanoelectronics, optoelectronics, data storage devices and computer memory, environmental energy and medicine.

1.6 Nano-dielectrics in polymer composites

Flexible composites based on a polymer matrix filled with nano-dielectrics are increasingly being used. In electronics and electrical engineering, they are used to suppress the spatial electric charge, to increase the density of the accumulated electric energy, to counteract partial electric discharges, to increase the thermal conductivity of insulating layers. In biomedicine, they are used in electronic skin, in elastomers (artificial muscles of robots, etc.). In general, in terms of design and application of materials, nanotechnology provides flexibility in tuning the dielectric properties of the composite by selecting the microstructure and distributing the filler in the polymer matrix [4].

A feature of the use of nano-structural fillers in polymers is the appearance of an additional factor for controlling the properties of a composite. This factor is the sharply increased volume fraction of interfaces between the embedded nanoparticles and the polymer. The fact is that the role of surface properties in nanoparticles dominates over its bulk properties due to the unsaturation of molecular bonds on the surface of nanoparticles, as a result of which their ability to chemically react with the nearest polymer molecules greatly increases. It should be noted that the possibilities of using polymeric materials filled with nano-dielectrics are still far from being fully disclosed, which contributes to the development of theoretical and experimental work in this area. At the same time, the microscopic mechanisms governing the macroscopic behavior of nanocomposites are also not completely clear and definite.

Unlike conventional composite materials, the properties of which, with known parameters of the polymer and filler (filler), can be calculated from models and formulas of a physical mixture, in composites with nano-dielectrics, the role of transition layers between a nanoparticle and a polymer matrix increases sharply, which limits the use of models of a simple physical mixture.

The point is that the presence of interfaces has a predominant effect on the macroscopic behavior of composites. In this case, the interface zone formed by two heterogeneous materials sharply increases as the size of the filler particles approaches the nanometer scale, since the number of atoms on the surface of the nanoparticle significantly predominates over the number of particles in its volume. It is known that atoms or ions located on the surface of a nanoparticle are characterized by free chemical bonds, which increases their chemical activity. Due to the interface effect, it is possible to control both the dimensional morphology of nanoparticles and the degree of their agglomeration. This applies to both zero-dimensional (0D) grains, one-dimensional (1D) fibers, and two-dimensional (2D) nano-plates. It is also possible to directionally change the spatial distribution of the filler in the polymer matrix, while achieving the desired properties of the composites by changing various properties of the composites due to the concentration and spatial configuration of the nanofiller [5].

In the theory of polymer composites with a dielectric filler, a sharp increase in the interface area with a decrease in the particle size is taken into account. For this reason, for nanodielectrics, the interfacial zone occupies a large volume fraction of the material, and this is what affects their macroscopic properties. At first glance, the interface between a nanoparticle and a polymer could be considered simply a transition zone, the properties of which are intermediate between those of a polymer and nanoparticles. However, in fact, with a large volume fraction of the interface, some properties of the composite are enhanced quite significantly, and are not a simple arithmetic average of the properties of the initial components. This means that a truly new material is formed in the interfacial zone. In addition, some dielectric properties such as electronic conductivity, interface polarization, dielectric degradation and breakdown are closely related to interfaces in composites, which should be analyzed at different spatial and temporal scales.

The configuration of polymer dielectrics is much more complex than the structure of crystals with regularly arranged atoms. The fact is that in a polymer material there are variations in size from a nanometer to a millimeter (from the length of a chemical bond (of the order of 0.1 nm) to a molecular chain with a size of tens of nanometers. All these configurations have different ability to move, characterized by different relaxation times in response.

With the introduction of nanoparticles, these conditions become even more complex due to the presence of various interfaces between the polymer and nanoparticles, which affects the process of relaxation of the response of the composite to any external impact both in spatial and temporal scales, including electrical conductivity, electrical polarization, electrical degradation.

As the measurement frequency increases, the dielectric constant decreases in accordance with the Debye equations, with the dissipation peak occurring in a certain frequency region. A number of dielectric degradation time can last from hours to many years.

It has been experimentally established that as the filler size decreases to nanosizes, the role of the physical and chemical structure at the interfaces inside the composites can significantly dominate the macroscopic properties. Various models have been proposed to explain the microscopic phenomena occurring in the interface zone.

The two-layer Lewis model [4] assumes that the interface zone is divided into two layers. The layer closest to the nanoparticle with a thickness of about 1 nm carries a high-density positive electric charge. due to strong electrostatic force; in this layer there is a sharp drop in the electric potential. In the outer (diffuse) layer, both positive and negative charges coexist, excited by electrical or thermal voltage. The thickness of this layer depends on the concentration of ions in the polymer matrix: it is small for polymers with high electrical conductivity, but for weakly conductive polymers, this thickness can reach 10 nm.

The Tanaka multilayer model [5] considers a spherical inorganic particle embedded in a polymer matrix. The layer closest to this particle is a transition layer, rigidly bound by chemical interaction with the polymer matrix. The second (intermediate) layer up to 10 nm thick consists of polymer chains constrained in their movement due to significant interaction with the first layer. The third (outer) layer is a more free-moving layer, consisting of polymer chains, which are weakly affected by the perturbing stress caused by the implanted particle. The thickness of the outer layer can reach several tens of nanometers.

Polymer composites filled with nano-dielectrics are successfully used in many areas of electrical engineering, electronics and biomedicine.

1. Composites with *high energy storage density*. Due to the flexibility and low cost of composite materials, polymer nanocomposites with a high permittivity and high breakdown strength are of interest for the electric power industry and compact electronics. For example, the ferroelectric polymer polyvinylidene fluoride (PVDF) can be used as a base material for the manufacture of nanodielectrics that store high energy. The fillers can be ceramic nanoparticles with a high dielectric constant (hundreds for TiO_2, $CaTiO_3$, $SrTiO_3$ and thousands for $BaTiO_3$ and its solid solutions. For example, a sandwich-shaped three-layer structure of $BaTiO_3$/PVDF nanocomposites with different content of $BaTiO_3$ in the polymer, which gradually increases layer by layer. Three-dimensional structures with $BaTiO_3$ nanoparticles were also obtained in polymer composites by increasing the permittivity.

2. Polymer nanodielectrics for *space charge suppression*. Injection from the electrode accompanied by the accumulation of space charge in dielectrics occurs commonly in high voltage direct current devices. The resulting volume distorts the local distribution of the electric field and, in places of increased field strength, accelerates the gradual degradation of the polymer chain. The introduction of inorganic nanoparticles into the polymer matrix provides suppression of injection by significantly reducing the space charge. In the experiments, nanowire oxides SiO_2, MgO or Al_2O_3 were introduced into the polymer, which effectively suppresses the formation of a space charge and equalizes the distribution of the electric field of high strength in the polymer.

3. Polymer nanodielectrics with *resistance to partial discharge*. Under conditions of high electrical voltage, it is difficult to obtain a uniform distribution of the electric field. In electrical insulation, there are many places where the local electric field strength is higher than the breakdown strength of air domains (3

kV/mm), for example, this is the winding terminal of a high-voltage generator and cable insulation. The result is a partial discharge that accelerates the degradation of the polymer chain and acts as a harbinger of serious malfunctions and problems. Therefore, the study of the property of resistance to partial discharges is of great importance for assessing the qualitative and long-term performance characteristics of polymer nanodielectrics in high-voltage equipment.

The addition of ceramic nanoparticles to the polymer matrix enhances the bond between the fillers and the polymer matrix. More importantly, the nanodielectric acts as an obstacle to high-energy charges, protecting the polymer from the direct impact of these charges. Depending on the localization of a partial discharge, it can be divided into internal and surface corona discharge, the former being mainly caused by the presence of voids, impurities and defects. To assess the ability of the surface of nanocomposites to withstand partial discharge, three main parameters are used: partial discharge current, surface roughness, and erosion depth. An experimental study of polymers and their nanocomposites with colloidal silica (SiO_2) shows that the partial discharge resistance improves markedly after the addition of a nanofiller. Layered silicate-polymer nanocomposites can effectively reduce surface roughness caused by partial discharge.

4. Polymeric nanodielectrics with *non-linear characteristics* use the dependence of conductivity and permittivity of the electric field voltage applied to the material. Electrical non-linearity is used to increase uniformity in the distribution of the electric field, making it possible to avoid voltage concentration in many high-voltage devices, both AC and DC. This phenomenon is used as protection against corona in motors and cables, as well as to protect the surface of the outer silicone rubber polymer insulator. Semiconductor nanofillers such as silicon carbide (SiC) and zinc oxide ZnO are added to the polymer matrix to create nonlinear characteristics. Carbon-based fillers, including carbon nanotubes and graphene oxide, are also used for field-regulating nanocomposites. In this case, the phenomenon of percolation is used, which is important for nanoparticles containing an insulating matrix and conducting and semiconductor nanoparticles. It is important to note that the percolation threshold depends on many factors, such as the morphology of the nanoparticles, the uniformity of the filler distribution, and the type of conduction between neighboring particles.

5. Polymer nanodielectrics with *high thermal conductivity*. Conventional polymer layers used for electrical insulation usually have low thermal conductivity, which can cause local overheating of devices. Increasingly compact arrangement of electronic components in integrated circuits leads to increased heat dissipation.

Therefore, composites that could combine good electrical insulation with high thermal conductivity are of considerable interest. Many fillers increase the thermal conductivity of polymer composites: metals (Ag, Cu), inorganic particles (BN, AlN, Si), carbon materials (nanotubes, graphene). Improving electrical insulating properties at high dielectric constant, low dielectric losses at high thermal conductivity are important for film capacitors for energy storage. Boron nitride (BN) nanolayers introduced into polymer nanocomposites have been found to increase thermal conductivity while maintaining electrical insulating properties. In this case, the thermal conductivity of polymer composites is strongly affected by the geometric distribution of fillers in the polymer matrix.

6. Polymer nanodielectrics in *biomedical systems*. Dielectric elastomers are flexible materials that change size or shape when subjected to an external electric field. Some of them, made from a soft and thin membrane placed with pliable electrodes, are materials used for artificial muscles and other robotic parts. It was found that in elastomeric nanocomposites, the control electric fields decrease as the deformation characteristics improve. In addition to applications in artificial muscles, the electromechanical properties of these soft dielectric materials are widely used as functional sensors to detect external stimuli of human movements or environmental conditions. In particular, capacitive-type sensors are preferred for various biomedical applications such as e-skin, health monitoring, and wearable equipment due to their advantages of low power consumption and better fault tolerance. The reason for the improvement in the characteristics of such materials is to increase the dielectric constant and reduce the rigidity.

Thus, many electrical properties of nanocomposites benefit from the inclusion of nanoparticles in polymers. The introduction of structural nanoparticles with their core and shell is one of the most effective ways to adapt the physical, mechanical, and electrical properties of the interface zones. In this case, the interface between the nanoparticle and the polymer matrix plays a decisive role in the properties of nanocomposites.

However, it is difficult to technologically ensure a uniform dispersion of the filler, since it is affected by the high cohesion energy of nanoparticles, i.e. bond energy between molecules, atoms or ions, which characterizes the strength of chemical bonds and their ability to withstand external influences. It is generally necessary to avoid the formation of agglomerates, which not only reduce the merits of the nanoscale, but also generate structural defects such as voids and impurities in the nanocomposites, which lead to deterioration of the long-term electrical and mechanical properties of the nanocomposites.

1.7 Summary

1. Nanomaterials, as a rule, are small particles (clusters) of materials consisting of 10=1000 atoms. Their properties depend on the number of atoms in cluster and on relative position of atoms, as well as on clusters shape and symmetry.

2. Nanoelectronics is rapidly developing field of electronics, which is engaged in development of technological and physical foundations for construction of integrated electronic circuits with element sizes less than 100 nanometers.

3. Nanoelectronics is the field of science and technology engaged in the creation, research and application of electronic devices with nanometer-sized elements, the functioning of which is based on the quantum effects.

4. Polycrystalline fine-grained materials with an average grain size of 50 to 150 nm are sometimes called *submicrocrystalline*, and if the average grain size becomes smaller than 50 nm, then *nanocrystalline.* In this case, the concept of "long-range order" in the arrangement of atoms of a substance can no longer be applied.

5. Quantum dimensional effects in the electronic structures are observed when the role of critical length l_{cr} is played by electron de Broglie wavelength (λ_e) when the size of a structure at least in one dimension has the order of λ_e. Thus, the quantum-dimensional effects are conditioned by wave nature of electrons.

6. The *nanocomposites* are solid formations consisting of basic matrix and nano-sized components that differ in their structural parameters and chemical properties. Mechanical, electrical, thermal, optical and other characteristics of nanocomposites differ significantly from properties of ordinary composite materials made of same basic substances or elements.

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1.9 Questions for self-examination

1. What is nanophysics? Give examples of 2D, 1D and 0D nanostructures.
2. Describe the ratio of surface and bulk atoms in nanoclusters.
3. What are the features of the structure of nanoclusters? Describe the optical properties of nanoclusters.
4. What is the role of the de Broglie wavelength of electrons for nanostructures?
5. Energy spectrum of electrons and density of their quantum states for 2D structures. Give an example of the implementation of a 2D structure.
6. Describe quantum threads - energy spectrum and density of quantum states. Give examples of implementation of 1D structure.
7. Describe quantum dots - energy spectrum and density of quantum states. Give an example of the implementation of a 0D structure.
8. What is single-electron tunneling? How to explain the Coulomb blockade?
9. What are the features of ballistic transport of charges?
10. Basic carbon nanostructures
11. List and explain the main features of nano-dielectrics in a polymer matrix.

Chapter 2. Peculiar electronic states in metals

Mane electrical characteristic of metals is the negative temperature coefficient of electrical conductivity. In metals, the electrons are practically free and chaotically move with Fermi speed. In the electrical field movement of electrons becomes partially directed: the drift of electrons superimposes over their chaotic movement. From direct proportionality of drift velocity to electrical field the concept of mobility follows which determines the measure of reaction of substance to electric charge transfer. Electromagnetic waves up to the optical range are almost entirely reflected from the surface of a metal that leads to the metallic lustre. Metals have high thermal conductivity caused by the high-mobility electrons; at that, the thermal conductivity is proportional to the electrical conductivity [1].

Classic electronic theory of metals is mostly consistent with quantum theory of electronic gas and electronic energy band theory of metals and successfully explains most properties of metals. However, in some cases, the experiments are confronted with the habitual simple explanations, and these cases are not only important in themselves but also allow to enhance the understanding of some peculiarities of electronic energy band theory. There is a special class of metals and alloys with the strong anomalous in different properties: this is the compounds of rare-earth metals, characterized by the incomplete 4*f*-shell. Their electronic properties are difficult to explain within existing concepts: the point is that these substances are intermediate materials between the magnetics and non-magnetics, as well as between the metals and dielectrics, while the valence electrons in them are found between the localized and free states. Investigation of these compounds helps to understand more deeply the nature as the metallic so the magnetic properties, and specify the conditions of “energy bands arrangement" in the metallic and dielectric states, as well as to investigate some peculiarities of electronic states in the crystals [2].

Below, as a quick reminder, in the first paragraph, the properties of common metals are listed and explained. But the main task of this Chapter to discuss the *highly unusual properties* of some metals and alloys that extend application possibilities of electronic energy band theory. Considerable attention is paid to the special electronic states in metals, such as the intermediate valence, heavy-fermions, valence instability, and so on. Superconductivity in metals and alloys are briefly discussed in connection of this effect use in electronics. Zero resistance nature of superconductors, magnetic field influence on them and mechanism of electron-phonon interaction are discussed. The high-temperature superconductivity is also considered as a basis for new components of electronic equipment.

Nanometals are metallic particles a few nanometers in size or thin films of the same thickness. These objects are of interest not only in connection with their special mechanical properties, but also due to unusual physical and chemical characteristics, sometimes significantly different from those of coarse-grained metals. Metal materials with magnetic properties are extremely interesting from the point of view of creating data storage facilities. Metals enclosed, for example, in a carbon matrix, acquire resistance to oxidation without losing their magnetic properties. Encapsulated or anchored nanometals are less susceptible to sintering at elevated temperatures. Thin metal films can be used in the electronics industry as compounds or as magnetic and electrical layers. Nanometals are used, including in energy sector, in manufacture of rocket engines, pyrotechnic materials, microelectronic films and coatings, the production of superconducting alloys and powder metals and alloys of increased strength. Any metal capable of forming extended flexible filament can be processed into nano-metal spheres using modern technology [3].

2.1 Basic electrical properties of metals

Metals are characterized by special kind of interatomic bonding – the metal type connection, in which crystalline lattice is formed by the positive ions while the valence electrons are delocalized throughout a lattice space. Therefore, metal can be presented as the lattice of positive ions crowded by "gas of electrons" that compensates forces of mutual repulsion of positive ions.

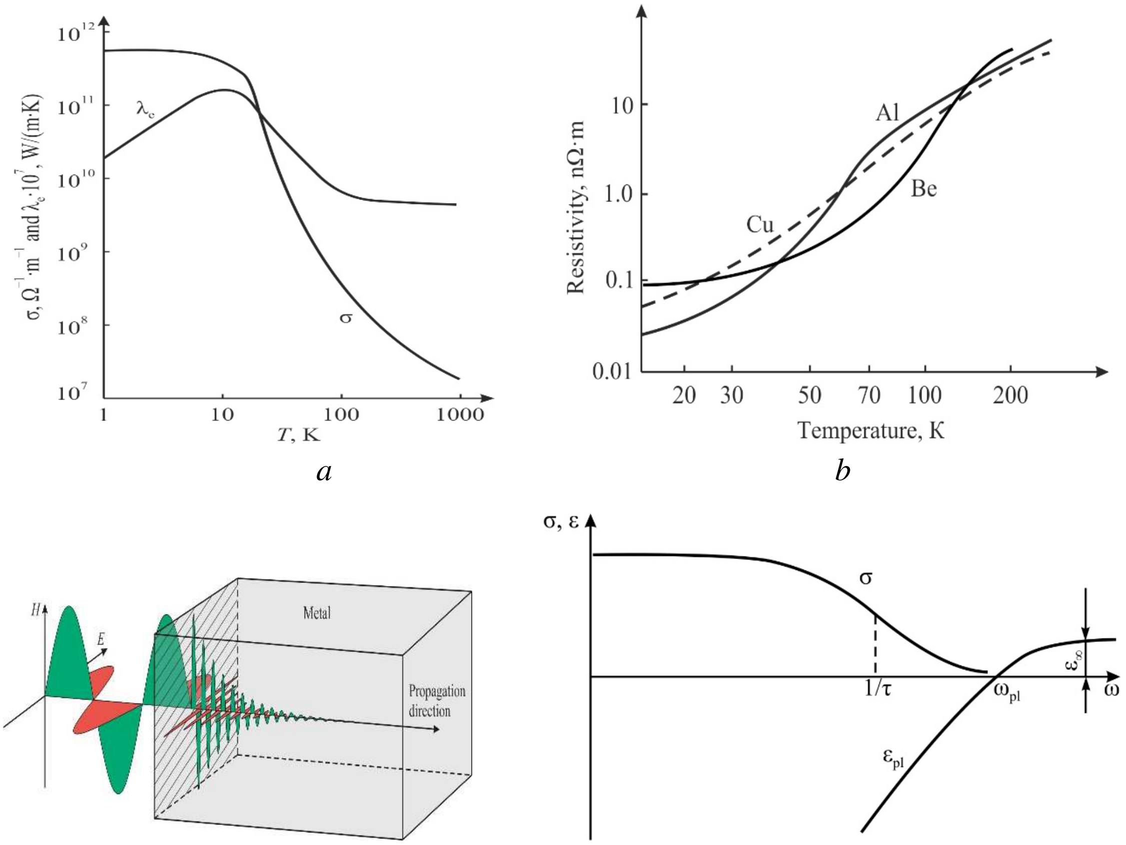
According to structure of electronic shells, metals can be divided into four groups: *s*-metals (alkaline metals and alkaline earth elements); *p*-metals (elements of third group); *d*-metals (transition elements); and the *f*-metals (also transition elements but of lanthanide group). Most of metals are crystallized in one of three structural types, namely; cubic, hexagonal dense packing and space-centred cubic lattice. In case of dense packing each ion of metal at equal distances has 12 nearest neighbours. The inter-atomic distances in metal structure characterizes the "metallic ionic radius." Optical range radiation is almost entirely reflected from metal surface, so that metals are opaque and have peculiar metallic luster. Being reflected from metal surface, the plane-polarized light becomes elliptically polarized. Some metals, such as gold (Au) in a form of very thin foil can be light translucent [1].

Electrical conductivity (or charge transfer) in metals is their main property which is described by the conductivity. It is the ability of material to conduct electrical current under the influence of constant voltage (not changing in time). If the substance is placed in the electrical field E [V/m], free charged particles – the carriers – under the force $F = qE$ get acceleration; q is charge of particle; in metals this is charge of electron: $q = e$. The acceleration of charges is directed towards the vector E for carries with positive charge $+q$ (i.e., for electronic holes or positive ions), or in the opposite direction for charge carries with negative charge $-q$. Directed in space motion of electrical charges is electrical current.

In the case of electronic conductivity, when only one sign of free charge carriers exist, the current density j, i.e., electrical charge that flows per unit time through unit area (oriented perpendicularly to vector E) equals to $j = ne\upsilon$, where n [m^{-3}] is number of charge carriers per unit volume of a substance (carriers concentration); υ [m/s] is the drift velocity, i.e., the average velocity of ordered movement of charge carries that arises under electrical field influence. This velocity usually is proportional to the field strength E: $\upsilon = uE$, where u is the proportionality factor called the *mobility* of charge carriers measured in [$m^2/(V\cdot s)$]. Above expressions can be represented as $j = \sigma E = E/\rho$, where σ [S/m] is specific electrical conductivity, $\rho = 1/\sigma$ [Ohm·m] = [$\Omega\cdot$m] is electrical resistivity,([S] = Siemens is the SI unit of conductivity). Specific conductivity σ or resistivity ρ defines the current density in material at given electrical field; at that, phenomenon of electrical conductivity is the electrical charge transfer [2].

Parameters ρ or σ are determined by the scattering process (losses) of electrical power in a matter. According to Joule-Lenz's law, the density of thermal energy p, [W/m^3], i.e., electrical energy that is converted into a heat per unit time and unit volume, is $p = E^2/\rho = \sigma E^2$.

Temperature dependence of conductivity can be described by the power law $\sigma(T) \sim T^{-1}$ which is explained by the scattering of electrons on the "dynamic" inhomogeneities of the lattice - phonons. But at very low temperatures this dependence show saturation, Fig. 1*a* becouse in case of deep cooling the dependence $\sigma(T)$ becomes depends on the concentration of "static" defects. When cooling metal, which has ferromagnetic impurities, at certain interval of temperature $\sigma(T)$ dependence can even show minimum (effect Kondo) [3].



a *b*

c *d*

Fig. 2.1. Conductivity different dependences: *a* – temperature change of σ and thermal conductivity λ_e in copper; *b* – temperature change of resistivity ρ of Cu, Be and Al; *c* – interaction and penetration of electromagnetic wave into a metal; *d* – conductivity σ and effective permittivity ε_{pl} frequency dependence in vicinity of plasma resonance

In some metals at low temperatures a *large conductivity* can be seen; Fig. 2.1*a* shows the specific resistance $\rho = \sigma^{-1}$ for convenience. This effect is different from the superconductivity and it is called the *hyperconductivity*. In fact, conductivity is the proportionality coefficient between the current j and applied electrical field: $j = \sigma \cdot E$. However, in the superconductors $E = 0$; as a result, parameter σ might be considered as an infinite quantity (only in DC). On the contrary, in the hyperconductor σ is quite certain parameter but it is unusual large. When describing temperature dependence, more convenient parameter is the resistivity $\rho = 1/\sigma$ shown in Fig.2.1*a*: at 77 K $\rho_{\text{Be}} < \rho_{\text{Cu}}$. The cause of such behaviour of Be is its largest among metals free electrons concentration: $n_e \sim 2.5 \cdot 10^{23}$ cm^{-3}. In the same way, but at low cryogenic temperatures best hyperconductor is Al: $\rho_{\text{Al}} < \rho_{\text{Cu}}$. At that, the advantage of hyperproducibility is that it cannot be suppressed by the magnetic field unlike superconductivity, which, as known, can be destroyed in the strong magnetic field. At cryogenic temperature 77 K (liquid nitrogen boiling point) the largest possible hyper conductivity (surpassing even the conductivity of copper) demonstrates the hyperconductor *beryllium* that is important in some applications.

Temperature dependence of thermal conductivity of metals, λ_e, [W/(K·m)], Fig. 2.1*a,* in addition to the their electrical conductivity, is also very important parameter for the electrical engineering and electronic equipment. Thermal conductivity of metals is conditioned mainly by the presence of high mobility electrons, and, therefore, λ_e is proportional to conductivity. The identity of λ_e/σ ratio for different metals is the Wiedemann-Franz's law: the ratio $\lambda_e/\sigma T$ is weakly dependent on temperature (because λ_e is practically independent on temperature). This ratio has same value for many metals and represents the Lorenz number: $L = (\lambda_e/\sigma T)$. For most metals at temperature 300 K this parameter equals $L \approx 2.4 \cdot 10^{-8}$ $W \cdot \Omega \cdot K^{-2}$.

Frequency dependence of conductivity, Fig 2.1*d*, is almost entirely corresponds to the electromagnetic waves reflection with the coefficient is $R = [(n-1)/(n+1)]^2 \approx 1$, where refractive index is $n = (\varepsilon\mu)^{1/2}$. Up to the optical range of electro-magnetic waves the conductivity of metals practically not changes with frequency, because electrons have very low inertia (due to their small mass). Since in the range of optical frequencies the magnetic permeability $\mu = 1$, the very large optical reflection of metals ($R \approx 1$) means that the effective dielectric permittivity $\varepsilon_{ef} \approx n^2$ is large (and negative). However, in the ultraviolet range of spectrum, the inertia of "electrons ensemble" (which is associated with the interaction with ionic lattice) shows the plasma resonance at frequency ω_{pl}. Frequency of this resonance (located approximately at 10^{16} Hz) is inversely proportional to the relaxation time τ_{rel} of electrons in plasma: $\omega_{pl} = 1/\tau_{rel}$. As a result, in the range of ultraviolet light conductivity of metals decreases with increasing frequency, Fig. 2.1*d*, and the metal gradually becomes transparent for harsh electromagnetic waves (*X*-rays).

Charge transfer description. Valence electrons in the ionic lattice of a metal are practically free, because the ions form energetically favourable lattice for electrons movement. The concentration of free electrons in metals is large (number of atoms per unit volume is approximately equal to 10^{23} cm^{-3}). Electrons can be treated as particles which weakly interact with each other; virtually they have no volume and move randomly through a crystal. The assumption that electrons practically do not interact with each other, seemingly, contradicts to Coulomb repulsion between them. But it should be also taken into account the Coulomb attraction of electrons to positively charged ions of crystal lattice. As quantum mechanical analysis shows, these joint actions in the strongly periodical structure of crystal make reasonable an assumption about “practically free electrons” (although this supposition has approximate nature).

Electronic gas exists in the thermodynamic equilibrium with crystal lattice that is established through the collisions of moving electrons and ions in lattice. Electrons in metal are always found in a movement, and they move even at lowest temperatures (near absolute zero). This quantum motion of electrons is chaotic, and different electrons move with different velocities. Most of electrons in metals move with Fermi velocity $\upsilon_F \sim 10^6$ m/s. This value can be defined from Fermi energy taking into account kinetic energy of electron: $(m_e \upsilon_F^2)/2 = E_F$. In the ideal metal with infinite conductivity, the electrical field cannot exist. To a real metal only very small electrical field can be applied (otherwise, huge electrical current would appear and melt the metal). Under the influence of external electrical field a current flows in metal, i.e., chaotic movement of electrons becomes partially directed: on disordered motion of electrons their drift is superimposed. To calculate corresponding current, one need to take into account the average velocity υ_{av} of electrons drift (at that, velocity of random motion of electrons is independent on electrical field). Since current density j is the amount of electricity passing per second through unit area of a conductor, then, according to this definition: $j = -n_e e \upsilon_{av}$. If current density is big enough, for example, $j = 1$ A/cm^2, calculations show that average drift velocity of electrons is only $\upsilon_{dv} \leq 10^{-3}$ cm/s. Thus, directional movement of electrons in the metals is very slow as compared not only with velocity of their chaotic movement but even in the macroscopic scale. The smallness of drift velocity is due to the fact that only a very weak electrical field can be applied to the metal.

Charge carriers mobility characterises the direct proportionality between the applied to metal field and caused by it current: $j = \sigma E$. Using the expression for current density, it is possible to establish that the average drift velocity of electrons in conductor is proportional to the force acting on them: $\upsilon_{dv} = (\sigma/en_e)E = uE$. Parameter $u = \sigma/en_e$ is the mobility which is the drift velocity caused by the influence of unit of field. Its unit can be clarified from formula $u = \upsilon/E$; as a result, in SI the dimension of mobility is $[u] = [\mathrm{m}^2/(\mathrm{s{\cdot}V})]$. It is seen that such unit of mobility difficult to relate with physical meaning of this phenomenon. If one continue to find physical sense of mobility unit using SI system, it can be written as $[u] = \mathrm{T}^{-1}$, i.e., return value of “Tesla” that is unit of magnetic induction in SI, because V·s = Wb (Weber) and

$Wb/m^2 = T$. Another possibility to find mobility unit in SI is also inconvenient for easy interpretation: $[u] = A \cdot s^2 \cdot кg^{-1}$.

On the contrary, in the Gauss system of units (CGSE), unit of mobility is estimated as [s/g] (second/gram), that is much more simple, and, hence, more understandable content. Really, mobility characterizes the increase of velocity (m/s) under force influence of: $\upsilon = u \cdot f$. The force is $f = ma$ and in SI has unit [N] = Newton, so in Gauss system force is $1N = 10^3\, g \cdot 10^2\, sm/s^2$; then mobility has simple unit: $u = \upsilon/f$, therefore $[u] = [s/g]$. In fact, mobility indirectly characterizes the opposition of a medium through which electrons drift under electrical field influence. If any braking force would be absent, the electron under electrical field will move with constant acceleration (such as in vacuum), but not with constant velocity as they really move in crystal. Mobility characterizes how charge carriers, being forced by electrical field to the directed ordered motion, can overcome their thermal chaotic motion that is characterized by continuous collisions with phonons and defects.Therefore, the mobility is the degree of freedom of electron’s directed motion in a media (while almost nothing prevents the electrons in their chaotic quantum Fermi motion) [2].

Analogy of a current, flowing in conductor, with a liquid, flowing through the pipe indicates that electrons in conductor move with some similarity of "friction". Thus, there are some reasons that brake field-induced directional movement of electrons inside a metal.

Analyzing these reasons and taking into consideration that mobility should be expressed through specific conductivity, it is possible to get: $\sigma = n_e e u$. Necessity to express the metal conductivity σ by means of two others parameters n_e and u is due to a fact that each of them can be found in independent experiments. Indeed, the concentration of free electrons n_e never changes with temperature: it is peculiar property of given metal. Conversely, another parameter, the mobility u, can vary with the change of temperature in hundreds and even thousands times. In addition, by cleaning metal from impurities it is possible to increase electrons mobility many times. That is why, it is important that two characteristics – number of electrons per unit volume n_e and their mobility u – allow independent measurement.

2.2 Necessary information from metals theory

High electrical and thermal conductivity of metals, as well as typical metallic luster indicate that electrons in a metal can be treated as free. Analysis of Ohm's law leads to same conclusion: when even a very small voltage is applied to metal it is always seen that current is proportional to voltage, and proportionality factor ($1/R$) is same as it is for increased values of voltage and current. If electrons in metal would be linked to specific nodes in a crystal lattice, then the threshold electrical field will exist, from which "normal" Ohm's law will begin to run. In other words, at lower electrical field the conductivity of metal would be less than at bigger field. The fact that such phenomenon is not observed testifies model of free electrons [1].

The Drude’s theory, supposing chaotic (thermal) motion of electrons and their drift under the influence of directional electric field, makes possible to conclude Ohm's law. In case of electrons collision with the imperfections in crystal lattice, the energy, accumulated during electrons acceleration in the electrical field, passes into crystal lattice, so that it becomes heated (Joule-Lenz’s law). Thus, classic electronic theory of metals can analytically describe and explain experimentally obtained basic laws of conductivity and power losses in metals. It can explain also the relationship between electrical conductivity and thermal conductivity of metals. Moreover, some others experiments confirm the hypothesis of electronic gas existing in metal, for example, the curvature of electron trajectory in the transverse magnetic field: electromotive force changes electrical resistance of a conductor.

Therefore, metals are different from other solid bodies by free electrons existence that practically are not connected with atoms but nearly freely move inside a metal. With a concept of free electrons not only electrical properties of metals, but other peculiarities can be explained, such as flexibility. Assuming that electrons in a metal represent the classic gas, Drude’s model offered metal as a "vessel" containing "gas" of freely circulating electrons that makes possible to get formulas for high frequency conductivity $\sigma(\omega)$ and for electronic contribution to thermal conductivity λ_e:

$$\sigma = \sigma_0/(1 - i\omega\tau); \qquad \sigma_0 = n_e e^2\tau/\mathrm{m}; \qquad \lambda_e = L\sigma_0,$$

where n_e is the number of electrons in 1 cm^3; $\omega = 2\pi\nu$ is the frequency of electrical field; σ_0 is the conductivity at low frequencies; τ is the free path of electron; L is the universal constant (Lorentz number). Thus, by introducing metal as a system, in which positive ions are fastened by means of freely mobile electrons, it is possible to explain basic properties of metals: elasticity, ductility, big thermal conductivity and large amount of electrical conductivity.

Quantum distribution of electronic gas. In the process of metal heating, the electrons, locating in lower energy levels, can not increase their velocity (by additional energy), because most of higher energy levels are already occupied. Occupied levels and free levels in electronic energy spectrum of metal are divided by the Fermi level. Thus, the only those electrons that located near the Fermi level can be thermally excited – only they can rise to the unoccupied states located just above the Fermi level.

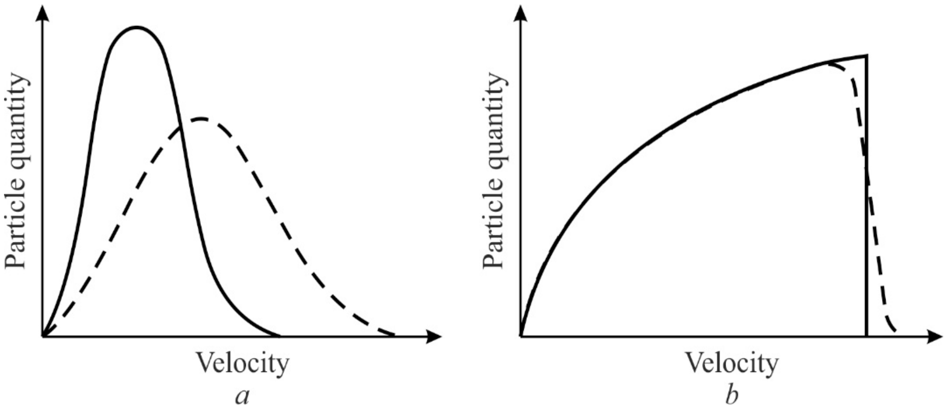


Fig. 2.2. Comparison classical Maxwell-Boltzmann distribution of gas molecules velocity (a) and quantum Fermi-Dirac distribution of electronic gas velocities (b); dotted lines corresponds to higher temperatures

Quantum distribution of electronic gas velocities is significantly different from classic distribution of molecules velocity in the normal gas, described by Maxwell–Boltzmann function. The point is that classic distribution is greatly dependent on temperature: at lower temperature the maximum of distribution is narrower than at higher temperature. Moreover, this maximum becomes more blurred and noticeably shifts toward higher velocities, Fig. 2.2*a*). In contrast, in case of quantum electronic gas distribution, the density of states at room temperature, Fig. 2.2*b*, *dotted line*, differs only a little from the density of states at absolute zero, Fig. 2.2*b*, *solid curve*.

However, during study electrical and thermal properties of metals, usually the distribution of energy but not the velocity is used [3].

Fermi energy level. To determine a number of free charge carriers in metal it needs to know the quantity of energy levels (states) of electrons in that conduction band which is actually occupied. Dependent on temperature and energy, the probability $w(T,E)$ of electron existing on the energy level E is determined by distribution function of Fermi-Dirac:

$$w(T,E) = \{1 + \exp[(E - E_F)/k_BT]\}^{-1},$$

where k_B is the Boltzmann constant, T is the absolute temperature; energy E_F is the Fermi level. As seen from this formula, at $T \neq 0$ the distribution function in level $E = E_F$ is $w = ½$.

In the *ground state*, i.e., at temperature $T = 0$ K:

- For energy levels which are located below the Fermi level, the distribution function is unity ($w = 1$), because $E < E_F$ and $\exp[(E - E_F)/k_BT \rightarrow 0$. This means that all levels, which lie below the Fermi level, at absolute zero are occupied by electrons.
- For energy levels which are located above the Fermi level, the Fermi-Dirac distribution function equals zero ($w = 0$), because, if the energy $E > E_F$ and temperature $T \rightarrow 0$, the function $\exp[(E - E_F)/k_BT \rightarrow \infty$, so the probability $w(T,E) \rightarrow 0$, i.e., at the absolute zero, all levels, lying above the Fermi energy, are empty.

Thus, in metals, at temperature $T = 0$ the Fermi level divides the conduction band on a half: entirely occupied lower part of a band, and entirely empty upper part of a band, without any energy gap between these parts. The Fermi-Dirac statistics should be used, only when the quantum effects are considered, and the particles (in this case – electrons) do not differ from each other. Quantum effects are found in the case, when the concentration of particles n is greater, than the quantum concentration n_q, while the distance between the particles is close to the de-Broglie wavelength, i.e., if the wave functions of particles are touching but *not overlapping*. Exactly this situation corresponds to the metals. As a result of electrostatic repulsion, the free electrons in a metal never come close to one another: each electron is surrounded by a free cavity, into which another electron can not enter. However, this cavity is partially filled by the positive charge of lattice, so the positive charge screens given electron from all others. Thus, due to the electrical repulsion force, the electrons move inside a metal with very rarely collisions between them.

Typically, Fermi-Dirac statistics is used at low temperatures, but in the case of metals this statistics should be applied at *normal temperature*. The point is that temperature ~ 300 K with correspondent energy k_BT ~ 0.03 eV looks as a very low for metals, because the Fermi energy in metals is large (E_F ~ 5 - 10 eV). In contrast to the ideal gas, in which any additional energy is absorbed by *all molecules*, in the metal absorbed heat ar other energy can excite only a *relatively small amount* of electrons located near the Fermi level. That is why, to raise the temperature of electronic gas, much less heat is required and in metals heat capacity is small, increasing linearly with temperature.

Fermi surface. Unlike classic electronic theory, the quantum mechanics shows that gas of electrons in a metal, under normal temperature. is found in a state of *degeneration*. In this state, the energy of electronic gas is practically independent on temperature, i.e., the thermal motion changes the electrons energy only a little. That is why, the thermal energy practically cannot heats the electronic gas, and this is clearly detected by measurement of thermal capacity. In the state, similar to the conventional gas, the electronic gas looks as if its temperature were several thousand degrees. According to the quantum statistics, gas of electrons cannot have more than two electrons with the same quantum parameters. Electrons occupy all allowed states of impulses, but not higher than limiting Fermi level. The Fermi surface, Fig. 3, is a boundary between the occupied and unoccupied states of electronic gas at the absolute zero. Therefore, the Fermi-surface is the *isoenergetic surface in a space of quasi-pulses* (p-space) which corresponds to the Fermi energy E_F: $E_s(p) = E_F$. Here $E_s(p)$ is the dispersion law of the conduction electrons where s is the number of energy band; so the Fermi-surface at temperature $T = 0$ K separates the occupied electronic levels from the empty levels.

Sometimes, when Fermi-surface representation, it is possible to restrict the task by using only one p-space, namely, the 1-*st* Brillouin zone, located just at the ends of vectors p which describes all non-equivalent states. If the Fermi-surface is completely housed in the one cell of p-space, then this surface is *closed*, Fig. 2.3*a*. In this case, the Fermi surface is the *sphere* with radius $k_F = (2mE_F)^{1/2}\hbar^{-1}$, which is determined by the concentration of valence electrons. If the Fermi surface intersects the boundaries of cell in the p-space, it is called *opened*, Fig. 2.3*b*. When the extended p-space is used, the closed Fermi surface is endlessly repeated from cell to cell.

In the impulse space, all states inside Fermi sphere of radius p_F are filled. The linear response of a metal to the electrical and magnetic fields or onto thermal gradient is determined by the shape of Fermi surface, because the electrical current is due to changes in the occupancy of the states near the Fermi energy.

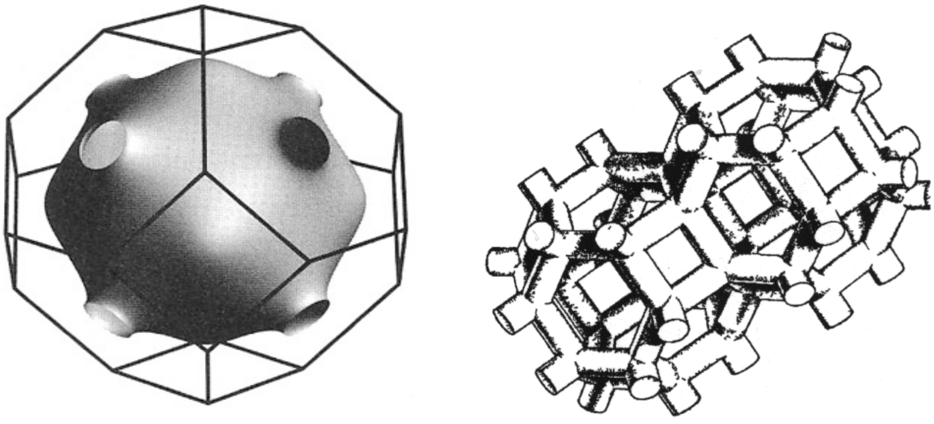

a *b*

Fig. 2.3. Closed (*a*) and opened (*b*) Fermi surfaces for copper and lead, respectively

Thus, the Fermi surface is the abstract boundary in the reciprocal space, which is useful to predict thermal, electrical, magnetic and optical properties of the metals and semimetals. The shape of the Fermi surface is derived from the periodicity and symmetry of crystal lattice, as well as from the occupation of electronic energy bands. The success of Fermi surface model is a direct confirmation of Pauli principle which allows maximum one electron per one quantum state. Most of electrons are placed inside the Fermi surface, and only some of them can be outside of it (in the strip of k_BT, Fig. 2.3)

Some important remarks to band theory of metals.

- Band theory utilizes a fact that electron has both properties of particle and wave, so, in case of close location to ions in a lattice, the wave properties of electrons necessarily manifest themselves. The Bloch wave functions, used in the one-electron band theory, is well true for the metals with *s*- and *p*-electronic shells, which have big length of orbital space with a considerable mutual overlap. However, in the case of metals with *d*- and *f*-shells, the use of band theory might be with cautious. tha conduction electrons in these metals (and in their alloys) have increased effective mass; moreover, other physical properties of these crystals might be very specific.
- The curvature of the Fermi surface is dependent on theallowed states density near it, and this curvature affects the electrical, thermal and magnetic properties of a metal. The more electrons are located near the Fermi surface, the more electrons can increase their energy during metal heating, as well as the more electrons can orient their spins in the magnetic field (that results in the paramagnetism of the electronic gas in metal).
- Metals always have some electrons on the blank levels above the Fermi level (that is why, the metals are good conductors of electricity). It means that metals have such Fermi surface, from which electrons can easily be transferred to the blank (allowed) higher energy levels. The current in conductor is carried by those free electrons which can be easily accelerated, moving through the allowed unfilled states.
- Decrease of electrical conductivity with increasing temperature is a typical property of metals. This dependence is due to the local thermal vibrations in a crystal lattice. Accelerated by the electrical field electrons are scattered on these vibrations, and, therefore, the velocity of electrons reduces. Raising temperature increases the thermal vibrations intensity, so the free path of electrons between two collisions decreases. Conversely, with temperature lowering, the interval between collisions (and corresponding relaxation time) increases, and conductivity increases. Electrical conductivity of any metal can be calculated, if the shape of Fermi surface and the relaxation time for these electrons are known. The Fermi surface permits also to evaluate the electrical and thermal conductivity of a metal at different conditions. Finally, the knowledge of the shape of Fermi surface is necessary to explain the peculiarities of metals structure and their absorption and reflection properties, as

well as to describe the superconductivity in some metals at low temperatures, and many others physical properties.

- Charge carriers in metals are the free electrons which are called also as the conduction electrons. They are typical quasiparticles? and their properties are substantially different from the "normal" electrons existing in a free space, although the electrical charge of conduction electron coincides with the charge of electron in a vacuum. However, the *energy* of "electron = quasiparticle" is the complex periodic function of the impulse. In the case, when electron is found in a free space, the surface of its equal energy is the sphere. For conduction electron in a metal, the surface of equal energy might be complicated, being correspondent to the surface of equal energy in the impulse space. The form of this surface and its size depend on the energy value that in its turn is dependent on the dispersion law of quasiparticle.
- Fermi surfaces of different metals can be quite various. In some metals, they resemble the billiard balls (K, Na, Rb, Cs), in others – the complex designs of various shapes (Au, Ag, Cu, Zn, Cd, and others). One of ordinary Fermi surfaces – for copper crystal – is shown in Fig. 3*a*. This example is chosen, because the copper has one of highest values of conductivity at 300 K, and copper is widely used in electrical engineering and electronics.
- The change of particle energy is equivalent to its impulse change multiplied by velocity. Therefore, to explain the complicated energy spectrum in a given metal, one needs to know the shape of Fermi surface, and superpose with this surface electron velocity. Increasing energy of any crystal (particularly, metal) can be described as the generation of new quasi-particles. The increase of conducting electrons energy in a metal is possible by the moving at least one electron under the Fermi surface into the external impulse space. At that, the appearance of electron beyond the Fermi surface is always accompanied by the unoccupied state in the filled part of a band – the hole, which can also be interpreted as a kind of quasiparticle – i.e., the antiparticle to the electron, which emerges from under the Fermi surface. Therefore, the increasing energy of a free electron in metal is always accompanied by the birth of *two quasiparticles*. Calling hole as a "antiparticle", one has in mind the possibility of recombination: in the case, when electron returns "into its place" (under the Fermi surface), the metal is returned again closer to its ground state, because both quasiparticles – electron and hole – disappear.
- Therefore, from full Fermi sphere, only those electrons should be selected, which are located directly beneath the Fermi surface, and in small distance from it. That is why, it is important to identify and explore just the *nearest neighbourhood* of the Fermi surface – those portion of impulse space, in which the quasiparticles –

electrons and holes – can coexist. The mechanism of current flow through a conductor might be rather intricate: due to the applied electrical field, the electrons, by infinitely small portions, increase their impulses (and energy); next, by the collisions with foreign atoms, dislocations, boundaries of crystallites and phonons (i.e., with any kinds of defects in crystal lattice) the electrons *return gained from electrical field impulse to lattice*. For electrons, located in the fully filled areas deep under the Fermi surface, such process is impossible: the Pauli principle of exclusion prevents them to leave their energy levels, so electrons can only move from their level to releasing level.

2.3 Metals with intermediate valence

When investigation the properties of rare earth metals, the main attention usually is focused on the phenomenon known as the "intermediate valence" or "heavy fermions". It is appropriate to remind that all electrons of atoms, which form a solid, can be divided into *two groups*: the electrons strongly bounded inside an atom (in the residue), and the electrons which can leave its atom: they either move to the another atom (i.e., from atom Na to atom Cl during formation of ionic rock salt crystal, NaCl), or form covalent bonds (such as in the germanium crystal). Electrons also might be *generalized* within crystal, this is what happens with the conduction electrons in metals. In all these cases, the conception of atom *valence* is employed, that is, the number of electrons that can be detached and moved away from native atom in the process of solid body formation. For example, the valence of Na is “+1” as in the ionic crystal NaCl so in the metal Na.

However, some substances are known, in which the outward electrons demonstrate a double, the *ambivalent* nature: keeping partly localized in the native atom, they also can demonstrate the intention to collectivization. To the systems with the *unstable valence* (or intermediary valence) the some compounds of rare-earth metals can be included (those elements that have uncompleted the 4*f*- electronic shells). These compounds have unique physical properties and anomalous characteristics, which can be accounted for *heavy fermions* formation: the extraordinary electrons, which effective mass in 10^2-10^3 times greater than the mass of free electron.

Historically, the study of this phenomenon began, when the peculiar α–γ phase transition in the metallic cerium was discovered. Most of phase transitions in solids are accompanied by the change in crystal symmetry, which means the changing in atoms packing in lattice (as well as the ordering of spins in the ferromagnetics, or the ordering of dipoles in ferroelectrics). However, the α–γ phase transition in Ce looks like an exception: when it happens, the ordering in the lattice symmetry not changes, but this transition is accompanied by an essential jump in crystal volume reaching 15%. Primary explanation of this phenomenon was the reconstruction of electronic structure of ionic residue during the α–γ transition in cerium. This concept with some additions and changes is still preserved, and even applied to the many other systems. At present time, rather wide class of compounds are found, in which the valence instability is accompanied by the strong anomalies of almost all physical properties of correspondent substances.

Among these systems, which by many features are close to the ordered magnetic states, some substances are found which are ready to pass into the superconducting state. This circumstance is quite unexpected: the antagonism between the magnetism and superconductivity is well known. However, this important fact is that not only normal, but the superconducting properties of these substances are quite unusual; these facts has led to the speculation that they are a new type of superconductors that differs from all known.

Metallic compounds with the intermediate valence and heavy fermions, in which the anomalous properties are most severe, include the UBe_{13}, in which uranium atoms form the cubic lattice while Be_{13} atoms are placed between them, creating almost regular polyhedron – icosahedron Be_{12} possessing another "extra" Be in the centre of this icosahedron. There are also some cerium compounds: the $CeAl_3$ possessing hexagonal lattice, the $CeCu_6$ with orthorhombic structure, the $CeCu_2Si_2$ with tetragonal lattice and some others. Besides, there are many systems with less-heavy electrons: they are compounds with the intermediate valence.

Anomaly properties of heavy electrons compounds.

Specific heat in metals with heavy fermions, at first glance, is surprising. The heat capacity is well known defining characteristic of solids: the temperature dependence of the *lattice* specific heat corresponds to Debye law: $C \sim T^3$ while the *electronic* contribution to the specific heat in ordinary metals very small and linearly increases with temperature: $C = \gamma T$. In sum, the specific heat of normal metals is

$$C = \gamma T + \xi T^3;$$

therefore, using more comfortable for graphic analyses scale $(C/T)(T)$, this dependence can be seen as:

$$C/T = \gamma + \xi T^2$$

and shown in Fig. 2.4*a* for the ordinary metals.

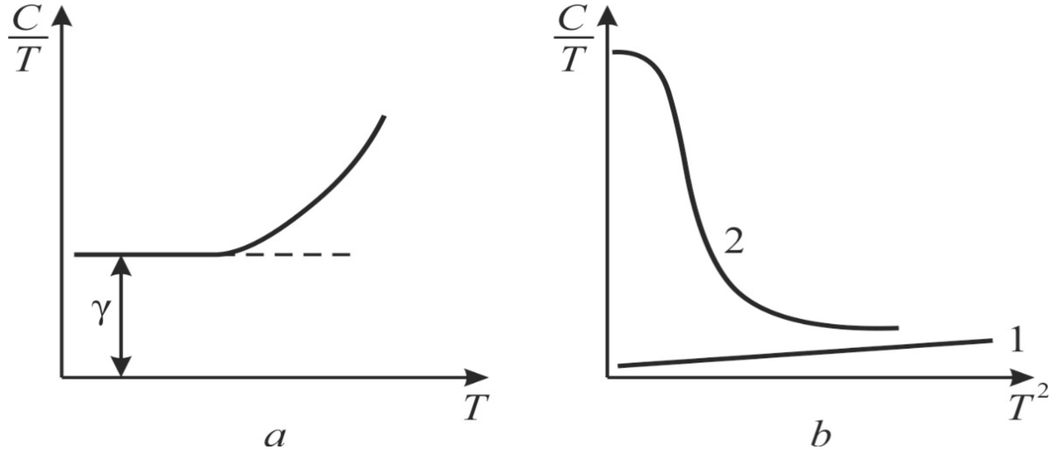


Fig. 2.4. Specific heat temperature dependence in various scales (*a, b*); compare normal metals (1) and systems with heavy fermions (2)

However, for the metals with heavy fermions, Fig. 2.4*b*, an another comfortable coordinates can be also used: $(C/T)(T^2)$. In this scale, it is convenient to observe the completely unusual growth of the electronic contribution to the heat capacity in the systems with heavy fermions. The comparison of temperature coefficients of specific heat in normal metals and in heavy-fermions materials at low temperatures are given in Table 2.1. In the conventional metals (Cu, Li), the proportionality coefficient $\gamma = C/T$ is about 1 mJ/mol·K^2, while in the transition metals like $CePd_3$ this ratio is greater by the order of magnitude: $\gamma \sim 10$ mJ/mol·K^2 which indicates a particular behaviour of the electronic subsystem already in the *transition metals*.

Table 2.1

Proportionality factor $\gamma = C/T$ and magnetic susceptibility χ in different metals

Crystal	Cu	Li	$CePd_3$	$CeAl_3$	$CeCu_6$	$CeCu_2Si_2$	UBe_{13}
γ, mJ/mol·K^2	0,695	1,63	35	1620	1500	1000	1100
æ, (T → 0) 10^{-3} CGSE/mol	0,008	0,03	1,5	36	27	8	15

It is noteworthy that the heavy-fermions systems have coefficient γ even greater by 2–3 orders of magnitude (and the same applies to their magnetic susceptibility). At that, the $CePd_3$ is a compound with the *intermediate valence,* while the $CeAl_3$, $CeCu_6$, $CeCu_2Si_2$ and UBe_{13} are the systems with *heavy fermions*. If the specific heat would be estimated like in normal metals, the observed values of γ will correspond to the effective mass of electron in 10^2–10^3 times grater than the mass of free electron. Unusual is also the temperature dependence of specific heat Fig. 2.4*b*.

Magnetic properties of heavy-fermions metals are also unusual. As well known, in conventional metals poswsessing collectivized electrons, the magnetic susceptibility æ of free electrons is almost independent on temperature: æ ≅ const, Fig. 5*a*, *curve* 1. That is because the æ (as well as the temperature coefficient γ of specific heat) is proportional to the effective mass of electron. However, in the *paramagnetic* metals, Fig. 2.5*a, curve* 2, the temperature dependence of magnetic susceptibility obeys Curie law: æ ~ $1/T$, i.e., parameter æ increases as temperature decreases (sometimes, such substances at low temperatures can even come to a state with magnetic ordering – ferromagnetic or antiferromagnetic).

In the systems with heavy fermions, at low temperatures the increase of æ(T) with decreasing temperature is also seen, but, unlike the paramagnetic, these increase comes to a saturation (stops at fixed temperature, Fig. 2.5*a*, *curve* 3). At that, any magnetic ordering in the systems with heavy fermions is not established (except for some special cases, such as U_2Zn_{17}), but the temperature change of susceptibility æ(T) enters onto a mode, peculiar in the conventional metals, when æ = const (such as in *curve* 1). It is necessary to note that quantity of this constant looks as abnormally large (Table 1). When $T \to 0$ the magnetic susceptibility in systems with heavy fermions may exceed the æ value of the paramagnetic susceptibility of conventional metals more than 1000 times.

Previously such a large value of paramagnetic susceptibility is supposed as the specific property of ferromagnetics. Among the "non-ferromagnetic" substances, the record shows metal Pd, in which at low temperature $\chi(\mathrm{T} \to 0) = 0.7{\cdot}10^{-3}$ CGSE/mol. However, it is necessary to note that palladium is nearly ferromagnetic metal: the adding into Pd only a few percents of iron makes it the typical ferromagnetic. Nevertheless, in the $CeAl_3$, for instance, the paramagnetic susceptibility in 50 times greater than in the Pd, although no ferromagnetism in this alloy can be observed. the heavy-fermions systems, instead magnetic ordering, become superconductors (recall that the classic case of superconductivity is incompatible with magnetism).

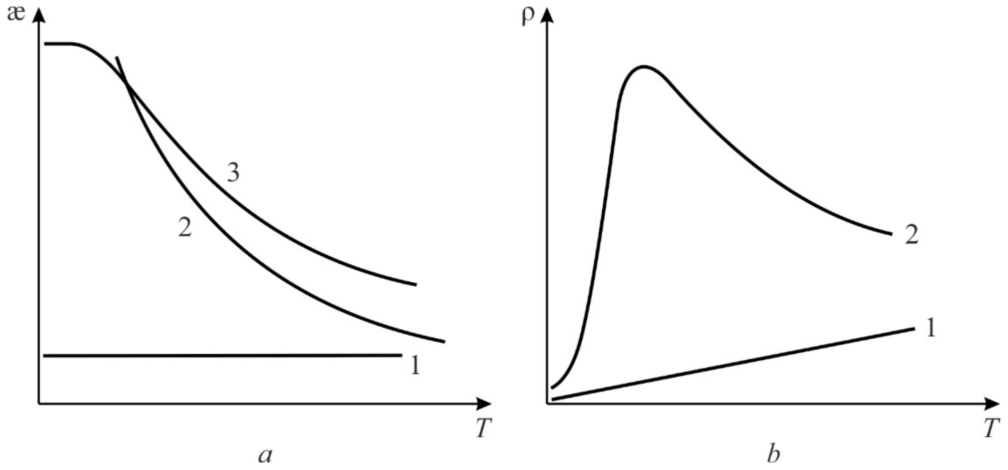


Fig. 2.5. Comparison of normal metals and heavy-fermions metals: *a* – temperature dependence of magnetic susceptibility: 1 – non-magnetic metal, 2 – paramagnetic with localized magnetic moments, 3 – heavy-fermions systems (in reality this susceptibility is situated much above than curve 2; *b* – temperature dependence or resistivity: 1 – normal metal, 2 –heavy fermions metal

Electrical conductivity of heavy fermions systems also impresses with its unusual behaviour. It should be recalled that in the conventional metals the specific electrical resistance ρ decreases with temperature fall approximately linearly. The resistance of the pure metals, ideally, in the case of $T \to 0$ tends to zero (Fig. 2.5*b, curve* 1) while in the case of impurities presence a small residual resistance can be observed. As stated earlier, the exactly *positive temperature coefficient* of a resistance (that means the negative temperature coefficient of conductivity) is the hallmark of the metal.

By contrast, in the semiconductors or dielectrics, the electrical resistance increases with decreasing temperature, and at $T \to 0$ tends to infinity. Similarly, at a sufficiently high temperature, in the heavy fermions metals ρ(T) dependence resembles the behavior of dielectrics or semiconductors, that is quite atypical for the conventional metals (Fig. 2.5*b, curve* 2). But at a certain temperature the ρ(T) reaches a maximum, and then, as in the metals, it decreases practically linearly in the low-temperature region.

Theoretical explanation of this unusual combination of properties of heavy fermions materials will be given later.

2.4 Electronic energy band theory and heavy fermions

It is assumed that each electron moves in a force-field of ions and all other electrons (except under consideration); at that, the paired interactions does not taken into account even for the nearest neighbouring electrons (these interactions are mathematically included in average field). In the one-electron approximation, the solution of the Schrödinger equation in the crystal are the Bloch functions, while energy eigenvalues form a power zones which filling is found by Pauli principle.

Band electronic spectrum allows construct the models of different variants of electronic spectra of crystals. There are several main cases:

I. Energy bands of electronic spectrum do not overlap, Fig. 2.6 *a*,*b*.

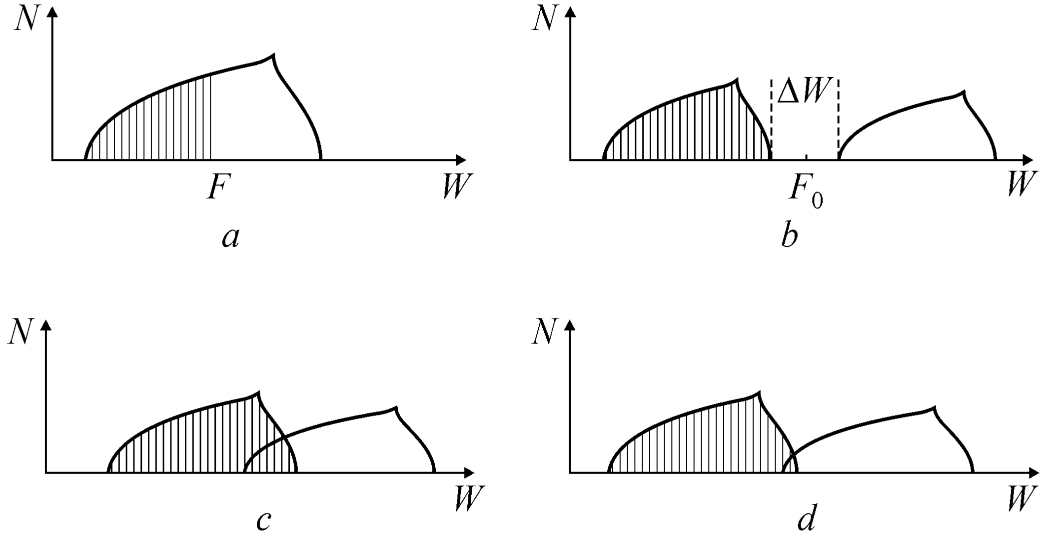


Fig. 2.6. Electronic levels in the spectra (filled levels are shaded): *a* – "true" metal with odd number of electrons in unit cell; *b* – dielectric or semiconductor with gap ΔW between valence band and conduction band; *c* – metal with even number of electrons in unit cell; *d* – semimetal

- Crystals with *odd number* of electrons per unit cell have the upper energy band filled with exactly half. The energy band has $2N$ vacations, lowest half of which is occupied by the electrons. The filled part from the unfilled part of valence band is separated by the Fermi level F.

- Crystals with an *even number* of electrons per unit cell are dielectrics or semiconductors, Fig. 2.6*b*. In the ground state (at $T = 0$ K) the energy bands are completely filled or empty. Therefore, the electrical field can not change the energy of electrons in the filled bands (since all the levels are filled), while in the empty bands there are no charge carriers. Upper filled band (valence band) and the nearest empty band (conduction band) are separated by the energy gap ΔW (forbidden band).

II. Bands of the electronic spectrum overlap, Fig. 2.6*c, d*.

- Crystals, as with the even, so with the odd numbers of electrons per lattice site, refer to metals. *Significant overlap* of the two bands (Fig. 2.4*c*) results in the situation, which is not very different from the model shown in Fig. 2.4*a*.

- In the event than *small overlap* of bands, crystals belong to *semimetals*, Fig. 2.6*d*. Their conductivity by the several orders of magnitude is lower than the conductivity of metals. For example, in the semimetal bismuth, the number of filled states in conduction band in 10^4 times smaller than in conventional metals, and, consequently, bismuth shows much lower conductivity. Other examples of semimetals are antimony and graphite. Under the influence of an electrical field, the electrons move in the semimetals within their area, but the lower density of states reducing their mobility.

Therefore, such crystals, which in the ground state have no partially filled bands, belong to the dielectrics or semiconductors. The metals and semimetals, by contrast, are characterized by the electronic spectrum with *partially filled* bands.

According to band theory, it is possible to make a conclusion that all properties of solids depend on the ratio of free electrons number to the number of states in the bands of electronic spectrum. If the quantity of electrons is just enough to fill a certain band *completely* (while their next band with higher energy remains empty), those crystals belong to the dielectrics or semiconductors. Inasmuch as the electronic states are localized, under the influence of electrical field no electrical current can flow in such crystals. At zero temperature in the dielectrics and semiconductors in the conduction band electrons are absent, while the valence band is completely filled (accordingly to Pauli principle: every energy level can hold only two electrons with opposite spins).

Another possible behaviour of electrons is realized in the metals, in which only the lower energy levels of conduction band are filled, while upper energy levels are available for electrons – without any energy gap. In this case, even an arbitrarily small electrical field can easily move electrons, so crystal exhibits metallic conductivity. It is appropriate to recall that highest energy level, occupied in the metal at zero temperature, is the Fermi level.

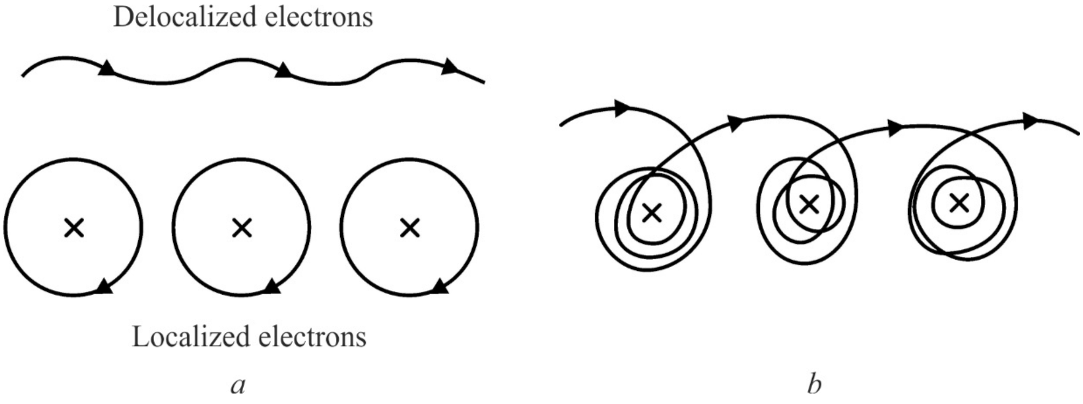


Fig. 2.7. Schematic representation of electron' movement: *a* – in metals with delocalized electronic states, *b* – in metals with heavy-fermions state

Therefore, for most of solids, the states of valence electrons are clearly described: in the metals (such as Na, Al, Pb), in the semiconductors (such as Ge and

Si) and in the typical dielectrics (such as NaCl). Metal type of electrons behaviour is symbolically illustrated in Fig. 2.7*a*: it shows the trajectories of the collectivized (delocalized) electrons and the electrons localized near atoms. Conception of delocalized states supposes that internal electrons of atomic residue have relatively small radius of their orbits and, of course, these orbits vary only slightly in the case of associations of atoms in a crystal.

However, quite another behaviour is possible for electrons, based in the external shells of atoms: they can be only partially tied with their native atoms so only for a while revolve around residue, but from time to time they move to neighbouring atoms like "free" electrons, Fig. 2.7*b*, and than return to their partially connected state. These electrons are almost delocalized.

Accordingly to electronic energy band theory, developed for crystal with entirely delocalized electrons, they move in the periodical field of ionic cores: the result is the formation of allowed and forbidden energy bands. Electrons by their energy tend to distribute closer to the bottom of energy band: and are described by same equation as free electrons: $E = p^2/m^*$, but with the effective mass m^* instead of free electron mass m_e. The value of the effective mass m^* is closely connected with the width of conduction band ΔE: $m^* \sim 1/\Delta \mathrm{E}$. If the impulse of electron runs a certain value (actually, in crystal $|p| \leq \hbar/a$, where "a" is the interatomic distance), the width of band is $\Delta E \sim \hbar^2/2ma^2$, i.e., the small effective mass meets the wide band, while the large effective mass corresponds to the narrow band.

However, another description of electrons properties in solids would be considered: the delocalized electronic states, the collectivized electronic states and the states of electrons localized in atoms. Despite the fact that this discussion concerns to metals, it make sense to consider whether all dielectrics are same. Each substance, including dielectric, is individually different from another substance by a specific set of attributes: way to get, optical properties, hardness, electrical conductivity, and so on. Hence, it is not evident whether the nature of the dielectric state is same in various substances. Correspondingly, in standard energy band theory, the dielectric is a substance, in which the valence energy band is entirely occupied, while located above it conduction band is empty and separated by the essential energy gap. However, not all dielectrics are arranged exactly by this way – another nature of the dielectric state is possible.

The point is that the description of electronic structure of solids is based on a conception that electron moves in the lattice created by regularly situated atoms or ions. If there are many electrons, it is assumed that they do *not interfere* with each other, and they are allowed to occupy energy levels accordingly to Pauli principle.

But in reality, all electrons interact with each other, so it is necessary to compare their interaction energy U with their kinetic energy characterized by the width of energy band ΔE. If $U < \Delta E$, then the simple energy band theory is applicable. If, on the contrary, $U > \Delta E$, the situation changes cardinally.

Formally, the energy band can be completed only partially, but the movement of electrons (that is required for charge transfer) is prevented by other electrons – electrons of neighbouring atoms. By their influence, they can "lock" each electron in the atom and make the dielectric property of crystal, although from the energy bands characteristics it would be a metal. These substances are the Mott’s dielectrics, named after English physicist H. Mott. The width of energy band ΔE depends strongly on the interatomic distance a; more precisely, on the ratio between a and corresponding radius of electronic orbital a_q: the smaller a_q/a, the narrower energy band.

Therefore, to obtain a status “dielectric crystals”, there is not only a single way, but at least two: (1) the complete filling of energy bands (in usual energy band diagram), and (2) the strong repulsion of electrons which leads to Mott-type of dielectrics. Metals with heavy fermions sometimes behave like Mott-type dielectrics (it suffices to recall dependence $\rho(T)$ shown in Fig. 2.5*b, curve* 2).

2.5 Specificity of rare earth metals

Electronic structure of the rare-earth elements is as follows: the typical valence of rare earth metals is “+3”, i.e., the three outer electrons can be detached from the rare earth atom and directed into the conduction energy band (or, in the compound, form chemical bonds).

As a result, the ion R^{3+} is formed, which usually keeps incomplete 4*f*-shell. For example, in the gadolinium ion (Gd^{3+}) instead of 14 electrons permitted in the 4*f*-shell, only partial filling of shell is observed: $4f^7$, while in dysprosium ion (Dy^{3+}) only 9 from 14 electrons exists: $4f^9$, Table 2. At that, the electrons of 4*f*-state strongly influence on the magnetic properties of correspondent crystals. If the 4*f*-shell is only partially filled, magnetic moments of electrons are not compensated, so total magnetic moment is nonzero.

So, such ions are similar to elementary magnets. It is clear that presence of these ions in crystal results in a fact that crystal is paramagnetic with localized magnetic moments, and at low temperatures these moments might be spontaneously ordered, making crystal either ferromagnetic or antiferromagnetic, or acquire more complicated ferrimagnetic structure.

Table 2.2

Electrons spins allocation in the shells of lanthanides

Z		4*f*	5*s*	5*p*	5*d*	6*s*
55	Cs	☐ ☐ ☐ ☐ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
56	Ba	☐ ☐ ☐ ☐ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
57	La	☐ ☐ ☐ ☐ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	↑ ☐ ☐ ☐ ☐	↑↓
58	Ce	↑ ↑ ☐ ☐ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
59	Pr	↑ ↑ ↑ ☐ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
60	Nd	↑ ↑ ↑ ↑ ☐ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
61	Pm	↑ ↑ ↑ ↑ ↑ ☐ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
62	Sm	↑ ↑ ↑ ↑ ↑ ↑ ☐	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
63	Eu	↑ ↑ ↑ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
64	Gd	↑ ↑ ↑ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	↑ ☐ ☐ ☐ ☐	↑↓
65	Tb	↑↓ ↑ ↑ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	↑ ☐ ☐ ☐ ☐	↑↓
66	Dy	↑↓ ↑↓ ↑↓ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
67	Ho	↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
68	Er	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
69	Tu	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
70	Yb	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	☐ ☐ ☐ ☐ ☐	↑↓
71	Lu	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ☐ ☐ ☐ ☐	↑↓
72	Hf	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ☐ ☐ ☐	↑↓
73	Ta	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ☐ ☐	↑↓

The valence instability of rare earth elements. This instability is caused by the *fluctuations* of a valence. In conventional rare earth compounds, the valence of rare earth ion is “+3” while 4*f*-shell is filled only partially. However, sometimes in the compounds, the rare earth elements exhibit the anomalous valences: “+4” or “+2”. For example, among crystals, based on cerium, there is the ionic compound CeF_4, in which cerium is clearly tetravalent. Another example, rare earth metal Eu even in its metallic modification can show corresponding to the valence “+2”. Among other things, it should be noted that europium is one of basic material of magnetic semiconductors: EuO and EuS, in which europium is bivalent.

The anomalous valence in the compounds is peculiar for rare earth elements locating in the beginning, in the end and just in the middle of rare earth elements group, Table 2.2. At the beginning of this period there are Ce and Pr; in the end of a period there are Tm and Yb, and in the middle of period the Sm and Eu are located. The quantum theory gives convincing explanation of this situation, which implies that such electronic states have anomalies in the valence stability, when 4*f*-shell appears or empty, or completely filled, or filled in exactly half.

Aforesaid can explain the nature of anomalous valence in the compounds of these elements. As if cerium would have normal "+3" valence, its 4*f*-shell will have only one 4*f*-electron. However, this configuration is competing with the empty configuration of 4*f*-shell, that is beneficial to pull away from ion still one (the fourth) electron. The result is the state of tetravalent cerium, in which its 4*f*-shell is empty. This situation is quite competitive, because its energy is close to the energy of conventional trivalent state.

Similar arguments show, that, for example, the compounds based on ytterbium ion that instead of valence "+3" (when 4*f*-shell has 13 electrons), might have advantageous condition for Yb^{2+}, in which 4*f*-shell is completely filled, i.e., $n_f = 14$, Table 2.2. Similarly, for europium the valence of Eu^{2+} state is competitive (and often preferred) before expected Eu^{3+}, because in the state Eu^{2+} has exactly half-filled 4*f*-shell and $n_f = 7$.

Similar energy states presence in the rare-earth ions with different valence significantly affects their properties, changing fundamentally all characteristics of correspondent substances. Exactly the instability of ionic valence state leads to the emergence of special class of systems with intermediate valence, and, in some special cases, heavy fermions.

Possible situation for metals is demonstrated in Fig. 2.8 (while for situation in semiconductors is shown in Fig.2.9).

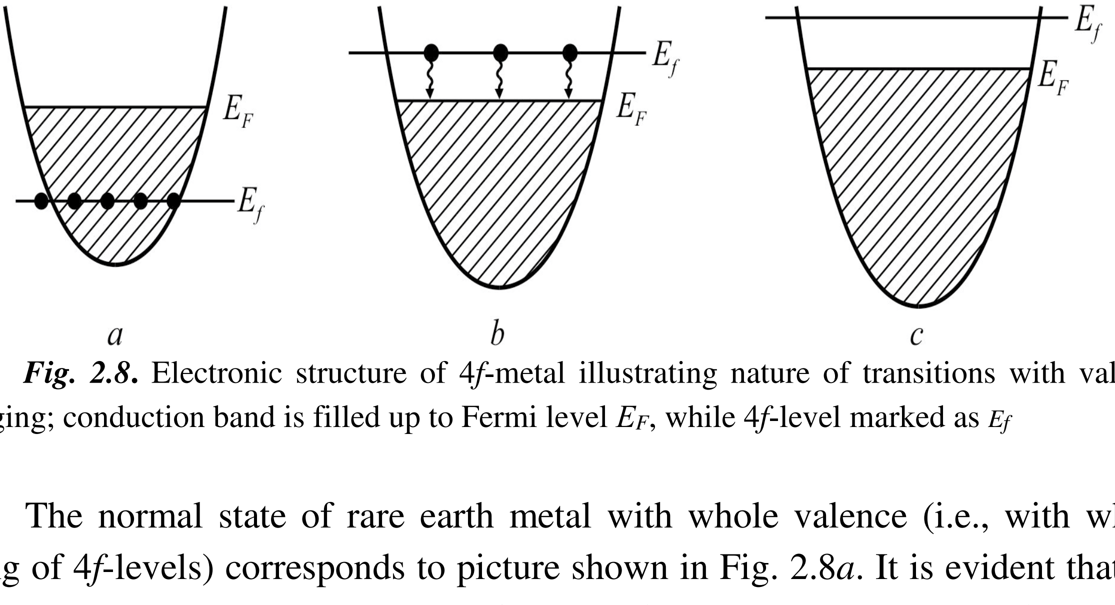


Fig. 2.8. Electronic structure of 4*f*-metal illustrating nature of transitions with valence changing; conduction band is filled up to Fermi level E_F, while 4*f*-level marked as E_f

The normal state of rare earth metal with whole valence (i.e., with whole filling of 4*f*-levels) corresponds to picture shown in Fig. 2.8*a*. It is evident that for such rare-earth metal the energy E_f of 4*f*-level is much lower than Fermi level E_F. Accordingly, in semiconductor, Fig. 2.9*a*, 4*f*-level is located in the forbidden energy band (energy gap) below the bottom of empty conduction band.

In the metals with the unstable valence, such situation is realized when the level E_f is located near the Fermi level E_F, Fig. 2.8*b* (or in the semiconductor E_f is located close to the bottom of conduction band, Fig. 2.9*b*). Complex configuration of 4*f*-orbital leads to the fact that some external conditions can move E_f level, for example, when pressure increases or temperature changes, this level as if floats up Fig. 2.6*b* and Fig. 2.9*b*.

If, due to this displacement, the E_f level rises sufficiently to cross the Fermi level of metal, Fig. 8*b* (or cross the bottom of conduction band of semiconductor, Fig. 7*b*), the energy of those electrons, which occupy the E_f level, becomes greater, than the energy of other states in the conduction band, located between E_f and E_F (most of them previously were empty). It's obvious that this is not profitable energetically, so the electrons will move from the E_f level to the empty states of the conduction band, Fig. 9*b*.

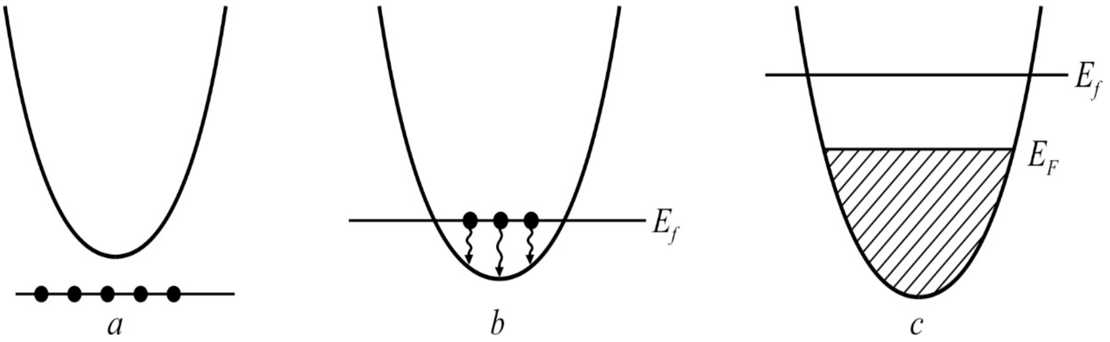


Fig. 2.9. Transition with the change in valence for compound that in initial phase is semiconductor with whole number valence

If the number of these empty states is big enough, this situation leads to the devastation of the E_f level, Fig. 2.8*b* and 2.9*b*. However, in the more general case, the electrons filling of E_f level are arranged by such a way that only one of E_f electrons leaves each ion. Due to this fact, in the conduction band, only one electron per ion can be found, Fig. 2.8*c* (in semiconductors with rare-earth element – Fig. 2.9*c*). This corresponds to the *increase by one* the valence of rare earth ion.

This change in the electronic state results in fundamental modification of crystal properties. Very often a possibility occurs for transition from the non-magnetic to magnetic state. Indeed, if initial situation (Fig. 2.8*a*) with localized electron on the 4*f*-level would remain unchanged, the system with localized magnetic moments can become ordered at low temperatures (leading, for example, to the ferromagnetism). At the same time, the situation with 4*f*-level devastation (Fig. 2.8*c*) would lead to the fact that the unpaired electrons left the 4*f*-level, so the localized in an ion magnetic moment disappears (Fig. 2.8*c*) that corresponds to the normal non-ferromagnetic metal.

Thus, the position of 4*f*-level relatively to the Fermi level determines the presence or absence of the magnetic properties in a system: at that, the possible shift of 4*f*-level (under temperature action, for example), may cause the phase transition from the magnetic into nonmagnetic state.

In the case of semiconductor, in the conduction band an initial state is empty, Fig. 2.9*a*, but after possible transition, Fig. 2.9*c*, some electrons appear in this energy band and next can move freely in a crystal. In other words, the valence transition will be also the transition of metal–dielectric type.

There are some systems, in which a new state of electrons is implemented exactly as described above; however, the transition with a change in the valence might be not completed in full, but *stopped on a "halfway"*. Really, there are some compounds which in the normal conditions (standard temperature and pressure) exhibit the *intermediate* situation. Many compounds with the unstable 4*f*-shell are known, in which the intermediate phase is realized, so this state demonstrates specific physical properties. Just in this case special electronic states are formed; and compounds with intermediate valence are identified as possessing of "heavy-weight" fermions.

Thus, when such a state of intermediate valence would occur, in which the 4*f*-level would be located very close to the Fermi level, this 4*f*-level will be filled only partially. For example, experiments show that, an average, 4*f*-electron level has only 1/3 of electrons. At that, a possibility arises, when the crystal, regularly or randomly, possesses atoms with two different types of 4*f*-electrons. If 4*f*-electron exists in the every third atom, so, in average, one atom holds only 1/3 of 4*f*-electrons. Compounds of this type really exist: they include, for example, very important for electronic technology crystals Eu_3S_4 and Sm_3S_4, as well as the well-known ferrimagnetic magnetite (Fe_3O_4).

At higher temperatures, the crystals Eu_3S_4 or Sm_3S_4 show rapid exchange by theelectrons, that looks like $Eu^{2+} \leftrightarrow Eu^{3+}$ transition and determines a conductivity of the metal type. However, at lower temperatures, these electrons become "freeze" in their centres, so the segregation of valence occurs, i.e., ions Eu^{2+} and Eu^{3+} now become different from each other and occupy in lattice fixed positions, alternating by a certain way. This "freezing"-type electronic transition is the phase transition that is accompanied by the restructuring of crystal lattice with the super-lattice arising and essential changing in the electrical properties. It is this transition that actually occurs in the magnetite Fe_3O_4 at temperature of 119 K. This transition has long been discovered, and it is the first experimentally studied metal–dielectric type of transition. Thus, the crystals with intermediate value of average valence can be arranged simply as alternation of ions with different but integer-valued valence. Such substances are the *mixed-valence* substances.

However, the systems with intermediate valence can be arranged differently. All ions, i.e., all centres of crystal lattice are completely equivalent; at that the concentration of centres is same as the unit cells, i.e., about 10^{22} cm^{-3}. Therefore, they are not doped but the principal system, and in each cell contains rare earth ion. Intermediate filling of 4*f*-level, i.e., the fractional number of 4*f*-electrons per one centre remains all times, but it captures the electron from 4*f*-level, some time (e.g., 1/3) holds it, and then throws out this electron into conduction band [9]. Then the probability of finding any ion in the state of “5f-electron” is 1/3 (while the probability of state “without 4*f*-electron” is 2/3), i.e., an average, the chance of 4*f*-level filling is 1/3.

This situation is symbolically illustrated in Fig. 5*b*: the electron moves in the conduction band, then it is captivated by the centre on closed orbit, almost being localized, some time it turns again on this orbit, and next jumps back into the conduction band, only to be caught again by some other centre, and, possibly, by the same centre. Thus, in the systems with intermediate valence all centres are equivalent but each of them shows the *valence fluctuations*, giving, in average, the fractional filling of 4*f*-state. With quantum mechanical point of view, this means that total electronic wave function Ψ is superposition of wave functions Ψ_f of the 4f-state and the state in conduction band Ψ_e, i.e., $\Psi = \alpha\Psi_f + \beta\Psi_e$.

The "weighting factor", with which the Ψ_f-function is included in this sum, determines the probability to find electron in the 4*f*-orbital, because the average number of 4*f*-electrons per one center is $n_{fl} = |\alpha|^2$. This process of constant conversion from the 4*f*-state of electron into the conduction band and back characterizes the probability of such transition, or the lifetime of electrons in the 4*f*-state. Through the uncertainty relation: $\Delta t \cdot \Delta E = h$ the finite lifetime of state means the uncertainty of its energy.

Explanation of heavy-fermions systems peculiarities. Abnormal behaviour of heat capacity, Fig. 4, as compared with conventional metals, follows from the fact that basic electrical properties of metals in dependence on temperature are determined by the electrons located in the energy range k_BT near the Fermi level. Indeed, in the conventional metals, at temperatures $T = 0$ all states inside Fermi sphere are occupied, while outside of it, when energy $E > E_F$, all states are empty. With temperature increase, the *redistribution* of electrons on the energy states starts, inasmuch as some electrons gain energy and move into the empty states above the

E_F. Accordingly, under the Fermi level the holes remain. At that, rather small number of states of electrons are exited: in range of $k_BT << E_F$.

However, in the systems possessing heavy fermions, due to the valence fluctuations, the number of states in the range k_BT is much greater: from two to three orders of magnitude more than in the conventional metals. Therefore, the factor γ showing the rate of heat capacity increases with temperature ($C = \gamma T$) is in many times larger (see Table 1). This huge value of γ, observed in systems with heavy fermions, becomes understandable, as well as the slightly smaller (due to the increased width of 4*f*-band) but still quite big values of γ in the compounds with intermediate valence.

As for the peculiarities of magnetic properties (see Fig. 2.5*a*), it should be noted that heavy fermions below certain temperature T^* are degenerated. Consequently, these fluctuations smooth out various sublevels, and stop the growth of the magnetic moment, that results in the saturation of magnetic susceptibility æ(T). Magnetic properties of heavy-fermions system cause also the anomalies in the temperature dependence of electrical resistance, Fig. 5*b*. The point is that the region of fluctuating transitions of electrons from the down level of Fermi level and back (which in ordinary metals is limited by the value of k_BT) in the crystals with unstable valence is significantly expanded.

Thus, the heavy fermions arise in such systems which contain the uncompleted 4*f*-shells (or 5*f*-shells), where the filling of electronic orbitals is unstable, so there is a proximity of the valence instability. These fermions have the record high value of the effective mass, at that, heaviest fermions are observed primarily in the compounds of cerium and uranium – just in the elements, located in the beginning of 4*f*- and 5*f*-periods. Among compounds with the heavy fermions there are as magnetics, so superconductors.

Mechanism of heavy electrons appearance right at the Fermi level can be rather complicated. Generally, different opportunities should be noted.

One is such situation when 4*f*-level itself goes to the Fermi level and at low temperatures forms energy district, where 4*f*-electrons are mixed with normal conduction electrons. In this version, the heavy fermions are primarily 4*f*-electrons themselves that are found near the Fermi level, and they are partially delocalized. In this case the interaction of 4*f*-electrons with other excitations in the crystal (phonons, conduction electrons, and maybe others) might play a special role. These types of interactions can result in the narrowing down of the energy band and, consequently, the effective mass of electron increases.

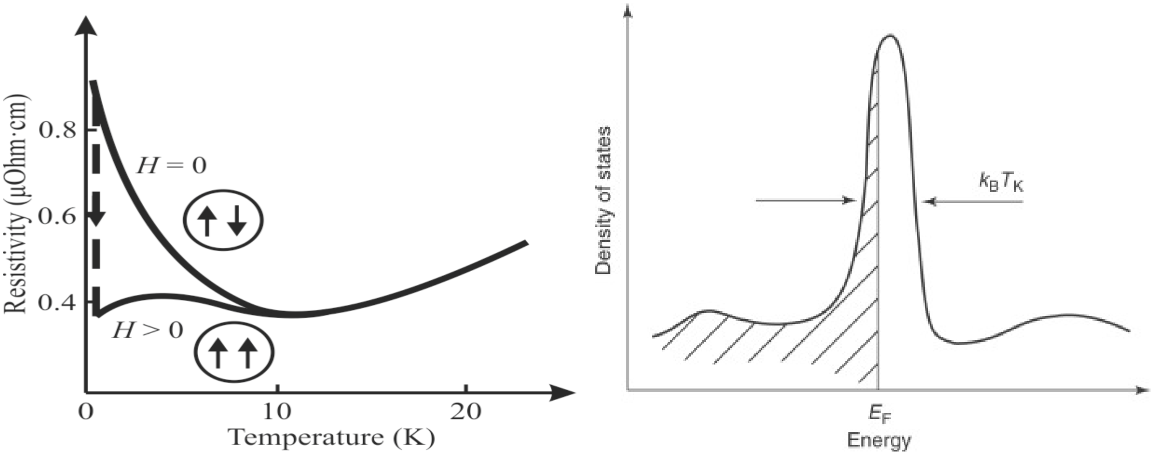
In another tested case – electron-phonon interaction influence – the effective mass increases due to the "polaronic" effect: electrical field of electron deforms the crystal lattice in its nearest surroundings, and then the electron moves in a crystal, surrounded by the "coat" of lattice deformations created by the electron itself. Similar interaction with conduction electrons can lead to the "electronic polarons" formation: the deformed lattice near heavy-fermion which additionally increases its mass.

The interaction of 4*f*-electrons between each other is another possible mechanism of their effective mass increase. Such interaction between the electrons may even results in a complete localization of some electrons, that is, their mass becomes “infinite” (Mott’s dielectric). However, if the limit of localization is not exceeded but only draws near, the crystal can remain a metal, but with a very narrow energy band and, correspondingly, with increased effective mass of charge carriers.

Kondo effect is directly related to the problem of heavy fermions. Consider the case of isolated *magnetic impurities* in the nonmagnetic metallic host (such as Fe^{+3} ions in the copper lattice). The hybridization between the conduction electrons and 4*f*-electrons, together with a large Coulomb repulsion between the 4*f*-electrons, may lead to the complete screening of magnetic moment, resulting in the singlet ground state. In this case, at low temperatures, the conductivity of copper does not increase with decreasing temperature as it usually happens in all metals, but vice versa decreases. This is the Kondo effect, seen in the non-ferrous metals containing impurities of magnetic ions. The scattering of conduction electrons by magnetic impurities becomes noticeable only at low temperatures, resulting in uncommon increase of electrical resistivity when temperature decreases, Fig. 2.10*a*, *curve* H =0 (at low temperatures the electrons scattering on phonons becomes not significant).

When temperature tends to zero, the magnetic moments of impurities can capture some of free electrons, creating the *opposite-spins* clusters (which reminds the structure of anfirromagnetic). Effective mass of moving through these clusters electrons largely increases, so the resistivity increases, Fig. 2.10*a*, *curve* H = O.

Applied magnetic field changes opposite orientation of coupled spins into their *parallel* orientation which partially suppresses effect Kondo, Fig. 2.10*a*, *curve* $H > 0$. At that, the *negative* magneto-resistance appears, shown by the vertical dashed line. Therefore, at low temperatures, when the background noise from phonons does not hinder to observe this effect in a pure form, Kondo effect testifies that the *opposite* orientation of adjacent spins promotes the increase of resistivity, while the external magnetic field gives rise to the negative magneto-resistance by means of magnetically induced parallel orientation of spins.

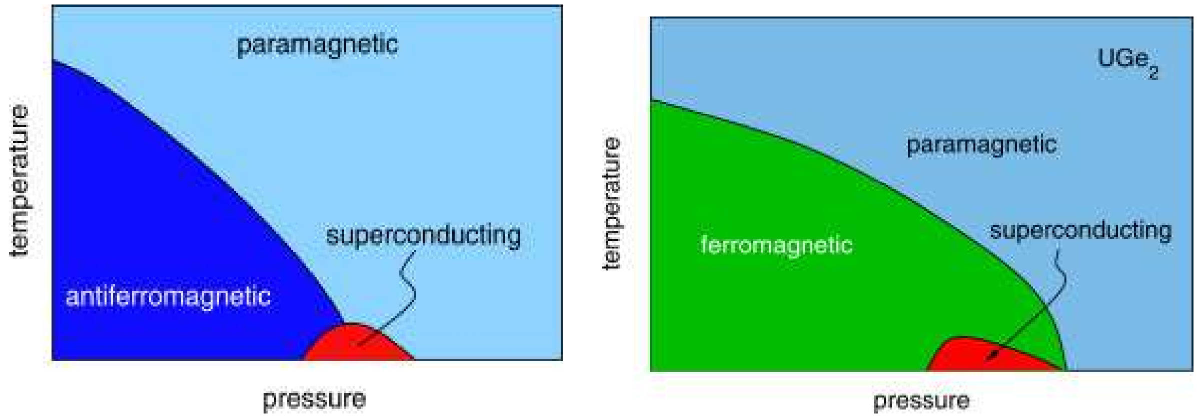


a *b*

Fig. 2.10. Kondo effect: *a* – magnetic field manages resistivity by suppressing electron capture effect (at $H = 0$) by external magnetic field ($H > 0$; *b* – local Kondo resonance at Fermi level in electronic density of states of metal with magnetic impurity.

Electronic energy band theory can describe the interaction between the conduction electrons and 4*f* or 5f electrons in terms of the Kondo Hamiltonian $\mathscr{H} = -JS\cdot s$, where S is the impurity spin and s is the conduction-electron spin, with an effective antiferromagnetic exchange interaction *J*. The resulting screening of the 4*f* magnetic moment by the spins of conduction electrons is dynamic effect, and can be visualized as being due to the virtual transitions between the localized 4*f*-level and the conduction electron states at E_F, leading to a resonance at E_F, i.e., so-called Kondo resonance, Fig. 2.10*b*. The binding energy of this singlet state can be expressed by characteristic temperature, i.e., the Kondo temperature T_K. At sufficiently low *T* (well below T_K) a local maximum of states is formed around the magnetic impurity, exhibiting increase in specific heat $C \sim k_BT/T_K$. By comparison with free-electron expression for parameter γ_0, temperature T_K plays role of *effective* Fermi temperature, $T_F = E_F/k_B$. The resonance is seen due to Kondo temperature T_K with height $1/T_K$. In the simple picture, the density of states of heavy-fermion compound may be viewed as the lattice-coherent superposition of local Kondo resonances.

Heavy electron superconductivity might be seen in the inter-metallic compounds containing the rare-earth ions possessing partially filled 4*f*- or 5*f*-shells: this is the *unconventional* superconductors. Due to the strong electrons correlation effects, they are characterized by extremely large effective mass of electrons. At normal pressure, these compounds might be as the antiferromagnetics (like $CeIn_3$) so the ferromagnetics (like UCe_2), passing at higher temperature into the paramagnetic phase (as at low so at high pressure), Fig. 2.11. However, under the conditions of *increased pressure*, when ions in a crystal lattice approach each other, in both cases, a condition arises for superconductivity appearance, Fig. 2.11. In this case, superconductivity appears at critical point, where antiferromagnetism is suppressed by the applied pressure.



a *b*

Fig. 2.11. Schematic phase diagrams: *a* – antiferroelectric $CeIn_3$ transforms as in paramagnetic so in superconducting phases]5]; *b* – ferromagnetic UCe_2 transforms as in paramagnetic so in superconducting phases

These superconducting phases might have different symmetry, and many such superconductors have been discovered. For instance, the compound UPt_3 and doped compound UBe_{13} is transformed from the antiferromagnetic into the superconductive phases. Unusual connection between the magnetism and superconductivity appears most clearly in compounds $CeIn_3$, $CePd_2Si_2$, $CeCoIn_5$ and related ones, which are the *non-centrosymmetric* crystals-superconductors. This phenomenon leads to novel classification of super-conductivity with the mixing of even and odd parity.

Usually, for example, in alkali metals, tin, copper, the effective mass of electrons m_e is close in magnitude to the mass of a free electron, differing from it at most by several times. However, it has recently been found that in some compounds ($CeAl_3$, $CeCu_2Si_2$, UBe_{13}, $CeCoIn_5$, URu_2Si_2, UPt_3 et al) the effective mass of electrons is almost a thousand times greater than m_e. This fact allows us to speak about "heavy" electrons. The properties of the compounds mentioned are very different from those of conventional metals: their specific heat capacity is several hundred times greater than the value expected for a conventional metal; the magnetic susceptibility is also great. At low temperatures, some of these compounds pass into a superconducting state, the nature of which differs from ordinary superconductivity. The nature of the large affective mass of electrons in such systems is related to the quantum nature of the magnetic interaction of electrons and heavy Ce, U, and Pt atoms.

2.6 Materials with unstable electronic spectrum

The crystals with a high density of the *excitonic states* looks like promising for the elaboration of high-temperature superconductors. In conventional superconductors – metals and metallic alloys – the phase transition into the superconducting state theoretically is limited by temperature of 25 K. The point is that at higher temperatures the Coulomb repulsion exceeds the attraction between the conductive electrons forming the Cooper pairs, which is due to the electrons interaction with a lattice, i.e., the electron-phonon coupling.

However, for a long time, theoretical investigations showed fundamentally different possibilities of electrons attraction in pair, namely, by means of *excitonic exchange*. Theoretically, with a such mechanism, the superconductivity can be obtained even at 300 K (currently, high-temperature superconductivity reaches temperature about 200 K). The term "exciton", when discussing a possibility of superconductivity, should be interpreted widely: it means *any polarized excitation* in the electronic subsystem of a crystal, including a variety of vibration modes of volumetric or surface type. Since the *classic* superconductors are the three-dimensional metals, while the excitons can be extended only in the dielectrics, the excitonic superconductor has to be *both metal and dielectric*, introducing a system of "crystal in the crystal". This subsystem is a complex substance, in which the metallic subsystem allows the free movement of electrons, while the dielectric subsystem is the environment for spreading of excitons binding the electronic pairs. In this case, the *dimensionality* of a matter should be decreased.

For the purpose of excitonic mechanism implementation to the superconductivity, two basic systems are offered:

1. *One-dimensional system* (1*D*, “needle”-like crystal, Little's model) is, for example, a long well-conductive molecule-thread with easily polarizable side radicals, which could provide the attraction of conduction electrons due to excitonic transfer. The presence of excitons makes it possible the origin of high-temperature superconductivity, as they can compensate the Coulomb repulsion of electrons. Unfortunately, to obtain the superconductivity in 1*D* crystal looks as almost impossible due to a fluctuations (this is so-called R. Peierls prohibition)

[**Note.** In the one-dimensional organic material (Bechgaard salt, $(TMTTF)_2ClO_4$) a superconducting phase was found at ambient pressure with transition temperature of $T_C = 1.4$ K. Several other such salts become superconducting only under external pressure, and it is experimentally shown that some exclusions from Peierls theorem are possible].

Nevertheless, in the 1*D* systems, the phase transition from the *quasi-metallic* phase to a *high-*ε *dielectric* phase is possible, and just this question will be discussed later.

2. ***Two-dimensional system*** (2*D*, "sandwich" crystal, V.L.Ginzburg model) consists of the "quasi-metallic" layers, surrounded on both sides by the dielectric layers, which should be carried out the excitonic exchange, contributing to the formation of Cooper-type pairs of electrons and the superconductivity in the metallic layers. The experimental verification of 2*D* models received full success: the investigation enables to find hundred materials with the superconductivity, including many high-temperature superconductors.

Electrical properties of 1*D* and 2*D* systems are proved to be extremely interesting, not only for the theory of phase transitions, but also for new applications in the electronics. Numerous studies results in the opening of several classes of quasi-1*D*, quasi-2*D* crystals with a *sharp anisotropy* of both σ and ε and various structural phase transition, caused by the instability of electronic spectrum with the electron-phonon and electron-exciton interactions.

Consider the model of ***quasi-one dimension metal***. In some 1*D* needle-like crystals at rather high temperatures (50–150 K) the conductivity shows a temperature peak, Fig. 2.12*a,* in which the value of $\sigma(T)$ is significantly higher, than the conductivity of any highly high-conductive metal (such as copper or silver). One might suppose that this huge conductivity at its temperature peak is due to the fluctuations of the superconducting state (but this phase, in the 1*D* system, as a rule, cannot be realized entirely). Calculations show that, following the one-dimensionality condition (ideally it is a thin wire), the "metallic" conductivity is incompatible with the one-dimensional system of any valence of metallic atoms in ground state (T = 0) but should acquire the properties of dielectric (R. Peierls theorem). Indeed, in the experiments, the quasi-one-dimensional conductive system at low temperatures mostly turns into the dielectric.

The example of such behaviour is shown in Fig. 2.12 for the quasi-one-dimensional organic metallic crystal: one of most studied one-dimensional conductors – the conductive polymer TTF–TCNQ (tetrathiafulvalene-tetracyano-quinodimethane). The anizometric ion $(TCNQ)^-$ demonstrates the strong acceptor properties, and it can form salts, in which the electronic transfer of charge is facilitated. Among many such salts that have a quasi one-dimensional structure, it should be noted the combination of $TCNQ^-$ with TTF^+, which at 300 K plays a role of well-conductive cation. Currently, many crystals-polymers of this type are investigated, and they form a class of quasi-one dimensional “metals"; however, most of them at low temperatures passes in the insulating phase.

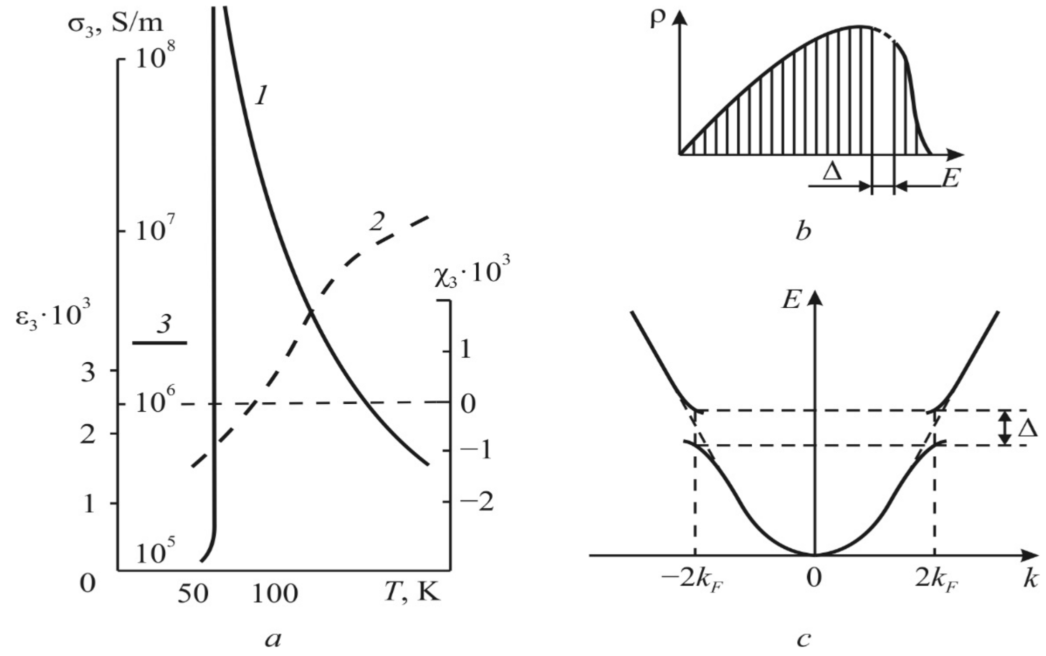


Fig. 2.12. Phase transition in TTF–TCNQ crystals: *a* – conductivity σ_3 (curve *1*), magnetic susceptibility χ_3 (curve *2*) and permittivity ε_3 (curve *3*); *b* – density ρ of electronic states with the energy gap Δ below transition temperature; *c* – energy gap in the electronic spectrum of quasi-one dimensional crystal

Needle-like crystals TTF-TCNQ have a strong anisotropy of their electrical properties. At high temperatures (on the side of metallic phase) the conductivity of this crystal along the “needle” (σ_3) and transverse to it (σ_1) different in about 500 times, while in the point of phase transition the ratio σ_3/σ_1 reaches 10^5. This anisotropy characterizes a degree of one-dimensionality of really studied crystal, which looks like “clot of joint needles”.

At low temperatures (on the side of insulating phase) the conductivity of TTF–TCNQ is very small, but the strong anisotropy becomes apparent in the dielectric permittivity. Measured in microwaves (when low-frequency relaxation processes can not give any dielectric contributions) near liquid helium temperature crystal TTF–TCNQ shows $\varepsilon_3 = 3200$ and $\varepsilon_1 = 6$. All characteristics in Fig. 12*a* are shown only for one direction – along a peculiar axis *3* of 1*D* crystal. It is important to note, that above transition temperature, the effect like "paraconductivity" is observed: the $\sigma_3(T)$ dependence is close to the Curie-Weiss law. However, such “paraconductivity” can not turn into the superconductivity below phase transition. At temperature T_C, instead of superconductivity, the $\sigma_3(T)$ dependence shows the discrete-steps breaks, when the conductivity becomes as small as in the dielectric.

In a place of large σ, below T_C, the *permittivity* ε_3 becomes abnormally high, and it practically does not vary with the temperature, Fig. 2.12*a*, curve *3*.

At low temperatures, an extremely high value of ε_3 in the TTF–TCNQ reminds the properties of displacement type paraelectrics (such as $SrTiO_3$ or $KTaO_3$). Note, that in the strontium titanate (and in the potassium tantalite as well) a large value of permittivity is observed (10^3–10^4) without any microwave dispersion. This is a result of "soft phonon" frequency critical decrease, which corresponds to the dynamic instability of *crystal lattice*. However, in the case of TTF–TCNQ, the cause of $\varepsilon \sim 10^3$ lies in the peculiarities not phononic, but *electronic spectrum*.

The magnetic susceptibility of TTF–TCNQ type crystals is small throughout all range of studied temperatures changes: from the paramagnetic to the diamagnetic susceptibility, Fig. 2.12*a*. This is significantly different from the 3*D* crystals (of V_2O_5 type) which also demonstrate the phase transition from high-temperature metallic phase to the low-temperature dielectric phase: V_2O_5 type crystals show the antiferromagnetic ordering in their low-temperature phase. Therefore, in the case of TTF–TCNQ, the nature of phase transition is different from the Mott transition, where the low-temperature phase also corresponds to dielectric phase with completely filled valence band.

The phononic spectrum of quasi-crystals, as it follows from the neutron scattering study, is characterized by a minimum in the $\omega(k)$ dispersion at a certain value of phonon quasi-impulse ($p = \hbar k$). This so cold W. Kohn anomaly is due to electron-phonon interaction, and it is observed at such quasi-impulse of phonons, which equals to twice quasi-impulse of Fermi electrons ($k = 2k_F$). (Note, that in the one-dimensional metals, the Fermi surface consists of two planes: $+2k_F$ и $-2k_F$). Electrons scattering with energy conservation can occur only between these planes, and it is accompanied by the change in impulse on $2\hbar k_F$. Just at this value of the impulse the electron-phonon coupling appears.

In the crystals TTF–TCNQ, as well as in other type of quasi-crystals, as temperature decreases, a Kohn anomaly (minimum in $\omega(k)$ dependence) becomes seen when phase transition approaches. This anomaly results in the multiplication of crystal unit cell at the transition to the dielectric phase with splitting-off the optical phonons branch (or branches). One of these branches becomes the "soft" mode, and this makes a connection of phonon spectrum with *charge density waves*, which leads to high ε_3 below the transition temperature.

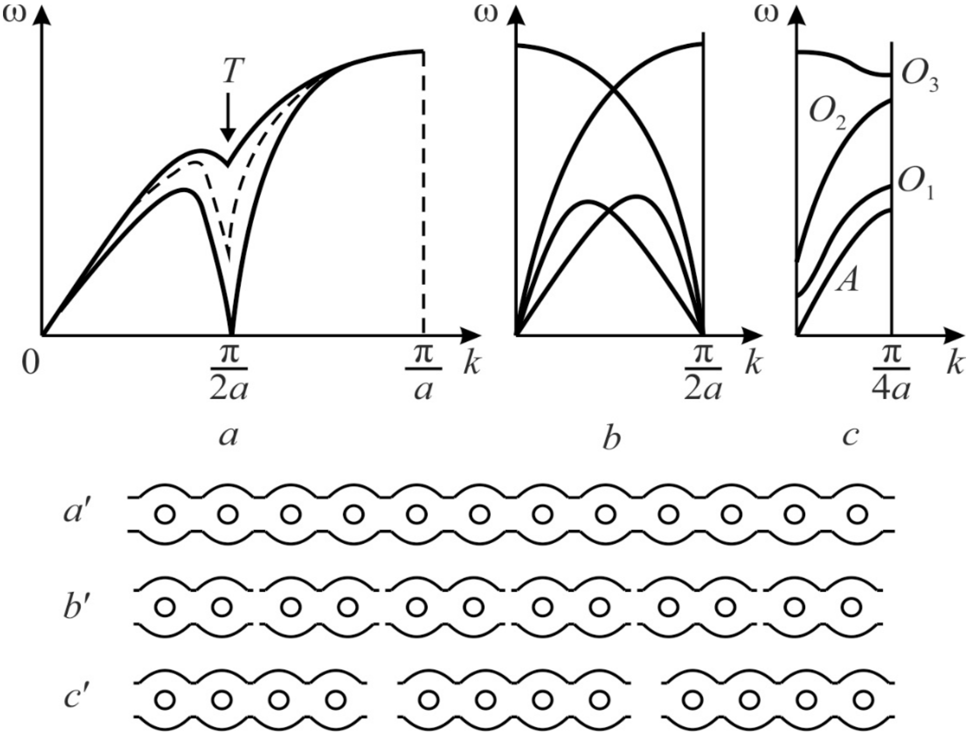


Fig. 2.13. Changes in phonon spectrum: *a* – temperature-dependent minimums (Kohn anomalies in acoustic mode), *b* –mode frequency at $T = T_C$ vanishes at wave vector $k = \pi/2a$ (virtual case); *c* – new phase appearance with four times smaller Brillouin zone and three optical modes, including two "soft" modes (O_1 and O_2); *a′*, *b′*, *c′* – modulated electronic structures in one-dimensional crystal that determines associated electron-phonon modes

This is illustrated in Fig. 2.13. When approaching to the phase transition from the quasi-metallic phase, the Kohn anomaly appears in the acoustic branch of the one-dimensional metal and gradually going down Fig. 2.13*a*. To simplify this model, the Kohn anomaly is shown here when the wave vector equals $k = \pi/2a$, but, in fact, such a coincidence can be only random, and usually is not observed.

Figure 13*b* shows the *intermediate* (virtual) case of branches splitting: from the "slowing down" acoustic branch the three optical modes and one acoustic mode are conceived. From the Fig. 2.13*c* it is seen that after the phase transition the unit cell becomes increased in 4 times, while two of splintered optical branches (O_1 and O_2) are the soft modes. In the started cell of one-dimensional metal (with lattice parameter *a*) all nodes are "neutral", and the electronic density is distributed evenly, Fig. 2.13*a′* (the metallic phase). Below the phase transition, the displacement of atoms occurs: in the doubling cell (virtual case) the atoms are grouped by two (Fig. 13*b′*); in the new formed lattice atoms are grouped by four (Fig. 2.13*c′* that corresponds to Fig. 2.13*c*). The redistribution of electronic density gives rise to such situation, when in the area of atoms "thickening" electronic density increases, and the negative effective charge arises, while to the area of atoms "depression" the positive effective charge corresponds.

By this way, the *wave of electronic density* appears, which in this (idealized) case is commensurate with the lattice parameter (exactly 4 times). However, in general, which can be implemented in all known experiments, the Kohn anomaly does not arise exactly at $k = \pi/2a$, but in the *arbitrary place* of the Brillouin zone. Therefore, the structure of the electronic density is modulated, i.e., it is *incommensurate* with the lattice parameter. This is the reason of instability of electronic spectrum.

The Kohn anomaly in the phononic spectrum is a well known characteristic of many superconducting 3*D* metals and alloys, in which the electron-phonon interaction is a main cause of the superconducting phase transition. However, in a given case, the lattice instability of Kohn anomaly type does not lead to the superconductivity, but to the dielectric phase appearance with the ultrahigh value of permittivity. This low-temperature “dielectric phase” of quasi-one dimensional metal has some properties similar to the superconductors: in such dielectric an energy gap discloses in electronic energy spectrum (Fig. 2.12*c*), but the pair of interacting electrons (or holes) is descended from *different bands*, while the Cooper interaction in the superconductors occurs between the electrons belonging to same energy band.

Therefore, the quasi-one-dimensional systems of radicals with metallic conductivity at lower temperatures turn into the dielectrics with the unstable electronic spectrum, which at elevated temperatures transforms into the quasi-metals. These properties, observed even at the microwave frequencies, are the evidence of their proximity to the superconductors, while the Kohn anomaly is the evidence of electronic nature of the phase transition.

The theory of one-dimensional conducting systems is developed long before their experimental realization. First time it has been shown by W. Peierls, who determined that the structure of a one-dimensional metal at low temperatures should be changed by such a way that it turns into an insulator. At that, the crystalline lattice must be reconstructed. Lattice distortion, caused by electron-phonon interaction, splits the partially filled energy band of the one-dimensional metal on a totally filled energy band and empty sub-band, which corresponds to the dielectric. In the Peierls theory, the Coulomb interaction of electrons does not taken into account. However, from the Mott theory, it follows that this interaction results in low-temperature instability of metallic phase. The defects in crystal lattice are also favourable for the insulating phase appearance instead of metallic phase.

With temperature decrease, in electronic spectrum of Peierls type insulator an energy gap Δ forms, which tends to have a maximum at temperature $T = 0$ K. This $\Delta(T)$ dependence further extends the analogy between metal-dielectric and metal-superconductor phase transitions. In addition, a phenomenon of "para-conductivity" is observed (curve *1* in Fig. 2.12*a*) that can be interpreted as the fluctuations of superconducting phase, occurring near transition from the quasi-metal to the high-polarizable insulator. This transition looks like disproportionate, because the value $2k_F$ is not a multiple to the π/a (a is the lattice parameter in conductive phase). Modulated by the charge density waves in the structure of dielectric (originated below a phase transition) cause the large and low-inertia high contribution to the dielectric constant.

In the vicinity of phase transition, the properties of one-dimensional structure are very sensitive to the fluctuations. Theoretically, for violation of long-ordering structure, a break of ordering originated only *in one point* is sufficient. However, in the real quasi-1*D* structures (thin, needle-like, but still macroscopic crystals in their thickness), the situation is another, and stability of a system to fluctuations significantly increased due to interaction between neighbouring "threads" of such structure. The degree of "three-dimensionality" is qualitatively assessed by high value of σ and ε anisotropy in these crystals.

Three-dimensional interaction not only can "extinguish" the fluctuations, but also can suppress the Peierls transition. Due to this suppression, in some quasi-structures, the superconductivity becomes possible: for example, polymer $(SN)_x$ is a quasi-1*D* superconductor, because dielectric phase in it does not occur, however $(SN)_x$ transition temperature is very small ($T = 0.3$ K). The impact of fluctuations onto the superconductive phase transition is minimal in the ordinary three-dimensional structures (3*D*), where, for ordering violation, a break should occur on some *surface* in a crystal. The 2*D*-structures, in terms of resistance to the fluctuations, are in the intermediate position, as for the destruction of ordering in them the “fluctuating break" should be on the *line* (but not at one *point*, as for l*D*-structures). Therefore, in the quasi-two-dimensional structures, the probability to obtain the superconducting state is greater than in the one-dimensional structures (while the probability of high-polarizable dielectric occurrence is lower than in the case of quasi-1*D* systems).

Currently, the two-dimensional structures of metal-insulator type are widely implemented, not only at macroscopic level (in the form of alternating metal and dielectric films), but also in a microscopic level (atomic layers). The latter are the most interesting as the systems with electron-phonon instability, leading to phase transitions. It is just in the 2*D*-structures a high-temperature superconductivity is discovered, which offers the great opportunities for technical applications in the cryogenic electronics.

The electron-phonon instability in the two-dimensional systems, like in the one-dimensional systems, might result in the phase transitions, analogous to Peierls transition. However, if in the 1*D*-structures, the metal-insulator transition is most typical, in the case of 2*D*-structures the transition of metal-semimetal looks more typical. In both cases, the transitions are conditioned by the electron-phonon interaction.

Dielectrics with superconducting phase transition. The peculiarity of electronic spectrum of the semimetals leads to the fact that in addition to their electron-hole "pairing" (when band gap formation, i.e., "dielectrization"), the electron-electron pairing with Cooper pairs formation is possible, resulting in the superconductivity. In the latter case, the attraction of electrons (arising due to their exchange by phonons) exceeds the electrons Coulomb repulsion.

Not only in the metals, but also in the crystals with the energy gap in their electronic spectrum (the semiconductors and dielectrics possessing increased concentration of charged carrier), at low temperatures their conductivity, instead of a smooth decrease to zero, can in spurts increase up to the infinite value. The coupling energy of Cooper pairs is caused by the electron-phonon interaction; as a result, the pair of electrons can not be scattered by lattice vibrations, which leads to the superconductivity, the *high permittivity* facilitates to the formation of Cooper pairs because increased ε dramatically reduces the Coulomb repulsion of electrons. At that, we should notice that the large ε at low temperatures is peculiar to the paraelectrics and virtual ferroelectrics.

Indeed, superconducting phase transitions in dielectrics first was discovered in the doped strontium titanate (the virtual ferroelectric with $\varepsilon \approx 40\,000$ at $T = 4$ K) and in the narrow-gap ferroelectrics-semiconductor (SnTe with $\varepsilon \approx 2000$). Although the temperature of superconducting transition in these materials not exceeds 0.3 K, the possibility of superconductivity in them is crucial. This fact was used in the following investigations and, finally, for high-temperature superconductivity invention just in the mixed oxides, which have typical for ferroelectrics possessing perovskite structure.

First of all, the superconductivity in dielectric was found in the complex oxides of tungsten type A_XWO_3 (where A is the alkali metal ions): the phase transition to superconducting state was seen in them at temperatures up to 7 K.

Then it is turned out that in other complex oxides the superconducting transition occurs even at $T = 13$ K, for example, in the $LiTi_{2-x}O_4$, and in a ferroelectric solid solution $BaPb_{1-x}Bi_xO_3$. Last composition is of interest not only because the superconductivity occurs in the material with a low charge carriers density, but due relatively high transition temperature.

As most ceramic materials, the $BaPb_{1-x}Bi_xO_3$ composition has high chemical and thermal stability; moreover, this ceramics can be obtained by the standard techniques (including in the form of thin films). Films of this ferroelectric-superconductor looks like one of promising material to use in various devices of cryogenic (helium) electronics.

Finally, the temperature of superconducting phase transition in the ceramic oxide compounds were essentially increased, initially up to 40 K (ceramic solid solutions $La_xBa_{1-x}Cu0_4$); next the superconductivity was obtained above nitrogen temperature (77 K). Mechanism of this superconductivity is supposed to be the *bipolaronic*: the Cooper electrons are bound in pairs like electrons in the metallic superconductors.

The discovery of high-temperature superconductivity in late 1986 in the polycrystalline oxide compounds, such as $YBa_2Cu_30_{7-x}$ at $T_C \approx 100$ K, has a significant impact on novel electronic equipment elaboration, providing a basis for new components.

Due to discovery of high-temperature superconductivity, the more quick computer memory devices, as well as the microwave converters and generators, tuneable electronic devices and many others devices can be constructed. Theoretically, it is possible to develop superconducting materials with operating temperature 300 K (available experimental data is contradictory).

2.7 Some aspects of superconductivity

Superconductivity is one of "cooperative" effects in the ensemble of conduction electrons, but it can not be explained by simple models within "independent electrons". Superconductivity is very interesting in science and important for technique in sense that superconductors have no skin effect so the energy losses are significantly reduced. In addition, as found by Josephson, the contact of various superconductors, separated by thin dielectric layer, can give effect of microwave generation, as well as enables the variety of sensory devices creation.

Theory of superconductivity in metals (having 3D lattice) is created much later after itsthis discovery. Conduction electrons form the Cooper pairs (that belong to bosons) and they can propagate in superconducting metals without any loss of energy [1]. However, according to theory, the temperature of superconducting transition cannot exceed 25 K (in agreement with experiments conducted with metals and alloys). This limit follows from the mechanism of electron-phonon interaction in the 3D regular structures. Indeed, for many years of research, either in pure metals or in metallic alloys there were no success to reach higher temperature of superconducting phase transition than 25 K. That is why, the application of metallic superconductors in power engineering, electronics and microwave technique necessarily requires the cooling of devices to liquid helium temperature (near 4 K). This leads to a very high cost of cryogenic devices. Nevertheless, the cryoenergetics with hardware elaborated for helium cooling and superconducting alloys of Nb_3Sn type are widely applied. In the microwave cryoelectronics, mainly the niobium is used (in the microwave resonators and millimetre range waveguides). In the devices based on Josephson's effect the lead, tin and other superconductors cooled by the liquid helium are applied.

In the contemporary cryoelectronics, for some electronic devices, the cooling by liquid nitrogen is also used (at temperature 77 K, which is hundred times less expensive than the helium hardware); this becomes possible after discovery of high-temperature superconductivity.

Zero resistance of superconductors. Temperature of phase transition into the superconducting state is critical temperature T_c. Most prominent pure metals–superconductors are lead, tin, niobium and some others. Note that conductors, which are best in normal conditions, such as copper, gold or silver, cannot turn into the superconducting phase: at very low temperatures they are only crioconductors. Most of known superconductors are the alloys and composite materials; their total number is up to several hundreds, and growing. In particular, the substances which belong to a family of high-temperature superconductors (HTS) consist of three, four, and even five components. In principal, due to high pressure technology, it is possible to transfer into the superconducting state even typical dielectrics, such as solid nitrogen and oxygen, but physicists expect the highest T_c in solid hydrogen (however, superconductive "metallic hydrogen" up to now is not reliable prepared).

The magnetic field influence. It was found that superconductivity in the metals can be destroyed not only by temperature growth, but also under the influence of magnetic field which is also the critical parameter, H_c. This effect is shown in Fig. 14*a* as a phase diagram of superconducting state *S* and normal state *N*. This diagram is built using the "normalized" temperature (ratio T/T_c) and "normalized" magnetic field (ratio H/H_c). However, such diagram is the characteristic only for superconductors of a *first type*. In the superconductors of a *second type* (that are not considered here) the dependence of T_c on the magnetic field is much more complicated [1].

Therefore, classic superconducting state can be realized only at very low temperatures and at relatively small magnetic fields. The fact, that magnetic field influences on the orientation of electrons spins: in the Cooper pairs, which are main cause of super-conductivity, spins of the interacting electrons obviously must have opposite orientation.

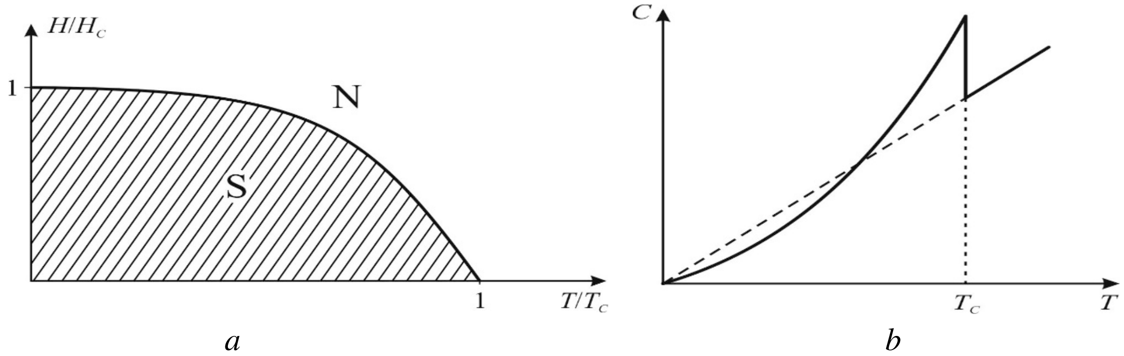


Fig. 2.14. Main characteristics of superconductors: *a* – dependence of superconducting phase S on relative temperature *T/T*c and relative magnetic field *H/H*c for superconductor of the first kind; *b* – specific heat capacity temperature anomaly in superconductor phase transition.

Anomaly of heat capacity at phase transition. The change of energy and entropy in the superconductor can be expressed through the magnetic interaction; firstly, because exactly the magnetic field H is able to destroy superconductivity and, secondly, the surface current in the superconductor creates magnetic moment M which completely compensates the applied to superconductor external magnetic field. Calculations show that in the point of phase transition into superconducting state the specific heat must show a jump, Fig. 2.14*b*, and this expectation is confirmed by the numerous experiments. Indeed, a maximum of heat capacity at the superconductor transition point exists despite the expected linear increase C(T) typical in metals (in normal metal electrons with their half-integer spin obey the Fermi-Dirac statistics which cause the linear dependence C= γT).

However, the notable fact is that not linear but the parabolic temperature dependence of the specific heat is seen below phase transition temperature Tc, i.e., in the superconducting phase follow Debye low C ~ T3. This fact clearly indicates that the statistics of electrons in the superconductor is changed: now it is the Bose statistics that is a characteristic for substances with the integer spin (Cooper pairs of electrons are bosons).

Meissner's effect. When temperature decreases below critical temperature T_c, the superconductor completely forces out of itself the magnetic field: first type superconductivity is incompatible with the magnetic field. Figure 15 demonstrates that when the “ideal conductor” (which is not a superconductor) first is exposed to the steady magnetic field, penetrating through it, Fig. 2.15*a* and then is cooled down, the magnetic field in it will be same, Fig. 2.15*b* (in this mental experiment the conductor is supposed as the diamagnetic).

However, the magnetic behaviour of a *superconductor* is quite different from the “ideal conductor”, Fig. 2.15*c,d*. When passing through the phase transition the superconductor will actively exclude any presence of magnetic field. The expulsion of magnetic field from the superconductor at phase transition from normal into superconducting state is the *Meissner’s effect*.

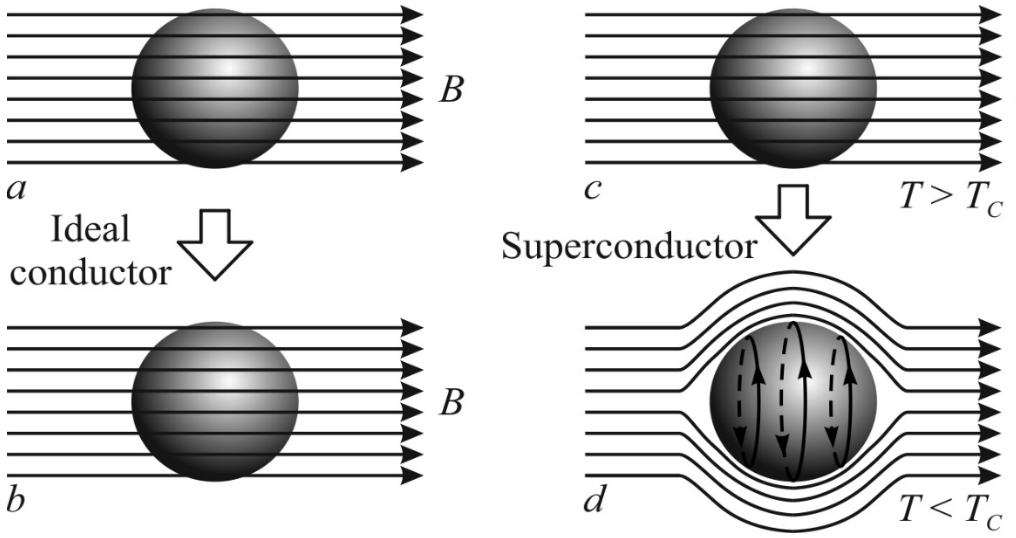


Fig. 2.15. Diagram explaining Meissner effect, magnetic field lines are shown by arrows: *a* – ideal conductor at elevated temperature; *b* – same conductor at extremely low temperature; *c* – superconductor above T_c; *d* – superconductor below T_c

As shown by the direct experiments, at temperatures $T < T_c$ under the influence of external magnetic field, regardless of how superconducting state is activated, inside of the superconductor any magnetization is always absent: $B = 0$. Otherwise this result is treated as *zero permeability* of superconductor, i.e., $\mu = 0$. This fact clearly demonstrates that superconductor as is quite different material from the "ideal conductor". Morweover, the first type superconductivity can exist, when external magnetic field is less than value of critical magnetic field ($H < H_c$), independently on previous history of a sample. Corresponding equilibrium state is thermodynamically stable, and it can be characterized within thermodynamic approaches.

Therefore, one can make important conclusion: superconductivity is such state of high conduction systems, in which always fulfilled two conditions:

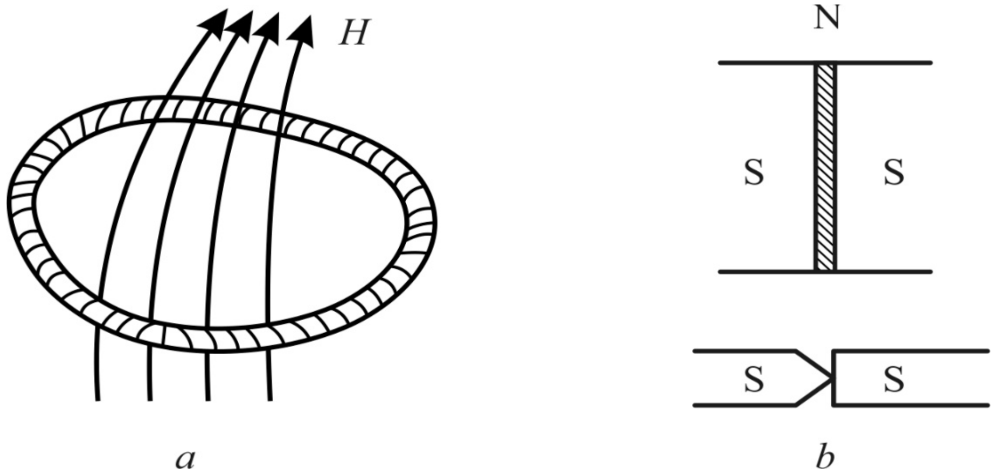
$$\rho = 0 \quad \text{and} \quad \mu = 0.$$

One of theoretical explanations of the Meissner's effect comes from Londons equations [1]. They show that the magnetic field, actually, can slightly penetrate inside a superconductor, but with the exponential decrease over distance of 20–40 nm. It can be described in the terms of special parameter: the Londons *penetration depth*.

As a rule, at rather strong magnetic field the superconductivity disappears, Fig. 14*a*. However, all known superconductors can be divided into two classes, according to the way how the magnetic breakdown occurs. In the Type I the superconductivity is abruptly destroyed, when the strength of magnetic field rises above the critical value H_c. However, in the Type II superconductors, the magnetic field exceeding the first critical value H_{c1}, converts the superconductor to peculiar *mixed state*, when the magnetic fluxes can penetrate locally in the material, but, as a whole, the superconductor remains as the non-resistive material up to the achievement of the second critical field H_{c2} (when the electrical current in the superconductor becomes too large). *Pure* metallic superconductors usually belong to the Type I while most of superconductive *alloys* belong to the Type II.

Quantization of magnetic flux. If one would take the ring of superconductive material and induces the current in it by the external magnetic field influence (Faraday's effect), this current will flow in the ring indefinite time, because any resistance in the ring is absent. To realize this experiment, the superconducting ring should be taken at temperature higher than the transition temperature ($T > T_c$); at that, the lines of magnetic field crosses the area of a ring, Fig. 2.16*a*.

Then the temperature might be lowered below the T_c and the source, creating magnetic field, is turned off. At the time when magnetic flux is switching off, starts its decrease with the inducing electromotive force in the ring with a current. This current will prevent the reduction of magnetic flux, so after external magnetic field turning off the magnetic flux in a ring will remain at the same level, because it is supported by a current flowing in the superconducting ring.



a *b*

Fig. 2.16. Quantum properties of superconductivity: *a* – frozen magnetic flux through the superconducting ring; *b* – schematic representation of Josephson contacts (weak connection)

If this ring would have a resistance *R*, after the turning off external field, the current in the ring (which has the inductance *L*) will disappear with the time dependence of exp(–t/τ), where $\tau \sim R/L$. Since the superconductor has $R = 0$, the time of current existence in ring is $t = \infty$. This means that the magnetic flux is "frozen" due to constant current in the superconducting ring. Moreover, this "frozen" magnetic flux is not any value, but has a certain value multiplied by $\Phi_0 = 2.07 \cdot 10^{-7}$ Gs/cm^2. This parameter is the *fundamental constant*, and this quantum of the magnetic flux that can be expressed through other fundamental constants: $\Phi_0 = hc/2e$. The quantization of magnetic flux identically confirms the *quantum nature* of superconductivity.

Josephson's effects. These effects also demonstrate a quantum nature of superconductivity. There are two Josephson's effects: stationary and non-stationary, and they both belong to a weak superconductivity – when two semiconductors are connected though any non-superconducting layer. This "weak coupling" can be the tunnel junction, thin-film narrowing, and, finally, a simple touching of one superconductor to another at a point, Fig. 2.16*b*.

The *stationary* Josephson's effect is a small current, passing through the poor connection, even if this weak link is the dielectric layer. Under created conditions, the weak link does not show electrical resistance when the movement of electrons in both superconductors is agreed *coherently*. Weak connection does not prevent superconducting electrons to be in the *same quantum ensemble*. In other words, the wave function of electrons is able to penetrate the weak connection from one superconducting area to another – this is the *interference*. All electrons in the macroscopic superconductor can be described by a single wave function (such as the electrons in individual atom).

The *non-stationary* Josephson's effect is the increase of current through a weak connection, when the voltage V is applied to it. Then, under the influence of applied voltage, in addition to the constant component, the *variable current* component appears, described by frequency ν, related to applied voltage by the ratio $\nu = 2eV/h$. The frequency of this generation is very high (located in the range of microwaves), and this frequency is a linear function of applied voltage. Non-stationary Josephson's effect can be used to generate microwaves in GHz range.

Electron-phonon interaction. It is important that in the superconductors an *isotopic* effect is discovered: this means that the temperature of phase transition depends on the mass of ions of crystal lattice. Such experimental data clearly indicate the active part of lattice oscillations (i.e., ionic cores) to create superconducting state. According to results of theoretical analysis, the interaction between electrons and lattice vibrations is a main reason of superconductivity in the simple metals and their alloys. Under certain conditions, the electrons-phonons interaction might have character of attraction. If this attraction is stronger than the Coulomb repulsion between electrons, it dominates between the charge carriers; as a result, at very low temperature the superconductivity looks as the more ordered and, therefore, energy more comfortable state.

For simplified analysis of the electrons and phonons interaction, lets initially assumed that in a metal at temperature $T = 0$ no thermally exited phonons exists (it is believed that nothing disturbs a lattice or nothing interacts with it). When the electron moves in crystal lattice with the wave vector $\mathbf{k}_1$, it can collide with stationary ion, and due to scattering process this electron will turn into another energy state with the wave vector $\mathbf{k}_1'$. In such a case, one can say that "electron generates" the phonon, which before the scattering was absent. Lattice is characterized by the invariant translations; therefore, the law of impulses conservation has to be implemented:

$$\mathbf{k}_1 = \mathbf{k}_1' + \mathbf{q}.$$

Next this phonon can be absorbed by the second electron with the wave vector $\mathbf{k}_2$, forcing him to move to state $\mathbf{k}_2'$. Since phonon was generated and next disappears, the electron's impulse before and after scattering must be same:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'.$$

It is considered that such scattering corresponds to electron-phonon-electron process, or otherwise, to the *indirect* electron-electron interaction which can be characterized by a diagram shown in Fig. 17*a*. At the time, when the electron goes from state $\mathbf{k}_1$ to state $\mathbf{k}_1'$, the oscillations in the electronic density occurs with a frequency

$$\nu = [E(\mathbf{k}_1) - E(\mathbf{k}_1')]/h,$$

where $E(\mathbf{k}_1)$ and $E(\mathbf{k}_1')$ are energies of initial and final state of electron.

Suppose that as a result of such fluctuations of electronic density in one place this density locally becomes increased. Positive ions of lattice will feel this temporary attraction that occurs in this place. They will move to it, and, having relatively big mass and inertia, will continue their moving even after the compensation of the local negative charge is achieved. This, in turn, results in the *excess of positive charge* in same place. Now it becomes the centre of attraction for electrons, to where they move towards from nearby regions. All this allows characterize the dynamic picture by such a way that looks as the *attractive interaction* between electrons.

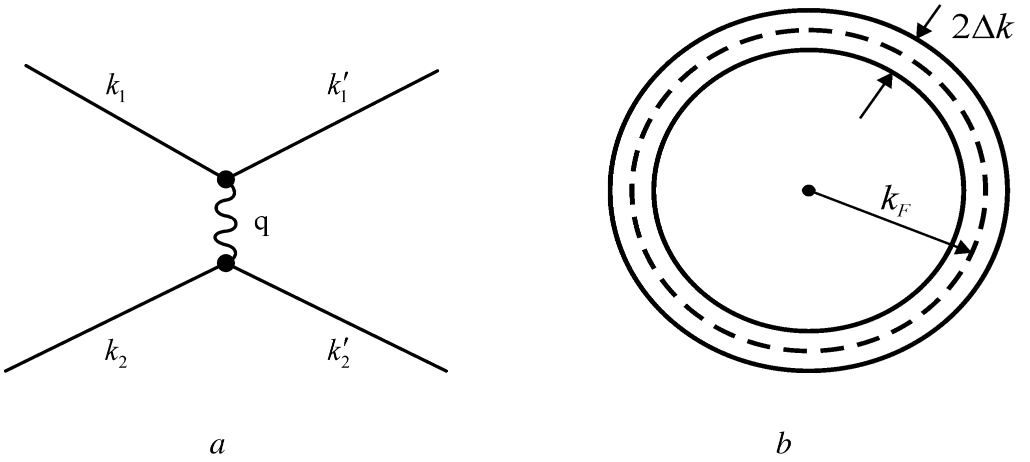


Fig. 2.17. Superconductivity mechanisms: *a* – diagram explaining electron-phonon-electron interaction in superconductors; *b* – schematic representation of Fermi surface in metal; interaction of Cooper electrons is possible just near this surface-layer

However, it should be noted that the attraction by this scheme is only possible if the distinctive frequency of such interaction is less than the own frequency of ionic subsystem (last is characterized by Debye frequency ν_D). In order to electron can move to the state $\mathbf{k}_1'$ from its initial state $\mathbf{k}_1$, first of all, this state should be free (Pauli principle). This is possible, as known, only *near the Fermi surface* (or in vicinity of Fermi energy) that can be simplistically represented as a sphere of radius k_F in the k-space, Fig. 2.17*b*.

Next it is possible to formulate the rule of electrons interaction via the phonons involving, or, finally, through the interaction with them. Those electrons, whose energy is different from the Fermi energy on the value $h\nu_D$, can attract together (rest of electrons continue to push off). Considerable attraction is peculiar only to those electrons, which energy states lie in a narrow spherical layer around the Fermi energy; its thickness $2\Delta k$ corresponds to energy $2h\nu_D$, Fig. 2.17*b*.

High-temperature superconductivity (HTS) is possible not in the classic metals, but in the other crystals – semiconductors and even dielectrics. In these uncommon cases, at low temperatures, the conductivity instead of smooth reduction to zero can be converted abruptly into the endless value (in spite of relatively small concentration of charge carriers). At that, the energy of electrons connection into the Cooper pair is carried out not by the electron-phonon-electron interaction, but through some others mechanisms (exciton type) wgich also can result in the superconductivity.

The crystals, which have high density of exciton states, looks like promising materials for the elaboration of high-temperature superconductors. For a long time theoretical predictions showed the possibilities of electrons attraction and Cooper pairs rising by means of exciton exchange. In principle, with such predicted mechanisms, the superconductivity can be obtained even at 300 K (currently, in 2017, high-temperature superconductivity reaches temperature of about 200 K).

When discussing the possibility of superconductivity, the term "exciton" should be interpreted widely: it means any polarized excitation in electronic subsystem of a crystal, including the variety of vibration modes of spatial or surface type. Since classic superconductors are the three-dimensional (3D) metals or alloys, while excitons can be extended only in dielectrics, the exciton superconductor has to be both metal and dielectric simultaneously, introducing a system of "crystal in the crystal". This system might be a complex substance, in which metallic subsystem allows free movement of electronic pairs, while dielectric subsystem is the environment for excitons spreading, which can join the electrons in pairs. In this case, the dimensionality of a matter should be decreased.

Among other possibilities, the exciton mechanism of electrons coupling in the Cooper pairs might be possible in the *one-dimensional* system (1D, needle-like crystal). It is, for example, the long well-conductive molecule-thread with easily polarizable side radicals that can provide attraction of conductive electrons due to excitonic exchange. The presence of the excitons makes it possible the appearance of high-temperature superconductivity, because the excitons can compensate Coulomb repulsion of electrons. However, the achievement of superconductivity in the 1D crystal is almost impossible due to thermal fluctuations (that is so-called “Peierls prohibition”). Nevertheless, in aome of 1D system, the phase transition from the quasi-metallic phase to the high-ε dielectric phase is possible: quasi-one-dimensional highly conductive (above T_c) system at low temperatures turns into “super-dielectric” with $\varepsilon \approx 2000$.

In the vicinity of the phase transition, the physical properties of one-dimensional structure is very sensitive to the fluctuations. Theoretically, in the 1D longitudinally-ordered structure the full disordering (with the violation of main properties) can occur just in one point. However, in reality, in the *quasi*-1D structures (thin, needle-like, but still macroscopic by their thickness crystals), situation changes, and the stability of system to fluctuations increases due to the interaction between the neighbouring "threads" of such structure. The degree of "three-dimensionality" is qualitatively assessed by the degree of anisotropy of conductivity and permittivity in these crystals. Three-dimensional interaction not only can "extinguish" the fluctuations, but also can suppress Peierls transition. Due to this suppression, in some of quasi-1D structures superconductivity becomes possible: for example, in the polymer $(SN)_x$ which is quasi-1D superconductor, the dielectric phase does not occur, however, temperature of transition to superconductivity is very small ($T = 0.3$ K).

The impact of fluctuations onto the phase transition of metal-dielectric type of crystals is minimal in ordinary three-dimensional structures, in which the violation of ordering should occur on certain *surface* inside a crystal. The 2D-structures, in terms of their resistance to fluctuations, are found in intermediate position, as for destruction of their ordering, i.e., “fluctuating break" should be seen on a *certain line* (but not in *a point* as for lD-structures). Therefore, in the quasi-two-dimensional structures, the probability to obtain the superconducting state is much greater, than in the one-dimensional structures.

Electrons formation into the Cooper pairs is promoted by the large permittivity (ε) which strongly reduces the Coulomb repulsion of electrons. As known, at helium temperatures, some of paraelectrics and ferroelectrics have very big permittivity. Indeed, the superconducting phase transitions in these dielectrics were first discovered in the doped strontium titanate (it has $\varepsilon \approx 40\,000$ at temperature $T \leq 4$ K), as well as in narrow-gap ferroelectric-semiconductor SnTe ($\varepsilon \approx 2000$). Although the temperature of superconducting transition in these dielectrics is less than 0.3 K, exactly a *possibility* of superconductivity in these cases looks fundamentally significant.

This opportunity is used to find the high-temperature superconductivity in the mixed oxides of the perovskite structure (which is a typical structure for ferroelectrics). High-temperature superconductivity (HTS) is discovered experimentally only in 1986, although the theoretical prediction of this phenomenon was long time before known as for two-dimensional (2D) so for one-dimensional (1D) non-metallic structures. Theoretically, the mechanism of electrons interaction by exciton exchange in these structures has no temperature limit.

Short history of HTS is shown in Fig. 18. Among superconductive two-dimensional systems (complex oxides), first several tungstates of A_xWO_3 type were discovered (A is alkali metal). Phase transition into superconductive state in tungstates was observed at temperatures up to 7 K. Then it is turned out, that in another complex oxides superconducting transition occurs even at temperature near $T_c = 13$ K, for example, in compound $LiTi_{2-x}O_4$ and in ferroelectric $BaPb_{1-x}Bi_xO_3$.

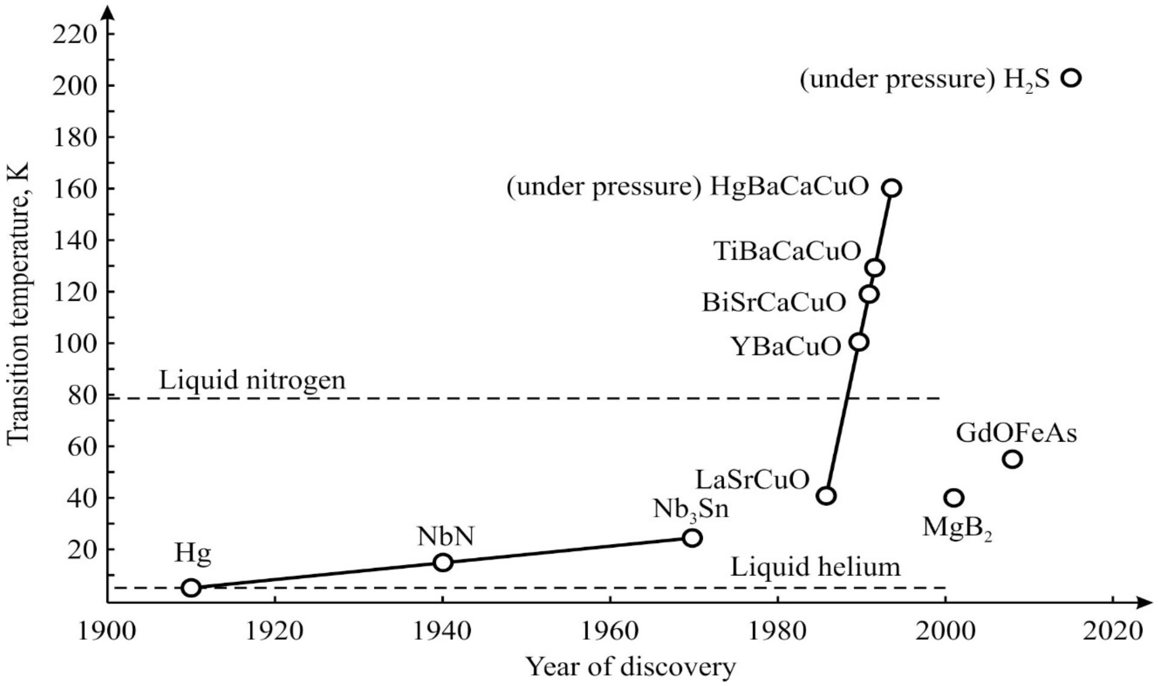


Fig. 2.18. History of superconducting materials research.

Finally, a significant increase of superconducting phase transitions temperature is achieved: firstly up to 40 K in ceramic compound $La_xBa_{1-x}CuO_4$, next superconductivity is discovered above nitrogen temperature (liquid nitrogen boils at temperature $T_c = 77$ K). Mechanism of this superconductivity is a bi-polyaronic type: polarons bound in Cooper pairs (like electrons in metallic superconductors). The discovery of HTS in the polycrystalline oxides, such as compound $Y_xSr_{1-x}CuO_4$ ($T_c \approx 35$ K, Nobel Prize for 1987 year) and $YBa_2Cu_3O_{7-x}$ ($T_c \approx 100$ K) becomes the basis for new components of electronic equipment.

In 2001, the superconductivity in the fusion MgB_2 (magnesium diboride) is discovered with relatively high transition temperature: $T_c = 40$ K. Crystal structure of these substance consists of boron and magnesium layers (before only certain compounds of copper and oxygen, so-called "cuprates" are believed to have HTS properties). In year 2008 several iron-based compounds become known as superconducting at high temperatures. At present, the reached "record" of HTS is 203 K: in hydrogen sulfide (H_2S) under pressure of 150 gigapascals. Theoretically, there is possibility of superconducting materials development with operating temperature of 300 K (available experimental information is controversial).

Thanks to high-temperature superconductivity discovery, it becomes possible to construct high-speed computer memory devices, microwave converters and generators, electronic sensors and others. Microwave technique from many of HTS mainly uses the composition, designated as "1-2-3" with chemical formula $YBa_2Cu_3O_{7-x}$. In Fig. 2.19 this is compound is designated as Y-Ba-Cu-O that has transition temperature slightly higher than 100 K. This transition temperature is sufficient for HTS application at temperature of 77 K, i.e., with cooling by liquid nitrogen. This type of cooling cost hundreds of times less than cooling by liquid helium. Moreover, at increased operating temperature of HTS, microwave devices can be applied in the space electronics. Technology of "1-2-3" composition is well developed: Y-Ba-Cu-O is prepared as thin poly- and mono- crystalline films, deposited onto dielectric substrates that have low microwave losses, such as MgO, $LaAlO_3$, Al_2O_3 (sapphire) and so on.

In high-frequency and microwave technologies conductors and superconductors are compared by their surface resistance R_S, measured in ohms. For ordinary metals the value of R_S is defined by skin effect, then

$$R_S = (1/2\rho\mu_0\omega)^{1/2},$$

where ρ is resistivity; μ_0 is magnetic constant and $\omega = 2\pi\nu$ is circular frequency. Thus, R_S in the conventional metals slowly increases with frequency as $\sqrt{\nu}$.

In the superconductors, particularly in the HTS, the skin effect is absent but there is another uncomfortable for microwave applications effect: the depth of penetration of electromagnetic field in the surface of superconductor. The reason is a presence in the superconductor not only the Cooper pairs of electrons (which do not cause any resistance), but also the ordinary electrons which make such a resistance. It is determined that at high frequencies in the superconductor R_S is nonzero, and it rather fast increases with frequency: $R_S \sim \nu^2$.

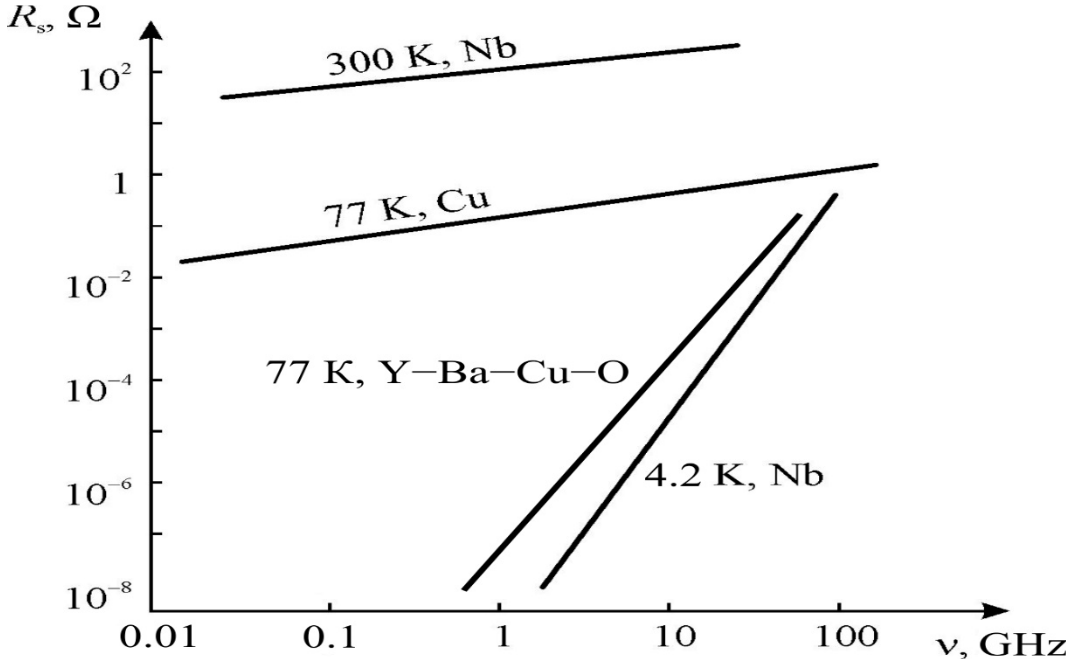


Fig. 2.19. Frequency dependence of surface resistance in superconductors and copper

Theoretical calculations are well documented experimentally. Frequency characteristics of best (at room-temperature) conductor copper at 77 K, as well as the niobium in the normal state (at temperature 300 K),and in the superconducting state (at liquid helium at temperature 5.2 K) are compared in Fig. 19. Most important in this figure is the frequency dependence of Y-Ba-Cu-O film: surface resistance increases with frequency very rapidly as in classic superconductor Nb, so in the HTS film. Therefore, at the millimetre waves (100 GHz and above) the superconductors have no advantage over a copper.

However, at frequencies lower than 20 GHz, the HTS electrodes have a significant advantage as compared to Cu (even being cooled to the liquid nitrogen, 77 K). At that, the electrodes made of niobium look better than HTS, but they need very expensive cooling by helium. Superconducting $YBa_2Cu_3O_{7-x}$ films deposited on dielectric substrates are successfully used instead of usual superconductive metals in the microstrip and coplanar microwave devices, allowing obtain a record high-quality filters, phase shifters with small losses of energy and other passive microwave devices. There are also some active devices based on the HTS films that use Josephson's effects.

2.8 Absorbing and reflection of EM waves in metals

Metals are interesting material for use in microwave absorbent composites as fillers for two main reasons. Firstly, their high conductivity σ makes it possible to ensure the absorption of EM wave by the increase in imaginary part of permittivity $\varepsilon'' = \sigma/\varepsilon_0\omega$, since from Maxwell's equation: rot $H = j + \partial D/\partial t$ it follows that losses caused by delay of polarization ($\partial D/\partial t$) and conductivity losses ($j = \sigma E$) are indistinguishable for EM wave. Secondly, several metals are ferromagnetics, and thus such a filler helps to reduce the reflection of EM wave from the absorbing composite.

It is quite obvious that a metal should be included in the composite only in the form of fine fraction (micro- or nano-particles). In this case, it is impossible to use macroscopic parameter σ of metal, but it can be predicted on the basis of knowledge about EM properties of metal in the frequency range, where $\sigma(\omega)$ undergoes dispersion, Fig. 2.1*d*. Metals are characterized by high reflectivity (R), which is due to their large conductivity, and, therefore, the part of incident EM energy (I) absorbed in metal (A), is small, since the energy of incident EM wave is the sum: $I = R + A$. At that, transmission (T) of EM wave is possible only in the exceptional cases (mentioned below). From the *microscopic* point of view, when explaining possible cases of metal interaction with EM waves, it is important to consider that in a metal the valence band of electronic spectrum overlaps with conduction band, but they are separated by Fermi level, below which are located the energy states of most electrons which fast reaction explains the interactions of metal with the EM field. However, this mechanism of EM wave interaction strongly changes in small metal particles. In the nano-scale fillers of metallic elements (of 0D, 1D and 2D configurations), used in the composite materials, the electronic spectrum is no longer continuous: instead of Fermi level the energy gaps arises in a spectrum, and its width and configuration depends on the particles size and on the configuration dimensions. In this case, the reaction of electrons to a high-frequency EM field, in part resembles properties of semiconductors and even dielectrics. In very small nano-particles the transition of electrons through the energy gaps is activated by thermal movement or by other external factors.

In microwave composites, the conductive fillers provide EM wave absorption due to ohmic losses. It is obvious that the conductor (metal, graphite, graphene, etc.) should enter the composite only in the form of a small fraction (micro- or nanoparticles). The mechanism of interaction of EM waves changes greatly in the case of small conductor particles. In this case, it would be incorrect in the calculations to use macroscopic data on the electrical conductivity (σ) of, for example, a metal, but the microwave losses created by its particles can be predicted on the basis of knowledge of the EM properties of the conductor in the frequency range where $\sigma(\omega)$ exhibits dispersion , Fig. 1*d*.

The particle sizes used in microwave absorbing composites are commensurate with or even smaller than the electron mean free path length. It is also important to note that during the drifting motion of the electron gas, not the acceleration, but the speed of the electrons is proportional to the electric field. That is why, the electrical conductivity is not proportional to the charge of an electron, but to its square ($\sigma \sim e^2$), while the deceleration of the electron drift in the electric field is equal to $m\upsilon/\tau$ and can be described by the equation: $m\mathrm{d}\upsilon/\mathrm{d}t = - m\upsilon/\tau + eE(t)$, solution the connection of which is shown in Fig. 1*d* as the dispersion of the conduction frequency $\sigma(\omega) = \sigma_0/(1+i\omega\tau)$, or:

$$\sigma'(\omega) = \frac{\sigma_0}{1+\omega^2\tau^2}; \;\; \sigma''(\omega) = -\frac{\sigma_0\omega\tau}{1+\omega^2\tau^2}, \;\; \sigma_0 = \frac{ne^2\tau}{m}.$$

The reduction of the real part of the conductivity is shown in Fig. 2.1*d*, due to the delay of drifting motion of electrons, and this leads to the *negative permittivity* of metals $\varepsilon'(\omega) = \sigma''(\omega)/(\varepsilon_0\omega)$, associated with the imaginary part of the conductivity. It is generally accepted that at a certain frequency, which is called the *plasma frequency* (ω_{pl}), the dielectric constant turns to zero $\varepsilon'(\omega) = 0$, crossing the abscissa axis and reaches the value eμ, which for various metals is equal to ε_∞ = 4-8. This behavior of the electronic gas in metals in very high-frequency EM field requires the introduction of the plasma frequency concept. If it is assumed that the limiting dielectric constant of metal is $\varepsilon_\infty = 1$, the plasma frequency can be estimated by the value $\omega_{pl} = (Ne^2/m\varepsilon_0)^{1/2}$.

Maxwell's equation (rot $H = j + \partial D/\partial t$) shows that the current density $j = \sigma E$ and the time derivative of the electrical displacement are additive quantities, and therefore the complex conductivity $\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ is related to the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$:

$$\varepsilon'(\omega) = \frac{\sigma''(\omega)}{\varepsilon_0\omega};\ \varepsilon''(\omega) = \frac{\sigma'(\omega)}{\varepsilon_0\omega};\ \varepsilon^*(\omega) = -\frac{ne^2/m\varepsilon_0}{\omega^2 - i\omega\gamma} = -\frac{\omega_{pl}^2}{\omega^2 - i\omega\gamma},$$

where $\varepsilon^*(\omega)$ is expressed in terms of the plasma frequency wpl and the damping coefficient of plasma oscillations: $\gamma = 1/\tau$. Microwave measurements show that the negative permittivity of highly conductive metals approaches several thousand, while it is only a few hundred for low-conducting magnetic metals.

The given description of plasma oscillations and the associated dispersion $\sigma^*(\omega)$ needs to be clarified, since it is necessary to predict the microwave properties of small metal particles used as fillers in absorbing composites. T

he thing is that plasmons in nanoparticles, starting with their certain size, are no longer registered. The reflection spectra of metallic elements change significantly as the size of metal particles decreases, especially when moving to nanoscale. At the same time, the conductivity drops sharply and plasma oscillations do not occur: nanoparticles of metallic elements cease to be metals.

First, they exhibit "semiconductor" and then even "dielectric" properties. It is obvious that a wide range of electromagnetic properties of nanoparticles can be obtained at these stages, especially if different technological methods are used to obtain agglomerates of particles having a quasi-one-dimensional or quasi-two-dimensional configuration. In the absence of the shielding property of the electronic gas (characteristic of a massive metal), the role of electron shells of ions in metal nanoparticles increases significantly. So, nanotechnology makes it possible to control the EM properties of matter. Absorption and transmission characteristics change especially strongly when moving to nano-sized metal particles.

The transmission of a part of the EM radiation falling on the conductor is possible only in the case of a very thin metal layer and, of course, when the frequency of the EM radiation is high enough. The analysis shows that the intensity of the incident wave (I_0) decreases exponentially during its propagation through the metal, resulting in a much lower intensity of the transmitted wave.

This happens because the metal strongly dampens the initial intensity of the wave. Obviously, the decrease in wave intensity is also related to the thickness of the metal layer, so the extinction coefficient is equal to $I(x) = \mathrm{I0}\exp(-4\pi kx/\lambda)$, where k is the attenuation constant. In connection with the weakening of EM waves in metal, such a parameter as the depth of penetration due to the skin effect acquires special importance.

This effect is manifested only in an alternating electric field and consists in the redistribution of the current density in the conductor: it becomes maximum near the surface of the conductor and decreases exponentially with increasing distance x from the metal surface. In the near-surface region, the current density j_0 decays exponentially, which is described as: $j(x) = j_0\exp(-x/\delta)$, where δ is the skin layer (or penetration depth) at which the surface current decreases to "$1/e$" (0.37) from its initial value.

As a result, the skin effect increases the effective resistance of the conductor, which is fundamentally different from a constant current that is evenly distributed along the conductor. The skin effect occurs due to opposing eddy currents caused by a change in the magnetic field. At a frequency of 10 GHz, when the length of the EM wave in vacuum $\lambda_0 = 3$ cm, the depth of the skin layer in good conductors is only $\delta = 0.6$–0.8 μm. The general formula for the size of the skin layer is as follows:

$$\delta = \sqrt{\frac{2\rho}{\omega\mu_0\mu}\left[\sqrt{1+\left(\rho\omega\varepsilon_0\varepsilon\right)^2}+\rho\omega\varepsilon_0\varepsilon\right]}, \tag{5}$$

where $\rho = 1/\sigma$ is the specific resistance. At low frequencies, when $\rho\omega\varepsilon_0\varepsilon << 1$ (that is, when the conductivity is large: $\omega\varepsilon_0\varepsilon << \sigma$), the value in brackets is close to unity, so above formula is more often given in the form: $\delta = (2\rho/(\omega\mu_0\mu))^{1/2}$.

However, in the case of smaller metal particles (i.e. for 0D, 1D and 2D nanoparticles), which become poor conductors under the influence of microwaves, the coefficient in brackets in formula (5) increases. As a result, at frequencies much higher than $\omega \sim 1/\rho\varepsilon_0\varepsilon$, the depth of the skin layer, instead of continuing to decrease, approaches the asymptotic value: $\delta \approx 2\rho(\varepsilon_0\varepsilon/\mu_0\mu)^{1/2}$.

This difference from the usual formula applies only to materials with low conductivity and such frequencies at which the EM wavelength does not greatly exceed the skin depth itself. It is this case that corresponds to nanosized metal particles and heavily doped semiconductors.

At the same time, for ordinary dielectrics and undoped semiconductors, the skin effect can be neglected in most practical situations. But in the opposite case of extremely high conductivity of the material, the length of the free path of the charge increases.

Under these conditions, an anomalous skin effect occurs, so the mechanisms described above, which lead to the formation of a normal skin effect, cease to work: the thickness of the layer in which the current is concentrated changes according to other laws. At normal temperatures, this phenomenon is expected in 2D graphene (which has no band gap) and in 1D nanotubes (where a ballistic charge transfer mechanism is visible).

Speaking about the possibility of using metal elements as fillers for absorbent composites, one cannot ignore ferromagnetic metals. They are of the greatest interest, since in them the dispersion of σ*(ω) manifests itself in a special way due to the interaction of the intrinsic magnetic moment of the lattice ions with the spins of free electrons. In addition, these fillers can provide increased permeability, determined by gyromagnetic resonance, which occurs in magnetic metal particles embedded in the polymer matrix.

This resonance manifests itself as a selective absorption of EM wave energy in the frequency range that coincides with the eigenfrequencies of the precession of magnetic moments in a given ferromagnet. The shape and width of the absorption maximum are determined by the collective spin-lattice nature of the magnet. In addition, in the case of magneto-dielectric composites, in which ferromagnetic particles are separated by dielectric layers, multi-resonance processes begin, which are strongly blurred in the frequency range.

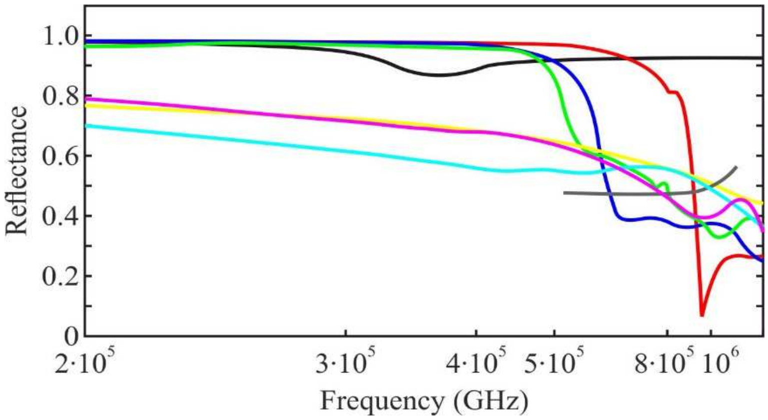


Fig. 2.20. Reflectance spectra of metals by lines: aluminum (black), silver (red), gold (blue), copper (green), beryllium (grey), cobalt (yellow), iron (cyan) and nickel (magenta)

The reflectance coefficient can be defined as efficiency of a material to reflect the incident light. This value depends only on complex refractive index (*n*) and damping constant (k) that is seen in equation: $R = [(n-1)^2+k^2]/[(n+1)^2+k^2]$. The study of metallic reflectance shown in Fig. 6 indicates that the process of $\sigma(\omega)$ dispersion not nearly as simple as the elementary theory predicts

The metal reflectance is related to the conductivity in accordance to above formulas: good-conductive metals have higher reflectance. But at a very higher frequency a sharp decrease in $R(\omega)$ is seen, Fig. 2.20. The fact is that in different metals the external electronic shells of metallic ions interact differently with free flying electrons in their free path, due to which the drift of electrons and their conductivity are created. At that, the direction of fast variable EM field changes during this free motion of electrons which they do not have time to make a collision, as the EM field already changes direction, so the free flying electrons cannot acquire drift velocity. It is at this time, when the influence of ions, having external configuration of inert gas, becomes very important (Au^{+1} repeats Rn shell, Cu^{+2} – Kr shell, Ag^{+1} – Xe shell, and Al^{+3} – Ar shell). But in the 3*d* and 4*f* metals, electronic configurations of ions contain uncompensated spins, which by their magnetic moment affect the dynamics of the drift motion of electronic gas. That is why, the EM waves reflection and conductivity of the ferromagnetics much less than in the high conductivity metals.

It should be noted that reflection spectra of metallic elements change significantly with decrease in the size of metallic particles, especially when going to the nano-sizes. At that, conductivity drops sharply and plasma oscillations do not appear: the nano-particles of metallic elements are no longer metals. At first, they exhibit the "semiconductor" and then even "dielectric" properties. It is obvious that at these stages a wide range of electromagnetic properties of nano-particles can be obtained, especially if using different technological methods to give to agglomerates of particles the quasi-one-dimensional or the quasi-two-dimensional configuration. Obviously, in the absence of screening property given by electronic gas (peculiar to the bulk metal) the role of electronic shells of ions in the metal-elements nanoparticles increases significantly. Therefore, nano-technologies make it possible to control EM properties of a substance. Absorbing and transmittance characteristics change especially strongly when going to nanosize metals.

The absorption of that part of incident EM radiation, which nevertheless penetrates into metal, from *microscopic* point of view, occurs mainly because the electrons of metal, exciting by the EM radiation both during their transition to the higher energy levels above Fermi level and during their subsequent return in the equilibrium state (with secondary emission of EM waves) interact with ionic lattice exciting its oscillations, i.e., convert some of EM energy into a heat. From the *macroscopic* point of view, the phase velocity of EM wave, penetrating into conductor, is *sharply reduced* in comparison with its velocity in vacuum, so much so that the length of EM wave in conductor (λ_m) becomes hundreds of times shorter than its wavelength in vacuum, Fig. 2.1*c*. This occurs due to the large conductivity, which in electrodynamics corresponds $\varepsilon''(\omega)$. (Note that the reduction of EM wavelength in a substance occurs in $|\varepsilon^*|^{1/2}$ times). Without a doubt, due to the huge step in the impedance at the "vacuum-metal" interface, as well as very small phase velocity of EM wave in a conductor, any EM wave falling on conductor (even in case of grazing incidence) refracts practically in the direction perpendicular to conductor's surface.

The transmittance of a part of incident on conductor EM radiation is possible only in the case of a very thin metal layer, and, of course, when the frequency of EM radiation is sufficiently high. Analysis shows that intensity of the incident wave (I_0) decreases exponentially while it propagates through metal, Fig. 5*a*, what leading to much lower intensity of transmitting wave. This happens because the metal strongly damp initial intensity of TM wave. It is obvious that decrease of wave intensity is related also to the thickness of metal layer, so extinction coefficient equals $I(x) = I_0\exp(-4\pi kx/\lambda)$, where k is the damping constant. In connection with attenuation and transmission of the EM wave in a metal, the parameter *penetration depth* due to the skin effect becomes especially important.

Therefore, in order to select the optimal materials for microwave absorbing composites, the various mechanisms of EM waves absorption in the materials are considered. In the dielectrics possessing by electronic polarization only, any absorption is practically absent, but such polymers are advisable as matrixes of composites. From the dielectrics having ionic polarization, only the ferroelectrics have big microwave absorption, increasing with frequency rise, that serves to benefit for shorter wavelength absorbers. Magnetic fillers in the composite can provide only small permeability, yet reducing reflectivity of a composite. Metallic elements in the form of micro- and nano-particles (fillers) have quite different properties than the bulk metals, but can provide both high absorption and significant permeability.

2.9 Summary

1. Negative temperature coefficient of electrical conductivity should be considered as the most characteristic electrical feature of metals, $\sigma(T) \sim T^{-1}$, i.e., the electrical conductivity decreases with temperature increase. In the case of a deep cooling, the $\sigma(T)$ dependence shows saturation, which level depends on the concentration of static defects in metal structure.

2. Metals have large thermal conductivity λ_e [W/(K·m)] caused by the high-mobility electrons; at that, the thermal conductivity λ_e is proportional to conductivity σ. The uniformity of ratio λ_e/σ for various metals is the Wiedemann-Franz's law.

3. Electrons in metals are always found in a fast movement; they move even at lowest temperatures (near absolute zero). This motion of electrons is chaotic, so different electrons move with different velocity. Usually electrons move with Fermi velocity: $\upsilon_F \sim 10^6$ m/s.

4. Electromagnetic waves, up to the optical range, almost entirely reflect from the surface of a metal, so that the metals are non-transparent for electromagnetic waves field, and demonstrate metallic lustre.

5. In the "ideal metal" with infinite conductivity, electrical field cannot exist. In the real metal, only a small electrical field can be applied, otherwise the huge transparent current will lead to metal melting. In presence of the external electrical field, the movement of electrons becomes partially directed; the drift of electrons superimposes over their chaotic movement. To calculate this current one need to estimate average drift velocity $\upsilon_{e\text{v}}$ (velocity of chaotic motion is independent on applied field).

6. Direct proportionality of electrons drift velocity to the strength of electrical field is characterized by the mobility. Exactly the mobility characterizes the resistance of a substance to electrons drift in direct electrical field. If inhibitory force would be absent, electrons will move in the electrical field with acceleration (such as in vacuum), but not with constant average velocity as they really move in crystals. So the mobility is the degree of electrons freedom in crystals.

7. Movement of electron in real metal under the external electrical field is not continuous but interrupted: as soon as electrical force appears, electron starts its moving with acceleration and its velocity gradually increases, but also the force of "friction" increases that is proportional to the electron's velocity. After relaxation time $\tau = m_e u$ the inhibitory force compensates completely acceleration force, so electron moves with constant velocity. The time constant, characterizing installing of steady state of electron movement in metal, is small: $\tau \approx 2\cdot10^{-14}$ s.

8. Parameter τ is the average time between two collisions of electron; by using its product by Fermi velocity υ_F, it is possible to estimate the average free path δ (middle distance between the electron collisions): $\tau\upsilon_F = \delta$. Charge transfer in the metals is carried out by the electrons and holes located near the Fermi surface; they take energy from the applied electrical field. As far as electrons (being excited by the external field) move to the empty higher levels, they are replaced by other electrons, previously located much deeper under the Fermi level.

9. Classic electronic theory of metals is based on Drude hypothesis about free electronic gas. This theory enables to explain and describe analytically most of experimental fact in metals,but cannot explain experimentally observed paramagnetic susceptibility and very small specific heat. Quantum mechanics show that electronic gas in metals under normal (and higher) temperature is found in the state of degeneration. In this state, the energy of electronic gas is almost independent on temperature, i.e., any alterations in thermal motion of ionic lattice almost not changes energy of free electrons.

10. Quantum mechanics explain why for metals normal temperature looks like very “low”: because Fermi energy of electrons in metals is large (about 5 - 10 eV). Electronic gas in metal is always degenerated; so energy distribution function at normal temperature varies only in narrow range k_BT near theFermi energy level. From Fermi surface electrons can be easily transferred to the allowed higher energy levels; that is why metals are good conductors of electricity.

11. Fermi surface in the space of impulses at 0 K separates the occupied by electrons ground states from their empty states. At non-zero temperature most of electrons, anyway, are placed under Fermi surface, and only some of them shift outside of it (in energy stripe k_BT). Fermi surfaces in different metals might have quite different form. In metal energy increase can be described as the birth of quasi-particles.

12. The increase of electrons energy in metal is possible by moving at least one electron under Fermi surface into external allowed level in the impulse space. At that, the appearance of this electron above Fermi surface is accompanied by unoccupied state below Fermi surface – the hole, which can be interpreted as a kind of quasiparticle that is the antiparticle as to born electron.

Therefore, the increasing energy of free electrons in a metal always is accompanied by the birth of two quasiparticles. Calling hole as the antiparticle, one has in mind possibility of its recombination, when electron will return "in its place" under Fermi surface, and metal again returns closer to its ground state, because both quasiparticles – electron and hole – disappear.

13. Metallic compounds possessing *heavy electrons* are important class of solids with anomalous properties which are difficult to explain within existing concepts. These substances are the intermediate ones between the magnetic and nonmagnetic materials, as well as between the metals and dielectrics, because most of their electrons are found amongst localized and free states.

Studies of these compounds help to understand fundumental properties of metals and magnetics, as well as to extend the conceptions of band theory for metallic and dielectric states by possible types of electronic states in crystals investigating.

14. Some compounds and metals are known, in which electrons have the binary, ambivalent nature: keeping largely localized (atomic) nature, they also can show the intention to collectivization. To the systems with unstable valence (or intermediate valence) belong some compounds of rare-earth metals and actinides, i.e., the elements that have incomplete 4*f*- or 5*f*-shells.

These compounds have unique physical properties and anomalous characteristics that explain formation of heavy fermions – peculiar electrons, that have effective mass in 10^2-10^3 times greater than mass of free electron.

15. Heavy electron materials are a specific type of intermetallic compound, containing elements with 4*f*- or 5*f*-electrons in the unfilled electronic bands. Electrons are one type of fermion, and when they are found in such materials, they are sometimes referred to as heavy fermions. These materials have a low-temperature specific heat whose linear term is up to 1000 times larger than the value expected from the free electron model. The properties of the heavy fermion compounds often derive from partly filled 4*f*- or 5*f*-orbitals of rare-earth or actinide ions, which behave like localized magnetic moments.

16. *Heavy fermion systems* are ones most remarkable manifestation of strongly correlated electron systems. These materials are compounds with the regular sublattice of 4-*f* or 5-*f* atoms (like Ce, Yb, or U). They are close to the *magnetic instability,* giving way to arising $p \Leftrightarrow f$ long-range magnetic ordering due to interactions between the 4-*f* or 5-*f* magnetic moments via the conduction electrons.

17. Conduction electrons in these metallic compounds behave as if they had an effective mass up to 1000 times the free particle mass.

This large effective mass is also reflected in a large contribution to the resistivity from electron-electron scattering. Heavy fermion behavior has been found in a broad variety of states including metallic, superconducting, insulating and magnetic states. Characteristic examples are $CeCu_6$, $CeAl_3$, $CeCu_2Si_2$, $YbAl_3$, UBe_{13} and UPt_3.

18 Several members of the group of heavy fermion materials become superconducting below critical pressure and temperature. Such superconductivity is unconventional. However, at high temperatures, heavy fermion compounds behave like normal metals, and their electrons can be described as a Fermi gas, in which the electrons are assumed to be non-interacting fermions. In this case, the interaction between the 4*f*-electrons, which present a local magnetic moment and the conduction electrons, can be neglected.

19. Superconductivity is one of "cooperative" effects in the ensemble of conduction electrons, and it cannot be explained by simple models of "independent electrons". In the technique superconductivity is interesting in sense that superconductors have no skin effect and can significantly reduce energy loss. In superconductors two effects are found by Josephson: (1) current, that flows indefinitely long time without any voltage applied across a junction that consists of two superconductors, parted by weak link; (2) when external voltage is applied, Josephson junction demonstrates effect of microwave generation. With these effects a variety of sensitive electronics devices are elaborated.

20. DC resistance of superconductor is zero: $\rho = 0$; respectively, its conductivity is the infinity: $\sigma = \infty$. This phenomenon was first discovered in mercury at temperature $T_c \sim 4$ K, but in some metals and alloys phase transition into superconducting state is observed at higher temperatures: for lead $T_c \sim 7$ K, for niobium $T_c \sim 9$ C. In alloy Nb_3Sn transition temperature is $T_c \sim 18$ K, while alloy Nb_3Ge shows highest observed temperature for metals: $T_c \sim 23$ K.

21. The non-stationary Josephson effect arises, if voltage V is applied to a weak connection; in addition to constant component of current the variable component appears that is determined by frequency ν connected with voltage by ratio: $\nu = 2eV/h$. This generation lies in ultra-high frequency range, and its frequency is linear function of applied voltage. Non-stationary Josephson effect is used to generate microwaves in GHz range.

2.10 References

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2.11 Questions for self-examination

1. Classification of metals. Basic conductivity ratios
2. Metals with high conductivity. Amorphous metal alloys
3. Temperature and frequency dependence of electrical conductivity Skin effect
4. Electronic gas in metals
5. Heat capacity and thermopower of metals
6. Zone theory of metals
7. Heavy fermions in metals and alloys
8. Superconductivity: the influence of a magnetic field
9. Superconductivity: Josephson effects
10. High-temperature superconductivity.

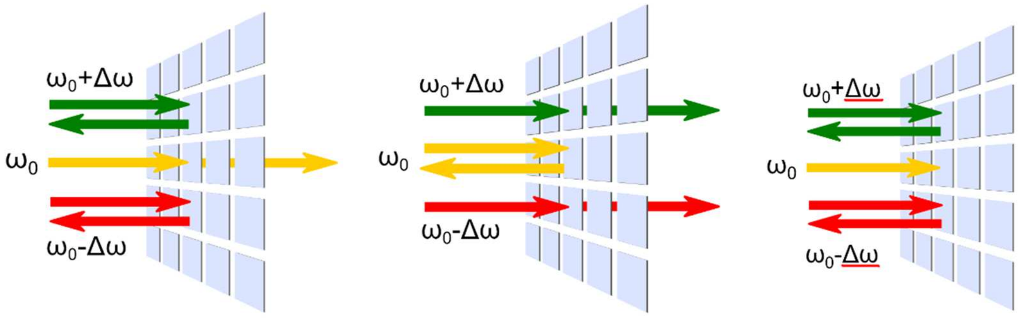
Chapter 3. Metamaterials in electronics

Contents

Metamaterials are the artificial created media elaborated for controlling of electromagnetic or acoustic waves propagation. Periodic structure of metamaterial includes the active (resonant) subwave-scale elements. Due to their special structure, the metamaterials have such electromagnetic, optical, acoustic or other properties, which can not be reproduced by known in nature homogeneous materials. Further, only metamaterials with special *electromagnetic* properties are considered (although *acoustic* metamaterials are also studied and are widely used).

As the special structure of electromagnetic metamaterials design, so the properties of actually received materials used in the structural elements, have a specific effect on the propagation of the electromagnetic radiation. This applies especially to such properties of metamaterials, which are not observed in the known bulk materials (at that, the especially impressive property of some metamaterials is the demonstration of negative refractive index in a certain frequency range.

As illustrative example, in Fig. 3.1 shows implementation of three microwave devices using metamaterial: filter that transmits only EM wave with frequency of ω_0, the filter which excludes the passage of only wave with this frequency, and the metasurface, which selectively absorbs an EM wave of only this frequency.



a *b* *c*

Fig. 3.1. Selected functionalities of metasurfaces: *a* — bandpass frequency selective surface; *b* — bandstop frequency selective surface; *c* — narrowband perfect absorber

3.1 Introduction

The term "metamaterial" comes from the Greek word "meta" which means "beyond": that is a material designed to have the properties not found in natural materials. Metamaterials are constructed from several elements made from different materials, usually using the composite technologies. At the same time, the resonant and connecting elements of such construction should be smaller than the wavelengths of a phenomena they affect; moreover, these elements are arranged in the repeating patterns. It should be noted that metamaterials get their special properties not so much from the properties of initial material components, but from the special design of their location. Manipulation by electromagnetic waves makes it possible to create the special geometry, size, orientation and location of the active elements that allows to reflect, block, absorb, amplify or bend the waves propagating in the metamarial, achieving such properties which go beyond the capabilities of conventional materials.

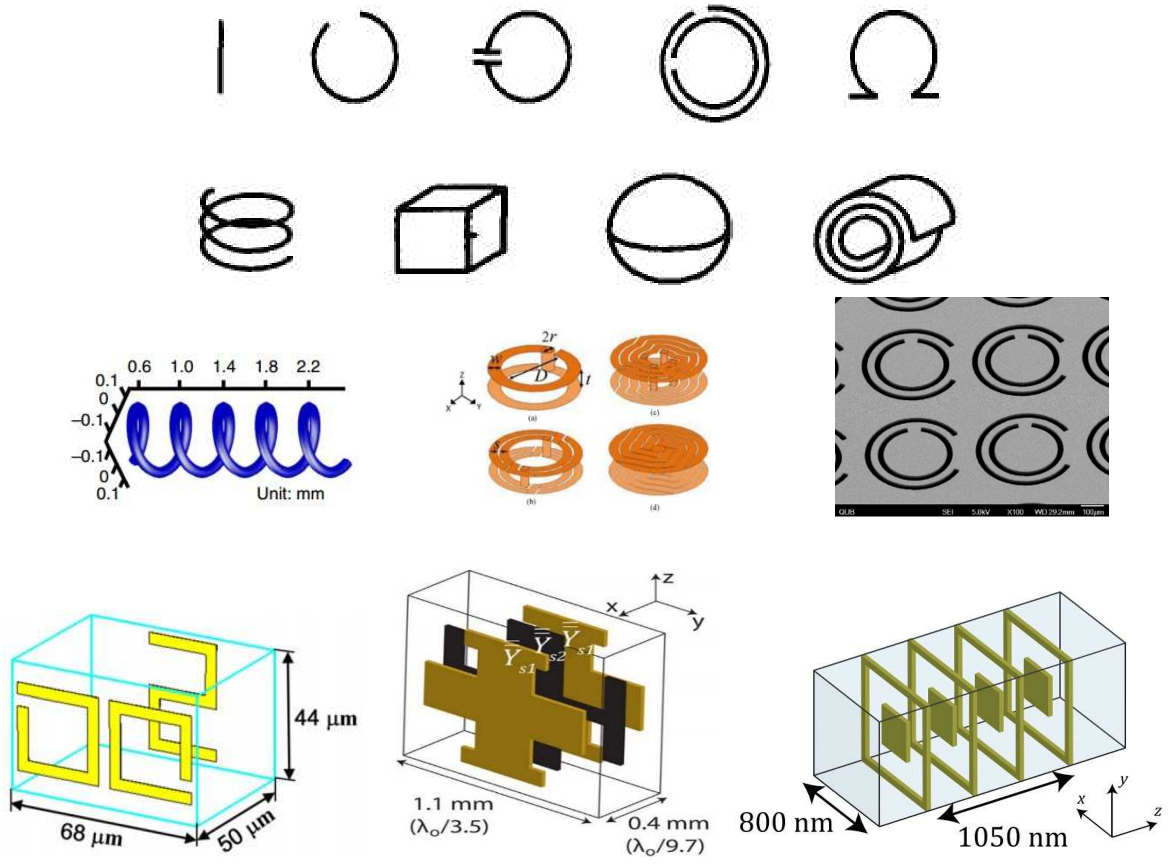
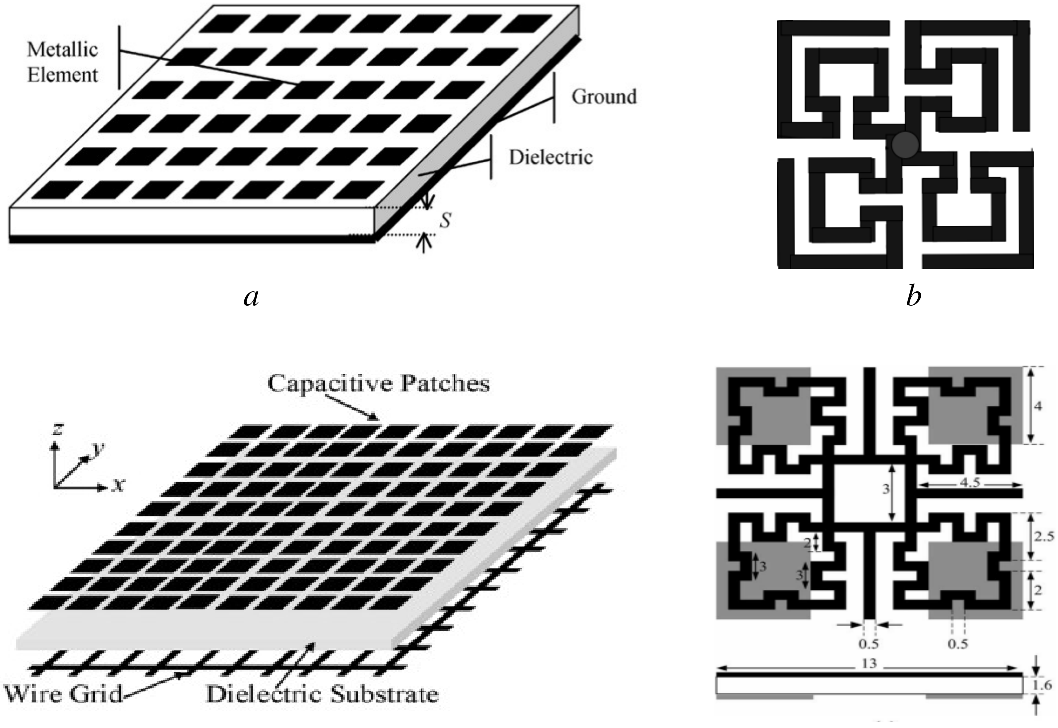


Fig. 3.2. Different elements from which metamaterials are constructed

The metamaterial can be obtained exclusively from the non-continuous and non-homogeneous medium: metamaterials always are the composites. Usually metamaterials are constructed from the *discrete* resonant micro- and nano- elements:

a sort of “meta-atoms", which *mimic* electromagnetic reaction of real atoms and molecules in the natural substances. Such "meta-atoms", Fig. 3.2, are grouped in the form of single or multilayered lattices, while their small size (less than wavelength of radiation) makes it possible to treat the created lattice as a *homogeneous* for given wavelength (by analogy with natural crystals), and use the concept of "effective medium" for characteristics calculating.

The applications of metamaterials are quite diverse: electromagnetic, optical, acoustic and medical devices, etc. However, only the *electromagnetic* metamaterials, which are intended for use in the microwave range, will be considered below. They act on the electromagnetic wave by specially arranged structural elements made of metals or dielectrics, these elements act on electromagnetic wave but remain less than the length of this wave. Fig. 3.3 shows an example of a combination of resonant elements with the formation of a metastpuktupa



a *b*

c *d*

Fig. 3.3. Frequency selective metamaterial: *a* – square-patch surface; *b* – miniaturized spiral-loop unit cell; *c* – miniaturized elements consisting of capacitive and inductive grids on opposite side of spacer; *d* – miniaturized unit cell with meandered layout

Metamaterials for microwave range typically consist of arrays of electrically conductive elements (i.e., wire cuts or loops), which have suitable inductive and capacitive characteristic. Revolutionary changes in the production technology and design methodology of electronic devices make it possible to achieve very high packing density of elements and compact dimensions of radio-electronics products in general.

Recently, quasi-two-dimensional (2D) materials, called *metasurfaces*, have gained great importance. These are the 2D analogs of metamaterials, defined as thin and dense 2D arrays of structural elements that have unusual and useful properties imparted by their constituent elements with typically resonant behavior (conventional metamaterials are defined similarly, but as bulk (3D) arrays). The size of the elements and their periodicity are sub-wavelength, so homogeneous or almost homogeneous metasurfaces reflect and transmit plane waves as uniformly polarizable sheets.

Of course, many functions of 2D metasurfaces can also be implemented using many layers of bulk 3D metamaterials. But metasurfaces have a number of advantages. First, 3D periodic arrays are difficult to implement because they are multilayer nanostructures. Secondly, the work of 3D metamaterials depends on the propagation of waves over considerable distances, and therefore is constrained by its own high losses, obviously accompanying resonances. Strong absorption by bulk metamaterials reduces many of their intended practical applications. On the contrary, 2D metasurfaces demonstrate much better ability to form EM flows than bulk metamaterials due to lower absorption. Thirdly, 2D structures are rather thin layers, which in microwave technology makes it possible to diversify technical solutions and allows many solutions for new designs.

3.2 Possible media with which EM waves can interact

In order to determine the position of *metamaterials* among others materials, the reflection, propagation and absorption of high-frequency EM radiation is discussed, when considering not ordinary specific substances (such as dielectrics, metals, semiconductors, ferrites, etc.), but as *media with certain electromagnetic parameters,* i.e., such as they are perceived by electromagnetic radiation during its propagation. This approach to the problem of EM waves interaction with environment is justified by the fact that in different frequency ranges the same substance can look like a different electromagnetic medium.

To classify whole variety of metamaterials, it is accepted to use the *signs* of effective values of their dielectric permittivity (ε) and magnetic permeability (μ), which are included in the Maxwell's equations as $D = \varepsilon_0\varepsilon E$ and $B = \mu_0\mu H$. To consider possible combinations of electromagnetic parameters of medium that determine the EM wave propagation, Fig. 3.4, shows four different cases in the rectangular coordinate system, where ε and μ axes are plotted (under the assumption that these parameters are isotropic).

All cases considered are highly idealized.

I ***quadrant*** corresponds to DPS (*double positive*) materials which:

- possess positive values for both $\varepsilon > 0$ and $\mu > 0$.
- have positive refractive index $n = (\varepsilon\mu)^{1/2} > 0$.

To begin with, it should be noted that outside the shaded area in Fig. 3.2 are the areas, where $0 < \varepsilon < 1$ and $0 < \mu < 1$, that is, they have a refraction index $n < 1$. This means that the phase velocity of EM wave exceeds the speed of light (which does not contradict the theory of relativity). With such a medium, a high-frequency EM wave can meet regions of electric or magnetic resonances, where its absorption and reflection is large (although not maximal). It is also appropriate to note that in superconductors it is customary to consider $\mu = 0$, since up to optical frequencies the EM field cannot penetrate in them. Particular cases, when at one or another specific frequency $\varepsilon = 0$ or $\mu = 0$ can be observed, are located in region of electric or magnetic resonance (slightly higher than the resonant frequency).

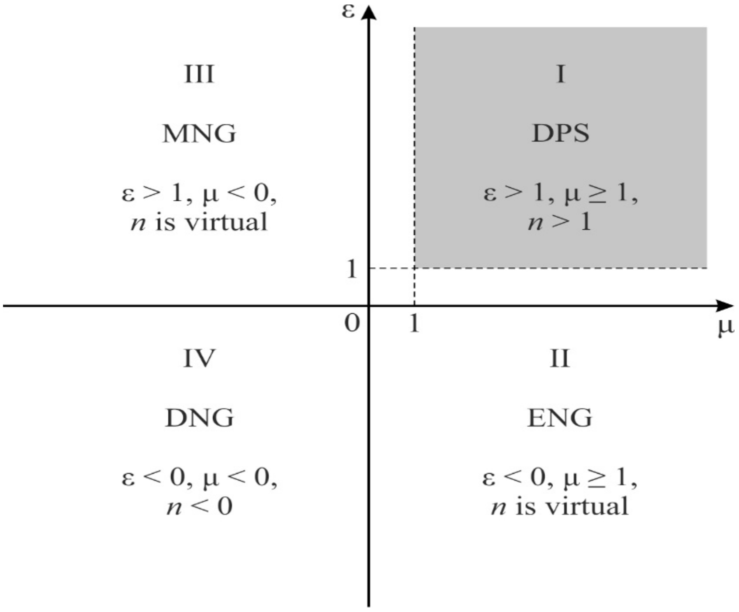


Fig. 3.4. Classification of media with which EM waves interact

Almost all dielectric, semiconductor and ferrimagnetic materials, where $\varepsilon > 1$ and $\mu > 1$, are identified in Fig. 3.4 by hatching (except for the rare cases of electric and magnetic resonances listed above). The vast majority of these substances are transparent for EM waves; usually these are some dielectrics with varying degrees of absorption of EM energy. In these ordinary materials, the parameters $\varepsilon(\omega)$ and $\mu(\omega)$ are fully defined for each particular case by one or other atomic or molecular structures. It means that their parameters are defined by *electrical polarization* (displacement of electrical charges with electrical moment formation) and by *magnetization* (orientation of elementary magnetic moments). Properties of atoms or molecules follow to fundamental laws of physics, and, at the absence of electric, magnetic and electro-acoustic resonances, they lead to *positive static values* of permittivity $\varepsilon(0)$ and permeability $\mu(0)$. In most frequency ranges, interesting for practical use, these parameters are, generally, greater or equal to unity ($\varepsilon > 1$, $\mu \geq 1$). But it should be noted that in any dielectrics there are peculiar regions of the EM spectrum (usually located in its optical part), where $\varepsilon < 0$ due to delay of resonant polarization, and then such a medium already belongs to quadrant II.

Everything that is located in the unshaded area of Fig. 3.4 can be attributed to the metamaterials of various types (exceptions are resonances of dielectric polarization and spin-orbital magnetism, which occupy only narrow frequency bands). It should be noted that the metamaterials are also created on the basis of ***resonant elements*** *packed in composites by special methods.*

II *quadrant* with ENG (ε-*negative*) characterizes materials which:

- possess negative value of $\varepsilon < 0$ but positive $\mu > 0$,
- have virtual (imaginary) refractive index that promotes EM waves reflection.

This phenomenon is possible both in the natural materials and in the artificially created media. First, the plasma has such characteristics; both the gaseous plasma and the plasma in solids. Such situation arises with highly mobile electrons in the metals and semiconductors. Exposure to them by a high-frequency electrical field leads to the *plasma resonance* and the dispersion of electronic gas. The least inertia of "free" electrons is a characteristic of metals and other conductors (graphite, graphene, etc.) which widely used in electronics as interconnectors and components of absorbing microwave composites. In semiconductors, the less dense electronic plasma leads to the resonance phenomena and dispersion at optical frequencies. When charge carries show their inertia, the *conductivity decreases*, at that, in usual metals conductivity decreases in the *ultraviolet* wavelength range (above 10^{16} Hz) so the electronic *polarizability of the deep ionic shells* in the ionic lattice of a metal becomes noticeable. However, in the *weakly conducting* metals and, especially, in the finely dispersed metals (usually used in absorbing composites), the inertia of electronic conductivity may appear already in the range of millimeter waves and even at microwaves.

The second case (usually in dielectrics), $\varepsilon < 0$ in a limited frequency range, in which the resonance of electrical polarization mechanism takes place. At that, the phase of dielectric response (which is the elastic displacement of closed charges) lags behind the phase of an applied field, which causes to *negative* value of ε. In case of the ionic polarization in dielectrics, their lattice resonance occurs in the frequency range of far infrared waves (~ 10^{13} Hz), while for electronic shells the polarization resonance going on in range of ultraviolet waves (frequencies greater than 10^{16} Hz): both these ranges are quite far from frequency range of metamaterials expected applications. Thus, at first glance, there is no basis for hoping to obtain resonant phenomena in *continuous homogeneous medium* as in the microwaves so in the visible optical range. However, it can be noted that in piezoelectrics their electro-mechanical resonance is possible, which also leads to a negative value of ε. Usually this resonance occurs at frequencies of 10^5–10^7 Hz (depending on the size of piezoelectric element); to realize this resonance at microwaves the piezoelectric resonators should have their size only a few microns. Microelectronic technology is responsible to realize this case.

Another case: the artificially created ε-negative media can be realized in the *ENG metamaterials* that will be described later.

III *quadrant* corresponding to MNG (μ-*negative*) materials which:

- possess negative value of $\mu < 0$ in some frequency range but positive $\varepsilon > 0$,
- have virtual value of refractive index that contributes EM waves reflection.

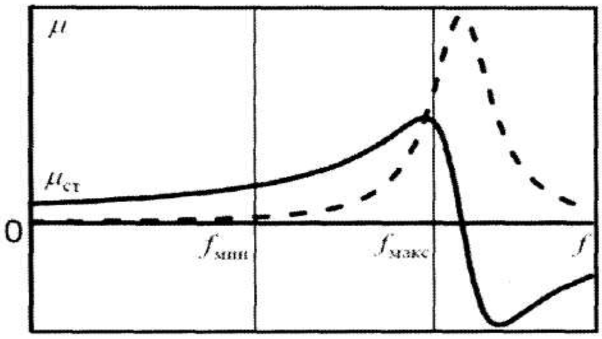
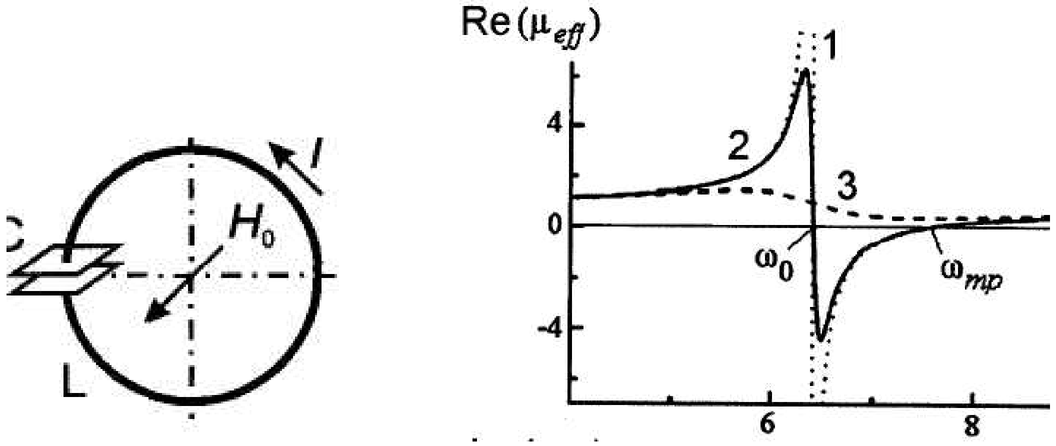


Fig. 3.5. Typical dependence of the real (solid curve) and imaginary (solid curve curve) magnetic permeability of ferrite at resonant dispersion (both positive, increasing with frequency part of μ and negative permeability above the resonance frequency are used in composite metamaterials)

Natural materials in which at certain frequency parameter $\mu < 0$ can be obtained are the ferrites (where ferromagnetism and antiferromagnetism coexist, conductivity not very big and $\varepsilon > 0$). In them, both the ferromagnetic resonance (at the beginning of microwave frequency range) and the resonance due to magnetic domains movement (in the megahertz range) are possible. In both cases, these resonances are accompanied by strong absorption of RF energy.

Artificial materials with control over μ sign and value have been known for a long time. Already in early works, it was noticed that ε increase in composite leads to the undesirable grows of reflection coefficient of electromagnetic radiation from such dielectric medium, while the opposite changes in μ and ε when metal particles are introduced into the medium reduce the reflection of EM waves. Therefore, it is desirable to increase magnetic permeability of medium by artificial "magnetic" iclusuins.



a *b*

Fig. 3.6. Configurations of single-turn oscillatory circuits for introduction into medium with controlled magnetic permeability (a) and its resonant characteristic (*b*) .

To do this, it was proposed to introduce miniature oscillatory circuits in the form of open loop with a capacitance, conventionally shown in Fig. 3.4*a*. The current induced in the coil in the counterclockwise direction is determined by the geometric parameters of the circuit through *C* and *L*. The capacitance can be formed by the coil itself, if it has dimensions close to resonant ones. A feature of circuits made up of open turns or loops are strongly pronounced resonant properties, Fig. 3.4.

As frequency rises above resonant, magnetic permeability *becomes negative*.

Therefore, both in II an III quadrants, the *single negative* (SNG) metamaterials are represented, which are characterized by either negative ε or negative μ. In the natural materials, as negative ε so negative μ arise due to the resonant dispersion, which is inevitably accompanied by losses, providing maximum absorption of energy in peculiar frequency range. In a such media, the electromagnetic waves decay very quickly (according to exponential law). As a rule, these materials are opaque to electromagnetic radiation, if their thickness is greater than characteristic exponential decay length of electromagnetic waves.

However, in the SNG metamaterials, in relation to EM wave losses, many various compromise solutions are possible, because electromagnetic resonances are artificially excited by small elements, which use the non-magnetic material ($\mu \approx 1$).

IV *quadrant* characterized the DNG (*double negative*) material,

- possess both negative $\varepsilon < 0$ and $\mu < 0$ in some frequency range,
- have negative value of refractive index $n = -(\varepsilon\mu)^{1/2} < 0$

The choice of precisely the negative sign at the square root of the product εμ could be justified, as it was done in the work [1]. For negative μ and ε, a simple replacement of μ with –μ and ε with –ε still gives a positive value for the index of refraction since $n = ((-\mu)(-\varepsilon))^{1/2} = (\mu\varepsilon)^{1/2}$ is might be positive. However, the square root has two solutions: one positive and one negative.

Thus, the simple solution when μ and ε are both negative, is to take the negative square root to get the index of refraction: $n = (\pm)\ (\mu\varepsilon)^{1/2}$ (so pick $n = (-)(\mu\varepsilon)^{1/2}$). However, there exists a more satisfactory solution in the *complex space.* Using complex notation, the result comes out more naturally with –μ expressed as $\mu\ e^{i\pi}$ and –ε expressed as $\varepsilon\ e^{i\pi}$, so that $n = [(-\mu)\ (-\varepsilon)]^{1/2} = (\mu\ e^{i\pi}\ \varepsilon\ e^{i\pi})^{1/2} = (\mu\ \varepsilon)^{1/2}\ e^{i\pi} = -(\mu\varepsilon)^{1/2}$.

Single-phase substances with simultaneously negative ε and μ do not exist in nature, but they can be created artificially – as metamaterials, which usually are represented by the artificial structures. Paradoxical from the ordinary point of view, the possibility of physical media existence possessing negative refractive index was theoretically substantiated by V.G. Veselago, who shown that this case does not contradict Maxwell's equations. Subsequently negative refraction was confirmed experimentally by J.B. Pendry, who created artificial constructions which double-negative properties.

If the composite material consists of discrete scattering elements, provided that their size is smaller than a wavelength, then, from the point of view of electrodynamics, this material can be considered as continuous one (but in limited frequency band). In electromagnetic sense, any physical medium appears to be continuous, if its properties can be described by averaged parameters, varying on scale much greater than the size and spacing of components that form the material.

The disadvantages of the first metamaterials based on the use of ring and rectangular resonators are the narrow frequency band and the high level of electromagnetic losses. To solve the problem of narrow band, many design options for resonant elements were proposed while their geometric dimensions were optimized.

With regard to the multi-frequency solutions, the fractal frames were used instead of split ring or square frames. There are some prospects for using in the metamaterials not only metallic resonant elements, but also composites filled with high-permittivity dielectric resonators (DR). At that, materials are known, in which the electromagnetic resonance in the DR can be accompanied by electroacoustic resonance in the same DR, if dielectric resonators are made of piezoelectric material.

3.3 ε-negative metamaterials

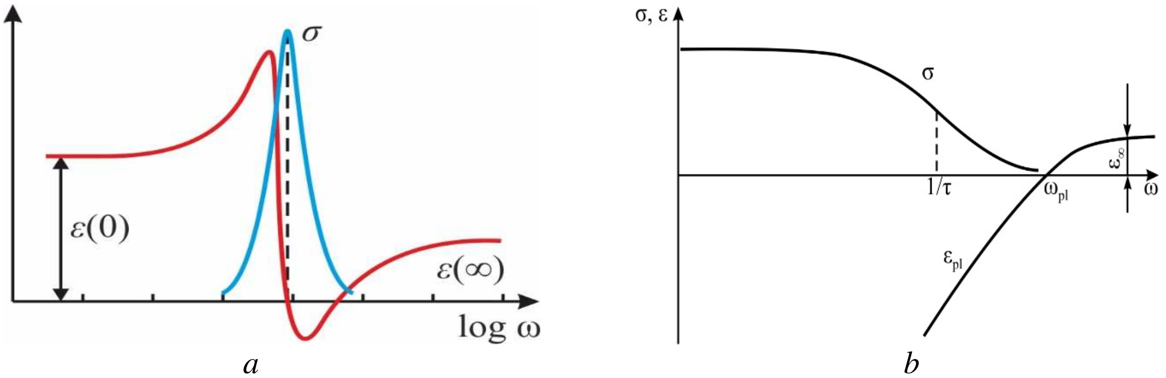
High-frequency electromagnetic waves perceive the permittivity as a negative value not only in the metamaterials, but also in the natural materials, which, firstly, demonstrate dispersion of resonant polarization, and, secondly, in the electric plasma of conductors.

Resonant dispersion of polarization, suown in Fig. 3.5*a*, is characterized by the fact that, at first derivative $d\varepsilon'/d\omega$ is positive, next at resonance point it changes sign to the negative value but after the anti-resonance the derivative $d\varepsilon'/d\omega$ again becomes positive. Therefore, permittivity passes through the maximum and minimum. In the region of resonance dispersion of permittivity, the effective conductivity is characterized by a sharp maximum $\sigma'_{max} = \varepsilon_0\Delta\varepsilon\omega_0/\Gamma$, locating *exactly at resonance frequency* of the oscillator describing this dispersion; where ω_0 is oscillator own frequency, Γ is the relative damping factor, while $\Delta\varepsilon = \varepsilon(0) - \varepsilon(\infty)$ is the dielectric contribution of oscillatory polarization mechanism.

When resonant dispersion occurs, in its initial stage the dielectric losses and effective conductivity increase due to the weakening of the elastic bonds between ions of a lattice when resonance approaches. As a result, at same value of electrical field the mutual shift of ions increases critically, and permittivity has a maximum. At the resonance frequency, the elastic bonds between ions no longer have enough time to manifest itself in a rapidly changing alternating electric field, so that the system of cations and anions looks like "electrolyte" (and maximum of conductivity is seen). Then, the phase of mutual displacement of ions changes in such a way that in the external alternating field the anti-resonance occurs, at which dielectric contribution of oscillator becomes *negative*, and effective conductivity decreases. With further increase in frequency, the ionic lattice no longer manages to respond to the rapid change in electrical field, but still the electronic quasi-elastic polarization of ionic cores establishes and provides a certain value of $\varepsilon(\infty)$.

Thus, in a certain frequency range, the *permittivity is negative.*

Electronic plasma in metals is the other case, when EM waves collide with the phenomenon of *negative permittivity*. Its sign is conditioned by conductivity decrease with frequency: $\sigma(\omega)$, that become apparent, as a rule, in the highest frequency region. In the rapidly changing electric field, the inertia of charge carriers begins to affect, that is why their movement at sufficiently high frequency of electrical field becomes no longer possible. Exposure to them by a high-frequency electrical field leads to the *plasma resonance* and the dispersion of electronic gas (in dielectrics electronics conduction has polaronic nature and "lags" at low frequency). The least inertia of "free" electrons is a characteristic of metals and other conductors (graphite, graphene, etc.), which widely used in electronics as interconnectors and components of absorbing microwave composites. In the semiconductors, less dense electronic plasma leads to resonance phenomena and $\sigma(\omega)$ dispersion at optical frequencies.



a *b*

Fig. 3.7. Frequency dependence of permittivity and conductivity: *a* – for resonance polarization dispersion; *b* – in metals in the vicinity of plasma resonance

It is important to note that the inertia of electrons can be detected by dielectric spectroscopy methods. When charge carries show their inertia, the *conductivity decreases*, at that, in usual metals conductivity decreases in the *ultraviolet* wavelength range (above 10^{16} Hz) so the electronic *polarizability of the deep ionic shells* in the ionic lattice of a metal becomes noticeable. However, in the *weakly conducting* metals and, especially, in finely dispersed metals (usually used in composites), the inertia of electronic conductivity may appear already in the range of millimeter waves and even at microwaves.

The following is a simplified model, which describes conductivity by using a conception of electronic plasma in solids. The plasma is a system of positive and negative charge carriers; at that, plasma can be *charged* (like electronic plasma in metals) or *neutral* (like electron-hole plasma in semiconductors). The density of charge carriers in charged plasma can reach 10^{22} cm^{-3}, while in neutral plasma charge carries density might be 10^{15}–10^{18} cm^{-3}. The plasma can be considered as a subsystem, which can interact with crystal lattice that facilitates its properties study. Characteristic property of plasma is the presence of *collective excitations* – plasma oscillations.

The model of Langmuir oscillations in electronic plasma in metals supposes that a *returning force* exists, arising when group of electrons possessing charge *e,* mass *m,* and density *N,* shifts from their equilibrium position on some distance relatively to the positively charged "non-moving" ionic lattice (in particular, this displacement can be induced by the external electrical field). The returning force, acting on displaced electrons, causes the oscillations of electrons around their equilibrium position with the plasma frequency $\omega_{pl} = (Ne^2/m\varepsilon_0)^{1/2}$. Experiment indicates that electronic gas in metals demonstrates its inertia at frequencies of 10^{16}–10^{17} Hz: at higher frequencies electrons have no time to follow electromagnetic field changing. That is why above the plasma frequency it is possible to determine the *permittivity* ε_{uv} in a metal due to the displacement of non-collectivized electrons (bound inside ionic cores).

Thus, conducting materials used in electronics as interconnectors, waveguides, antennas and components of absorbing microwave composites show some ohmic losses in a whole frequency range including terahertz range. The degree of electromagnetic energy absorption due to conductivity effect on high-frequency properties of metals can be found using dielectric spectroscopy method. At that, in the simple metals (or other conductors) *complex permittivity* follows Drude-Langmuir model for free charge carriers absorption:

$$\varepsilon^*(\omega) = -\,(Ne^2/m\varepsilon_0)/(\omega^2 - i\,\omega\gamma) = -\,\omega_{pl}{}^2/(\omega^2 - i\,\omega\gamma)$$

where N is the concentration of charge carries, e is their charge, m is the effective mass, $\gamma = 1/\tau$ is the damping factor of plasma oscillation, τ is the scattering (life) time of charge carries, ω_{pl} is plasma resonant frequencyand ω is angular frequency.

Accordingly, from above model, *complex conductivity* can be determined: $\sigma^*(\omega) = i\,\omega\varepsilon_0\varepsilon^*(\omega)$, or otherwise

$$\sigma^*(\omega) = \frac{\sigma(0)}{1 + i\omega\tau}, \text{ where } \sigma(0) = \frac{Ne^2\tau}{m} = \varepsilon_0\omega_{pl}^2\tau\,,$$

The low-frequency conductivity $\sigma(0)$ remains frequency independent in the case when $\omega << 1/\tau$, i.e., practically in the entire frequency range used in electronics. At that, the conductivity makes contributions both to the real and imaginary parts of permittivity

$$\varepsilon'_{\mathrm{pl}}(\omega) = \varepsilon_{\mathrm{uv}} - (\omega_{\mathrm{pl}}\tau)^2, \quad \varepsilon''_{\mathrm{pl}}(\omega) = \omega_{\mathrm{pl}}{}^2\tau/\omega,$$

where ε_{uv} is the contribution to permittivity of polarization of deep electronic shells of ions making up the metal crystal lattice (ε_{uv} is detectable in ultraviolet frequencies). Thus, in metals and other conductors, the plasma contribution to permittivity is *negative,* while plasma contribution to the dielectric losses, of course, is positive but at low frequencies (far from resonance) it is small.

Graphs of $\sigma(\omega)$ and $\varepsilon(\omega)$ change are shown in Fig. 3.5*b*. Frequency behavior of *conductivity* resembles the *relaxation* dispersion of permittivity: at frequency $\omega = 1/\tau$ the conductivity decreases by a half while near the frequency of plasma resonance conductivity vanishes. Frequency dependence of plasma contribution to *permittivity* resembles *resonance* dispersion but only *above* natural frequency of oscillator. The fact is that in the electrically conductive media, below frequency of plasma resonance, charge carriers shield the electrical field, so phase of their displacement in the applied alternating field corresponds to the *negative* contribution to permittivity, which is the greater the higher concentration of charge carriers and lower frequency.

At plasma resonance frequency ($\omega = \omega_{pl}$), the permittivity of metal equals zero: $\varepsilon'(\omega) = 0$ due to *compensation* of negative dielectric contribution from free charge carriers by the positive contribution to permittivity from the polarization of ionic cores: $\varepsilon_{cor} = \varepsilon(\infty)$. When frequency increases above ω_{pl}, the permittivity ε_{cor} gradually gets its full value; next, with a subsequent increase in frequency and its approach to *X*-ray values any polarization has no time for establishing, and $\varepsilon'(\omega) \rightarrow 1$.

It is worth noting that plasma oscillations of electrons can be quantized, so the model of quasi-particle can be introduced: the *plasmon*, which is elementary excitation of plasma oscillations. The formula for plasma resonance frequency $\omega_{pl} = (Ne^2/m\varepsilon_0)^{1/2}$ shows that it is proportional to square root of charge carriers concentration. In highly conductive metals ($N \sim 10^{22}$ cm^{-3}) this frequency is located in ultraviolet part of a spectrum, but for weakly conducting metals frequency ω_{pl} is lower. In semiconductors, which have charge carrier concentration of 10^{15}–10^{17} cm^{-3}, the plasma resonance frequency is seen in the visible optical range. The charge carriers mass has essential influence on the resonance frequency, so that in the semiconductors, possessing small effective mass of electrons, the frequency of plasma resonance is increased.

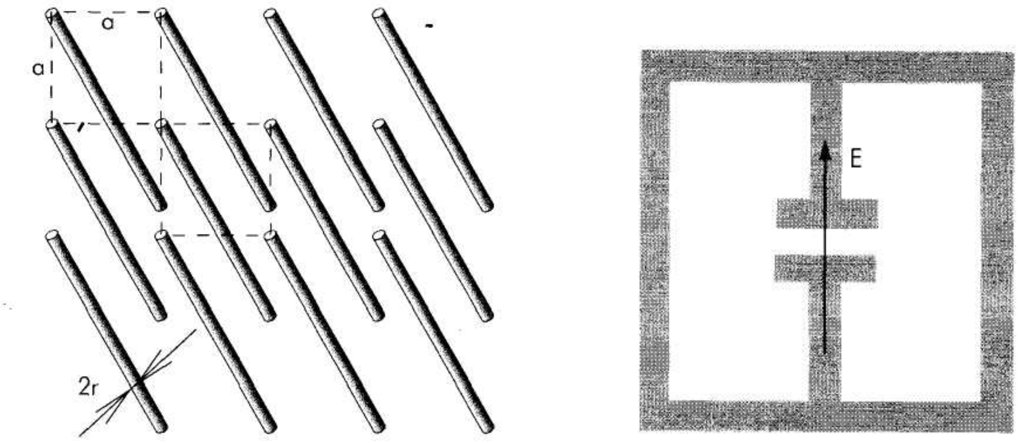
Since at plasma resonance frequency permittivity is zero ($\varepsilon = 0$), the reflection of electromagnetic waves from crystal practically is absent; in practice, this means that quasi-particle – plasmon – leads to minimum of reflection coefficient of semiconductors in optical range. At that, frequency ω_{pl} can be determined from the minimum of the reflection, characterizing by ratio of charge carriers concentration to their effective mass. Besides, in the *heavily doped* semiconductors, the presence of free charge carriers *decreases* their optical refractive index. Such negative contribution of plasma to the permittivity at optical frequencies is especially significant in those semiconductors, in which effective mass of electrons is small (usually these are semiconductors of $A^{III}B^{V}$ type). Effect of plasma onto refractive index decrease is used in the integrated optics to obtain planar optical light guides.

Artificially created electromagnetic media, imitating properties of dielectrics, have been studied for a long time. At that, by special selection of the shape and design of metallic elements, it is possible to achieve both *positive* and *negative* values of permittivity. The term "artificial dielectrics" has long been used to denote artificial materials with a pronounced *electrical reaction*, while the elements used, and the structural features of artificial dielectrics are very reminiscent of those material compositions that are now called metamaterials.

Developers implemented experimentally the idea of modeling the phenomenon of EM waves (in particular, light) passage through a "dielectric structure" by the replacing a real crystal to spatial grating of metallic elements, while choosing the correspondent parameters and the radiation wavelength λ based on the principles of similarity, i.e. the distance between the elements and the size of elements must be small in compared with λ. Metallic elements were considered as a physical model of atoms or molecules of a crystal. For example, gratings of small scattering particles (simulating molecules) with a lattice period much smaller than EM wavelength were considered. Such a lattice was assumed to be as analogue of continuous medium, subjected to two important requirements, necessary to obtain the effect of artificial dielectrics from metallic elements: the distance between elements in the lattice and the size of elements must be less than wavelength. At present, exactly these requirements are typical for the metamaterials as well.

Subsequently, it turned out that artificial dielectrics do not need to have a regular lattice, but they can be the composite of inclusion particles, randomly distributed in the matrix, so that in this case they can also have unusual interesting properties. It should also be noted that when concentration of electrically conductive particles in the dielectric matrix exceeds the *percolation threshold* (at which the particles directly touch each other or have a strong capacitive coupling), at rather low frequencies the current begins to flow through the composite material, and it turns into the artificial conductor with some complex conductivity (term percolation means the flow of current through a medium with electrically conductive inclusions). The conductivity of percolation materials can be controlled constructively and with the help of an external magnetic or electric field. Such materials are used in various electrical devices as well as in Stealthy technology.

One of artificial media with a negative ε is the system of thin metal wires arranged in parallel, Fig. 3.8*a*. The use of many thin conductors opens up the possibility for plasma simulation with similar calculation of effective permittivity. In particular, for meta-structure based on the aluminum conductors with a radius 1 μm and spacing between them 5 mm, plasma frequency is approximately 8.2 GHz.



a *b*

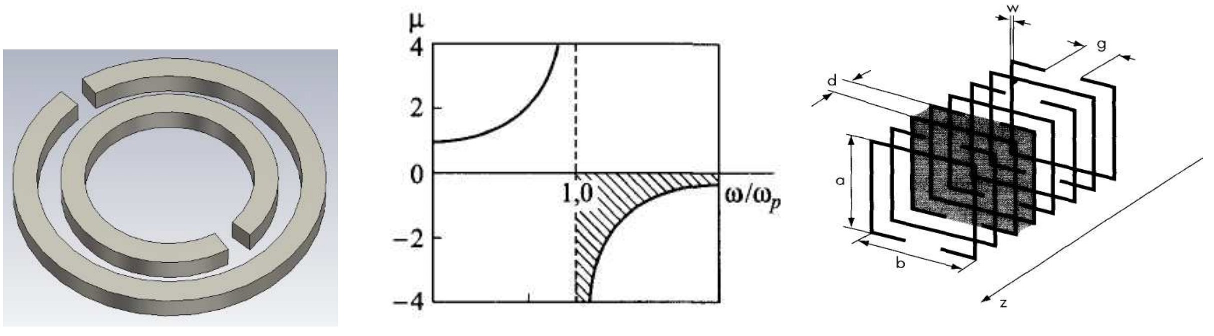
Fig. 3.8. Metamaterial elements imitating negative electrical permittivity in certain frequency range: *a* – set of thin metal wires in dielectric matrix; *b* – capacitive element simulating negative permittivity

Along with considered metallic-wire structures, other designs of artificial ENG materials are also known. For example, Fig. 3.6*b* shows a structure, in which inductive loops, formed by two split frames, create mutually opposite magnetic fields, which cancel each other out. As a result, the response of element depends only on the electrical component of electromagnetic field incident on it. Respond is formed mainly by capacitance of a cut in combination with active resistance of frame material; at that, this construction provides *dynamically* negative sign of capacitance in a certain frequency range. The metamaterial based on these elements is described, which has negative value of ε in terahertz range. In it, with inter-element interval of 50 μm, the external dimensions of frame were only 36 μm, and the width of a cut in central bridge was 2 μm.

3.4 μ-negative metamaterials

Some gyrotropic substances with the positive permittivity and negative permeability in a certain frequency regimes are the prototypes of MNG media. Various ring and ring-like structures with a negative *effective* magnetic permeability have long been used as building blocks in manufacture of microwave lenses. Currently, the main structures used to obtain MNG media are thin metallic cylinders, nested split rings, rectangular frames, etc.

The split ring resonator (SRR) shown in Fig. 3.9*a* is a basic structure, in which the capacitance between two rings is compensated by the inductance of this structure, generating the secondary magnetic field – either amplifying the initial field or counteracting it, which leads to the positive or negative effective values of the effective permeability. The frequency dependence $\mu(\omega)$ can be described as the $\mu(\omega) = 1 - \omega_r{}^2/\omega^2$, where ω_r is the resonant frequency. At that, parameter $\mu_{ef} \to \infty$ (if loss is absent), is determined by the parameters of a given element of device.



a *b* *c*

Fig. 3.9. Metamaterial elements imitating negative magnetic permeability in certain frequency range: *a* – double ring split resonator (SRR); *b* – frequency dependence of effective magnetic permeability of medium with resonators; *c* – metallic slit frames with alternating orientation of section of elements

Figure 3.9*b* describes the emergence, increase and resonant decline of effective magnetic permeability, and its transition to a negative value above the resonant frequency of inductive elements of metastructure. There are a large number of magnetic resonance structures developed for microwave metamaterials. One of these structures is shown in Fig. 3.9*c*.

3.5 Double negative metamaterials ($\varepsilon < 0$, $\mu < 0$)

In the metamaterials, a very interesting idea is realized: the possibility to obtain the *negative refractive index* for microwaves or light. These means that in these materials the electromagnetic wave, for example, light is not refracted as usual, i.e., it deviates not to the right, but to the *left* at negative angle, Fig. 3.8*a*. Therefore, these materials are often referred to as the materials with negative refraction (Negative Index Materials – NIM) or Left-Handed Materials (LHM). V.G.Veselago, who theoretically predicted the existence of such metamaterials, called them "left media". The point is that in usual medium the directions of the electric field vector ***E***, the vector of magnetic field ***H*** and the wave vector ***k*** form the right triplet, that is, they can be described by right hand fingers (RHM). On the contrary, in the metamaterial these vectors form the left hand triplet. However, in the left hand material, LHM, the Poynting vector ***S,*** which shows direction of energy propagation, remains in right triplet, Fig. 3.10*b*.

The negative refractive index *n* is due to strong spatial dispersion in the мetamaterial, and negative values of ε and μ. Due to both permittivity and permeability have negative sign, these materials sometimes called "double negative" (doubly negative - DNG). In metamaterials, the phase velocity of waves is directed in opposite side relative to the group velocity, therefore, these materials are also referred to as "reverse" media (“backward-wave media – BW-media).

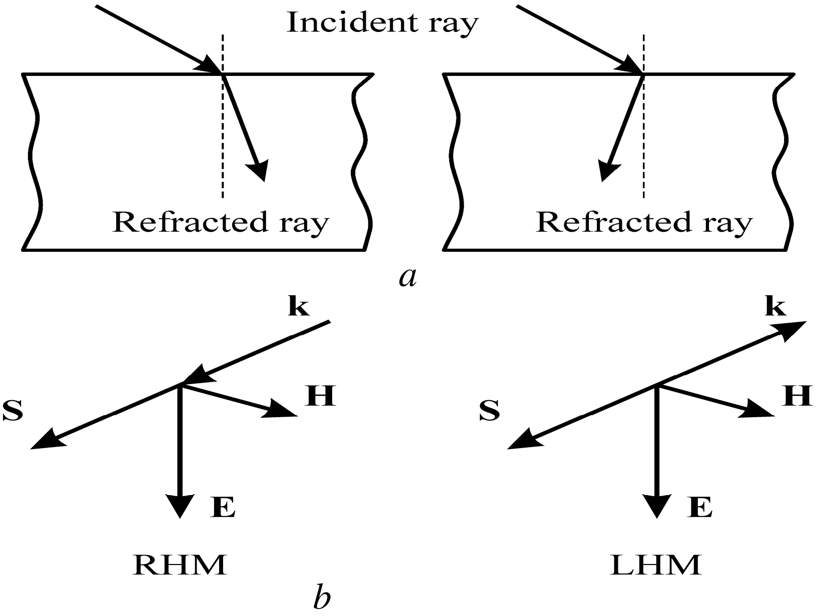


Fig. 3.10. Effect of light refraction in conventional RHM material and LHM metamaterial: *a* – direction of rays in medium; *b* – orientation of electromagnetic field vectors in ordinary RHM material and LHM metamaterial

Main feature of metamaterials is their resonant response to the external electromagnetic field, and what is most surprising, is their response at optical frequencies not only to the electric, but also to the magnetic field of light. Hence the term “electromagnetic metamaterial” indicates the manifestation of their properties when interacting with an electromagnetic field. Metamaterials interacting with optical frequency radiation are usually called *photonic* or optical metamaterials. Similarly, metamaterials, which respond to acoustic waves, are called *acoustic*. The main way to obtain most of the known metamaterials is based on their “assembly” from a huge amount miniature discrete modules, cells or even nanoparticles. These modules (cells, even nanoparticles) are sometimes called “meta-atoms”. It is clear that they are not real atoms, but are composed of them, i.e. are made of ordinary substances - metal and dielectric. The sizes of metaatoms are significantly exceed atomic dimensions. They form a spatial structure (matrix) like an artificial crystal lattice, so the number of meta-atoms even in a small piece of metamaterial reaches 10^3-10^9. It should be noted that meta-atoms *do not have a chemical bonds* with each other, in contrast to atoms in polyatomic molecules of ordinary materials. This explains the difference in technologies for obtaining conventional materials and metamaterials. The former are obtained by metallurgical or chemical synthesis from atoms of chemical elements, the latter by assembly of artificial meta-atoms obtained by micro- and nanotechnologies.

It is important to note that metamaterials imitate a homogeneous medium for EM radiation; for this, the sizes of metaatoms and the distances between them are chosen to be less than the operating wavelength of the radiation, and the smaller the sizes, the better the uniformity condition is satisfied. Externally, meta-atoms are tiny formations (nanoparticles) of wire segments, strips, plates, rods, disks, rings, spirals, balls, films, coatings, multilayer structures, they can be in the form nanoclusters; finally, they can be in the form of some system of holes in flat elements (for example, they can resemble a fishing net. It is important that the configuration and properties of the meta-atoms of electromagnetic metamaterials ensure that they perform the functions of simple capacitors, inductors, oscillatory circuits, or miniature (nano) resonators.Thin layers of metamaterials deposited on a substrate are called metafilms or metacoatings.In the simplest case, a metafilm is a patterned single-layer film of metal, semiconductor, dielectric or magnetic material on a dielectric or semiconductor substrate.The pattern pattern is determined by the configuration of the above electrical (radio) Metamaterials can be considered as composites, the heterogeneous medium of which contains inclusions, but in this case, unlike other types of composite materials, inclusions are miniature, nanosized electro (radio) elements. Due to such inclusions, metamaterials have unique electro(radio)-physical and optical properties due to resonant interaction with an electromagnetic field. Multiple local amplification of the field in the region of the resonating metaatom leads to various nonlinear effects. It was commonly believed that metamaterials do not exist in nature; they are artificial formations, but recently there have been reports of discoveries of such materials in wildlife, in particular, in the eye tissues of some marine animals. The mineral opal is a kind of metamaterial, like a photonic crystal.

Microwave devices need to use specific artificially created materials of a special design, which have negative effective values of dielectric permittivity and magnetic permeability. These structures consist of miniature split ring frames which act as the magnetic dipoles and straight wire segments. This approach is based on the fact that if a composite material consists of discrete scattering elements, the size of which is smaller than the radiation wavelength, then in a limited frequency band this composite can be considered as continuous from point of view of electrodynamics. Thus, a medium is electromagnetically continuous, if its properties can be described by averaged effective parameters varying on a scale much larger than the dimensions and spacing of the components that form the material.

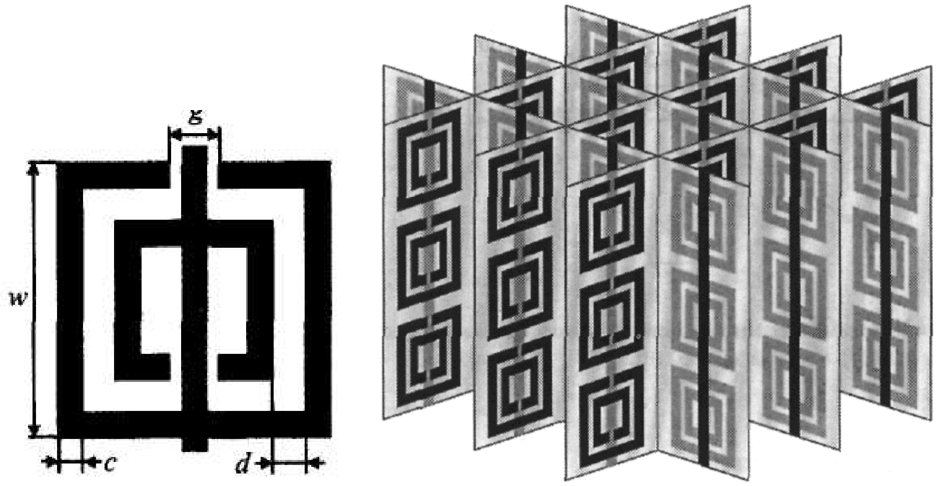


Fig. 3.11. Practically implemented meta-structure for research in microwave frequencies

The combination of structural elements makes it possible to create a material which has negative refractive index in the centimeter range of electromagnetic waves. One of these metacomposites, consisted of a dielectric base, in which there were many metal rods and split rings arranged in a strict geometric order. The rods, in fact, were the antennas interacting with electrical component of electromagnetic field, and the split rings were antennas which responded to the magnetic component. The main dimensions of all elements and distance between them are less than the wavelength, and entire system as a whole had negative effective values of ε and μ.

Numerous works are devoted for properties of substances with a negative refractive index investigation; they have attempted to evaluate their possible practical applications. However, the main disadvantages of the first metamaterials based on the use of ring and rectangular SRR are the narrow frequency band, high levels of electromagnetic losses, bulkiness and impracticality for microwave technical applications. To solve the problem of narrow band, many variants of magnetically sensitive elements were subsequently proposed.

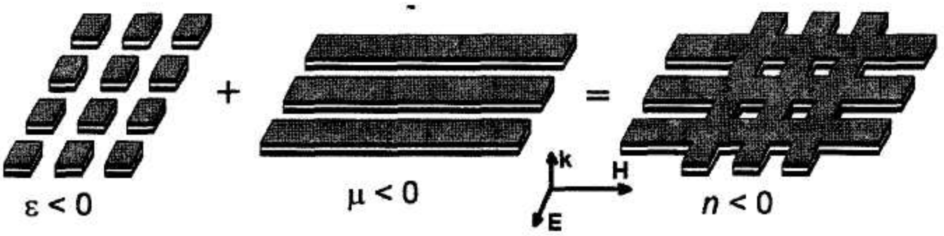
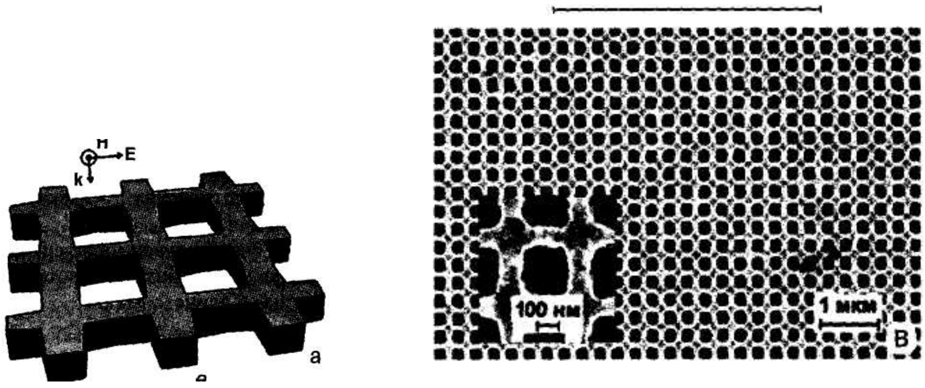


Fig. 3.12. A scheme for obtaining a mesh metamaterial by combining electrical and magnetic elements (meta-atoms) in the appropriate orientation of the electromagnetic field vectors necessary to create the effect of negative refraction.

As example, Fig. 3.12 on the right shows a lattice with $n < 0$ having rectangular holes, which can be obtained by combining “electric meta-atoms” (on the left in figure) in the form of short plates with $\varepsilon < 0$ oriented along the electric field, and “magnetic meta-atoms” in form of metal strips directed along magnetic field.

The combination method is possible: a lattice with rectangular holes is obtained by superimposing “magnetic metaatoms” in the form of extended paired metal strips directed along the magnetic field, on “electric metaatoms” in the form of extended metal strips directed along the electric field. Magnetic and electric metaatoms of similar configurations were considered separately in previous sections. Thus, a new metamaterial in the form of a lattice with rectangular holes is assembled from crossed paired metal strips. Since this material resembles a fishing net in its appearance, it is often referred to as such (“fishnet metamaterial”). Another version of the mesh metamaterial is shown in Fig. 3.13.



a *b*

Fig. 3.13. Configuration of the mesh metamaterial and the orientation of the incident radiation vectors, at which the effect of negative refraction is observed (*a*); top view of the experimental sample of the lattice, inset - enlarged image of the unit cell (*b*)

In addition to the reproduced here known way of obtaining the broadband absorber, based on the rectangular resonant metallic frames, separated by the capacitive gaps, one can try to develop fundamentally other way to obtain the very specific broadband absorber, located just at the boundary between UHF (Ultrahigh Frequency range) and MW (microwave range). In this case, the main difficulties, arises in most difficult long-wavelength part of frequency range, due to large size of resonant elements (even made from metamaterials) can be overcome due to the high dielectric permittivity of resonant elements themselves.

1. There might be some prospects, if one uses in the metamaterials, instead of metallic resonant elements, the composites filled by a set of regularly located dielectric resonators (DR) prepared from high-permittivity materials ($\varepsilon = 30 - 300$).

2. At that, among materials, suitable for DR manufacture, the piezoelectrics can be used, in which the electromagnetic resonance in the DRs is accompanied by the electroacoustic resonance*) in same DR that significantly expands the variety of metamaterial properties. It can be noted that in piezoelectrics the electro-mechanical resonance is possible, which also leads to the negative value of ε. Usually this resonance occurs at frequencies of 10^5–10^7 Hz (depending on size of piezoelectric elements); so to realize these resonances at microwaves the piezoelectric resonators should have the size only a few microns. However, microelectronic technology is responsible to realize this case.

3.6 Metasurfaces

The unique interaction of *inhomogeneous* metamaterials with EM waves exceeds the capabilities of naturally occurring materials, which are usually *homogeneous.* The universal tool for imparting a certain polarization response to surface is the division of this surface into elements, each of which has the polarizable inclusion with carefully selected parameters. With planar structures, the deeper control of electromagnetic waves is provided due to the special design of subwavelength inclusions, since they can be densely spaced and allow the creation of fields with better spatial resolution. In general, such inclusions have both electric and magnetic polarizations, and allow full control of both reflected waves and transmitted waves with great potential for a new generation of microwave and optical devices. Similar planar metamaterial structures are conditionally called *metasurfaces*. Broad possibilities of controlling the propagation of EM waves are shown in fig. 3.14.

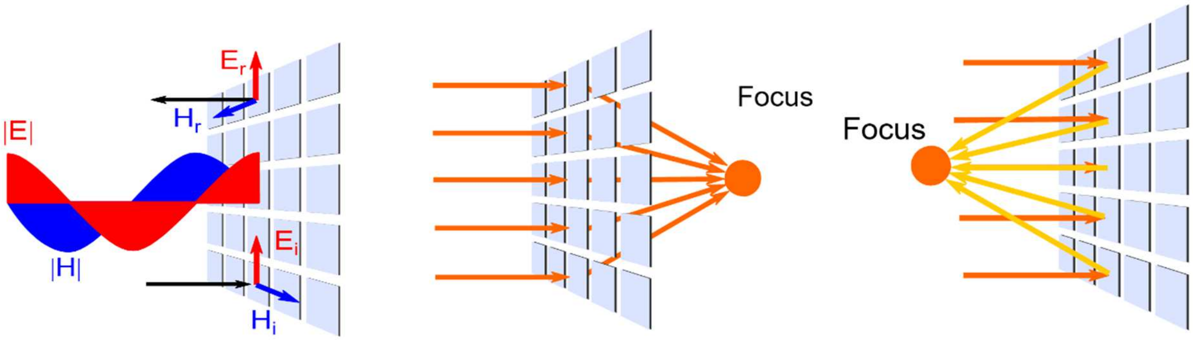
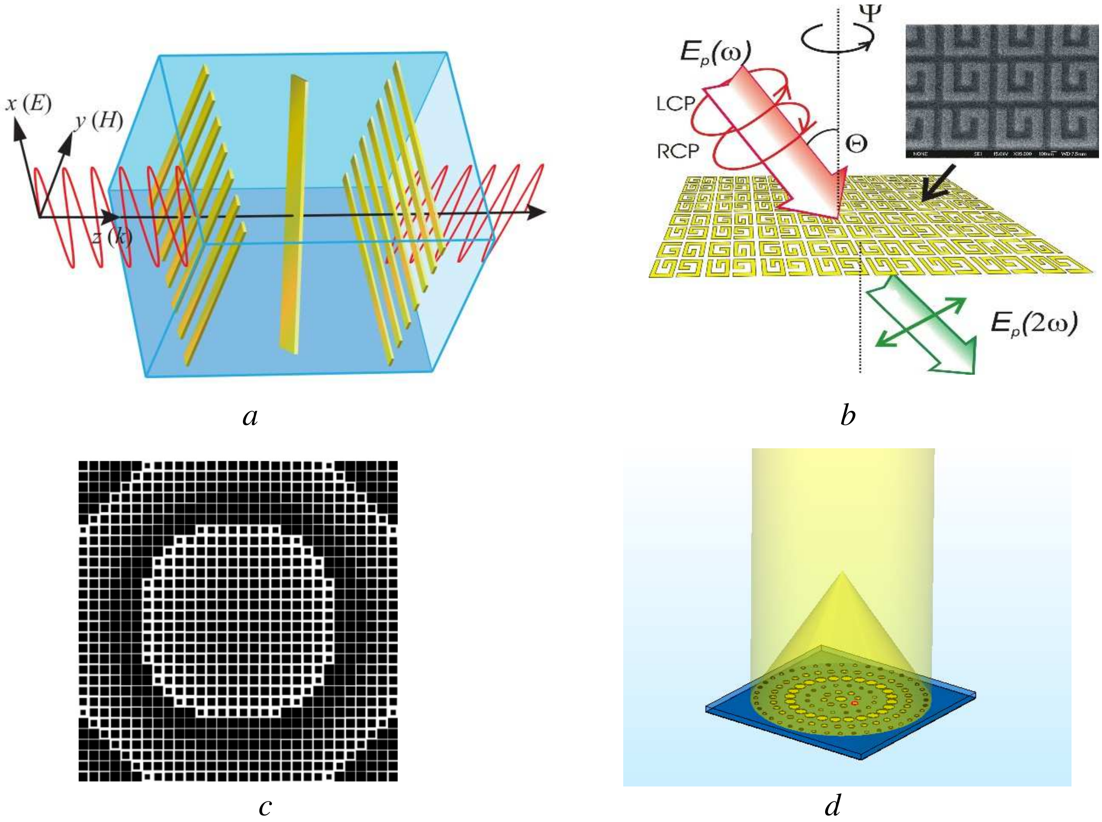


Fig. 3.14. EM wave is incident on: *a* – opaque high-impedance surface; *b* – focusing transmittance array; c – focusing reflective array;

These materials are used in the radio-electronics at microwave frequencies due to their ability to manipulate EM waves. The metasurfaces are artificial composite materials, which consist of metal-dielectric plates with a single-layer or multilayer structure which thickness is of EM wavelength order. Metasurfaces are able to control the propagation of EM waves in surrounding media. It is possible to variate the wave impedance of metasurfaces by forming special cells and their specific arrangement; such control makes it possible to use metasurfaces in the camouflage absorbers, and also in the reflectors, polarizers and modulators of EM waves.

The exceptional ability to block, absorb, concentrate, scatter or direct EM waves as on surfaces in grazing incidence so in the space, both in normal and oblique incidence of EM waves, is due to the *strong interaction* of metasurfaces with electric and magnetic fields. In its turn. these abilities are due to the resonant properties of elements used in the metamaterials, and their geometric arrangement. To do this, the resonant cells are designed with the required impedance in order to control the phase or group velocity. Cells are arranged in such a way that they can direct or separate waves in certain directions, or they are used for scattering control. By choosing the sizes, shapes and materials of unit cells of metasurface, various effective refractive indices of the surface can be achieved, and the surface can be shaped to perform various functions.

As a convincing example in Fig. 3.15 shows two devices on metacarriers



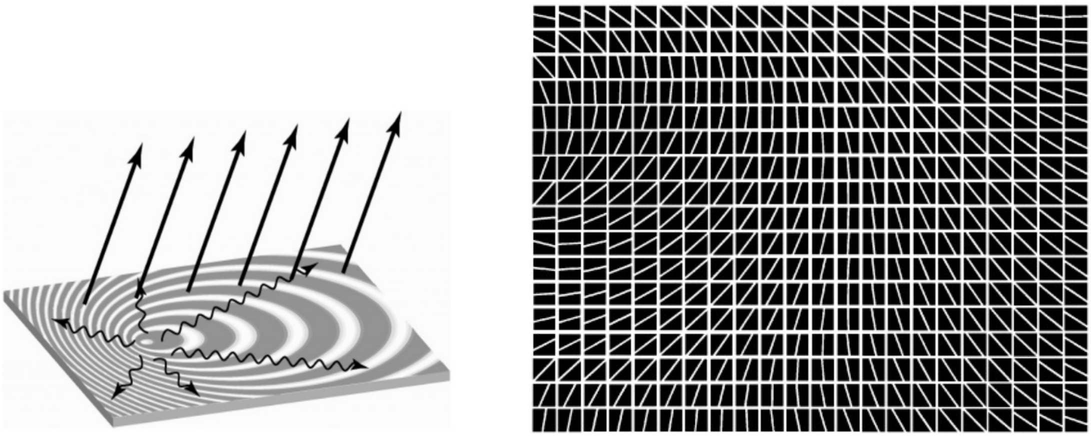
a *b*

c *d*

Fig. 3.15. Different possibilities of metasurfaces: *a* – exhibiting optical activity; *b* – metasurface-induced second-harmonic generation; ***c*** – metesurface for reflected beam focusing; *d* – its implementation

In addition to the surface waves, the metasurfaces are used to manipulate EM waves in the free space. For example. the reflection phase of EM waves hitting the metasurface is controlled for use as polarization transducers. Incoming linearly polarized waves can be rotated 90° to their orthogonal polarization or converted to circularly polarized waves. In addition to controlling the absorption or scattering of electromagnetic waves, the metasurfaces can also be used to radiate waves into free space by converting the surface waves into radiation modes as a leaky wave antenna with high degree of radiation pattern control. as shown in Fig. 3.16.

Metasurfaces have the unique ability and distinct advantage as a medium for emitting electromagnetic waves into free space, in addition to their wide application in the manipulation of surface waves and waves in free space. Antenna systems for many applications need a lot of amplification to meet requirements of communication link. Large flat arrays are used in many antenna systems due to their large aperture size and narrow beam-width. However, feed systems are usually made more complex to minimize loss and provide phase control for each antenna element to determine the beam pattern. Leaky wave antennas allow for the elimination of mains power for certain applications, instead using the traveling wave method, Fig. 3.16.



a *b*

Fig. 3.16. Metasurfaces with modulated surface impedance, employed for holographic leaky-wave antennas: *a* – operation principle of holographic metasurface: *b* – modulation of anisotropic surface impedance with slit-patches to control polarization of radiated wave

Impedance of metasurfaces. When a wave from free space is incident on a surface, its reflection and transmission are determined by the effective properties of a surface, which can be described in terms of its *impedance.* Frequency selective surfaces consist of subwavelength periodic metal-dielectric structures that provide an effective surface impedance, which can be specifically designed and controlled for various applications.

High-impedance surface will be considered firstly. It is desirable that the metasurfaces have compact geometry and lower profiles. However, this is limited by the presence of a conductive ground layer, located under radiating elements. Due to the effect of image currents, the distance of a quarter wavelength is required between the metasurface and ground plane. If the metasurface is located too close to ground, then the radiation of image currents will destructively interfere with its properties, resulting in the impedance mismatch.

The high impedance surface consists of periodic subwavelength metal regions supported by a ground plane, with a conductor passing through the center of each unit cell, as shown in Fig. 3.17A. These flat high-impedance metasurfaces are associated with corrugated surfaces which allow control over the scattering and propagation of surface waves. The corrugated surface is the metal plate with periodic vertical slots having a sub-wavelength step. With quarter-wavelength slots, a short circuit at the bottom end of the surface is converted to the open circuit at the top end, resulting in high impedance.

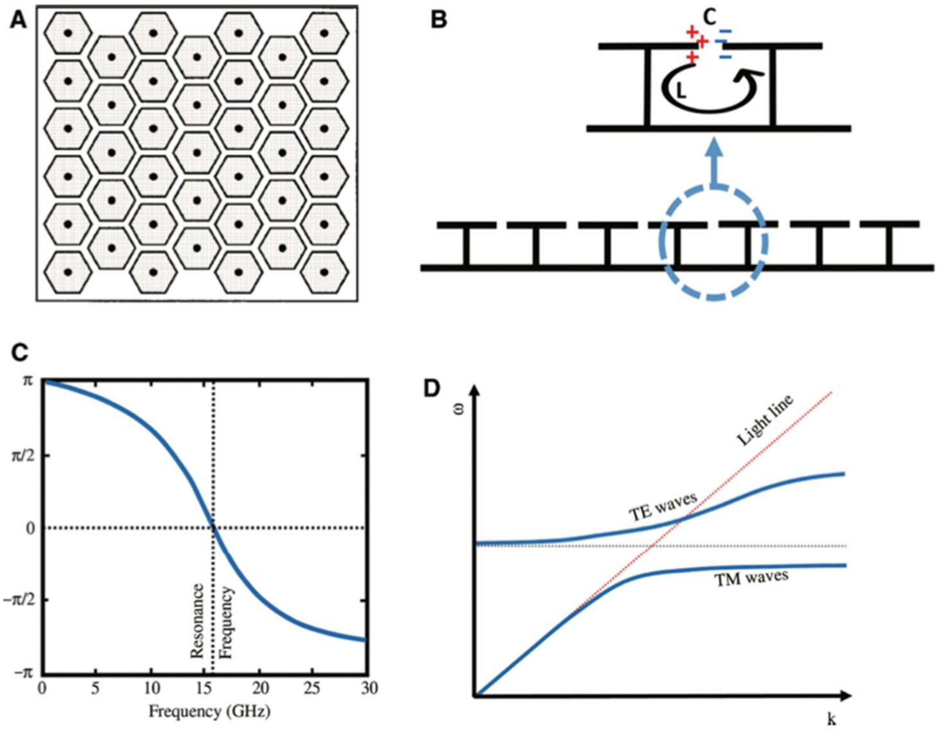


Fig. 3.17. High impedance surface with surface wave suppression: A –- top view; B – side view with an enlarged image of a resonating elementary cell; C – surface reflection phase at normal incidence; D – dispersion curve showing the band gap between TE and TM modes.

The behavior of high impedance surfaces can be understood as follows: each section connects to adjacent sections, providing an effective surface capacitance. They are also connected to their neighbors via a conductive path including vias and a ground plane, which provides effective surface inductance. The side view of the high resistance surface with an enlarged unit cell is shown in Fig. 3.17B. Corresponding equivalent circuit can be considered to be a parallel *LC* circuit, where *L* and *C* are controlled by the geometry of metal areas and by the thickness of substrate. The ambient field in the gap between adjacent patches contributes to the *capacitance*, and current path from the patch to ground through vias contributes to the *inductance*.

The resonant frequency of parallel *LC* circuit is equivalent to an open circuit with infinite impedance, so the reflection phase is 0 at normal incidence, as shown in Fig. 3.17C, unlike the conventional metal reflector, whose reflection phase is π. This property is equivalent to the magnetic conductor, but with limited bandwidth, and is often referred to as artificial magnetic conductor, since tangential magnetic field is zero on the surface, and not the electric field (as is typical for electrical conductor). This unique property is useful for applications, because the image current at surface is added in phase with the current at antenna, eliminating the need for a quarter-wave separation between the antenna and ground plane.

In addition to providing unusual reflection phase, high impedance surfaces can also be used to control the surface waves. These structures have a band gap between the first band supporting transverse magnetic waves and the second band supporting transverse electrical waves, plotted and shown in Fig. 3.17D.

The TM strip does not reach the edge of the TE strip, but stops just below it. For the TE band, it tilts up before crossing the light line, resulting in a gap between the TE and TM surface waves below the red line. In other words, no surface waves are supported in the bandgap, and this interesting property can be exploited in applications such as decoupling nearby emitters. High impedance surfaces have the advantages of small profile, light weight, and low cost, making them extremely suitable for application to vehicles, buildings, etc. as microwave absorbers. One example of a frequency selective surface with a conductor substrate that provides a high impedance response and is used as a microwave absorber is shown in Fig. 3.17C. A thin, high-impedance surface microwave absorber consists of frequency-selective surfaces backed by a sub-wavelength ground layer.

Passive metasurface absorbers have an advantage over classical microwave absorbers, which have a thickness of quarter wavelength, so that the electric field of incoming wave is maximum in the lossy layer. Absorbers based on metasurfaces can significantly reduce the thickness of usual absorber by using resonant designs to increase electric field at the surface. Near the resonant frequency, interaction between electromagnetic waves and surface increases, increasing losses associated with resistive materials on surface. In general, metasurface-based absorbers have the advantages of low profile and light weight with a simple metal construction. However, there are limitations in their absorption band width, absorption rate and air breakdown at high power.

For some applications, it is necessary to absorb not only normal and angular incidences of EM wave, but also the surface currents on metal case of a system must be carefully absorbed, since a simple gap or any break in surface can act as hindrance slot antenna and allow surface waves to penetrate and further radiate into surrounding systems, resulting in interference. Metasurfaces that absorbs propagating *surface* waves is called a surface wave absorber.

Camouflage is one of the most intriguing and widely publicized aspects of electromagnetism continues to be the possibility of creating an invisibility cloak. The first proposed designs were based on the concept of transformational optics and used 3D anisotropic metamaterials. However, these cloaks were too bulky and narrow-banded and suffered heavy casualties. An alternative method, known as "mantle cloaking", has been proposed that uses ultra-thin metasurface screens positioned some distance above the object to be cloaked.

The surface reactance of the metasurface shield was used to negate the reactance of object at some distance from its surface. By tuning thickness and reactive parameters, it was shown that it is possible to generate "out-of-phase" or destructive interference waves to compensate for scattering from "one atom thick" graphene metasurface (among other structures) even at terahertz frequencies. Because the impedance matching occurs at only one frequency, it is difficult to obtain broadband masking. In this direction, varactors were used to adjust the capacitance of the metascreen to slightly increase the bandwidth.

Another method of camouflage, called "plasmon cloaking", is to cover objects with a metasurface that has spatially varying refractive index. Essentially, the idea is to create a cloak that can reconstruct the phase of the scattered wavefront to match the expected wavefront, if the object were replaced by a flat mirror.

Plasmonic cloaks often have opposite polarization of the object they are cover. Passive metasurfaces, while effective, failed to meet the two main requirements of a true "invisibility cloak" - the ability to provide broadband masking across the entire visible spectrum and to cover an object of arbitrary shape and size. The ones listed are only effective for a certain narrow part of the spectrum and mask objects of a certain shape or size that are relatively small. To obtain a wider bandwidth would require the metasurface to have an almost constant impedance over a wide range of frequencies.

3.7 Summary

1. Metamaterials are the composites, in which heterogeneous medium contains inclusions, but in this case, unlike other types of composite materials, inclusions are the miniature, sometimes even nanoscale *radio-elements*. Due to these inclusions metamaterials have unique electrophysical and optical properties, caused by the *resonant interaction* with electromagnetic field.

2. The electromagnetic *metamaterials* are artificially structured in special way mediums that electrical and magnetic properties are significantly different from original structural materials. For example, metamaterial can have *negative refractive index* that is never observed in natural materials. Internal structure of metamaterials plays important role in the formation of characteristics and parameters.

3. Metamaterials are constructed from the *discrete* resonant micro- and nano-elements: a sort of “meta-atoms", which *mimic* electromagnetic reaction of real atoms and molecules in the natural substances. The "meta-atoms" are grouped in the form of single or multilayered lattices, while their small size (less than wavelength of radiation) makes it possible to treat the created lattice as *homogeneous* for given wavelength (by analogy with natural crystals), and use the concept of "effective medium" for characteristics calculating.

4. The *double positive* (DPS) materials possess positive values for both $\varepsilon > 0$ and $\mu > 0$. They have positive refractive index $n = (\varepsilon\mu)^{1/2} > 0$. Almost all dielectric, semiconductor and ferrimagnetic materials, where $\varepsilon > 1$ and $\mu > 1$, belong to DPS, except for rare cases of electric and magnetic resonances. The vast majority of these substances are transparent for EM waves; usually these are some dielectrics with varying degrees of absorption of EM energy.

5. The *ε-negative* (ENG) materials are characterized by negative value of $\varepsilon < 0$ but positive $\mu > 0$, so they have virtual (imaginary) refractive index that promotes the EM waves reflection. ENG phenomenon is possible both in the natural materials and in the artificially created media. First, the plasma has such characteristics including plasma in solid state matirials and second *ε-negative* materials can be created artificially.

6. The *μ-negative* (MNG) materials possess negative value of $\mu < 0$ in some frequency range but the positive $\varepsilon > 0$, so they have virtual value of refractive index that contributes EM waves reflection. First, the *natural materials,* in which at certain frequency parameter $\mu < 0$ can be obtained, are ferrites in which ferromagnetic resonance at the beginning of microwave frequency range is seen/ Second, MNG can be created artificially as metamaterial.

7. Summarizing, we note that *single negative* (SNG) metamaterials are characterized by either negative ε or negative μ. In the natural materials, as negative ε so negative μ arise due to the resonant dispersion, which is inevitably accompanied by losses, providing maximum absorption of energy in peculiar frequency range. In a such media, the electromagnetic waves decay very quickly (according to exponential law). As a rule, these materials are opaque to electromagnetic radiation, if their thickness is greater than characteristic exponential decay length of electromagnetic waves.

8. The *double negative* (DNG) metamaterial possess both negative $\varepsilon < 0$ and $\mu < 0$ in some frequency range, and have *negative value* of refractive index $n = -(\varepsilon\mu)^{1/2} < 0$. However, the square root has two solutions: one positive and one negative. Using complex notation, the result comes out naturally with $-\mu$ expressed as $\mu\ e^{i\pi}$ and $-\varepsilon$ expressed as $\varepsilon\ e^{i\pi}$, so that $n = [(-\mu)\ (-\varepsilon)]^{1/2} = (\mu\ e^{i\pi}\ \varepsilon\ e^{i\pi})^{1/2} = (\mu\ \varepsilon)^{1/2}\ e^{i\pi} = -(\mu\varepsilon)^{1/2}$.

9. Metasurfaces are quasi-two-dimensional (2D) metamaterial, which consists of densely packed flat arrays of resonant subwave elements. The electromagnetic properties and functionality of such metasurfaces are determined by the structure and features of resonating elements, as well as by type and degree of their coupling, moreover, they are also affected by the underlying substrate.

10. Metasurfaces can provide complete control over reflected and transmitted EM waves, and they can be designed to have many desirable properties that replace bulky traditional components.

11. The structure of electromagnetic fields outside closed surface is completely determined by the electric and magnetic components that are tangent to the surface. Each infinitely small area of the surface can be associated with an equivalent EM source of secondary field, and such closed surface can be "infinite" plane, separating two homogeneous half-spaces. The off-surface EM field can be controlled not only by changing the EM sources, but also by properly designing the tangent fields. The desired distribution of electromagnetic fields is achieved through proper design of artificially structured surfaces.

3.8 References

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3.9 Questions for self-examination

1. What are metamaterials and how they are created?
2. What is the place of double-positive materials in general classification?
3. What are places of single negative materials in general classification?
4. List and explain the choose of media for EM waves interaction.
5. ε-negative metamaterials.
6. μ-negative metamaterials.
7. Double negative metamaterials.
8. Benefits of metasurfaces.
9. Implementation of metasurfaces.
10. Areas of of metasurfaces use.

Chapter 4. Multiferroics in electronics

Contents

Some classes of structurally ordered solids, whose properties are widely used in *functional electronics*, namely: the ferromagnetics, ferroelectrics and ferroelastics, despite the completely different nature of structural orderings, arising in them, demonstrate a number of *similar* properties: the anomalies in physical properties in vicinity of phase transition to the ordered state, the appearance of domains, the presence of hysteresis, etc.

Traditionally, they are combined into one common group of substances with common name ***ferroics***, according to common prefix "ferro" in English terminology (ferromagnetics, ferroelastics, ferroelectrics). Substances, in which functional magnetic, electrical, and elastic properties coexist, can have remarkable properties for electronics applications, and it is these materials that this Chapter is concerned with.

***Multiferroics** are the class of crystalline solids, in which at least two of three ordering parameters coexist: magnetic, electrical, or mechanical.*

Previously electric and magnetic ordering in solids are considered separately: the point is that electric charges of electrons and ions are responsible for the *charge* effects, whereas magnetic charges are absent, so only electron *spins* govern magnetic properties. The field of multiferroics has greatly expanded in last years, particularly with discovery of many different types of multiferroic materials.

Next, we consider, in particular, such materials, which have both magnetic and electric ordering - the magneto-ferroelectrics, which are now more often called by the name of wider class of multiferroics. The connection between magnetic and electric subsystems in the multiferroics, which manifests itself in form of magnetoelectric effects, makes it possible to control the *magnetic properties* of a material by using the *electric field*, and vice versa, to modulate electrical properties by magnetic field.

Previously, magnetoelectrics and multiferroics were of interest to relatively narrow circle of specialists, since very small magnitudes of magnetoelectric effects, as well as rather low temperatures, at which they manifested themselves did not allow to talk about their practical application. One of reasons was low temperature at which magnetoelectric effects were manifested, and another reason was the need to apply very high controlling fields.

But in recent years, there has been a surge in research activity in this area, which has found expression in numerous reviews and special issues of journals devoted to multiferroics.

The reason for this interest is due, on the one hand, to significant progress in understanding of physical mechanisms of magnetoelectric interaction in the multiferroics, and, on the other hand, to discovery of materials, which under normal conditions and moderate values of magnetic and electric fields, exhibit such magnetoelectric properties that allow magnetoelectrics specific practical applications in spin electronics, magnetic memory and sensor technology. Perhaps, the earliest studies of multiferroics were discovery of large ferroelectric polarization in epitaxial films of $BiFeO_3$ ferromagnetic and ferroelectricity with magnetic ordering in $TbMnO_3$, which proved their *compatibility*.

It should be noted that total number of high-temperature multiferroics is still small, and those, which exhibit magnetoelectric properties at room temperature, are characterized by low (or zero) magnetization and significant losses due to finite conductivity. In this regard, the search of new scenarios for magnetoelectric phenomena in solid body implementation is relevant, among which the mechanism of formation of electric polarization, which is associated with spatially modulated spin structures (spin cycloids) and is similar to the flexoelectric effect in liquid crystals, deserves special attention.

The point is that distortion of orientational structure, corresponding to cycloidal spatial modulation of director, generates electric polarization. The occurrence of electric polarization during spatial modulation of magnetic ordering parameter is called flexo-magneto-electric (nonuniform magneto-electric) effect. This phenomenon is universal for all magnetically ordered media and operates not only in multiferroics, but also in centrosymmetric magnetic dielectrics, which makes it possible to expand significantly the class of magnetoelectric objects.

In addition to scientific interest in their physical properties, the multiferroics have potential for applications as actuators, switches, magnetic field sensors, and new types of electronic memory devices.

4.1 Basic definitions

Multiferroics are defined as materials, which exhibit more than one of the basic ferroic properties in the *same phase.* The basic properties, implying different types of various structural elements self-ordering in substance, include:

- *ferromagnetism* – spontaneous magnetization, which can be switched by the applied magnetic field;
- *ferroelectricity* – spontaneous electric polarization, which is switchable by the applied electric field;
- *ferroelasticity* – spontaneous deformation, switchedable by applied mechanical stress.

In fact, these three main types of structural self-ordering are greatly complicated by other categories:

- *antiferromagnetism* – spontaneous magnetization, completely compensated in different sub-lattices, but which can be turned into ferromagnetic state by magnetic field applying;
- *ferrimagnetism*, in which the antiferromagnetism and ferromagnetism coexist in same phase;
- *antiferroelectricity* – spontaneous electric polarization, which is completely compensated in different sub-lattices, but can be converted into ferroelectricity by applied electric field;
- *ferrielectricity*, in which the antiferroelectricity and ferroelectricity coexist in the same phase.

In the case of *ferroelastics*, analogous situations are possible but up to now are little studied.

Multiferroics include many combinations of listed cases of structural dipoles and spins orderings. For example, "ferroelectrics-ferroelastics" and "ferromagnetics-ferroelastics" are formally the multiferroics, but they are usually considered simply as the *magnetoelectric* materials. In fact, the term "multiferroics" is used to describe such materials, which are both ferromagnetic and ferroelectric. Moreover, in a number of studies, multiferroics also include the combinations from minor series, such as antiferromagnetism or ferr*i*magnetism.

In this textbook, intended for bachelors, masters and PhD students, it is advisable to first recall the basics of ferromagnetism, ferroelectricity and ferroelasticity, which are given in the next three sections 4.2–4.4 in short volume and small print.

4.2 Elements of ferromagnetism

Magnetism is special kind of physical interaction from a distance between moving electrical charges (that creates magnetic moment), as well as the interaction between particles and bodies with naturally existing magnetic moments. Magnetic interaction is characterized by the magnetic field. There is no complete symmetry between magnetic and electrical fields. The sources of electrical field are electrical *charges*, but similar single "magnetic charges" are absent in a nature. That is why, the sources of magnetic field are also electrical charges, but only the *moving charges* (even if this movement is hidden in the elementary particles). Cyclically moving charges create *magnetic moment*, also called the *magnetic dipole*.

Any material is magneto-sensitive in its nature, i.e., interacts with external magnetic field and has certain magnetic property. In every matter an elementary circular currents exist, such as rotation of electrons around nucleus (orbital magnetism) and electrons fictitious rotation around their own axis (spin magnetism). These movements lead to orbital and to spin magnetic moments, both created by the electrons. Basically, exactly the magnetic moment of *electronic shells* of atoms determines magnetic properties of any material, because this moment in thousand times greater, than the magnetic moment of atomic *nucleus*. That is why exactly the peculiarities of *electronic structures* of atoms stipulate the differences in magnetic properties of substances [1].

Magnetic materials are widely used in many areas of technologies: electronics, electrical engineering, information, computing and measuring instruments, and others. In recent years it is seen a qualitative "jump" in the development of magnetic materials and creating on this basis new types of electromagnetic and magneto-electronic devices with unique properties, due to scientific discoveries physics of magnetic materials and advanced technologies.

The current stage of magnetic devices development is characterized by the transition from discrete magnetic components using to homogeneous magnetic environments application, when magneto-polarized charge carriers by their directional movement create magnetic domains. Low-inertia reorientation of magnetic domains is widely applied in magnetic electronic devices. Small size of magnetic domains with combination of their high mobility can create on their basis various *functional devices* that have large memory (10^{9}-10^{10} bits) and high density of information (10^{8}-10^{10} bits/cm^{2}), as well as characterized by great speed of processing ($10^{12.}$-10^{8} bit/s) [2].

Further progress in the creation of materials with new properties is due to development of *nanotechnologies* for super-small elements. This progress is associated with the changes in a structure of matter, affecting its fundamental properties. Currently it becomes possible to "manage" properties of substances by their fragmentation (dimensions) decrease. At present, most of technical implementations of nanoelectronic elements are observed just in the magnetic electronic devices [3]. Based on microelectronics and nanoelectronics, one of promising areas of functional electronics is the *magnetic electronics* developing that is qualitatively new stage in creation of components to build broad class of logical and storage devices, as well as various information processing devices.

At present, magnetic materials with large magneto-optical effects are synthesized that combine good transparency of material in visible and near infrared regions of spectrum. On this basis many advanced magneto-optical elements and devices are developed: magneto-optical drives, controlled banners, printers, deflectors, integrated optics elements, various converters, etc. Due to a variety of types of magnetic materials, their properties and manufacturing methods promote creation new items and devices. At that, magnetic electronics requires development of electronic equipment thorough the knowledge of physics of magnetism, features of magnetic interaction in solids, getting control over manufacturing technology materials with different properties and exact understanding of modern technology and trends.

This Section focuses on physical fundamentals of magnetism in solids, on the processes that determine principles of magnetic electronic devices, as well as on operation characteristics, requirements, scope and prospects of development of magnetic devices.

For quantitative description of magnetic phenomena in solids the *axial vectors* are introduced: magnetic field H, magnetic induction B, magnetic moment M, magnetic flux Φ and magnetization J. The *magnetic field* is specified by its direction and strength; it characterizes magnetic effect, created by electrical currents or by internal magnetic properties of materials. The symbols B and H are used for two distinct but *closely related* fields. At that, in SI units the vector H is measured in amperes per meter [A/m] while vector B is measured in Newton per meter per ampere: [N/(m·A)] = tesla [T]. Magnetic induction B sometimes is also called as "magnetic field" (it is, most commonly, defined in the terms of Lorentz force, acting on moving electrical charges).

The *magnetization* (magnetic polarization) is also axial vector field that expresses the density of permanent or induced magnetic dipole moments in magnetic *material*. It can be compared with electrical polarization, which is the measure of response of a material onto electrical field. Magnetic moment per unit volume is represented by the vector M.

By formal analogy with used for dielectrics *polar* electrical vectors ($D = \varepsilon_0\varepsilon E = \varepsilon_0 E + P$, $\varepsilon = 1 + \chi$, where D is electrical induction, E is electrical field, P is electrical polarization, ε is permittivity and χ is dielectric susceptibility), the *axial* magnetic vectors are also joint by material *tensors of second rank*: permeability μ and magnetic susceptibility æ:

$$B = \mu_0\mu H = \mu_0 H + J, \qquad J = \mu_0 æ H,\ \mu = 1 + æ.$$

As permeability so magnetic susceptibility are *relative* values; therefore, they are *dimensionless*. In vacuum relative permeability $\mu = 1$, since at the absence of substance magnetic susceptibility is zero: æ = 0. Similarly, without any substance, relative dielectric permittivity of vacuum $\varepsilon = 1$ and dielectric susceptibility $\chi = 0$.

However, the analogy between electrical and magnetic phenomena is purely formal. Electrical dipole is a system of two separated in space electrical charges, equal in their magnitude and opposite in their sign. Conventionally electrical dipole is indicated by an arrow: it is *polar vector*. Magnetic dipole is formed by the *movement* of electrical charges, roughly representing circular electrical current: it is *axial vector*. For both types of dipoles (electrical and magnetic) the *potential* of correspondent fields decreases with distance as $1/r^2$. However, by this factor their similarity ends. In the *macroscopic* examination magnetic dipole can be represented by electrical current in a closed circuit. At that, in the *microscopic* processes, properties of magnetic matter might be caused also by the internal ("hidden") forms of electrical charges movement that is possible to describe only in *quantum mechanics*.

Microscopic magnetic dipole can be created:

- by change in the orbital moment of electronic shell of atom (ion, molecule) that results in the *diamagnetic* component of magnetization;
- by "own rotation" of elementary particles represented by spins of electrons that leads to the *paramagnetic* or *ferromagnetic* components of magnetization;
- due to the presence of magnetism in some of atomic nucleus (it should be noted that *nuclear magnetism* is very weak).

Thus, in atomic scale, electrons can create two types of magnetic moments ("microscopic currents"): the *orbital* moment that is due to electrons rotation round atomic residue, and the *spin* moment due to a natural magnetic momentum of electron. Practically magnetism is characteristic of *electrons* orbital and spin magnetic moments. Protons and neutrons also have own magnetic moments, but nuclear magnetism, as compared with electronic magnetism, is very small (about thousand times weaker), because thenetic moments relates the mechanical moment and therefore is *inversely proportional to mass* of particles. In this way magnetic moment of particle the smaller, the greater mass. Therefore, magnetic properties of a matter are determined mainly by the electrons, as electron roughly three orders of magnitude lighter than lightest atomic nuclei – proton. The energy of magnetic interaction of microscopic particles, though it is smaller than energy of electrical interaction, is still large enough to affect the structure of a matter. Since any stable system tends to minimize its energy, the internal magnetic moments in substances strive for maximum compensation. For instance, in basic energy state of helium atom (state $1s^2$) both the spin and the orbital electronic moments are zero, so the only *induced by external field* magnetic moment can arise. The same is applicable to hydrogen molecule H_2. Thus, in the atoms or molecules with *completely filled electronic shells* as total spin moment so total orbital moment are zero.

Summary spin magnetic moment in the *completely* filled orbitals (two, six, ten, fourteen electrons) is totally compensated. Therefore, in most substances electronic orbitals of atoms and molecules, normally, are entirely filled ("self-organized") with the *even* number of electrons (filled *s-, p-, d-, f-* shells contain respectively 2, 6, 10, 14 electrons). Nevertheless, there are some quite uncommon (but very important for practical use) exceptions of stable but only *partially filled d-* and *f-* shells of atoms, in which uncompensated total spin magnetic moment can exist.

Accordingly to electromagnetic induction law, the external magnetic field creates in a substance *induced* microscopic electrical current, which magnetic field is directed *oppositely* to applied field (such reaction of a matter to applied magnetic field exists always). Faraday identified this effect as ***diamagnetism***. Prefix "*dia-*" means the opposition to externally applied field, or deviation of magnetic field lines: external magnetic field aspires to turn round of diamagnetic. That is why, diamagnetic *repels from any pole* of permanent magnet (it is pushed out of magnetic field but with a small force, because this effect usually is very small). In the diamagnetics, magnetic induction becomes *smaller than in vacuum.*

Second, if atoms (or molecules) of a matter have particles with natural nonzero magnetic moments (spin, or orbital, or both), external magnetic field will aspire to orient them *along the field.* The result is additional magnetic moment appearance that is collateral to external field; these materials Faraday called ***paramagnetics***. The prefix "*para-*" means "consistency" of magnetism in substance with magnetic field lines; in the paramagnetic magnetism becomes *stronger than in vacuum*, at that, the magnetic field as if *draws* into paramagnetic. At that, the paramagnetic is *attracted by any pole* of permanent magnet. As phenomenon of diamagnetism exists always, so such this attraction indicates the preference of paramagnetism over diamagnetism (almost in all cases when both effects take place).

The dependence of magnetization on magnetic field ($J = \mu_0 æH$) for some typical cases is shown in Fig. 12.2. Induced in a matter by external field magnetic moment can be both as positive so negative. Figure 12.2*a* shows the comparison of magnetization in external field for diamagnetic and paramagnetic. In both cases to obtain *noticeable effect* applied magnetic field requires to be large (hundreds of [Oe] = *oersted*).

Significant magnetic properties, even in small external magnetic field, can be seen in such substances, which have *strong internal magnetic interaction* between particles – carriers of own magnetic moment (atoms, ions, molecules). Through this interaction, such situation might be energetically favourable when the ***involuntary ordering*** of internal magnetic moments occurs (without action of external magnetic fields). In these cases, the strong magnetism usually can be seen. Dependence of magnetization in the ***ferromagnetic***, induced by the external magnetic field, is shown in Fig. 4.1*b*: even if the strength of external magnetic field is only one oersted, induced magnetization in thousands of times greater than in the diamagnetic or paramagnetic substances. Faraday has shown that ferromagnetic is *attracted to both poles* of permanent magnet.

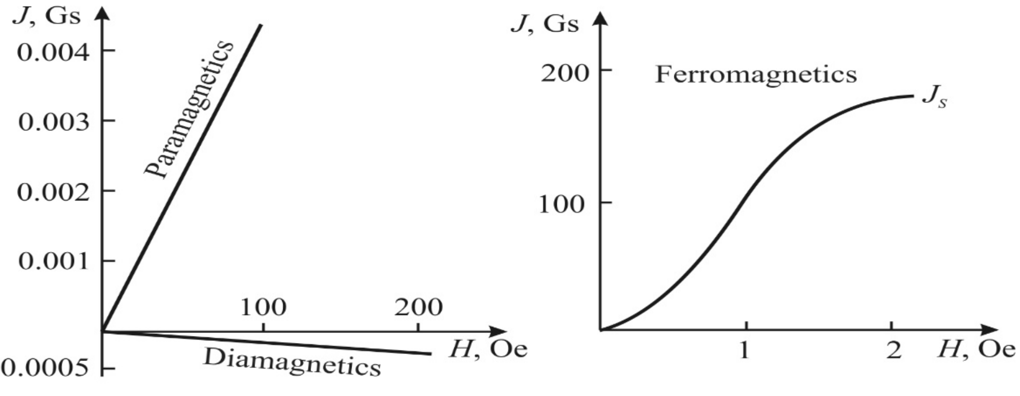


Fig. 4.1. Field dependence of magnetic moment induced in: *a* – diamagnetic and paramagnetic, *b* – ferromagnetic

Therefore, in the diamagnetic, any proper magnetic moments of particles are absent: its magnetization is induced exclusively by the external field. This moment disappears very fast when external field removal – at time of about 10^{-14} s. As to the paramagnetism, it is conditioned by the existence in material intrinsic (natural) magnetic moments, which are, however, completely disordered if the external magnetic field is absent, as shown in Fig. 4.2*a*. The magnetization of the paramagnetic (as diamagnetic) is also *induced* by the external magnetic field due to *orientation* of existing natural magnetic moments. However, external magnetic field orients only a small part of natural moments and, after magnetic field switching off, the induced magnetism in paramagnetic disappears, but not so fast as in the diamagnetic (at time 10^{-9}–10^{-2} s).

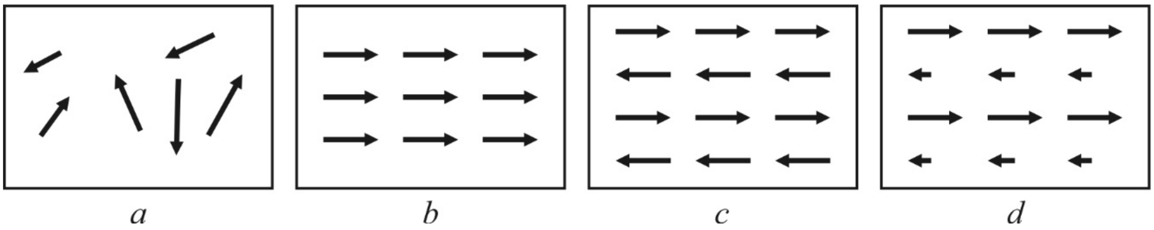


Fig. 4.2. Schemes of magnetic moments ordering in different lattices: *a* – paramagnetic; *b* – ferromagnetic; *c* – antiferromagnetic; *d* – ferrimagnetic

In some solids, their magnetic structures can be characterized by different types of *spontaneous* magnetic ordering. Crystal or polycrystal, in which natural magnetic moments are oriented in parallel to each other is ***ferromagnetic,*** Fig. 4.2*b*. Accordingly, the ***antiferromagnetic*** has neighbouring atomic magnetic moments oriented in antiparallel, Fig. 4.2*c*. Moreover, ferromagnetism and antiferromagnetism can *coexist* in a single structure; such material is the ***ferrimagnetic***, in which the compensation of atomic magnetic moments is incomplete, Fig. 4.2*d*. Related substances are known as ***ferrites*** that are very important for technical applications. Except for relatively simple collinear ferromagnetic, atomic and electronic structures of antiferromagnetics and ferrimagnetics might have more complicated and even non-collinear magnetic structures (i.e., spiral, triangular, etc).

Thus, magnetic properties of substance is divided into a *weak* magnetism (diamagnetism and paramagnetism) and *strong* magnetism (ferromagnetism, antiferromagnetism and ferrimagnetism). The magnetization of materials differs significantly from dielectrics polarization. For comparison it should be pointed out that in case of electrical polarization in dielectrics *static* dielectric susceptibility is always positive ($\chi > 0$); that is why, the static permittivity of any material surpass one ($\varepsilon > 1$). However, while a matter is magnetized, depending on the nature of magnetism, the value of magnetic susceptibility æ can be as positive so negative. So in a substance *static* magnetic permeability μ can be both greater than one ($\mu > 1$) and less than one ($\mu < 1$). Superconductors (in which electrical resistivity is zero, $\rho = 0$) formally is characterized by value $\mu = 0$ (it has $æ = -1$) being supposedly the "ideal" diamagnetic. The complexity of atomic structure of a matter, constructed from wide variety of particles, leads to many forms of magnetic structures. While consider properties of solids, usually the general term *"magnet"* is used.

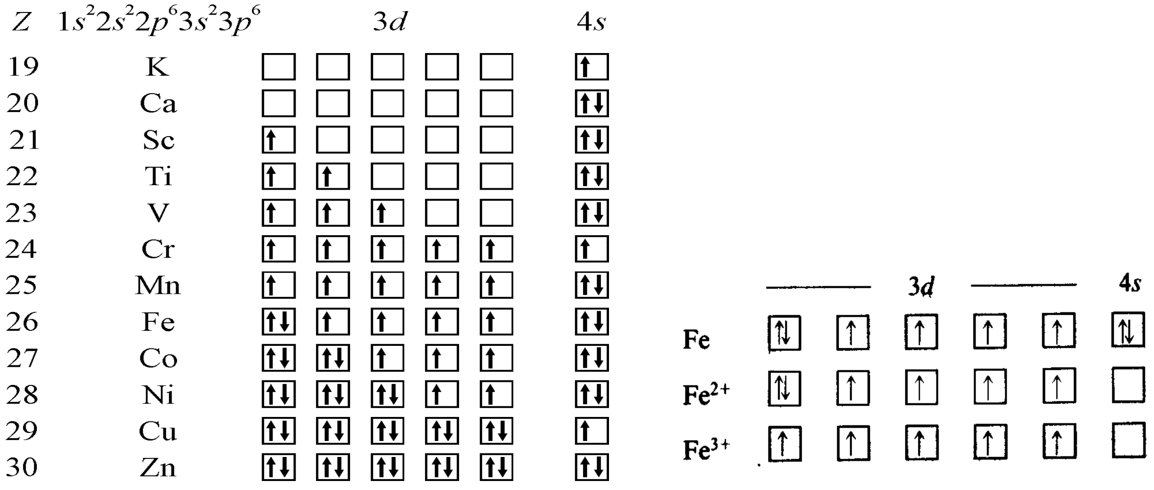
Spins in electron and nuclear. If a primary physical cause of diamagnetism is the *orbital* motion of electrons in atoms and ions, the paramagnetism is conditioned by the *spins moments* of particles. The value of spin is denoted by letter *s*, particle with spin ½ and electrical charge *e* has magnetic moment $\mu_B = e\hbar/2mc$. This value (called as Bohr magneton), equals ~10^{-20} erg/Gs. It should be noted that electronic magnetic moment is unusual vector, because it can be oriented in a space only by two ways: either on the field or against it. The ratio of magnetic moment of particle to its mechanical moment is the constant "γ" that is *magneto-mechanical ratio* (or gyromagnetic ratio). Its unit in SI is "radian per second per tesla": [rad/(s·T)]. However, very often other term *gyromagnetic ratio* is used for different but closely related quantity, namely, the *g*-factor, which unlike γ is dimensionless.

Magnetic moment of atom is expressed by formula $\mu_{at} = \gamma\hbar J = g\mu_B J$, where $\hbar J$ is total angular momentum, which is the sum of orbital moment $\hbar L$ and spin moment $\hbar S$. Bohr magneton is determined as $\mu_B = e\hbar/2m$ that is very close to spin of free electron. Value of *g*-factor for electron is defined as $g = -\gamma\hbar/\mu_B$, and it is called also the *spectroscopic splitting factor*. For electrons $g = 2.0023$, but usually the value $g = 2$ is used.

The *nuclear magnetism* should also be mentioned for better understanding the nature of particles *interactions,* an examining not only electrical but also magnetic properties of materials is necessary. According with experiments, "classic" size of nucleus is about 10^{-13} cm that is negligibly small as compared to size of atom (10^{-8} cm). Since mass of cores in four orders of magnitude greater than mass of electron, it might be considered (while electronic processes are studied) that atomic core as "infinitely heavy". This approach is so called "*adiabatic hypothesis*", when condensed matter theory is applied to justify electronic spectrum. Electrical fields in atomic nuclei are very large, and it is determined by the number of protons in nucleus. However, nuclear magnetism is smaller in thousand times than electronic magnetism, so in technical applications, as a rule, magnetism of cores can be ignored.

At that, it is necessary to mention, that, in general, magnetic interactions are much smaller than electrical interactions. Actually, the energy of magnetic interaction in atom is appreciated as $U_{mag} \approx \mu_B^2/a^3$, where μ_B is Bohr magneton and a is average distance between electrons. Energy of electrostatic interaction between two electrons in same conditions equals $U_{elec} = e^2/a$. The ratio of these two energies is $U_{mag}/U_{elec} \approx \alpha_Z^2$, where $\alpha_Z = e^2/\hbar c \approx 1/137$ is Sommerfeld constant ("fine structure constant"), characterizing the strength of electromagnetic interaction between charged elementary particles. Thus, magnetic interaction of electrons is much smaller than their electrostatic interaction. In physics of magnetism it is important because small "fine structure constant" results in small value of diamagnetic susceptibility. It can be shown that this susceptibility is estimated as $\text{æ}_{\text{dia}} \approx \alpha_Z^2 \approx (1/137)^2 \approx 5\cdot10^{-5}$ that is well consistent with experimental data.

Lanzheven-Curie paramagnetism, being relatively weak manifestation of magnetism, is most directly related to the strong phenomenon of ferromagnetism. One reason of own magnetic moment existence in the atom (or ion) might be electronic spins, which are *not compensated* in the non-completely filled d-shells or f-shells. For example, in the *transition metals*, listed in Fig. 4.3, non-compensated atomic magnetic moments are due to some of $3d$-electrons. Orientation of spins in first period of transition metal is shown schematically. Limiting number of $3d$-electrons is ten, so in d-shell up to five electrons may have same spin orientation (as it is seen in case of manganese and chromium) before filling these states by electrons with opposite orientation.



a *b*

Fig. 4.3. Location spins of electrons in orbitals in transition metals: *a* – $3d$-electrons in atoms are arranged with parallel orientation of spins; *b* – distribution of $3d$ spins of electrons in two-valence and three-valence iron ions

Quantum mechanical calculations show that for transition metals a convergent orientation of electronic spins in *d*-shell corresponds to the energy minimum (as more stable state). In case of chromium, for example, configuration $3d^5 4s^1$ exists but not $3d^4 4s^2$. Similarly, copper atom has electronic configuration $3d^{10} 4s^1$ but not $3d^9 4s^2$ as one might expect.

In atoms K and Ca 3*d*-orbital is *empty* while in atoms Cu and Zn 3*d*-orbital is completely filled (spin magnetic moments of electrons in this case are totally compensated). This means that *atoms* K, Ca, Zn and Cu are not paramagnetic. In others listed in Fig/ 4.3 atoms, their 3*d*-orbital is not completely filled. The exact calculations of 3*d*-electrons distribution is complicated, but the manner of these electrons distribution is expressed by the Hund's rules, following to which 3*d*-electrons are arranged in the 3*d*-shell according to their magnetic spins [1]. Pauli principle does not allow the existing in one energy state two electrons with same spins. Thus, electrons with same spin direction should be *separated in space*. However, due to Coulomb interaction, the energy of electrons with same spin directions is reduced. Thus, average potential energy of oriented in parallel spins might be less than in the *antiparallel orientation*. As an example, the Mn^{2+} ion may be taken. The 3*d*-shell of this ion has five electrons, so this shell is filled exactly half. Spins of electrons can be oriented parallel, if electrons occupy *different states*; in the 3*d*-shell exactly five different states are allowed that are characterized by the orbital quantum number $m = 2, 1, 0, –1, –2$. Each of these states can be occupied by one electron. In this case, it might be expected that total spin will be equal to $S = 5/2$, and, because $\sum m = 0$ the only possible value is $L = 0$ that is observed experimentally.

Since magnetic properties of atoms are due, primarily, to the spins of electrons, then uncompensated spin orientation, Fig. 4.3, allows evaluate magnetic moment of atom. For example, single titanium atom has magnetic moment of two spins (two Bohr magnetons, $2\mu_B$), while single cobalt atom has own moment of three spins ($3\mu_B$). Up to five 3*d*-electrons in atoms can be placed with parallel orientation of spins preservation. Second electron in each state should be oriented in antiparallel.

Up to now, mostly magnetic moments of *atoms* are considered. The *ions* of 3*d*-metals, have varying valence, and, depending on this they can have different number of uncompensated spin moments. This fact is significant for magnetic materials synthesis with various purposes. Very important example is shown in Fig. 4.3*b*: distribution of spins in the 3*d*-shell for two different iron ions: Fe^{+2} and Fe^{+3} as compared with atom of iron (Fe). It is seen that two-valence iron has total magnetic moment $4\mu_B$, while three-valence iron might be characterized by $5\mu_B$. It should be noted that in Fig. 4.3*b* only simplified model is shown, because it does not take into account the *spin-orbital interaction*. Taking into consideration this interaction (and according to experiments), magnetic moment of Fe^{+2} is dependent on a given crystal, once it might have 4.4 μ_B, while in other case Fe^{+3} can have 12.9 μ_B.

Rare earth elements atoms and ions also might have uncompensated spin moments, but located in the 4*f*-orbital. Electronic structure of rare-earth compounds is as follows: typical valence of rare earth metals is "+3", i.e., three outer electrons can be detached from rare earth atom and directed into conduction band (or form chemical bonds in the compound). As a result, the ion R^{3+} is formed, which usually keeps incomplete 4*f*-shell, location of spins in the 4*f*-shells for lanthanides is shown Fig. 4.4. For example, in the gadolinium ion (Gd^{3+}) instead of 14 electrons permitted in the 4*f*-shell, only partial filling of shell is observed: $4f^7$, while in the dysprosium ion (Dy^{3+}) only 9 from 14 electrons exists: $4f^9$.

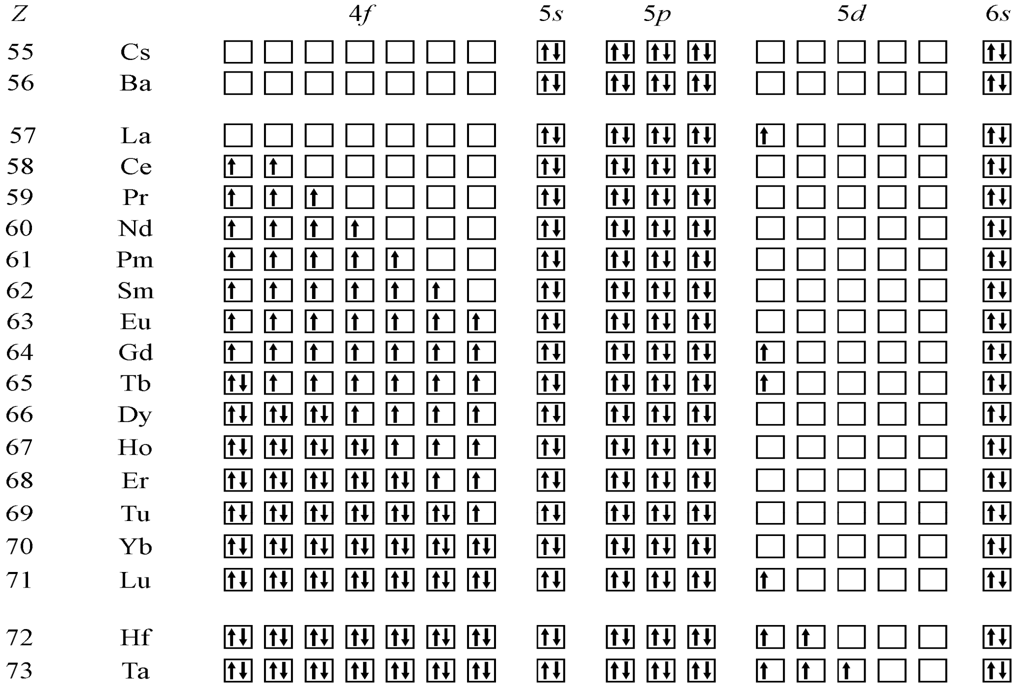


Fig. 4.4. Electrons spins allocation in orbitals of lanthanides

Since the *f*-states are located rather close to atom's nuclear, they have small radius: a_0 ~ 0.4 Å. It is much smaller than the distance between atoms in solids, which usually is about 3 Å. Therefore, it looks like *f*-electrons do not involved in chemical bonding, and it would seem that their state can be considered as localized, so they belong to the ionic residue. By analogy with Mott type of dielectrics, *f*-electrons can be regarded as being located far on the "dielectric side" of Mott type transition. The nature of chemical bonding and the type of crystal lattice (that determines metallic or dielectric properties) should have been identified only by three valence electrons. At that, the electrons of *f*-state strongly influence on the *magnetic properties* of correspondent crystals. If *f*-shell is only partially filled, the magnetic moments of electrons are not compensated, so total magnetic moment is nonzero. So, such ions are similar to the elementary magnets.

It is clear that the presence of these ions in crystal results in a fact that crystal is paramagnetic with localized magnetic moments, and at low temperatures these moments might be spontaneously ordered, making crystal either ferromagnetic or antiferromagnetic, or acquire more complicated ferrimagnetic structure. It is noteworthy that the first two *f*-elements in the table Cs and Ba do not have "stationary" electrons in their *f*-shell. However, its very presence leads to significant features in the behavior of these elements in the compounds used in the functional electronics, in particular, in the ferroics. As in La, their *f*-shell might be virtually "visited" by electrons and affect the properties of correspondent ions in the compounds.

The *ions* of various rare earth elements have quite similar chemical properties, since their outer electronic shells should be identical: they all have configuration $5s^2 5p^6$ (similar to neutral xenon atom). The radius of trivalent *ion,* when transition from one element of this group to other, gradually reduces from 1.11 Å in cerium to 0.94 Å in ytterbium. This phenomenon is the *lanthanoid compression*. This fact allows to *manage properties* of crystals which contain rare earth elements by selecting lanthanide ion with need radius for a given crystal.

Table 4.1.

Experimental data as to number of Bohr magnetons in lanthanides

RE ion	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
Moment, in μ_B	0	2,4	3,5	3,5	–	1,5	3,4	8,0	9,5	10,6	10,4	9,5	7,4	4,5	0

Experimentally found values of magnetic moments of rare earth elements ions are shown in Table 4.1. Magnetic properties of rare-earth ions are very appreciable. In lanthanum (La) that is starting element of rare earths group 4*f*-shell is empty, but in cerium atom 4*f*-shell already has one electron. Further, the number of 4*f*-electrons consistently increased in each next element of up to ytterbium (Yt), which has 13 electrons in its 4*f*-shell, and lutetium (Lu) in which 14 electrons completely fill 4*f*-shell. It is obvious that ions La^{+3} and Lu^{+3} are diamagnetics while all other *ions* of rare earth elements (from Ce^{+3} to Yb^{+3}) belong to paramagnetic [8].

The difference between magnetic properties of rare-earth (4*f*) metals and transition (3*d*) metals is that the radius of 4*f*-shell equals only ~ 0.3 Å, and this shell is *hidden* under the outward electronic shells. Therefore, widely used in engineering ferr*i*magnetic materials (ferrites) that are synthesized with rare earths elements have highest electromagnetic *quality factor Q* (i.e., small loss of electromagnetic energy at microwaves). In rare earth ferrites there is rather weak connection of deep-seated *active magnetic* 4*f subsystem* with lattice thermal movement (phonons) that mainly touches external electronic shells. External electromagnetic field excites exactly 4*f* magnetic subsystem, which being partially screened from phonons losses less energy: at microwaves rare earth ferrites have much higher quality factor than ferrites based on transition metals in which 3*d* shell is not shielded from ions thermal movement.

Various magnetics. Magnetic crystals and polycrystals with high ordering of spin and orbital magnetic moments demonstrate so called "strong" magnetism. In this case permeability is large and correspondent materials can be the sources of strong magnetic fields that widely used in engineering. When considering paramagnetics, it was shown that some atoms, which electronic shells are not completely filled, have their own magnetic moments and behave as small permanent magnets. The degree of magnetization of such crystal is determined by total magnetic moment that is the vector sum of atoms magnetic moments.

Natural magnetic moment have atoms and ions of *transient groups* of Periodic Mendeleyev Table, because they are characterized by unfilled inner electronic shells that available to hold unpaired electrons spin. The example is iron atom, in which 26 electrons move around nucleus; eighteen of them fill inner orbitals (as well as in argon atom). However, in the 3*d*-shell of iron atom only 6 of possible 10 electronic states are occupied, so the 3*d*-shell in iron is not filled completely, as there are four empty states, see Fig. 4.3*b*. Moreover, four magnetic moments of electrons in 3*d*-shell of Fe atom are *self-ordered*, making a system with uncompensated magnetic spins. Such feature of 3*d*-shell that determines big *intrinsic magnetic moment* of atom is peculiar to several elements of iron group.

If the crystal is formed from such atoms that have natural magnetic moments (like iron), different ways of magnetic moments orientation might be realized. The simplest types of regulation in two-dimensional case are shown in Fig. 4.2. The tip of arrow shows the north pole of magnet linked with atom. If magnetic moments are oriented randomly, as shown in Fig. 4.2*a*, then total magnetic moment of crystal is zero (this corresponds to paramagnetic). When one apply magnetic field to such a crystals, the *forced ordering* of magnetic moments occurs with their overwhelming focusing according to field that creates deposit in total magnetic moment (paramagnetism). In Fig. 4.2*b* the ordered structures are shown too simplistic – only as a comparison with disordered structures.

Different ordered structures are shown more detailed in Fig. 4.2. In the simplest *ferromagnetic* structure, Fig. 4.5*a*, all magnetic moments of atoms are directed equally. Examples of such ferromagnetics are metals: Fe, Ni, Co, Gd and Dy. These strictly magnetically ordered metal crystals can behave like permanent magnets (if they have single-domain structure). Simplest ordered *antiferromagnetic* structures might be also collinear, but magnetic moments in them are directed oppositely, so they are totally self-compensated, as it is shown in Fig. 4.5*b*. Axis, at which all these moments are directed, is the *antiferromagnetic* axis. Typical representatives of crystals with antiferromagnetic structure are some oxides of transition metals (Mn, Ni, Co, Fe) and many of their fluorides, chlorides, sulfides, selenides and others.

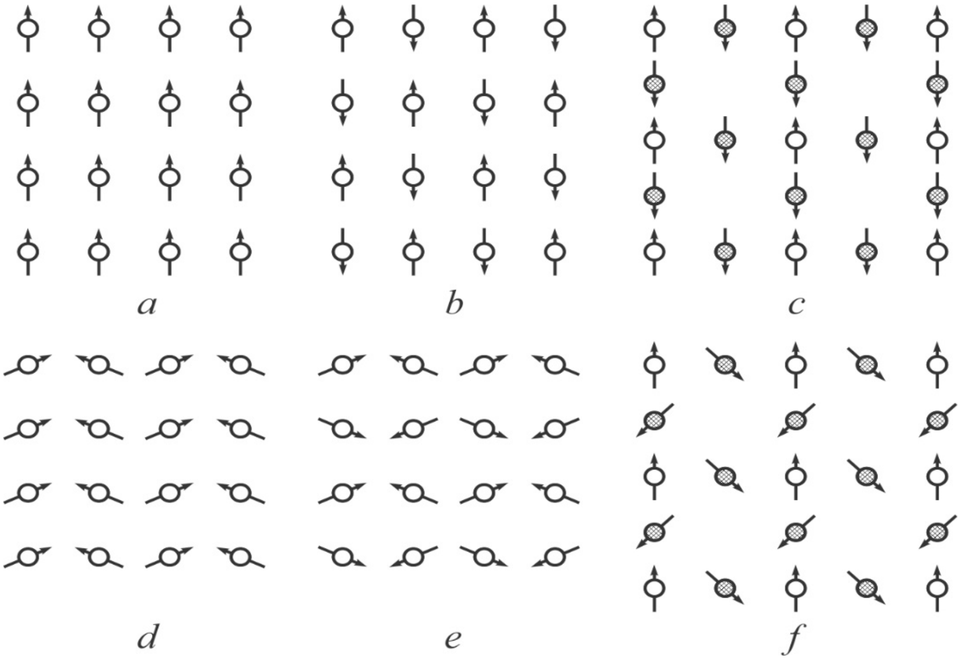


Fig. 4.5. Different types of ordered magnetic structures (explanations are in text)

Crystallographically all magnetics that have structure with similar direction of their magnetic moments might be presented as *magnetic sublattices*. In illustrated case in Fig. 4.5*b* some of magnetic moments of atoms are directed "up", forming one sublattice, while atoms with opposite direction of their magnetic moments form another sublattice. These two sublattices consist of atoms that are located in the equivalent positions (two *equivalent* magnetic sublattices). In general, magnetic structure may contain several sublattices, formed by atoms that crystallographically located in *non-equivalent positions*. Magnetic sublattice is a set of all atomic magnetic moments that can be obtained using parallel translations at distances that are divisible to period of unit cell. In the collinear *ferrimagnetic* structure, Fig. 4.5*c*, the neighbouring atoms also show antiparallel orientation, but *total* magnetic moment of elementary cell of crystal is *different from zero.* Therefore, this structure has spontaneous magnetization, as magnetic moments of ions that belong to different sublattices are non-compensated.

Partial compensation of magnetic energy may be conditioned by several ways. First, elementary magnetic cell may account different numbers of ions belonging to two sublattices (magnetic moments of ions in this case might be same). Second, magnetic moments of ions of two different sublattices may have different size. Most often both causes are observed, as shown in Fig. 12.11, *c*. Ferr*i*magnetism usually is called as *non-compensated antiferromagnetism* that better reflects the nature of this phenomenon. Shown in Fig. 4.5*a, b, c* types of magnetic structures belong to *collinear* magnetic structures. There are also different types of *non-collinear* magnetic structures, and some of them are shown in Fig. 4.5*d, e, f. Weakly* non-collinear magnetic structure (Fig. 4.5*d*) is inherent to the weak ferr*i*magnetics, and they are characterized by small resultant magnetic moment (in Fig. 4.5*d* it is directed upward). This causes a slight slanting of antiferromagnetic ordering of magnetic moments sublattices. Weakly non-collinear magnetic structure is seen in Fe_2O_3 (hematite), in crystals $FeBO_3$ and FeF_3, in carbonates $MnCO_3$, $CoCO_3$, $NiCO_3$, in orthoferrites $RFeO_3$ as well as in orthochromites $RCrO_3$ (R is rare earth element).

There are also such weakly non-collinear antiferromagnetic structures (Fig. 4.5*e*) that have no resultant moment. At that, triangular (corner) structures shown in Fig. 4.5*f* belong to *strongly* non-collinear magnetic structures. In this case magnetic lattice is formed by blackened atoms, divided into two sublattices, which magnetic moments are directed at angle to each other; as a result, magnetic moment can be created, and it is antiparallel to moment of third sublattice. All these are very special cases of ferromagnetic structures. There are also more complicated cases of "screw" and "helical" magnetic ordering that is not considered here.

Ferromagnetism. It is necessary to consider, why in some materials (ferromagnetics) natural magnetic moments of individual atoms become spontaneously ordered, while in other materials (paramagnetics) – no ordering is observed. When permanent magnet is placed in constant magnetic field, then its magnetic moment tends to take a position, coincident with direction of applied field. In the majority of crystals, containing *d*- and *f*-atoms, each structural unit has own magnetic moment that creates around itself magnetic field. If this field would be large enough, it can force magnetic moments of nearest neighboring ions to be oriented in parallel. This happens in case, when energy of interaction of magnetic moments of neighboring ions is larger than energy of thermal fluctuations (k_BT) in crystal lattice. It is determined that two types of interaction between magnetic moments of neighboring ions might exist: *dipole* interaction and *exchange* interaction. Exchange interaction is a purely quantum effect, and, usually, it is stronger than dipole type of interaction.

Among *d*-metals ferromagnetics are Fe (T_C = 1040 K), Ni (T_C = 630 K), Co (T_C = 1600 K) while among f-metals are only Gd (T_C = 293 K) and Dy (T_C = 87 K). In most of them, the carriers of ferromagnetism are the uncompensated ions spins *associated with orbital moments of electrons* belonging to crystal lattice. As known, electronic magnetism is manifested as in spin so in orbital moments. Magnetization of ferromagnetic summarizes magnetic moment *M* consisting of ordered magnetic moments of electrons and appropriate mechanical moment *P*. Ratio *M/P* equals $-q\mu/2m$, if magnetization is caused by orbital magnetic moments of atoms but equals $-q\mu/m$, if magnetization is caused only by spin magnetic moments.

There are some important experiments related to these assumptions:

1. Magneto-mechanical effect (*mechanical moment* arising at magnetization) was studied by Einstein and de Haas. The iron rod was hung on elastic string inside solenoid; when magnetized, the rod turns and twists the string. If direction of magnetic field changes, the direction of rod rotation also changes. From this experiment the value of gyromagnetic ratio is determined as $M/P = -q\mu/m$ that implies that this effect is caused by the *spins* of electrons.

2. In the reciprocal experiment the magnetization of iron rod occurs in case of its rapid rotation. This means electrons aspiration (representing so called "whipping tops" with angular momentum) to be oriented in the direction of axis of rod rotation. Along this experiment as mechanical, so magnetic moments of electrons were oriented. This also confirms the *spin* model of magnetization.

3. In another experiment, previously magnetized rod was subjected to rapid heating above Curie point. As a result, previously oriented "whipping tops" acquire random direction, so the demagnetization stimulated rotational momentum of rod that can be directly measured in experiment. In this case also the gyromagnetic ratio indicates that ferromagnetism is due to spin momentum of electrons.

However, convincing calculations show that *only spins interaction cannot provide their parallel orientation* that is main characteristic of ferromagnetic at temperatures below Curie point. Theory is obliged to assume (F.R. Weiss) that stable orientation of spins can be caused by the *molecular field,* which is the non-magnetic in its nature. As it was first shown by Y. Frenkel, the forces that compel orientation of magnetic moments have electrostatic nature. The spontaneous orientation arises as a result of the *exchange interaction* of spins and orbital moments of electrons in a crystal lattice. Exchange interaction is repeatedly considered in quantum mechanics, for example, to describe constitution of hydrogen molecule. In case of small particles that have magnetic moment (such as electrons) their arrangement in the magnetic field is determined by a fact that projection of spin vector on magnetic field direction can take only two values: ± $(1/2)\mu_B$. For two-electron system in the H_2 (as example) it can not be specified which of two electrons has definite state. However, following Pauli principle, two electrons can not be located on single energy level having same spin quantum number. In quantum mechanics this is taken into account by introducing *anti-symmetrical wave function*, i.e., when two electrons interchange their wave function must change its sign.

Exchange interaction has electrostatic nature, however it is not a simple Coulomb-type, but the quantum interaction. During mechanism of exchange interaction direction of electronic spins of neighbouring atoms are co-ordinated. Such interaction is titled as “exchange” because in process of interaction between neighbouring electrons magnetic atoms looks like their *places are changing*. The result of exchange interaction is the establishment of electronic spin moments orientation in parallel to each other, so *spontaneous magnetization* arises without any external field.Since both spin and orbital moments of electrons are interrelated, it can be argued that spontaneous magnetization is created by the ordering of magnetic moments of atoms. While heating to Curie temperature lattice thermal motion destroys orderly setting of atoms, established by exchange interaction. It follows that the greater exchange interaction in ferromagnetic, the higher should be its Curie temperature at which magnetic ordering becomes destroyed.

In the *exchange integral* both positive and negative members are included, so it might have both positive and negative signs. This sign identifies what kind of spins orientation of electrons, involved in the bonding exchange, is energetically more favorable: parallel (that corresponds to ferromagnetism) or antiparallel (corresponding to antiferromagnetism). Thus, exchange interaction characterizes the difference of Coulomb energy between parallel and antiparallel orientation of spins. For ferromagnetics and antiferromagnetics exchange integral has opposite sign. Since exchange interaction occurs only in case of *overlapping orbitals*, it follows that this interaction has *short-range nature:* between adjacent orbitals. Conversely, spin-type interaction (between own magnetic dipoles in lattice of magnetic ions) is called as *long-range* dipole-dipole interaction. Thus, main magnetic interactions are as exchange interactions (short-range) so dipole-dipole interactions (long-range).

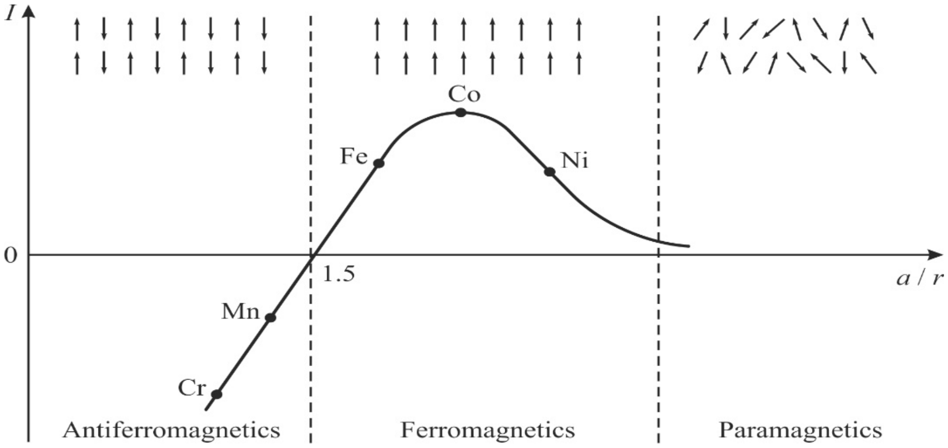


Fig. 4.6. Calculated data for exchange integral for iron group ferromagnetics

Results of exchange integral calculation in dependence on ratio of lattice constant *a* and radius *r* of 3*d*-shell for different metals of iron group is shown in Fig. 4.6. It can be seen that just for ferromagnetic metals – iron, cobalt and nickel – exchange integral is positive, i.e., parallel location of spins for neighboring atoms appears energetically favorable [9].

The value of exchange integral correlates with the Curie temperature, Table 4.2: the greater exchange energy, the higher ordered structure of spins can resist to action of thermal phonons. Indeed, greatest value of exchange integral is observed in cobalt with Curie point of about 1400 K. Exchange integral is smaller in the iron (T_C = 1040 K), while the lowest it is in nickel (T_C = 630 K). The density of electronic states (partially filled orbitals) in the ferromagnetic must be big enough in order to the kinetic energy cannot exceed exchange energy.

Interestingly, that *manganese* (and others representatives of 3*d*-metals, in which ratio a/r < 1.5) is not ferromagnetic, but the value of exchange integral in Mn is very close to Fe, Fig. 4.6. Therefore, if the lattice constant of manganese would be slightly increased, then ratio a/d will be more than 1.5, and manganese will become ferromagnetic. Experiment confirms this expectation: the ferromagnetism in Mn arises after its doping by a small amount of nitrogen, that causes some increase of manganese lattice parameter. Similarly, many manganese-based alloys are also ferromagnetics, in spite of they have no one component, which is ferromagnetic in pure crystal. For example, very important in technique is the alloy Mn-Si-A1, as well as compounds MnSb, MnBi and some others, containing manganese atoms on distances larger than atoms of pure manganese.

Apparently, for emergence of ferromagnetism, it is important to have certain "optimum" in atomic distance in crystal lattice. When atoms approach too close one to another (Ti and Cr), then in their electronic energy band a significant dispersal appears with a rapid increase of kinetic energy, and ferromagnetism is absent. The point is that atoms are located too far from each other, and the exchange interaction becomes insufficient for ferromagnetism. At that, in the iron group of metals, only the spins interaction (i.e., the dipole-to-dipole attraction) is not large enough for ferromagnetism formation. Thus, the presence of unfinished internal electronic shells in some atoms, as well as *positive sign* of exchange integral (that results in the parallel orientation of spins) is the necessary and the sufficient conditions when ferromagnetism can exists.

It needs to recall, that magnetization J (density of magnetic moment M in sample) is defined as total magnetic moment per unit volume, induced by external field H (in which measurement is performed). Magnetic "response" of crystal to applied field H is characterized by magnetic susceptibility æ, since $J = \mu_0 æ H$. However, in ferromagnetic materials æ >> 1, and, therefore, magnetic susceptibility practically equals to the permeability that follows from ratio $B = \mu_0 \mu H$, so that in ferromagnetics $æ \approx \mu$ and $B \approx J$.

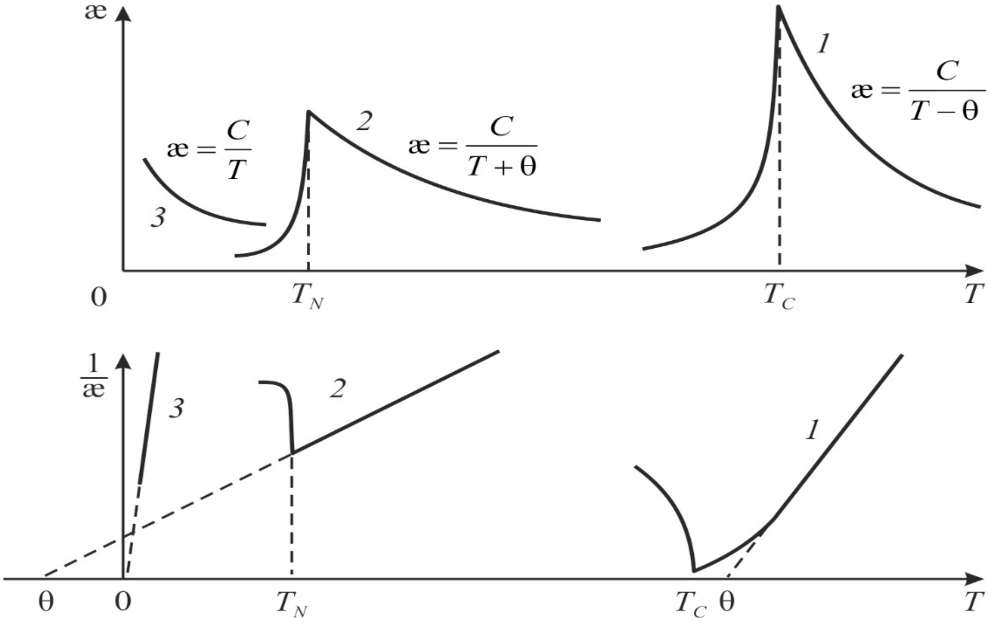
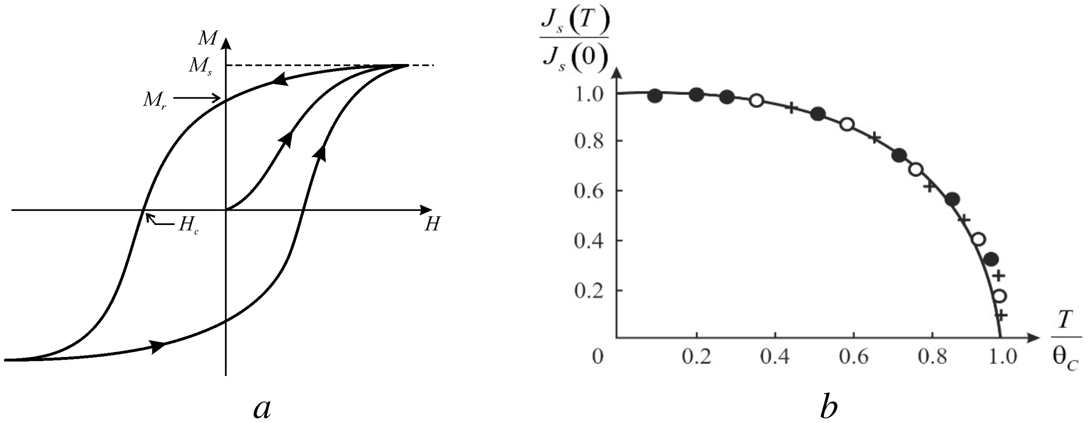


Fig. 4.7. Temperature dependence of magnetic susceptibility and inverse susceptibility for various magnetic materials: *1* – ferromagnetic, *2* – antiferromagnetic; *3* – paramagnetic (θ is Curie-Weiss temperature, T_C is Curie temperature, T_N is Neel temperature)

Permeability temperature dependence in some magnetics is shown in Fig. 4.7. While cooling from high temperatures (i.e., cooling from disordered paramagnetic phase), the permeability (and magnetic susceptibility) of ferromagnetic first increases and reaches maximum at Curie temperature T_C. In the paramagnetic phase, above phase transition point the *Curie-Weiss law* is fair: $æ \approx \mu = C/(T - \theta)$, where C is Curie-Weiss constant and θ is Curie-Weiss temperature. Once crystal is ferromagnetic, then spontaneous *internal magnetic field* H_{sp} appears, so measured in a *small* external magnetic field **æ** ≈ μ below its sharp maximum rapidly decreases with temperature lowering due to *saturation* process occurring in H_{sp}. (However, in the *strong* measuring magnetic field μ ≈ **æ** continues its smooth increase, so sharp maximum $\mu(T_C)$ is seen but only in small magnetic field). In temperature dependence of *inverse* magnetic susceptibility, near phase transition the increase of æ(T) becomes a little slower, and, therefore, $\theta \neq T_C$.

- Phenomenon of magnetization backlog when magnetic field is changing is *magnetic hysteresis*. Fig. 4.8*a*. To destroy the residual magnetism M_r, it is necessary to apply the counter field H_c that in ferromagnetic can reverse its magnetization. This field is the *coercive field* (retentive force). Shown in Fig. 4.8*a* closed curve, describing the reversal cycle, is the *hysteresis loop*. The area of this loop is proportional to work which external field spends to reverse polarization in the unit volume of ferromagnetic. During reversal process, this work *turns into a heat* and characterizes *hysteresis losses*. Therefore, in case of repeated reversal magnetization, ferromagnetic becomes heated, and the more intense the bigger the area of hysteresis loop. Heating is a result of *internal friction* that occurs at continuous reorientations of magnetic domains. At higher frequencies the ferromagnetic is heated additionally: due to *Foucault currents* arising in ferromagnetic which usually is good conductor.



a *b*

Fig. 4.8. Magnetic hysteresis (*a*) and temperature dependence of spontaneous magnetization (*b*) for different magnetic materials: ● – iron, ○ – nickel, + – cobalt

Depending on the shape and area of hysteresis loop, the ferromagnetic materials are divided into the "soft" materials (small coercivity) and the "hard" materials (with high coercivity). Different application of magnetic materials requires different types of magnetization curve. Materials used in the electrical transformers and electrical machines should show a *quick response* to magnetic field, because they have to change their magnetization many times per second. This might result in partial loss of efficiency and material heating; especially, if ferromagnetic is rather "hard" (with increased coercive field).*Temperature dependence of spontaneous magnetization.* Magnetization that arises below Curie point is the *spontaneous:* $J_{sp} \approx B_{sp}$. Temperature dependence of spontaneous magnetization in iron, nickel and cobalt is shown in Fig. 4.8*b*. On the vertical axis the relative value of magnetization is designated; dependence of J_{sp} on T/θ is depicted by the *same curve* for these three ferromagnetics. As temperature increases, the magnetization decreases and in Curie point (as well as above it) becomes zero.The temperature, at which phase transition occurs from ferromagnetic ordered state into paramagnetic disordered state is the *ferromagnetic Curie point*, T_C. Above this temperature a substance ceases to be ferromagnetic and behaves just like many others paramagnetic solids. Afterwards, when cooling to temperature below critical, spontaneous magnetization arises again, and dependence $J_{sp}(T)$ is restored. In other words, spontaneous magnetization of material decreases with increasing temperature and vanishes at the critical point.

The value of saturation in the $J_{sp}(T)$ curve depends on fundamental properties of ferromagnetic. Since this value corresponds to magnetization inside domain, it does not depend on the method of ferromagnetic sample preparation. This feature of spontaneous magnetization temperature dependence is explained by F. Weiss: in ferromagnetic the *internal* (molecular) field exists which aspires to orient all elementary magnets along one direction. This field is directly proportional to existing magnetization. Thermal fluctuations seek to destroy the orientation of elementary magnets, and the more intense, the higher temperature. The violation in ordering means less spontaneous magnetization, but, for its turn, it decreases the field which organizes magnetic dipoles. Thus, there is a kind of "positive feedback": the aspiration for magnetization to zero as temperature rises is progressively increasing with decreasing magnetization. On the contrary, when temperature decreases, magnetization gradually increases. To explain internal (or molecular) Weiss's field existence, it is insufficient to consider only the magnetic forces, acting between elementary dipoles. Calculations show that magnetic forces between spins cannot play a vital role for internal forces; according to Weiss's theory these forces for about three orders of magnitude smaller than it is necessary to overcome the action of heat disordering. As it is considered before, the electrical forces also act between electrons that stipulate for their exchange interaction.

Antiferromagnetism. In the case of negative sign of exchange integral, the antiparallel orientation of spins in the lattice sites of crystal is more profitable, Fig. 4.7. Spins are ordered, but no spontaneous magnetization occurs because magnetic moments of neighboring spins compensate each other, Fig. 4.2*c*. Such crystal has two magnetically opposite sublattices that are interpenetrated. The most studied antiferromagnetics are listed in Table 4.2.

Table 4.2.

Neel temperature of some antiferromagnetics

Crystal	T_N, K	**Crystal**	T_N, K
MnO	122	$KCoF_3$	125
FeO	198	MnF_2	67,34
CoO	291	FeF_2	78,4
NiO	650	CoF_2	37,7
$RbMnF_3$	54,5	$MnCl_2$	2
$KFeF_3$	115	VS	1040
$KMnF_3$	88,3	Cr	311

The antiparallel arrangement of spins is formed in structure of spontaneously at temperature below *Neel temperature* (T_N), in competition with chaotically disordered thermal motion. When antiferromagnetic is heated above Neel point ($T > T_N$), the uncompensated spins which partially fill *d*- or *f*-shells, form something *like paramagnetic* system which is characterized, however, by a *special* temperature dependence of magnetic susceptibility: $æ = C(T + \theta)$, where C is Curie-Weiss constant. At that, θ is the characteristic temperature, which in contrast to paramagnetic phase of ferromagnetics is located in the *negative* range of Kelvin temperature scale, Fig. 4.7, curve *2*.

As the examples of antiferromagnetics, we can mention some *d*- and *f*-metals: Cr with Neel temperature $T_N = 311$ K, Mn with $T_N = 100$ K, and their numerous compounds. Antiferromagnetics are also many oxides of *d*- and *f*-metals: MnO with $T_N = 122$ K, FeO in which $T_N = 198$ K, NiO with $T_N = 650$ K – this is highest Neel temperature.

It should be noted that antiparallel spontaneous orientation of electronic spins in the closely located ions strongly *reduces the electrical conductivity* – antiferromagnetic below Neel temperature is turning from conductors to the semiconductors (or dielectric). In the disordered (paramagnetic) phase antiferromagnetic does not have any band gap in their electronic spectrum (as metal). However, as temperature decreases and transition to antiferromagnetic phase occurs (at Neel point), in electronic spectrum of most antiferromagnetic *compounds* the *energy gap opens*. Therefore, Neel phase transition in antiferromagnetics might be simultaneously the "dielectric-to-metal" phase transition. At that, electrical conductivity in the antiferromagnetic phase is thousands of times lower than in magnetically disordered (conducting) phase.

However, permeability of antiferromagnetics is small ($\mu \approx 1$) that is obviously insufficient for their technical application as magnetic materials. The smallness of permeability is consequence of the fact that at low temperatures (in antiferromagnetic phase) the atomic magnetic moments of sublattices *totally compensate* each other, so the resulting magnetic moment is zero. When temperature rises and antiparallel orientation of spins become disordered, the value of magnetic susceptibility æ increases and reaches maximum at Neel point, Fig. 4,7, while the disordering of their spins becomes like in paramagnetic. Simultaneously, the movement of valence electrons (which in the antiferromagnetic phase are constrained by strongly ordered opposite spins) becomes free, so when transition into disordered (paramagnetic) phase crystal turns into conductor.

Ferrimagnetism. In addition to totally magnetically compensated antiferromagnetics, there are many crystals and polycrystals, in which the magnetic moments of sublattices, although being directed opposite to each other, have significantly difference in their magnetization, Fig. 4.2*d*. These materials have rather complicated structures with varying kinds of atoms that form them, and with variable number of uncompensated electrons in the *d*-shells (or *f*-shells). These magnetics show properties *similar to ferromagnetic materials,* because they hold spontaneous magnetization and total magnetic moment in their lattice is nonzero. These substances, being very important for applications, are the *ferrimagnetics*; some of them are listed in Table 4.3.

Table 4.3.

Curie temperature T_C and magnetic saturation induction B_S at 4 K in some ferrimagnetics

Crystal	T_C , K	$4\pi B_S$, Gs
Fe_3O_4 (magnetite)	858	6400
$CoFe_2O_4$	793	6000
$MgFe_2O_4$	713	1800
$CuFe_2O_4$	728	2000
$MnFe_2O_4$	573	7000
$Y_3Fe_5O_{12}$	560	2470

Therefore, magnetic moments of ferrimagnetics are directed antiparallel, but they are non-compensated. Electronic interaction in such lattices is known as the *indirect exchange interaction,* at which there is no direct overlap of magnetic ions wave functions. However, the overlap of wave functions of diamagnetic anions (for example, O^{-2}) with wave functions of magnetic cations (for example, Fe^{+3}) enables the exchange interaction *through the virtually excited state*. The 2*p*-shell of oxygen ion in its main state is completely filled, and, despite the overlap with iron ion wave functions (*p*-orbitals of O^{-2} and two *d*-orbitals of Fe^{+3}), any exchange interaction between them is absent. However, in the *excited* state, one of *p*-electrons of oxygen transfers to the 3*d*-shell of iron ion. In compliance with the Hund's rules, those electron has to move which spin is antiparallel to the spins of electrons in the half-filled shell of ion Fe^{+3}. Leaving 2*p*-shell, the electron, due to negative exchange interaction, orients spins of neighboring iron ions. The intensity of indirect interaction increases with the extension of overlapping of electronic shells, i.e., with the *strengthening of covalent bond*. Because covalent bonds are non-central, the indirect exchange interaction reaches maximum when three interacting ions are not collinear. Therefore, the compensation of magnetic moments is not complete in the complex structure of antiferromagnetic.

Permeability of ferrimagnetics, being less than values of permeability in typical ferromagnetics, nevertheless, is rather big for successful technical applications: $\mu \sim 10^2$-10^3. As to another physical properties (hysteresis, nonlinearity, domain structure), the ferrimagnetic is close to ferromagnetic, but its magnetization decreases with temperature rise non-monotonically (as in ferromagnetics), sometimes passing through zero before reaching final Curie temperature, Fig. 4.9.

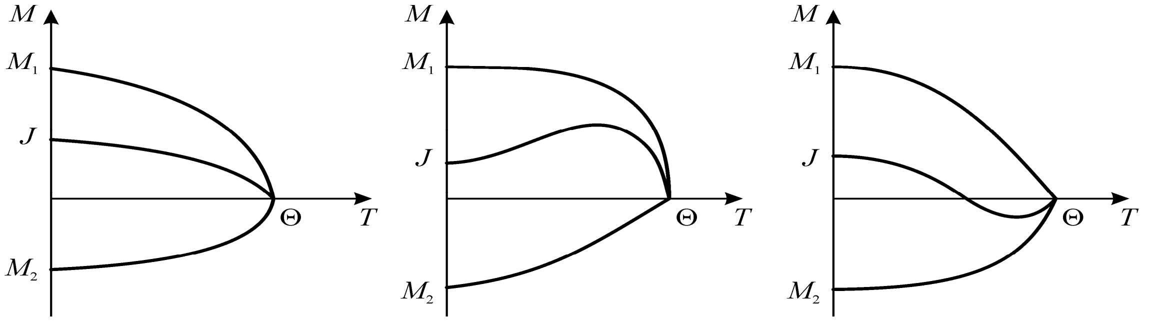


Fig. 4.9. Different types of temperature dependence of magnetization in the sublattices (M_1 and M_2) and resultant spontaneous magnetization (J) of ferrites

Several different sublattices that exist in ferrimagnetic make temperature dependence of spontaneous magnetization rather complicated, as compared with conventional ferromagnetism, seen in Fig. 4.9. This is due to the fact that temperature dependence of spontaneous magnetization may be different for various sublattices of ferrimagnetic. It is necessary to remind that most of ferr*o*magnetics are metals (with high conductance) and, therefore, they cannot be used at increased frequencies due to high losses conditioned by Foucault currents. Therefore, for electrotechnical applications (frequency 50 or 60 Hz), and, especially, for mobile (transport) electrical engineering (frequency of 400 Hz) the iron, permalloy or any ferromagnetic metal are divided into the separate plates (or even into thin foil) with the electrical insulating layers between the plates (or foil). One of possible ways of ferromagnetic metal using at the radio frequencies is to reduce losses from Foucault current by using micron-sized ferromagnetic particles pressed together with polymer (*magneto-dielectric composites*). Nevertheless, this technology cannot prevent losses from Foucault currents in the microwave range (where magnetic materials are widely used, particularly in information and computing technique).

However, extremely necessary insulating properties are achieved exactly in ferr*i*magnetics by combination of depressed conductivity with rather strong magnetism in *elementary crystal cell.* Therefore, main advantage of ferrimagnetics is rather high permeability with a significant manifestation of magnetic properties, combined with high enough electrical resistance. This is especially important in microwave technology as provided small loss of electromagnetic energy. In technologies, the ferrimagnetics usually are called *ferrites,* and most important representative of them is *magnetite* $Fe_3O_4 = FeO{\cdot}Fe_2O_3$. Its unit cell is ferrospinels that has cubic lattice formed from eight molecules of $FeO{\cdot}Fe_2O_3$. In this mineral the negative oxygen ions form face-centred lattice, in which compound Fe_3O_4 has one divalent (Fe^{+2}) and two trivalent (Fe^{+3}) iron ions. As shown in Fig. 4.3b, the atom Fe as well as the ions Fe^{+2} and Fe^{+3} have different number of uncompensated spins. One sublattice of ferrite contains one half of trivalent iron ions, another sublattice – second half of trivalent iron ions and divalent iron ions. Magnetic moments of sublattices are antiparallel. Therefore, the magnetic moments of trivalent iron ions are compensated, but spontaneous magnetization is caused by magnetic moments of divalent iron ions.

In various ferrites with a structure of magnetite the divalent iron ions Fe^{+2} can be substituted by divalent ions of other metals, such as Mg^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} and Cu^{+2}. General formula of ferrites with spinel-type structure is $MeO{\cdot}Fe_2O_3$, where Me is the divalent metallic ion. Just the divalent metal ions cause spontaneous magnetization of many ferrimagnetics. Some of ferrites (manganese and nickel ferrites) have rather high permeability: up to several thousands. In others ferrites usually $\mu \sim 100$ (however, ferrites based on zinc and cadmium are not ferrimagnetics).

Ferrites based on *rare earth elements* are of great scientific and technological interest. It is necessary to remind that rare earth elements (or lanthanides) are the elements of third group with numbers 57 -71 (La, Ce, Nd, Sm, etc.). To them, by similar properties, scandium Sc and yttrium Y are attributed. As the alloys, so compounds of these elements have pronounced magnetic properties. Their difference from the magnets of iron type (3*d*-metals) lies in that magnetic moment of lanthanides (4*f*-metals) is determined mainly *by spin properties of electrons,* while importance of orbital moment is smaller (nevertheless, orbital moment also has some influences on their magnetic properties). From fourteen rare earth elements the *ferromagnetism* is observed only in six of them (gadolinium, erbium, dysprosium, holmium, thulium and terbium) but in most of them (except gadolinium) at a certain temperature the ferromagnetism turns into the antiferromagnetism. In the gadolinium, like in iron, the ferromagnetic state occurs *directly* from the paramagnetic state (at temperature of 290 K). Five rare earth elements (cerium, praseodymium, samarium, europium and promethium) are antiferromagnetics. Magnetic moments of lanthanum and lutetium are zero (they are diamagnetics). So magnetic properties of rare earth metals are quite different and complicated.

4.3 Basics of ferroeletricity

Traditional and comfortable modelling of ferroelectric is the assumption of its *spontaneous polarization* P_S, direction of which can be switched by externally applied electrical field. Currently, there is opinion as to another nature of ferroelectricity: it might be assumed that structure of ferroelectric is able to demonstrate such nonlinear polar response to externally applied field, as if the *switching of polarization* occurs in it. However, in this tutorial it is better adhere to *traditional theory* of ferroelectrics as crystals with reversible spontaneous polarization.

It should be noted that other than in the ferroelectrics internal polarization is peculiar to the electrets and pyroelectrics. However, unlike residual polarization of electrets, the cold spontaneous polarization represents the *stable thermodynamic state* of polar dielectrics. Indeed, residual polarization in electrets disappears during their heating or irradiation, while spontaneous polarization looks like a structural feature of polar crystal. Really, its value can be changed under external influences, but then it completely restores when initial conditions return. It should be recalled that the pyroelectricity is one of possible manifestations of polar crystals peculiar structure. However, applied electrical field can not change the direction of spontaneous polarization in the *linear* pyroelectric, which persists up to the melting of a crystal. Being the *non-linear* pyroelectric, the ferroelectric not only switches its P_S in electrical field, but shows a significant change in P_S temperature dependence, until it completely disappears well before the melting of a crystal.

Ferroelectrics are the subclass of pyroelectrics, in which polarized state is not stable enough but it is quite labile. This polarized state can be changed by many external influences: electrical field, temperature and pressure.

Two types of phase transitions. In the vicinity of phase transitions, the substance, firstly, allows considerable control of its parameters by the not very strong fields that is used in electrically and magnetically controlled devices; secondly, the substance is very sensitive to changes in temperature, pressure, humidity, etc. that is used in various sensory devices. Due to enormous anomaly of dielectric properties observed at phase transitions, dielectric spectroscopy requires special measurement methods and software for obtaining information about physical properties of object under study (critical frequency and attenuation, critical relaxation time, etc.).

According to the *condensed state physics*, the nature of phase transitions can be like that. The degrees of freedom of atomic particles in solids can be divided into two groups. For some degrees of freedom the interaction energy of particles U_{int} is smaller in comparison with thermal motion energy k_BT. In this case, i.e, at $U_{int} << k_BT$ the appropriate degrees of freedom behave as the collection of particles, i.e., as the "almost ideal gas", and the applicability to use the model of *quasi-particles* is justified. Conversely, when $U_{int} >> k_BT$, then appropriate degrees of freedom are ordered, but their movement, too, can be described by the introduction of quasi-particles. In other words. both of these cases correspond to the ordinary state of crystals and it is possible to describe, for instance, the phenomena of electric charge transfer (electronic or impurity ionic), as well as the phenomena of electrical polarization, by involving the dynamics of the crystal lattice (phonons).

However, if the energy of particles interaction approaches to changing with temperature thermal motion energy ($U_{int} \sim k_BT$), the theoretical description of dynamic phenomena in a solid becomes complicated: exactly this case usually corresponds to the *phase transitions*.

As known, in almost all substances at a definite temperature the significant change in physical properties occur and as a rule it is not a gradual but *abrupt*: this spasmodic change of properties is a phase transition. The “liquid ⇔ steam” (vaporization) phase transition is a typical example while another example is the "liquid ⇔ crystal" transition (crystallization). Both transitions refer to the *first order* (PT-I), in which the phases before and after transition point *differ significantly* from each other. At that, one phase replaces another phase just because it is more favourable energetically. To make this change happen, the essential energy barrier, separating these phases, should be overpass so the *stepped changing* of entropy should take place with a heat release (or absorption). Moreover, in the neighbourhood of first order phase transition the overcooling (or the overheating) is theoretically expected and seen experimentally.

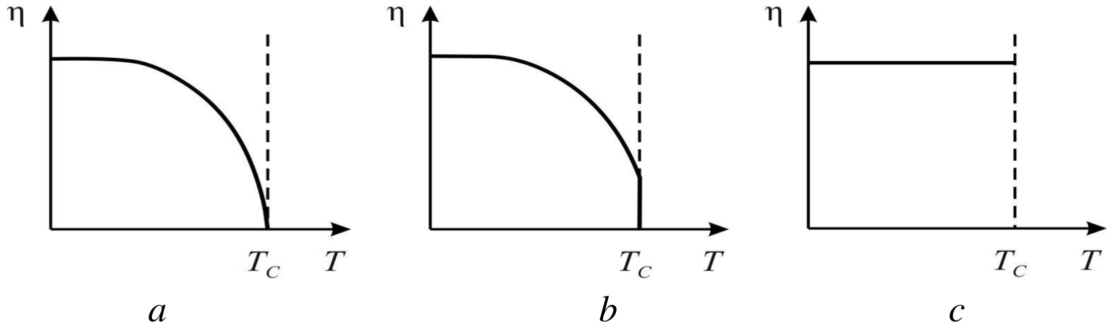


Fig. 4.10. Temperature dependence of ordering parameter for PT-II (A); PT-I close to PT-II (B) and for PT-I (C)

Ordering parameter η may vary differently with temperature changing, as it is illustrated in Fig. 4.10. The characteristic feature of PT-II is the *continuous* change of this parameter with temperature in the ordered phase Fig. 4.10*a*. On the contrary, idealized case of PT-I corresponds to the case when ordering parameter changes by *jump*, Fig. 4.10*c*. But it should be noted that in many experimental situations the $\eta(T)$ dependence very often changes by one of "*intermediate*" ways, shown in Fig. 4.10*b*. In this case, the phase transition is the *transition of first order, close to transition of second order*. Here the ordering parameter η first changes with temperature increase gradually, but than abruptly falls down to the disordered phase.

Phase transition of second order can be accompanied by the multiplication of crystal unit cell size. Then the volume of unit cell of low-symmetry phase (more ordered) increases in 2, 4, 8 times, as well as the translational symmetry of unit cell also changes. Based on microscopic changes in a structure, phase transitions are divided into *order-disorder type* and *displacive type:* theoretical justifications for this division will be given below. Nevertheless, it should be noted here that a clear border between the displace and order-disorder types of PT can not be determined. In terms of crystal symmetry, there are no differences between them: when analizing structure, always an average position of atoms is taken in consideration. So it is no matter how this averaging is performed: by the discrete way or by the continuous way. As to some other properties, especially, the dynamics of PT in case of displacive type of transition and in order-disorder type of transition vary considerably.

However, for solid state physics, more ordinary are the phase transitions within same physical state, which takes place as in the crystals so in the liquid crystals. Of particular interest are the phase transitions, at which a *new property* appears in crystal, for example, polar phase with the ability to electrical controlling (hysteresis loop) in case of transition from paraelectric phase to ferroelectric phase. This type of transitions is related to PT-II model: at Curie temperature ($T = T_C$) one phase ceases to exist, but it is replaced by another phase. In the point of transition both phases can not be clearly distinguished, but when system moves away from this point, the difference between properties of phases gradually increases. Second-order transitions are gradual and smooth; they do not show any temperature hysteresis and not accompanied by the discontinuous jump in the energy or in the volume of a crystal. Nevertheless, as a result of this transition, the new physical property appears: crystal becomes ferroelectric, ferromagnetic, ferroelastic, superconductive, etc. When a ferroelectric phase transition is studied by the dielectric spectroscopy, the sample is exposed to the external electrical field and the “uncertainty” of phases at Curie point of ferroelectrics is expressed as a huge maximum of permittivity (as well as in the point of ferromagnetic phase transition the maximum permeability is huge).

When microscopic characteristics of any phase transition are discussed, a *regulating* (*ordering*) *parameter* η should be considered. In crystals, it is the measure of structural deviation from the state of highest symmetry. Depending on what kind of microscopic interactions gives rise to the PT and what changes of structure take place, the ordering parameter η acquires different physical meaning. For example, in ferroelectrics ordering parameter may correspond to the degree of electrical dipoles regularity, in ferromagnetics parameter η describes the ordering in system of magnetic moments (spins), etc. Ordering parameter may have also broader content; for example, in case of PT with the aggregate conversion this parameter characterizes the degree of regularity in a mutual arrangement of atoms or molecules.

Domains and spontaneous polarization. An important feature of ferroelectrics, which suggests them as electrical analogue of ferromagnetics, is their spontaneous division into a plurality of domains. Within each domain, the spontaneous polarization P_S is same, but in various domains P_S has different orientation. The subdivision of ferroelectric structure into great number of domains is energetically advantageous, since the single-domain crystal would create in environment external electrical field (as in case of electrets). Obviously, energy of this field decreases with diminution of size of domains. Externally applied electrical field causes, at first, the junction of randomly oriented ferroelectric domains into one domain; next its polarization reaches saturation. As seen in Fig. 4.11*a,* after external field switching off polarization tends to maintain its constant direction. If polarity of externally applied field would be changed, polarization, without changing its absolute value, will change its direction abruptly.

For such "forced" change in the direction of P_S, that is, for ferroelectric polarization reversal, it is necessary to apply electrical field of a certain value, which is the *coercive field* E_C (see Fig. 4.11*a*). Sometimes the value of this field reaches very large values, and then the ferroelectric cannot be repolarized and behaves like the pyroelectric. However, during such "hard" ferroelectric heating, as it approaches the temperature of Curie point T_C, its coercive field E_C mush reduces, and, therefore, close to Curie point it becomes possible to observe hysteresis. The coercive field E_C as well as the P_S in ferroelectric becomes zero, if $T = T_C$. The pyroelectric, however, has no Curie point, and until electrical breakdown its internal polarisation does not change direction – such crystal rather can be destroyed than change the direction of polarization.

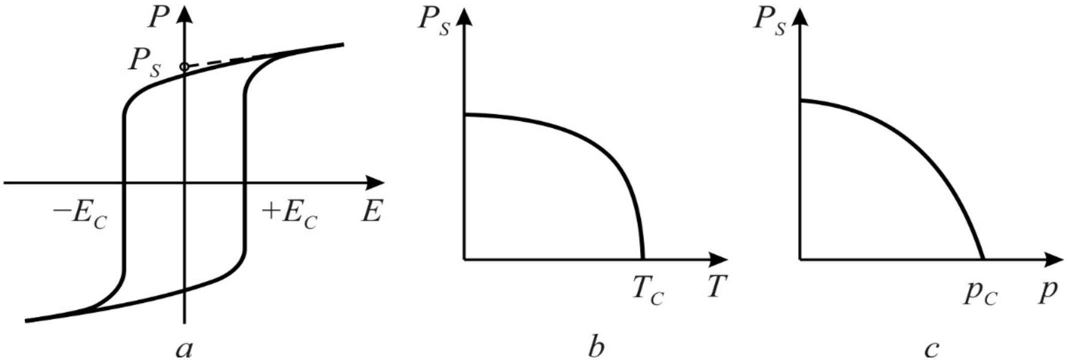


***Fig. 4.11.*.** Ferroelectric polarization dependence on electrical field (*a*) and spontaneous polarization dependence on temperature (*b*) and pressure (*c*)

It is therefore believed that availability of dielectric hysteresis is *necessary and sufficient property* of ferroelectric state. If temperature exceeds the critical value T_c then as hysteresis loop so ferroelectric state disappears. In same way on ferroelectric P_S affects increase of hydrostatic pressure, Fig. 4.11*c*. In contrast, linear pyroelectric does not change its polarized state under a pressure up to being destroyed. Summarizing, it might be concluded that ferroelectric is a special, nonlinear pyroelectric. Ferroelectrics are significantly different from linear pyroelectrics of tourmaline or lithium sulphate types.

In case of *active dielectrics applications*, first of all, ferroelectrics or close to them dielectrics have largest interest. In fact, exactly in ferroelectrics their "transforming functions" are most pronounced. For example, the greatest value of piezoelectric module is observed in Rochelle salt crystals and in the ferroelectric antimony sulfoiodide (SbSI). The highest values of pyroelectric coefficients are also seen in ferroelectric crystals (threeglycine-sulphate). Therefore, for thermal infrared receivers manufacture that use pyroelectric effect just the ferroelectrics (nonlinear pyroelectrics) are applied. The most applied piezoelectrics are also ferroelectrics, in particular, the ferroelectric ceramics of PZT-type ($Pb(Zr,Ti)O_3$). In optical detectors (that use photo-polarization effect) also some of ferroelectric crystals are applied, while for optical holograms recording ferroelectric crystals strontium-barium niobate and lithium niobate are employed.

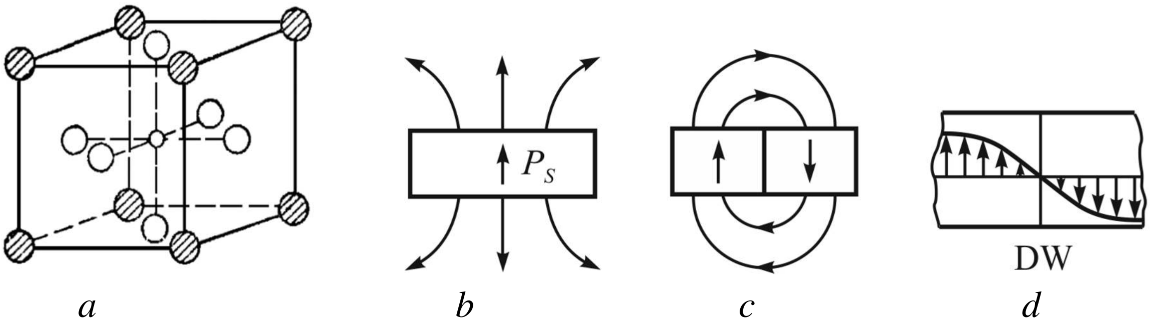


Fig. 4.12. Crystal structure of perovskite ABO_3 (*a*); domain structure of ferroelectrics: *b* – single-domain crystal creates depolarizing electrical field in surrounding area; *b* – in two-domain crystal depolarizing field is reduced; *c* – domain wall in vicinity of which P_S gradually changes its direction to opposite

In the perovskites which have general formula ABO_3 small size cation B^{+4} is surrounded by the octahedron formed of six oxygen ions O^{-2} (Fig. 4.12*a*). Any displacement of particular "ferro-active" ion B^{+4} makes great contribution to the dipole moment of unit cell in which spontaneous polarization occurs. The significant shift of small size tetravalent cation in the octahedron is conditioned by the fact that surrounding very small ion B^{+4} large anions O^{-2} leave considerable space inside octahedron for ion B^{+4} easy displacement. This effect causes to appearance of spontaneous polarization in the perovskites.

Ferroelectrics properties are considerably dependent on their ***domain structure.*** The origin of multidomain structure in ferroelectric crystal below phase transition is energetically favourable. Single-domain crystal (Fig. 4.12*b*) creates an electrical field in the surrounding space (like electrets), to which spent some energy W_1. As can be seen from Fig. 4.11*c,* the energy of external field in a two-domain crystal is smaller than in single-domain crystal. Thus, in case of many-domain structure the total energy of crystal must be reduced.

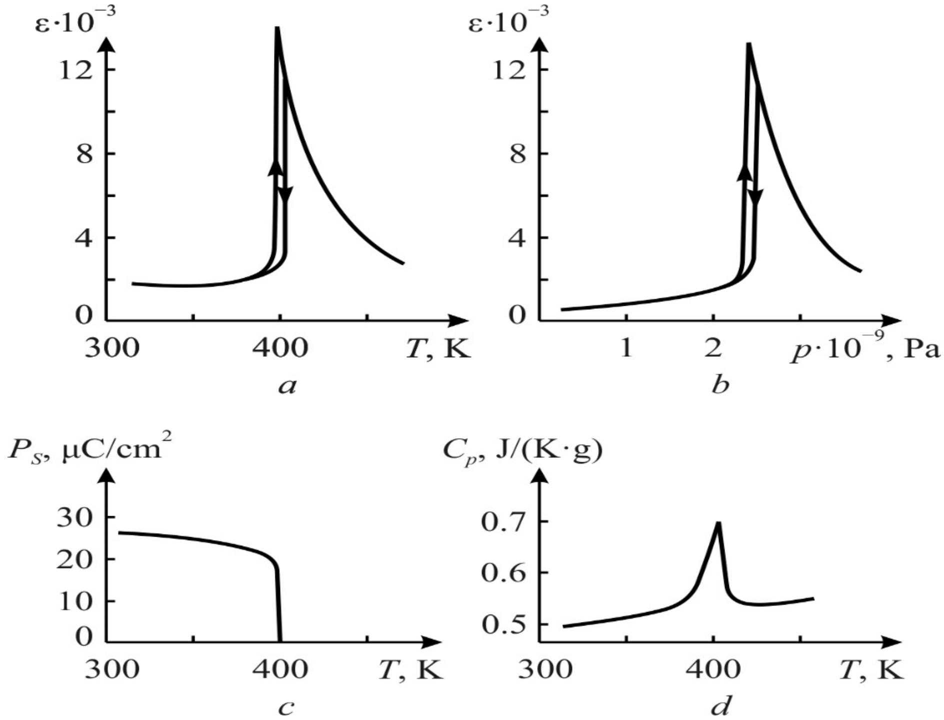


Fig. 4.13. Basic characteristics of barium titanate: *a, b* – permittivity dependence on temperature and pressure; *c, d* – spontaneous polarization and specific heat dependences on temperature

This reduction in energy is limited by the growth of energy W_2, expended on the formation of domain walls that separate regions with different directions of P_S, Fig. 4.12*d*). The average size of domains (at which the sum $W_1 + W_2$ is minimal) depends on temperature, structural defects and electrical conductance of dielectric, as well as on environment properties. Multidomain structure in ferroelectrics is relatively stable; at that, the equilibrium state of ferroelectric domains usually corresponds to domain size from a few hundredths of millimetre to several millimetres.

Barium titanate ($BaTiO_3$) is one of many ferroelectrics with perovskite structure. In the Curie point of barium titanate, its permittivity shows step increase and gradual decrease in the paraelectric phase, Fig. 4.13*a*. As temperature increases, the spontaneous polarization first gradually declines and then abruptly falls to zero at phase transition, Fig. 4.12*c,* but not smoothly as in Fig. 4.10*a*, since in this case phase transition is of the first order. Heat capacity shows typical for ferroelectric phase transition maximum Fig. 4.12*d*.

Paraelectrics and soft lattice made. Above the Curie point, a paraelectric phase is observed in ferroelectrics,, but there are crystals (related to barium titanate), in which they are paraelectrics in entire temperature range. Non-polar ionic crystals with ε ~ 100 (and much above) occupy special place among dielectrics with high permittivity. Typical representatives of such dielectrics are rutile (TiO_2) and perovskite ($CaTiO_3$). It should be noted that these crystals are characterized by increased electronic (optical) polarization: $\varepsilon_{opt} > 5$. Moreover, microwave permittivity of rutile and perovskite is strongly temperature dependent with negative *TC*ε. Paraelectric crystals belong to dielectrics with particular temperature dependence of their permittivity, described by Curie-Weiss law: $\varepsilon(T) = \varepsilon_1 + C/(T - \theta)$, where θ is Curie-Weiss temperature, *C* is Curie-Weiss constant and ε_1 is a part of permittivity practically independent on temperature. This equation is in good agreement with experimental data, Fig. 4.14*a*.

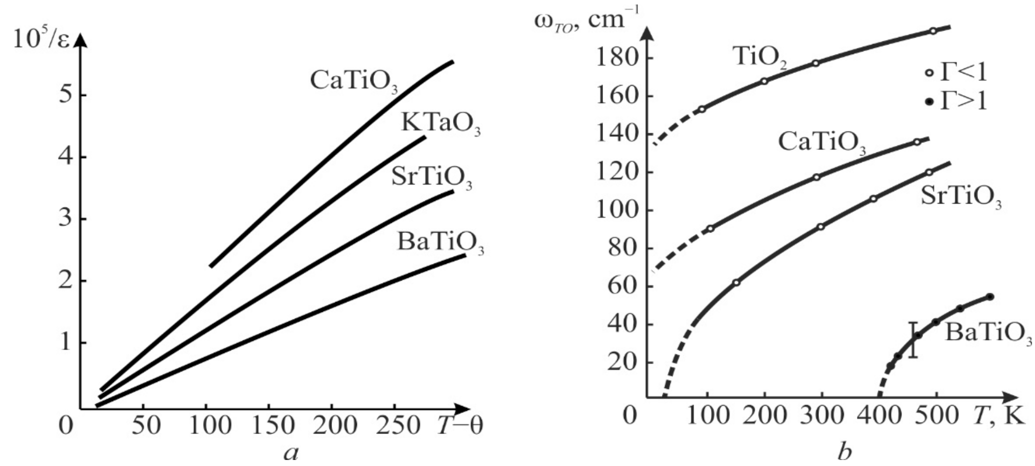


Fig. 4.14. Temperature dependence of inverse permittivity (*a*) and frequency ω_{TO} (*b*) for paraelectrics TiO_2, $CaTiO_3$, $SrTiO_3$ and ferroelectric $BaTiO_3$ (in paraelectric phase); Γ is oscillator damping factor, 1 cm^{-1} = 30 GHz

For example, dependence ε(*T*) in $CaTiO_3$ (perovskite) can be described in broad temperature range, if in above formula one put $\varepsilon_1 = 60$, $C = 4\cdot10^4$ K and $\theta = -90$ K. Calcium titanate can be considered as material *close* to paraelectrics. However, in *typical* paraelectrics, which include, for example, $SrTiO_3$ or $KTaO_3$, the Curie-Weiss temperature is positive ($\theta > 0$ K), whereas $CaTiO_3$ is distinguished by a fact that it has negative characteristic temperature ($\theta < 0$ K). In most of paraelectrics at temperature of $T = T_c \approx \theta$ (that is *critical temperature*) phase transition occurs to ferroelectric (or antiferroelectric) phase. That is why paraelectricity usually is associated with ferroelectricity. Just as the ferroelectrics, the paraelectrics can be divided into two basic classes. The paraelectrics of *displace type* are ionic (not dipole) crystals, in which, however, ionic-covalent bonds between atoms are very significant. They usually show *first-order* phase transition and relatively *flatter* ε(*T*) dependence in their paraelectric phase that characterizes by a *big* Curie-Weiss constant: $C \approx 10^5$ K.

These properties of displace type paraelectrics can be explained by dynamic theory of lattice vibrations. Central point in this theory is the idea that phase transition arises due to crystal lattice losses its stability relatively one of *transverse* optical vibrations. This is reflected in the decrease of frequency ω_{TO} with decreasing temperature, and it is assumed that at temperature $T \rightarrow \theta$ the frequency $\omega_{TO} \rightarrow 0$. The relationship between frequency and temperature is described by Cochran law: $\omega_{TO} = \mathrm{A}((T - \theta)^{1/2}$, where A is temperature coefficient of frequency. This dependence is confirmed by many experiments, Fig. 4.13*b*. Direct connection between the permittivity and temperature dependence of transverse optical lattice mode frequency in paraelectrics i.e., the correlation of $\varepsilon(T)$ and $\omega^2{}_{TO}(T)$ is seen while two parts of Fig. 4.13 comparison. The frequency of transverse optical vibration mode in ionic lattice, which tends to zero when temperature $T \rightarrow \theta$, is the *"soft" vibration mode*. Using Liddeyn-Sachs-Teller relation: $\varepsilon(0)/\varepsilon(\infty) = [\omega_{LO}/\omega_{TO}]^2$, it is possible to show that Cochran law gives rise to Curie-Weiss law: $\varepsilon(T) \approx C/(T - \theta)$. To explain the possibility of frequency ω_{TO} reducing in the perovskites, one needs to use the *polarizable* ion model, in which interaction of electronic shells has significant effect on repulsive force of ions. This interaction can cause a condition, at which the force, conditioned by polarization of ions, reduces, so that allows assume $\omega_{TO}(T) \rightarrow 0$ and, respectively, to $\varepsilon(T) \rightarrow \infty$. In this sense, it might be understood expression "wasting of crystal stability": when small external perturbation (i.e., external electrical field) leads to great response; big polarization and large ε. Table 4.4 summarizes the comparative parameters of the soft modes in paraelectrics and ferroelectrics.

Table 4.4.

Some ferroelectric crystals and their properties

Ferroelectric / parameter	P_S, μC· cm⁻	T_C, K	θ, K	C, 10^{-4}, K	E_g, eV	$A2\pi$, GHz · K^{-12}
$CaTiO_3$:	–	–	–90	4,5	2,2	170
$SrTiO_3$	–	–	35	8,4	3,2	180
$BaTiO_3$	30	400	388	12	3,3	75
$PbTiO_3$	80	780	730	15	3,1	90
$KNbO_3$	30	685	625	18	3,4	95
$LiNbO_3$	70	1500	–	–	3,6	–

The electronic band gap energy W_g is also given in Table 4.4 to characterize the electronic conductivity of given crystals. The coefficient A describes temperature dependence of ferroelectric "soft mode" frequency ω_{TO}, which determines permittivity dispersion in paraelectric phase: $\omega_{TO} = A\sqrt{(T - \theta)}$. It is seen that frequency of transverse optical phonon ω_{TO} would be zero, when crystal at its cooling from paraelectric state reaches temperature θ. However, in the experiment this is not observed due to phase transition occurs *before*: at temperature $T_C > \theta$. However, it should be noted that the difference $T_C - \theta$ usually is little, so frequency ω_{TO} turns out to be very small in comparison with other frequencies of crystal lattice.

Thermodynamic theory based on the Landau's theory supposes that thermodynamic potential of ferroelectric $\Phi(T,P)$ can be represented as a series in powers of ordering parameter P (polarization):

$$\Phi(P) = \Phi_0(T) + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6, \tag{1}$$

where α, β, and γ are coefficients of series. Analyzing this expansion, it is possible to make a conclusion as to *critical dependence* of parameter α on temperature: $\alpha(T) = \alpha_0(T - \theta)$, where α_0 is independent of temperature coefficient. Due to polynomial form of free energy presentation, Landau's theory allows not only quantitatively describe changes of crystal properties near phase transitions, but also predict many physical characteristics. At that, according to Landau's theory, the type of phase transition (PT-I or PT-II) is determined by the *sign* of coefficient β at the fourth degree of ordering parameter. When phase transition PT-II would be considered, second Landau parameter β is positive, so in this case the parameter γ in the polynomial (1) becomes unnecessary and one can put $\gamma = 0$ as well as $\beta = const > 0$.

First-order phase transition (PT-I) is characterized by polynomial (1) with parameters $\beta < 0$, $\alpha = \alpha_0(T - \theta)$ and $\gamma > 0$. In this case, the sustainability of a studied system is provided by next term $\frac{1}{6}\gamma P^6 > 0$ in the expansion, because just this ensures stability of all phases. When these relationships detailed study, some special points for $\Phi(P)$ function and for its derivatives can be found. If instead of the image of the function $E(P)$ the more convenient coordinates $P(E)$ would be used, polar phase existence will be explained by the region of instability, that corresponds to dielectric hysteresis loop like in Fig. 6.1A and Fig. 6.6. Accordingly, the permittivity depends on the field strength. Thus, main characteristics of ferroelectrics in their *polar phase* (hysteresis loop and $\varepsilon(E)$ dependence) do not depend on what type of phase transition undergoes in the Curie point.

To study the polynomial (6.6) describing PT-I, it is necessary to find singular points for both the function Φ(P) and its derivatives:

$$\partial\Phi/\partial P = E = \alpha P + \beta P^3 + \gamma P^5; \tag{2}$$

$$\partial^2\Phi/\partial P^2 = \partial E/\partial P = 1/\chi \approx \varepsilon = \alpha + 3\beta P^2 + 5\gamma P^4; \tag{3}$$

$$\partial^3\Phi/\partial P^3 = \partial^2 E/\partial P^2 = 6\beta P + 20\gamma P^3; \tag{4}$$

$$\partial^4\Phi/\partial P^4 = \partial^3 E/\partial P^3 = 6\beta + 60\gamma P^2 \qquad (5)$$

The first condition for the phase stability $\partial\Phi/\partial P = 0$ leads to equation of fifth degree (2); its roots are equal to:

$$P_1 = 0; P_{2,3,4,5} = \pm\sqrt{\frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\gamma}} \qquad (6)$$

To analyze the second stability condition $\partial^2\Phi/\partial P^2 = 0$, it is necessary to study the conditions for the extrema of equation $E(P) = 0$ which can be found from (4):

$$P_{6,7,8,9} = \pm\sqrt{\frac{-3\beta \pm \sqrt{9\beta^2 - 20\alpha\gamma}}{10\gamma}}\,. \qquad (7)$$

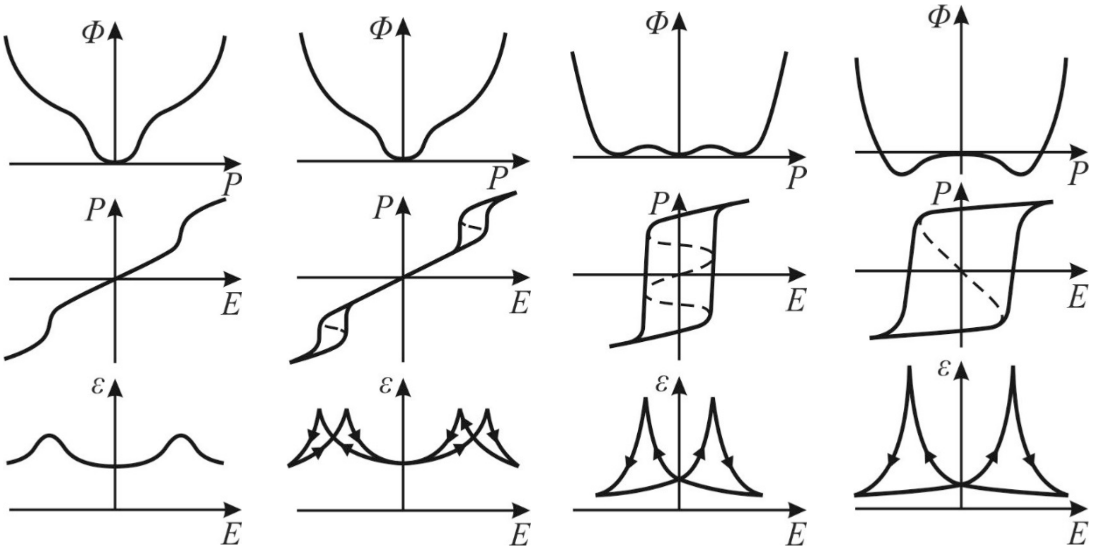
In turn, extrema of dependence $\partial E/\partial P$ are special points of expression (6.9):

$$P_{10} = 0; P_{11,12} = \pm\sqrt{\frac{-3\beta}{10\gamma}}\,. \qquad (8)$$

And finally, from expression (6.10) it is possible to obtain

$$P_{13,14} = \pm\sqrt{\frac{-\beta}{10\gamma}}\,. \qquad (9)$$

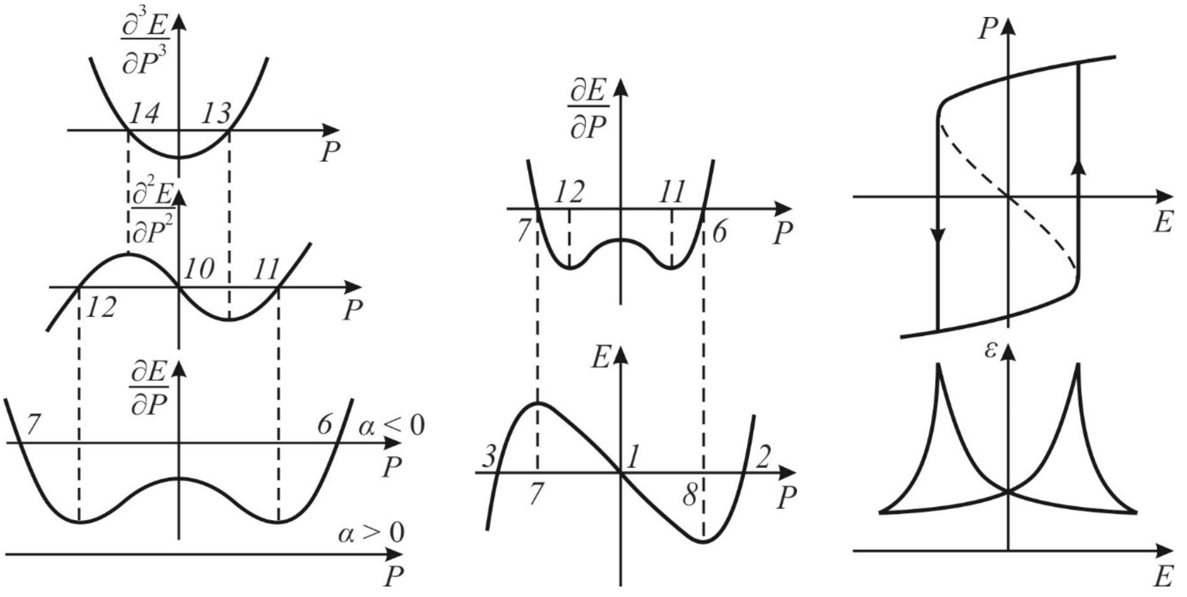
Fourteen special points (extremes, kinks, intersections with axes) characterize many different variants of $\Phi(P)$ dependence, which arise in the vicinity of PT-I when the ratio between coefficients α, β and γ changes. Before further analysis, it is advisable to introduce the ***generalized parameter*** $\varsigma = \alpha\gamma/\beta^2$, which makes it possible to trace how the thermodynamic potential and its derivatives change (depending on the combination of Landau parameters). It should be noted that this investigation might have grate interest for the *nonlinear dielectric spectroscopy*, when exactly the dependence of dynamic permittivity on electrical field is important.



$\varsigma = 0.4$ **$\varsigma = 0.3$** **$\varsigma = 0.2$** **$\varsigma = 0$**

Fig. 4.15. Dependence of $\Phi(P)$ characteristic on generalized parameter $\varsigma = \alpha\gamma/\beta^2$

As seen in Fig. 4.15, just at phase transition point, i.e., at $T = T_C$, the parameter $\varsigma = 0.2$, while at Curie-Weiss temperature $T = \theta$ this parameter is zero ($\varsigma = 0$). In the Fig. 4.15, it is shown how, starting from high-temperature nonpolar (paraelectric) phase (when $\varsigma = 0.4$) when the crystal gradually is cooling to the ferroelectric phase ($\varsigma = 0.2$) the change in $\Phi(P)$ and its derivatives occur, when generalized parameter passes through the values $\varsigma = 0.4, 0.3, 0.2, 0$.



a *b* *c*

Fig. 4.16. Thermodynamic analysis of ferroelectric phase transition of first kind: A, B – derivatives describing phase transition parameters, numbers at intersections correspond to roots of equations (6.8–6.10); C – explanation of dielectric hysteresis and dynamic dielectric permittivity $\varepsilon(E)$

Continuing above analysis, note that all the roots of equations (4) and (5) are valid are determined by formulas (8) and (9) since $\beta < 0$ and $\gamma > 0$. Therefore, equations roots P_{13} and P_{14} determine respectively the minimum and maximum of the function $\partial^2\Phi/\partial P^2$, while the roots of P_{10}, P_{11} and P_{13} determine the maximum and two minimums of $\partial E/\partial P$ function as shown in Fig. 4.16.

Further analysis depends on Landau parameter α temperature changing.

In the ***polar phase*** of PT-I ferroelectric, at *sufficient distance* from the critical point T_C (when $T < \theta$ and $\alpha < 0$), as follows from formula (7), the equation (3) has only two real roots (P_6 and P_7) of the four. In this case, dependence $E(P)$ is characterized by minimum at P_6 and maximum at P_7 and also intersects the P axis at three points: $P_1 = 0$; $P_{2,3,4,5} = \pm [-\beta \pm (\beta^2 - 4\alpha\gamma)^{1/2}/2\gamma]^{1/2}$ (other roots P_4 and P_5 in the expression (6) are imaginary since $\alpha < 0$. Further, presenting the functional dependence $E(P)$ as $P(E)$, obtain a situation with instability region (dotted line in

Fig. 4.16*c*) and the hysteresis loop. Accordingly, dynamic permittivity also changes, but in the *vicinity* of PT-I the variations of polarization $P(E)$ and permittivity $\varepsilon(E)$ are complicated as can be seen from Fig. 4.17. But far from the phase transition, both the hysteresis loop and dynamic permittivity nonlinearity in the PT-I and PT-II ferroelectrics are qualitatively similar.

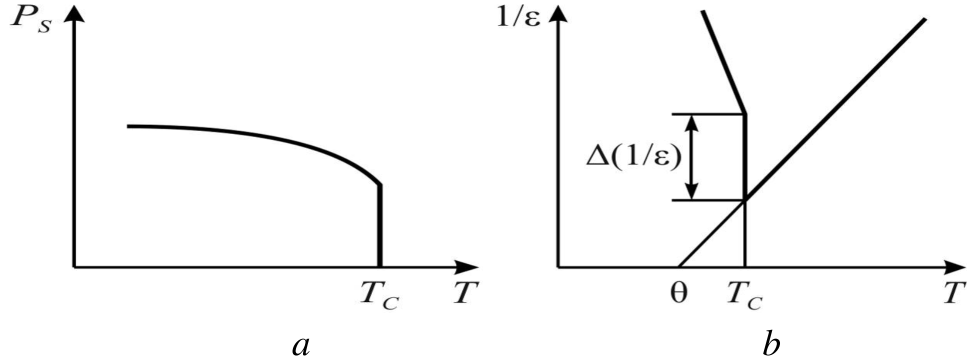


Fig. 4.17. Temperature dependence of spontaneous polarization (*a*) and inverse permittivity (*b*) in PT-I ferroelectrics

Now discuss spontaneous polarization and permittivity temperature dependence, Fig. 4.17. At the phase transition point, the potentials of the polar and nonpolar phases should be the same, i.e. $\Phi(P) = \Phi_0$ at $P = 0$. Therefore, from equation (1) it follows $\alpha + 1/2\beta + 1/3\gamma = 0$. Substituting into this expression the value for P_S obtained from formula (6) while note that the roots $P_{2\text{-}5}$ and the root P_1 are side solutions, we can obtain an equation relating all three parameters $\alpha_C = \frac{3\beta^2}{16\gamma}$, where α_C is first parameter Landau at $T = T_C$. It should be noted that first order phase transition occurs not at temperature $T = \theta$ (when parameter $\alpha(T) = 0$) but at the value α_C That is why, in case of PT-I the transition temperature T_C is *higher* than Curie-Weiss temperature θ. At that, spontaneous polarization arises at $T = T_C$ by a *jump*, and the size of this jump equals $\Delta P_S = \frac{3\beta}{4\gamma}$, Fig. 4.17*a*.

Permittivity also shows a jump at temperature T_C, and its graded change is $\Delta\varepsilon = \frac{4\gamma}{3\beta^2}$; correspondingly, at PT-I is not expected that permittivity becomes infinite (as predicted in case of PT-II) but has a maximum seen at T_C which equals $\frac{16\gamma}{3\beta^2}$ (more detail calculation of all these jumps of ferroelectric parameters is given, for example, in [13]). Most studied ferroelectric which has phase transition nature close to PT-I is barium titanate. The temperature maximum of permittivity in pure $BaTiO_3$ occurs at $T_C = 400$ K, while Curie-Weiss temperature ($\theta = 388$ K) is below on 12 K. Curie-Weiss constant in barium titanate equals C = 1.2·10^5 K and temperature maximum of permittivity is $\varepsilon_{max} = 10^5$.

Polar structures of crystals. Non-centrosymmetric structures are formed owing to the compensation of atomic electronegativity by the polar-sensitive bonding emerging in the process of polar crystal formation (while it is growing from the liquid or steam state of a material). At that, dependently on the chemical composition of a crystal, the variety of combinations may occur between the ions of crystals possessing by two- or three-dimensional polar-active constructions (which, when external actions exerts on them, can produce the electrical responses, describable by the tensors of different ranks). Polar structures of crystals are the demonstration of *mixed ionic-covalent bonds* between their ions.

These bonds are strongly directional and, therefore, such structures lead to the different manifestations of the asymmetry and complexity of polar crystal structures. When electrical field is affected on the "persistantly arranged" polar structure, its electrical polarization usually looks like a linear effect (as in the ordinary dielectrics). However, the exception are the ferroelectrics, in which the *switching* of their “gently arranged" polarization is seen: their low-stable enantiomorphic structure can change its polar-sensitive direction. Outwardly this event manifests itself as dielectric *hysteresis loop*, Fig. 4.1*c*, which allows measure the ability of polar-sensitive structure to react on the external actions and indirectly can characterize its features. An increase in the intensity of thermal motion in the crystal lattice leads to the destruction of polar-sensitive bonds strength in ferroelectrics, while in the pyroelectrics they remain until the crystal melts. An increase in pressure also leads to the destruction of these bonds, Fig. 4.11*c* since the ferroelectricity is accompanied by the increase in crystal volume.

As known, in applied electric field, the ferroelectrics demonstrate reorientation of their polarity-activating bonds with the pronounced nonlinear response: exactly this was served for introducing of spontaneous polarization concept and to name the corresponding group of crystals as ferroelectrics. Shown in Fig. 4.18*a,b* two opposite positions of internal bonds orientation are quite stable, which is confirmed by coercive field E_C measured along hysteresis loop investigation. As known. two-position (*a* and *b*) of stability of polar moment orientation is used for ferroelectric memories devices. The switching of two orientations of polarity-sensitive bonds occurs, if the applied field exceeds the coercive field, Fig. 4.18*c*.

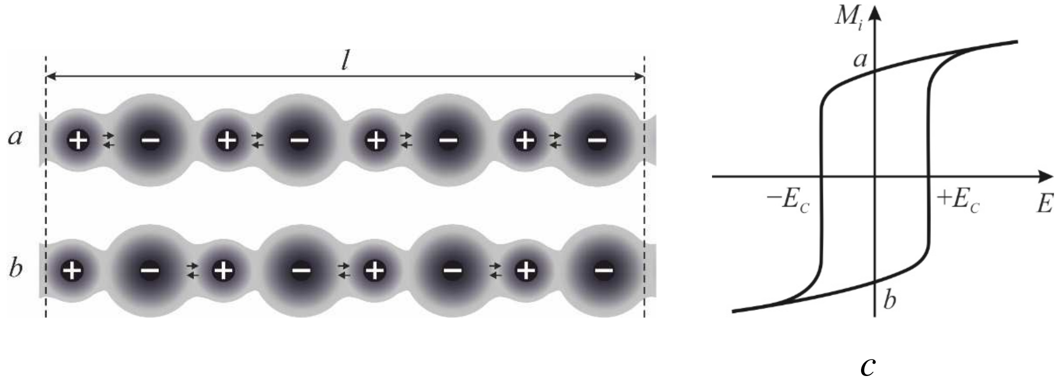


Fig. 4.18. Model description of two opposite orientations of polar bonds in ferroelectric; directions *a* and *b* are indicated on dielectric hysteresis loop

Above modeling makes it possible also to describe also the antiferroelectrics, Fig. 6, which in the strong electric field can be reversibly transformed into the ferroelectric state. Stability of the antipolar state is characterized by value of electric field capable to switch antipolar phase into polar. Notable feature of antiferroelectrics is the decrease in their volume during phase transition from non-polar to antipolar phase (on the contrary, ferroelectrics volume of in their polar state increases). Thus, applied electric field, converting antiferroelectic into ferroelectric, significantly changes the volume of a matter that is used to obtain large electromechanical and electrocaloric effects. In general case, when phase transition is forced by external electric field from paraelectric phase to ferroelectric phase, the jump in volume leads to change crystal temperature (this is clearly seen from relationship $PV = RT$: at constant P the change of V changes T). Usually this electrocaloric effect produces temperature change of 1-2 degrees, and this is not enough to be used in technology. However, electrically controlled jump in volume at antiferroelectric⇔ferroelectric transition at least doubles this temperature jump which is good for applications [9].

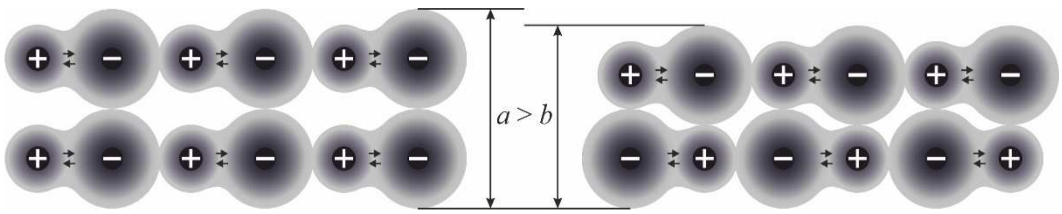


Fig. 4.19. Comparison of polar ordering (*a*) lattice with antipolar ordering (*b*): it is seen that $a > b$

The polarity-activating bonds arrangement explains also a number of other features seen in the polar crystals: the structural proximity of piezoelectrics and pyroelectrics; the chemical anisotropy of polar crystals; the frequency dependence of polar crystals permittivity; the microwave absorption in polar dielectrics; the possibility of electric control by thermal and elastic properties; the heat capacity increase due to fluctuations of polar clusters; the negative thermal expansion coefficient at low temperatures; the reduced thermal conductivity due phonons scattering on to polarity-activating bonds; the effect of polar bonds on electric conductivity; the action of polar bonds on the dielectric losses in microwave dielectrics.

Antiferroelectrics are close to ferroelectrics by their physical nature, structure and chemical composition. However, in the antiferroelectric $P_S = 0$, since spontaneous polarization that occurs during phase transition is totally compensated within a single unit cell. Inasmuch as the energy of antipolar state is not very different from the energy of polar phase, external influence can turn antiferroelectric into the ferroelectric. For example, phase transition from antipolar to polar state can be induced by strong electrical field ($E > E_{cr}$); in this case, the *double hysteresis loop* is observed, Fig. 4.20 *f*.

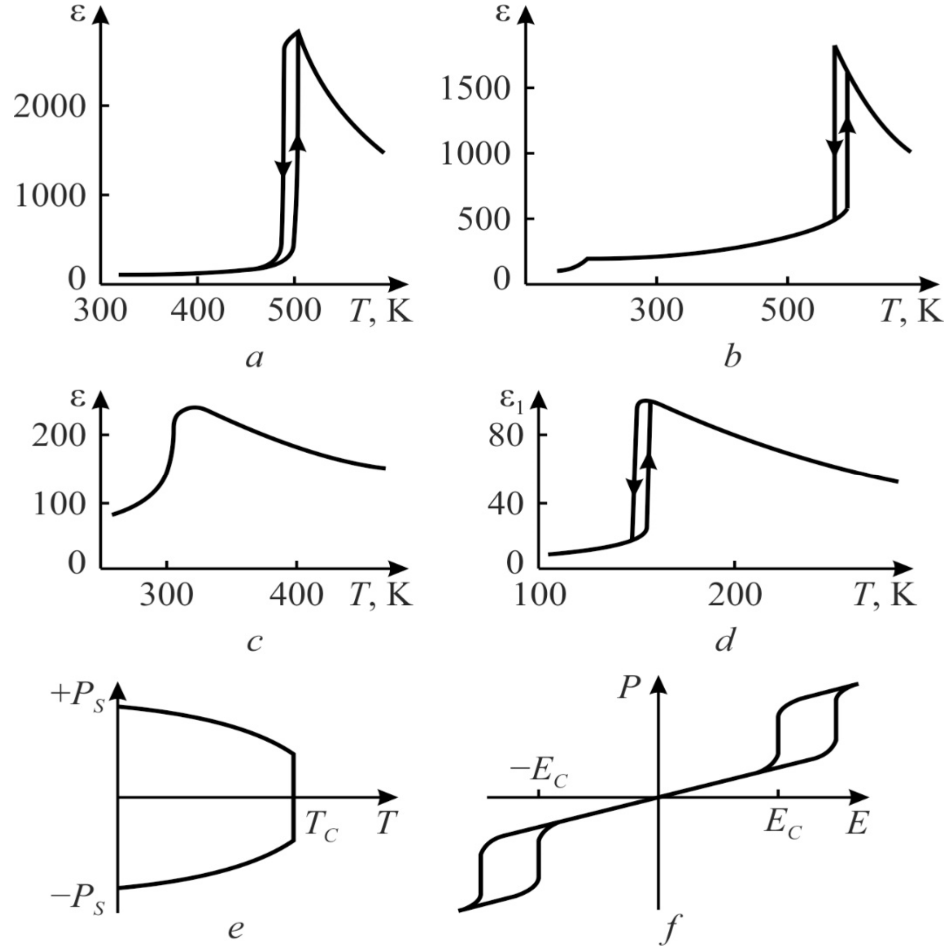
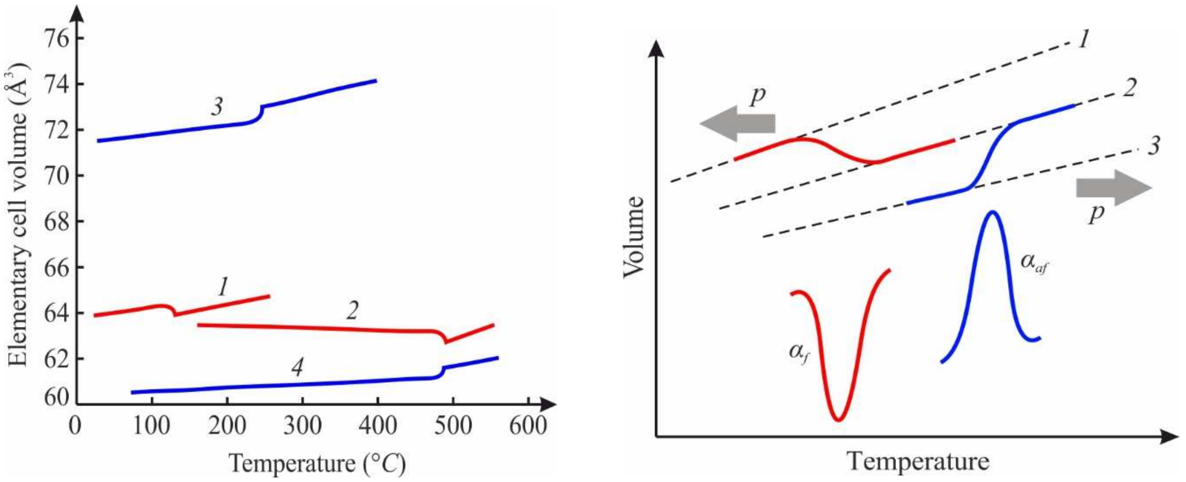


Fig. 4.20. Temperature dependence of permittivity in antiferroelectrics $PbZrO_3$ (*a*), in $NaNbO_3$ (*b*), $PbMgWO_6$ (*c*) and NH_4PO_4 (*d*), as well as spontaneous polarization compensation of in unit cell of antiferroelectric (*e*) and double hysteresis loop (*f*)

Phase transition between antiferroelectric and ferroelectric can occur not only under the influence of electrical field, but sometimes it is a result of temperature change. This situation is observed, for example, in sodium niobate ($NaNbO_3$, Fig. 4.20*b*). Antiferroelectric phase in this crystal exists between temperatures of 630 K and 80 K. Below temperature of 80 K crystal $NaNbO_3$ turns into the ferrielectric phase, when ferroelectric and antiferroelectric states coexist.

However, most often, antiferroelectric phase occurs upon cooling from paraelectric phase, usually with the "multiplication" of crystal unit cell. Therefore, below Curie point the size of antipolar phase unit cell in 2, 4 or 8 times bigger than the unit cell in paraelectric phase. Spontaneous polarization in this case is compensated by the displacement of opposite charges within new enlarged unit cell.



a *b*

Fig. 4.21. Temperature expansion in ferroelectrics: *a* – unite cell volume in ferroelectrics $BaTiO_3$ (*1*) and $PbTiO_3$ (*2*) as well as in antiferroelectrics $PbZrO_3$ (*3*) and $NaNbO_3$ (*4*); *b* – anomalies in volume change $V(T)$ and in □(T) during phase transitions: *2* ⇒ *1* – paraelectric-ferroelectric transition: *2* ⇒ *3* – paraelectric-antiferroelectric transition. Designations: *1* – $V(T)$ dependences for polar phase, *2* – $V(T)$ dependences for non-polar phase, *3* – $V(T)$ dependences for antipolar phase, α_f –thermal expansion minimum at ferroelectric transition, α_{af} – maximum at anti-ferroelectric transition, shaded wide arrows indicate the direction of T_c displacement with pressure *p* increase

As was mentioned, in ferroelectrics the negative thermal expansion coefficient $\alpha(T)$ is characteristic seen in the vicinity of phase transitions T_c, but antiferroelectrics show opposite $\alpha(T)$ anomaly, Fig. 4.21*b*. In ferroelectrics, the volume of lower-temperature ordered phase becomes greater in comparison with the volume of higher-temperature disordered (paraelectric) phase. Upon transition from nonpolar cubic to polar tetragonal structure, ferroelectric $BaTiO_3$ and $PbTiO_3$ crystals elongate along *c*-axis but shorten along two *a*-axes; however, volume of these crystals increases. At that, dynamical structural disordering of internal polarity in $BaTiO_3$ (which have cubic structure as a basic) shows the intensive fluctuations along four axes of [111]-type. The hydrostatic pressure, applied to $BaTiO_3$ below its Curie point (in polar phase), returns this crystal into paraelectric non-polar phase, in which, naturally, configurational entropy is larger. At that, Curie temperature T_c decreases with increase of hydrostatic pressure that occurs with the rate –5 K/kbar; as a result, at room temperature polar phase in $BaTiO_3$ already disappears at pressure of 30 kbar: it is "squeezed out" (in ferroelectric $PbTiO_3$ the rate of T_c decrease with pressure is –8 K/kbar).

Figure 4.21*b* explains symbolically these processes, which are fully consistent with the concept of configurational entropy. Naturally, that volume increase in the polar phase during ferroelectric transition is accompanied by the minimum of thermal expansion coefficient, Fig. 4.21*b*. On the contrary, in case of antiferroelectrics, the volume of antipolar phase at temperature at T_c decreases; correspondingly, in phase transition, parameter $\alpha(T)$ demonstrates maximum. The density of antiferroelectric not decreases (as in the case of polar crystals) but it increases, so the entropy in antipolar phase decreases also. Accordingly, hydrostatic pressure shifts the T_c to the high-temperature region: for antiferroelectric $PbZrO_3$ with the rate of +4.5 K/kbar.

Thus, in antiferroelectrics, owing to unit cell "multiplication" in comparison with original (non-polar) phase, the polar shifts of ions during phase transition are compensated at the elementary level, so total spontaneous polarization is absent ($P_S = 0$). In this connection it is necessary to note, that in at phase transition from paraelectric to ferroelectric state multiplication of elementary unit cell usually is not observed: each unit cell below Curie point becomes polarized in a same way, and this effect is summarized in crystal, forming $P_S > 0$. This means that in antiferroelectrics the critical reduction in the frequency of vibrational soft mode occurs not in the center of Brillouin zone (as in ferroelectrics) but on the boundary of Brillouin zone, and, therefore, the size of antiferroelectrics Brillouin zone decreases as a result of crystal symmetry lowering below phase transition.

Ferrielectrics are crystals, in which spontaneous polarization P_S is compensated only partially – by analogy with ferrimagnetics that are characterized by partial compensation of their spontaneous magnetization. Therefore, ferr*i*electric is not entirely compensated antiferroelectric. To ferr*i*electrics sodium niobate ($NaNbO_3$ below 80 K), tungsten oxide WO_3, $PbCd_{1/2}W_{1/2}O_3$ and some other isostructural compounds are related.

The structural diversity of perovskite oxides opens up wide possibilities for studying and applying the functions of ferroelectrics and multiferroics. Competition between different order parameters leads to a wide variety of phases and induces enhanced responses to external influences such as mechanical stress, magnetic and electric fields. The control of electronic and lattice degrees of freedom can give the desired properties and provide access to emerging physical phenomena.

Since the functions of polar materials are determined primarily by their polarization response to external stimuli, most research has focused on controlling polar lattice distortions. In some perovskite oxides, the polar distortions coexist with non-polar tilts and rotations of oxygen octahedra. The interaction between non-polar and polar instabilities raises the question of how to create materials using their bond. Ferroelectrics are essentially degenerate antiferroelectrics exhibiting ferroelectric properties. Capacitors with such a dielectric have a threshold switching field similar to ferrites. These materials open up a wide field of new applications, for example, in devices that operate similarly to a transfluxor and represent an electrically controlled circuit impedance. Controlling the transfer of polarization through two or more ferroelectric sections connected in series is a new basic means for storing and gating electrical signals and, in general, a means for controlling the impedance of a circuit in any predetermined manner. With the help of control signal, such capacitor can be converted from a ferroelectric capacitor to a linear capacitor and can take on any intermediate level of polarization between these two limits; in addition, it is able to control the flow of AC power according to its settings. In such devices, both switching and holding properties are present, as well as a threshold switching field. Research into ferroelectric storage media has led to the discovery of a class of ferroelectric materials that require a minimum threshold field to switch. This property has not yet been observed in conventional ferroelectrics and is comparable to similar properties found in ferrite cores. Therefore, ferrielectricity can find applications in computer logic devices.

4.4 0utlines of ferroelasticity

The ferroelastics are crystals that in their structural properties are close to the ferroelectrics. Phase transitions in them are accompanied by critical changes in the *elastic constants* of these crystals. Thus, at temperature below critical T_C, the *spontaneously deformed state* arises, just as spontaneous magnetization arises in the ferromagnetic or spontaneous polarization occurs in the ferroelectric. By analogy with ferroelectrics, these materials are called the *ferroelastics*.

In the ferroelastic phase transition from one direction of spontaneous deformation into another direction can be realized by external *mechanical stress* applying. As ferroelectric, so ferroelastic below temperature T_C are divided into mechanical domains, where spontaneous strain has different direction. Like analogues process of ferroelectric domains orientation (under electrical field influence), the uniform mechanical stress can make a single-domain ferroelastic.

Thus, ferroelastic is spontaneously deformed crystals which deformation can be reoriented by the external mechanical influences.

If the sign of strain X is changed, the sign of spontaneous deformation x_S also changes. Mechanical rigidity of ordinary crystals is large enough, so that their deformation is very small and *linearly* depends on mechanical stress (according to Hooke's law, Fig. 9.32, *a*). Conversely, the mechanical stiffness of ferroelastic *in one peculiar direction* of crystal is small, and, therefore, deformation increases sharply in case of increasing correspondent stress X, Fig. 9.32, *b*). However, after certain coercive force X_C attainment, the stiffness increases again, and a hysteresis characteristic is observed with the nonlinear saturation of $x(X)$ characteristics.

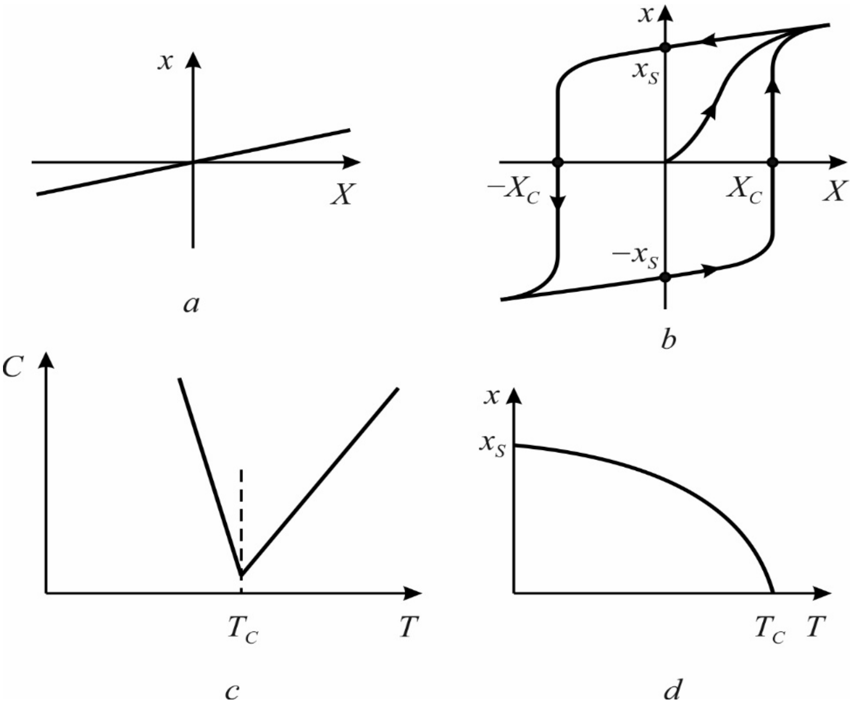


Fig. 4.22. Key features of ferroelastics: *a* – linear dependence of $x(X)$ in ordinary crystals; *b* – mechanical hysteresis in ferroelastic; *c* – temperature dependence of critical component of elastic stiffness in vicinity of phase transition; *d* – spontaneous strain temperature dependence

After external stress removing, unlike conventional crystals, immediate restoration of un-deformed state does not observe in the ferroelactics: for some time, they can save their spontaneous deformation $+x_S$. In order to change strain direction (from $+x_S$ till $–x_S$), it is necessary apply to a crystal the opposite sign mechanical force that exceeds coercive strain X_C. Therefore, ferroelastic long time can exist in one of the two spontaneously deformed states: in the state of tension ($+x_S$) or in the state of compression ($-x_S$). Over time, however, the ferroelastic domains arises, and total (macroscopic) spontaneous deformation gradually relaxes to average value of $x = 0$, approaching to original (zero) point of mechanical hysteresis, Fig. 4.23 *b*.

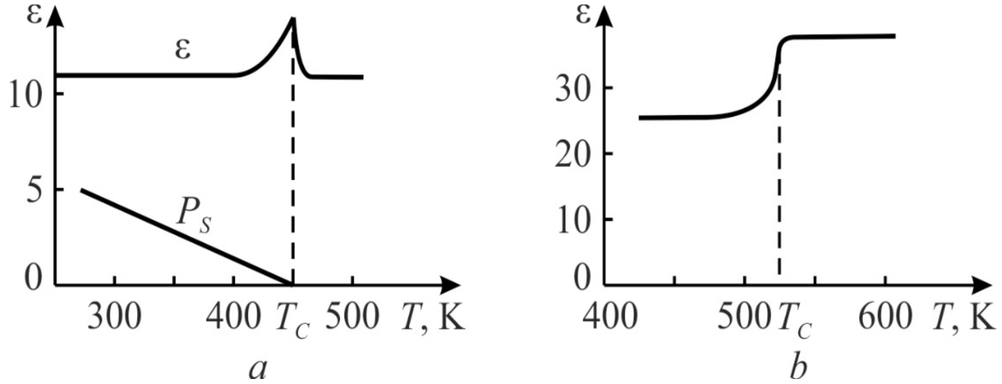


Fig. 4.23. Temperature dependence of permittivity and spontaneous polarization in gadolinium molybdate (*a*); ε(*T*) dependence for lead orthophosphate (*b*)

The *ordering parameter* of the ferroelastic phase transition is one of components of crystal mechanical deformation. Therefore, the ferroelastics in the vicinity of phase transition may not have either dielectric or magnetic anomalies. However, due to the symmetry change at phase transition, particularly, because of appearance (or change) of piezoelectric effect, small anomaly in the permittivity in vicinity of ferroelastic phase transitions can be observed, Fig. 333*b*. For example, such change in ε takes place in the ferroelastic lead orthophosphate ($Pb_3(PO_4)_2$).

In ferroelastic gadolinium molybdate ($Gd_2(MoO_4)_3$, sometimes used in optoelectronis, main parameter of phase transition is mechanical deformation, but as a consequence of ferroelastic transition the spontaneous polarization also arises, Fig. 4.23*a*. It is interesting to note that unlike conventional ferroelectric crystal in this case spontaneous polarization P_S increases while cooling not accordingly to Landau dependence $P_S \sim (T_C - T)^{1/2}$ (as in ferroelectric or ferromagnetic) but linearly: $P_S \sim (T_C - T)$.

Ferroelectric phase, that arises in this case as "by-effect" of ferroelastic transition, is the ***improper ferroelectric***. In case of improper ferroelectric transition the ordering parameter is not vector quantity (polarization) as well as it is not the tensor physical quantity (component of deformation) but it is the *mixed* parameter. Thus, the improper ferroelectric $Gd_2(MoO_4)_3$ is the ferroelastic and the ferroelectric simultaneously. Small peak in permittivity near phase transition (Fig. 4.23*b*) is observed in this crystal only at low frequencies, when crystal is free to deform in electrical field – as electromechanical contribution to permittivity ε_{EM} from the piezoelectric effect. In microwave frequency range, where piezo-deformation in crystal has no time to occur, the dependence ε(*T*) for $Gd_2(MoO_4)_3$ has no significant anomalies near its phase transition.

In the ferroelastic spontaneous deformation changes with temperature according to law: $x_S \sim (T_к - T)^{1/2}$, Fig. 4.22*d*. Therefore, strain component x_S in the ordered phase of ferroelastics changes by similar law as spontaneous magnetization M_S in ferromagnetics or ferroelectric spontaneous polarization P_S.

Main parameter that is critically changed at the Curie point (similar to the permittivity of ferroelectric or magnetic permeability of ferromagnetic) in case of ferroelastic is a component of elastic compliance tensor s_{ijkl} that causes spontaneous deformation in crystal at temperature below T_C. Temperature dependence of elastic stiffness tensor critical component c_{ijkl} (inverse to elastic compliance s_{ijkl}) is shown in Fig. 4.22*c* for one of ferroelastics. As the 1/ε of ferroelectrics or the 1/μ of ferromagnetic, this option (1/*s*) of ferroelastics at Curie point tends to zero.

Critical reduction of elastic stiffness components in the *paraelastic* phase determines the reduction of sound velocity (υ_{sound}) in a certain directions of crystal. In some cases, in the vicinity of ferroelastic phase transition sound velocity reduces down to 300...400 m/s (in this connection, it is appropriate to remind that in the ordinary crystals $\upsilon_{sound} \sim$ 4000 m/s while in water $\upsilon_{sound} =$ 1500 m/s). After transition from paraelastic into ferroelastic phase the velocity of sound rises again, but still remains much lower than in most of dielectric crystals. All this shows that peculiar mechanical properties of ferroelastics are caused by the soft mode in the *acoustic* lattice vibrations, which frequency is critically reduced in the vicinity of phase transition – as well as in ferroelectrics spontaneous polarization is a result of decrease in the frequency of transverse *optical* lattice vibrations mode.

Ferroelastic transitions can be both the second and the first order. In ferroelastic lead orthophosphate ($Pb_3(PO_4)_2$) phase transition of first-order type (PT-1) takes place at 450 K with a jump in deformation. However, in another ferroelastic $BiVO_4$ its transition at 530 K is the second-order transition (PT-2). As mentioned above, below transition temperature in the ferroelastic additional ferroelectric phase can arise. Thus, ferroelastics have the property of spontaneous deformation of the crystal lattice below the phase transition temperature from a more symmetrical paraelastic phase. phase into a ferroelastic phase. As a result of such a transition, ferroelastic domains appear in the crystal, which differ in the orientation of the crystal lattice. But, since the location of the domains is determined by the initial symmetry of the crystal, the symmetry in the crystal is generally preserved. Under the influence of an external mechanical stress, the domains can change their orientational state, which determines the nonlinear character of the dependence of the deformation on the mechanical stress. It becomes like a hysteresis loop. Thus, ferroelastics are mechanical analogues of ferroelectrics and ferromagnets.

The low velocity of sound indicates significant sensitivity of ferroelastic to external influences. That is why they can be used in the optics as *light deflectors,* designed for spatial scanning of light beam. Elastic waves can be excited crystal using a piezoelectric (usually in frequency range of 30 - 300 MHz), and they form a kind of *optical diffraction grating,* whose pitch depends on the frequency of controlling electrical field. By varying the frequency of ultrasound, it is possible to control the angle of light beam deflection passing through crystal. Besides deflectors, ferroelastics and paraelastics can be applied as sensors of pressure and strain, as well as in other measuring devices.

4.5 Magnetoelectric effects

Theoretically, the symmetry does not forbid the simultaneous coexistence of magnetic (spin) and electric (dipole) ordering in crystals, as pointed out by Landau and Lifshitz (1959), and soon confirmed experimentally. Currently, materials with a coexistence of magnetic and ferroelectric ordering – multiferroics – provide an efficient route for the control of magnetism by electric field. In recent years, key discoveries in theory, synthesis and characterization techniques have led to a new surge of interest in these materials. Different mechanisms, such as lone-pair, geometric, charge-ordering and spin-driven effects can support multiferroicity.

However, fundamental physical mechanisms of ferromagnetic and ferroelectric phenomena might bee seen as essentially different.

Difference in the mechanisms of ferromagnetism and ferroelectricity. As known, in the externally applied electric field, the electric polarization occurs in any dielectric, but only polar (non-centrosymmetric) dielectrics can be polarized in the non-electric way. Moreover, to explain this phenomenon, it is considered that the term "spontaneous polarization" (P_S) should be used, similarly to the ferromagnet spontaneous magnetization. The basis for this term was discovery of dielectric hysteresis in the Rochelle salt crystal about 100 years ago as an analogue of magnetic hysteresis. Exactly the similarity of these phenomena and due to the possibility of spontaneous polarization magnitude measuring from hysteresis loop substantiate this concept application to the ferroelectrics (which as ferromagnetic now referred to as so-called ***ferroics***) .

However, later the concept of "spontaneous polarization" was unreasonably applied to the pyroelectrics (which formally resembles the permanent magnets), but in pyroelectrics spontaneous polarization cannot be directly measured. Nevertheless, the ferroelectrics are undoubtedly a subclass of pyroelectrics, and their structures are united by *sole polar axis* presence in their structure. In addition, the big family of polar (non-centrosymmetric) crystals include the piezoelectrics, which in many aspects have noticeable closeness to pyroelectrics, so sometimes even the mutual transformation between them becomes possible, such as mixed wurtzite ⇔ sphalerite structures in the zinc blende.

It should be noted that at first sight and on basis of established ideas the similarity between ferroelectricity and ferromagnetism is purely external, and the only based on this similarity (due to hysteresis loop) they can be conditionally combined with the term "*ferroic"*.

Firstly, the magnetic charges do not exist in nature, so that in the absence of external influences the spontaneous magnetization can exist in equilibrium state for arbitrarily long time. On the contrary, spontaneous polarization, sooner or later, should be screened by the ubiquitous free electric charges, and in the equilibrium state P_s does not show up electrically. It is this circumstance that underlies a fundamental difference between these phenomena (although researchers are trying to unite them in the mulferoics (remind that crystallography not prohibit their joint existence).

Secondly, the magnetic field H and magnetic induction B (created by closed microscopic or macroscopic electric currents) are the axial vectors. In contrast, the electric field E and polarization P are the polar vectors, created by existing in nature electric charges. The electric field E is the gradient of electric potential, which starts and ends on electric charges. The macroscopic electric polarization P is Induced by electric field, and, in accordance with Lorentz relation ($E = \beta P$), any polarization should be accompanied by macroscopic electric field E, which necessarily sets in motion free electric charges.

Thirdly, attributed to the ferroelectrics spontaneous polarization (only on the basis of hysteresis loop) was applied to pyroelectrics unfoundedly, because ferroelectrics is only a subclass of pyroelectrics. If it would be true, pyroelectric will look like electric analogue of permanent magnet (which is surrounded by magnetic field). However, in the equilibrium state (when any external influence is absent), as pyroelectric so ferroelectric are not surrounded by the external electric field. This can only be explained for ferroelectrics, which are divided into domains. However, the absence of ambient field around pyroelectric would be explained by free charges screening, then this means that in equilibrium state no macroscopic polarization will be seen. In this regard, one can remember about the electrets, which really generate external electric field (consistent with their internal field) for considerable time. However, there is fundamental difference between pyroelectrics and electrets: the pyroelectric is capable to create polarization under non-electric action, being itself in the equilibrium state, which is naturally acquired during crystal formation from the liquid or gaseous phase, and disappearing only when the pyroelectric melts. At that, the pyroelectric effect can occur in the polar crystal infinite number of times. On the contrary, the *residual* polarization of electrets is established artificially by special technology: as a result, their polarized state is non-equilibrium and temporary: if electrets are exposed to heat, the depolarization current is generated by it only once, and electrets cease to be polarized. With a good reason, it can be assumed that ferroelectrics are special case of pyroelectrics, having, in contrast to them, the reversibility of in the direction of activating their polarity bonds. It can be considered that the ferroelectrics are such subclass of pyroelectrics, which break down into domains.

The fact is that when electric measurements of polar structure parameters (voltage or current), it is necessary to obtain the vector type response from a scalar action, as for example in the case of uniformly heating pyroelectric. However, in the polar-neutral piezoelectric, such a response, which allows one to measure its polarity, is possible only if its thermal deformation is partially limited by rigidly fastening polar cut of this crystal on the non-deformable substrate. This method of thermo-piezo-polarization is used to obtain an artificial pyroelectric effect, and a similar method is also possible to obtain the volumetric piezoelectric effect in the polar-neutral crystals such as quartz. It is assumed that in the polar and polar-neutral crystals, a peculiar arrangement of inter-atomic bonds exists, which drive in them the electric response onto the non-electric actions. It was shown that the mixed covalent-ionic (polarity-sensitive) bonds, which form polar or polar-neutral crystal, are the consequence of structural compensation of nearest ions electronic structure dissimilarity, giving the opposite contribution to electronegativity. It is this feature, that causes in polar crystals many electric, mechanical, thermal and optical properties, which are quite different from ordinary dielectrics.

Magnetoelectric interaction existence in some crystals is currently not only in doubt, but also is used in electronics. Although the magnetoelectric materials are not necessarily themultiferroics, all multiferroics (combining ferromagnetic ferroelectric properties) are the magnetoelectrics, that is, applied electric field causes a change in the magnetization proportionally to its magnitude.

Before discussing actually the multiferroics, it is necessary to consider other magnetoelectric phenomena and materials, in which electric field changes magnetic properties, and vice versa:

- Electric polarization, associated with magnetic inhomogeneities, and micromagnetic structures, such as domain walls, vertical Bloch lines, and magnetic vortices.
- The effects of electric field influence on the magnetic domain structure was observed in the ferrite garnets films, namely, the displacement of magnetic domain walls is seen, controlled by electric field, as well as the slope of domain wall plane.
- In rare-earth ferroborates, at their spin-reorientation phase transitions, the anomalies were observed in dependences of electric polarization in this class of compounds.
- Magnetic phase transitions and magnetoelectric effects can be due to the spatially modulated spin structures, for example, in the $BiFeO_3$ (bismuth ferrite), which, due to wide variety of magnetoelectric effects, is very convenient as the model object for theoretical studies.
- Bismuth ferrite is also of practical interest as basis for such magnetoelectric materials creating, which are associated with high temperatures of electrical (T_C = 1080 K) and magnetic (T_N = 640 K) orderings. A remarkable property of bismuth ferrite is the spin cycloid, generating spontaneous electric polarization due to the flexo-magnetoelectric effect.

Connection possibilities for ferroelectricity and magnetism. As already noted, the ferroelectric is characterized by the spontaneous electric polarization, which can be switched by applied electric field. As a rule, such polarization arises together with the *structural distortion*, which breaks in material the symmetry inversion upon phase transition from initial centrosymmetric phase. For example, barium titanate, $BaTiO_3$ in its initial phase has perfect cubic perovskite ABO_3 structure with Ti^{4+} ion in the B position in the center of oxygen coordination octahedron, and has no electrical polarization. But in the ferroelectric phase, Ti^{4+} ion is displaced from the center of octahedron, causing polarization. This is because the B cation has empty *d*-shell electronic configuration (so-called d^0 configuration), which actually promotes the formation of covalent bond. So exactly *B-site cation* can be called as "ferroelectrically active".

It is very important to note that it is the d^0 configuration which prevents the formation of multiferroics, since the magnetism arises precisely due to *partially filled d*-shells of transition metals. Therefore, it is not surprising that in the multiferroics a quite different physical nature of ferroelectricity should be used.

Thus, other mechanisms are required to circumvent indicated opposition between ferromagnetism and ferroelectricity.

It might enumerate such physical mechanisms;

Lone-pair multiferroics use the ferroelectric displacement which is due to the A-*site cation* (in this case, just it is "ferroelectrically active"). In this case. the magnetism is due to the partially filled *d*-shell at the B-*site* ("ferromagnetic active" iob). Examples include the bismuth ferrite, $BiFeO_3$, as well as the $BiMnO_3$ and $PbVO_3$. In these materials, the A-site cation (Bi^{3+} or Pb^{2+}) has so-called stereochemically *active lone pair* of $6s^2$-electrons, and corresponding shift of A-site cation is facilitated by energy-reducing distribution of electrons between formally empty $6p$-orbitals of A-site and filled O $2p$-orbitals.

"Geometric" ferroelectricity refers to such a situation, in which the driving force of structural phase transition to polar phase is not usual formation of ion-covalent polar bond, but the rotational distortion of polyhedra. In the perovskites, such distortions occur, when the A-cation is small; as a result, located around it oxygen octahedrons change their rectangular formation, so that one octahedron rotates to the right while neighbor rotates to the left. At that, in the layered materials, such rotations can lead to *common polarization*. Such "geometric" ferroelectrics include layered barium—transition metal fluorides, $BaMF_4$, where M is: Mn, Fe, Co, Ni, Zn, which have ferroelectric transition at large temperature (of about 1000 K) and the magnetic transition usually to antiferromagnetic state at low temperature (of about 50 K). Since the structural distortion is not caused by the hybridization between *d*-site cation and anions, then it is compatible with the existence of magnetism in the B-site, allowing for multiferroic behavior. Another example is the hexagonal rare-earth manganites of general formula $RMnO_3$, where R = Ho, Lu or Y. These manganites undergo phase transition at temperature of about 1300 K, which consists in the tilt of the MnO_5 bipyramids. This slope is due to polar corrugation of R-ion layers, which gives the spontaneous polarization. Such ferroelectrics are called *improper*, since the ordering parameter does not have polar character. In this case, the multiferroic phase occurs due to triangular antiferromagnetic ordering (usually below 100 K).

Rare-earth multiferroics have quite different type of magnetism, in contrast to most of magnetoelectric compositions, which have usual magnetism of transition metal *d*-electrons, but show special mechanism of ferroelectricity. It turns out that the ordinary ferroelectric can be combined to introduce another type of magnetism, namely, the use of a rare earth ion with a partially filled *f*-shell at the position A. An example is $EuTiO_3$, which, although not ferroelectric at ambient conditions, becomes it at small voltage or by expanding its lattice constant, for example, by replacing some of Eu by the Ba in the A positions.

Multiferroic due to charge self-ordering is observed in the compounds, containing magnetic ions of *mixed valence*. At high synthesis temperature, the valence electrons of a material are, naturally, delocalized, and materil conductivity is high. But as temperature decreases, the electrons become localized onto different cationic positions and in orderly manner, so that the material becomes dielectric. In the event, when the structure of localized electrons, appeared during cooling of a magnet, turns out to be *polar*, then a kind of the charge-ordered ferroelectricity arises. In this case, cations are magnetic, and, therefore, ferroelectric state, of course, is the multiferroic. An example of such a material with ordered charge is $LuFe_2O_4$, in which the Fe^{2+} and Fe^{3+} ions are located in such a way that they lead to polar ordering of charges below temperature of 330 K. With further decrease in temperature below 240 K, the ferromagnetic spin-orbital ordering also arises. It is also assumed the existence of similar charge-ordered polarity in the magnetite Fe_3O_4 and in the magnetic compound $(Pr,Ca)MnO_3$.

Flexoelectric effect in solid dielectrics arises during bending due to gradient of mechanical deformation. In the magnetically ordered media, the flexoelectric effect is due to appearance of *spin cycloid*. In this case, in media without a center of symmetry and without a preferred polar direction, the magnetic ordering can also generate electric polarization. This manifests itself in ferroelectric anomalies, which are observed in various spontaneous and magnetically induced spin-reorientation phase transitions that occur in the rare-earth magnetics.

Dynamic multiferroic effect, namely the fast cross-control between electric and magnetic dipoles in a solid, is introduced by the dynamics of multiferroic domain walls. Related to this problem is also the electric dipole-active magnetic resonance, called as electromagnon.

Composite multiferroicы. Obtaining high magnetization and spontaneous polarization with a strong coupling between them at *room temperature* is a difficult task. Therefore, to achieve need multiferroicity, researchers are increasingly turning to the composites, which combine magnetic materials with ferroelectric materials. For example, thin magnetic films are deposited on the ferroelectric substrates or even the multilayer structures are created, including the layer-by-layer growth of atomic-scale multiferroic consisting of separate layers of ferroelectric and magnet (for example, the antiferromagnetic $LuFeO_3$, alternating in superlattice with ferrimagnetic but nonpolar $LuFe_2O_4$). Another possibility for creating a composite is the core-shell ceramics, in which the magnetoelectric composite is formed in situ during synthesis. In such systems, very strong magnetoelectric coupling can already be achieved on a microscopic scale, and the switching of magnetization by means of electric field has been observed. The point is that the magnetoactive grains are surrounded by the ferroelectric shell. The strong magnetoelectric coupling is due to the magnetic exchange interaction in core-shell interfaces, which leads to increased operating temperature.

4.6 Different types of multiferroics

In theory, it is need to explain the coexistence of ferroelectricity coupled with magnetic ordering. Recall that conventional ferroelectricity is accompanied by the *distortions of the lattice* of ions carrying different charges; in this case, below phase transition structural deformation leads to a violation of *spatial inversion symmetry*. But the mechanisms of a second type exists, which are caused by *electronic degrees of freedom,* and, except *time inversion*, during the phase transition break also spatial symmetry of electronic state even in centrosymmetric structures. The difficulty lies in the fact that both mechanisms can exist simultaneously, so that the signs of symmetry reduction of both ionic and electronic mechanisms of ferroelectricity are found in the same multiferroic. In the improper ferroelectrics, the spontaneous polarization is the by-product of another structural (or electronic) primary phase transition, unlike the proper (intrinsic) ferroelectrics. where symmetry lowering can be explained by the polar distortions.

In type I multiferroics, the proper ferroelectricity and usual magnetism arise through different physical mechanisms, and, therefore, they arise at *different* temperatures. The independent occurrence of ferroelectricity and magnetism means that these two properties can exist independently on each other. Such multiferroics exhibit the *linear* magnetoelectric effect. It should be noted that spontaneous electrical ordering (ferroelectricity) usually appears at higher temperature, while the magnetic ordering (usually antiferromagnetic) is established at lower temperature. For example, in bismuth ferrite $BiFeO_3$, the ferroelectric Curie point is $T_C = 1100$ K, and the antimagnetic Neel point is $T_N = 640$ K. The yttrium manganite, $YMnO_3$ ($T_C = 914$ K, $T_N = 76$ K) belongs to same type of multiferroics, but in it the nature of ferroelectricity refers to "improper", since it is secondary effect arising from another (primary) structural distortion.

Type II multiferroics are characterized by simultaneous appearance of magnetic and electrical ordering. It is assumed that the leading interaction is the magnetic one, and it is it that breaks the inversion symmetry thereby creating ferroelectricity. Naturally, the ordering temperatures for both phenomena *coincide*. A typical example is $TbMnO_3$, in which magnetic spin helix, which is accompanied by the ferroelectric polarization, appears at 28 K. It is important that both effects in the type II multiferroics are *strongly coupled*, since they are generated by same phase transition.

Table 4.4.

Different multiferroics, designations T_C - Curie temperature, T_N - Neel temperature

Critical temperature			
Material	**Ferroelectric T_C [K]**	**magnetic T_N or T_C [K]**	**Type of ferroelectricity**
$BiFeO_3$	1100	653	lone pair
h-$YMnO_3$	920	80	geometric (improper)
$BaNiF_4$			geometric (proper)
$PbVO_3$			lone pair
$BiMnO_3$			lone pair
$LuFe_2O_4$			charge ordered
$HoMn_2O_5$	39		magnetically driven
h-$HoMnO_3$	873	76	geometric (improper)
h-$ScMnO_3$		129	geometric (improper)
h-$ErMnO_3$	833	80	geometric (improper)
h-$TmMnO_3$	>573	86	geometric (improper)
h-$YbMnO_3$	993	87	geometric (improper)
h-$LuMnO_3$	>750	96	geometric (improper)
K_2SeO_4			geometric
Cs_2Cd_{I4}			geometric
$TbMnO_3$	27	42	magnetically driven
$Ni_3V_2O_8$	6.5		
$MnWO_4$	13.5		magnetically driven
CuO	230	230	magnetically driven
$ZnCr_2Se_4$	110	20	
$LiCu_2O_2$			
$Ni_3B_7O_{13}$			

Ferroelectricity here is "improper" and manifests itself with rather small spontaneous polarization. An inverse effect has also been reported in the Mott charge-transfer dielectric, where the charge ordering phase transition to the polar ferroelectric case leads to the magnetic ordering, again creating a close relationship between the ferroelectric and, in this case, antiferromagnetic ordering.

Symmetry breaking is always associated with formation of ferroic ordering. When electric dipole moment arises in the ferroelectrics, the inversions break the *spatial symmetry*. When ferromagnetic emerges from paramagnet, the *time symmetry* is broken (i.e. time reversal is broken). Symmetry breaking is usually described by the ordering parameter (in the first case, by polarization *P,* and in the second case, by magnetization *M*). However, in many real cases, a lot of equivalent ground states can arise, which can be chosen by appropriate conjugate field; electric or magnetic for ferroelectrics or ferromagnets, respectively. Ferroics are often characterized by the behavior of different ordering parameters upon inversion of space and time. The spatial inversion operation reverses the direction of polarization (therefore, polarization phenomenon is antisymmetric with respect to spatial inversion), leaving magnetization unchanged. As a result, the *nonpolar* ferromagnetics and ferroelastics are invariant under the spatial inversion, while the polar ferroelectrics are not. On the other hand, time reversal operation changes sign of *M* (which is, therefore, the antisymmetric with respect to time reversal), while the sign of *P* remains unchanged. Therefore, non-magnetic ferroelastics and ferroelectrics are invariant under time reversal, while the ferromagnetics are not.

The multiferroics are both space-inversion and time-reversal anti-symmetric, since they are both ferromagnetic and ferroelectric. The combination of symmetry breaking in the multiferroics can lead to a coupling between the ordering parameters, so that one property of ferroic can be controlled with the conjugate field of another. The ferroelastic *ferroelectrics*, for example, are piezoelectric, meaning that the electric field can cause the change in shape, or the pressure can induce the voltage. The ferroelastic *ferromagnets* exhibit similar piezomagnetic behavior. Particularly attractive for potential technologies is the control of magnetism using the electric field in the magnetoelectric multiferroics, since electric fields require less energy and much faster than their magnetic counterparts.

4.7 Multiferroics application

The study of magnetoelectric multiferroics is a very hot topic. It is interesting not only from the point of view of fundamental physics, but the magnetoelectric coupling in the multiferroics is promising also for many potential applications in electronics. The discovery of materials which possess two or more ferroic properties (magnetzation, polarization and strain), where various ferroic quantities are possibly coupled, became appealing in past few decades. They are referred to as multiferroics and have potential applications in the non-volatile memories, in the high sensitivity ac magnetic field sensors, and in the microwave devices, such as filters, oscillators and phase shifters, etc.

The applications listed below are generally based on the use of magnetoelectric coupling. Of particular importance are the switching processes, which allow the manipulation of magnetic properties of material using the electric field and vice versa. An important research goal is to minimize switching times to the nanosecond range, which is typical time scale needed for modern electronics such as following generation storage devices. The physics of these processes is described by the dynamics of domains and domain walls.

Magnetism control by electric field served as the main impetus for research into what the magnetoelectric coupling is used for. The fact is that the use of electric fields to control requires much less energy than the control by magnetic fields, which require electric currents. In the application of heterostructures, consisting from ordinary ferromagnetic metals and multiferroics, a significant progress has also been made in controlling of magnetism orientation using electric field, as well as in controlling the magnetic state, for example, by changing from antiferromagnetic to ferromagnetic states. The related parameters of magnetic and ferroelectric ordering in thin films of the multiferroics can be used to develop magnetoelectronic spintronic devices: tunneling magnetoresistance sensors and spin valves with tunable electric field functions. Typical device consists of two layers of ferromagnetic materials separated by a thin ≈ 2 nm tunnel barrier made of thin multiferroic film: in this case, the *spin transfer* through the barrier can be controlled electrically. In addition, the multiferroic layer can be used asm the exchange bias pinning layer. Since the orientation of antiferromagnetic spins in the multiferroic layer can be electrically tuned, the applied electric field is used to control the magnetoresistance. Multiferroics make it possible a[so to create such state memory elements in which data is stored in both electric and magnetic polarizations.

High frequency devices. Multiferroic composite structures are promising for use as highly sensitive ac magnetic field sensors, and also in the electrically tunable microwave devices such as steerable antennas, filters, oscillators and phase shifters, with the advantage that these devices are tunable electrically rather than mechanically or magnetically.

Multiferroics for fundamental physical research. As is known, the spin magnetic moment is fundamentally inherent in the electron, but the question of electric dipole moment existence in electron remains open. Therefore, to search for this moment of the electron, it is proposed to use the fact that individual electron is, as it were, a "multiferroic" with electric dipole moment, and the symmetry prescribes that its dipole take same axis as magnetic moment. In one study, the (Eu,Ba)TiO_3 multiferroic is used, and the change in the resulting magnetic moment was measured upon switching of ferroelectric polarization in the applied electric field. This made it possible to determine the upper limit of electric dipole moment of an electron. This value is important because it reflects the degree of violation of time reversal symmetry in the Universe, which is of interest to Particle Physics.

In the elementary Particle Physics, it has been shown by using multiferroic that unusual geometric ferroelectric phase transition in the hexagonal manganites shares symmetry characteristics with the supposed phase transitions of the early Universe. As a result, the hexagonal manganites can be used to conduct laboratory experiments to test various aspects of the Universe Physics: the mechanism of formation of cosmic strings and the aspects of cosmic strings evolution have been confirmed, which can be studied by observing their counterparts - lines of intersection of the multiferroic domains.

Various electronic effects in the multiferroic films are due to a combination of ferroelectric polarization with a small bandgap, consisting of peculiar *d*-states of transition metals. For example, the photovoltaic effect and photocatalysis were found in the bismuth ferrite, as well as its sensitivity to the surrounding gaseous medium was found which is important for sensors. There are known developments of multiferroic films for solar cells, in which energy conversion is based on efficient separation of carriers due to the presence of ferroelectric polarization,

4.8 Summary

1. In addition to electricity, the magnetism is manifestation of electromagnetic interaction. This interaction becomes apparent as moving electrical charges *influence* each on other at a *distance* by the magnetic field. Microscopic sources of electrical field are electrical charges (electrons or protons). Microscopic sources of magnetic field are orbital and spin magnetic moments of elementary particles, atoms and molecules. In macroscopic scale magnetic field is created by electrical current or by permanent magnets.

2. Classic statistical physics proclaims that electronic systems can not have thermodynamically stable magnetic moment, but this assertion contradicts to experiments. Quantum mechanics that explains stability of atom, account for magnetism as in the atoms so in the macroscopic bodies. In atoms and molecules magnetism is caused by:

- spin magnetic moments of electrons (*spin* magnetism);
- moving electrons in shells of ions and atoms (*orbital* magnetism);
- spin magnetism of some nucleons (*nuclear* magnetism).

Nuclear magnetism is very small as compared to electronic magnetism, but it is still used in the instrumentation as a method to study of matter by the *nuclear magnetic resonance* method and to obtain *very deep cooling* by nuclear demagnetization method.

3. All substances, but in varying degrees, respond to external magnetic fields, so they can be characterized by a certain *magnetic susceptibility*. However, usually only those substances are called as magnetics, in which ions or atoms without any external magnetic fields influence have *unpaired* electronic spins. Existence of non-compensated spin magnetic moments in some atoms or ions is caused by *partially filled* 3*d*- or 4*f*-shells.

4. *The substances with magnetic ordering* of different types:

- *ferromagnetics,* in which due to exchange interaction the parallel orientation of magnetic moments of atoms or molecules exists that is energetically favorable in macroscopic areas (domains);
- *antiferromagnetics*, in which exchange interaction is such that in two or more sublattices of crystal are oriented anti-parallel that in sum shows zero magnetization;
- *ferrimagnetics* that in contrast to antiferromagnetics cannot reach full compensation of magnetic moments of sublattices, so these materials, generally, have non-zero spontaneous magnetization.
- substances with *magnetic ordering of different types*: spin glasses, superparamagnetic ensembles of particles, molecular magnets and clusters, plasma, elementary particles (in solid state physics magnetic properties of plasma and elementary particles are not considered).

5. *Paramagnetic* susceptibility is *positive* (æ ~ +($10^{-12\cdot}$...10^{-1}), typically it characterizes such atoms and ions that have internal permanent magnetic moment. This susceptibility depends strongly on temperature, usually, by Curie law: æ ~ K/T. However, for most metals their paramagnetic susceptibility is originated by "free electronic gas”, equals approximately æ ~ + (10^{-6} … 10^{-5}) and does not depend on temperature that is explained by Pauli mechanism of paramagnetism.

6. Magnetic crystals and polycrystals with ordered spin and orbital magnetic moments show *"strong" magnetism* – in sense, that their permeability can be large, and they can be a source of strong magnetic fields that is widely used in engineering. The degree of magnetization of these crystals is determined by total magnetic moment that is vector sum of atomic magnetic moments. Proper magnetic moment has atoms of transient group of Periodic Mendeleyev Table, because they are

characterized by non-completely filled inner electronic shells, which are available to hold unpaired electrons spin.

7. In simple *ferromagnetic* structures all magnetic moments of atoms are directed equally. Examples of such metals are ferromagnetics Fe, Ni, Co, Gd and Dy. These magnetically ordered metals behave like permanent magnets (in case of single-domain structure). Simplest ordered *antiferromagnetic* structures are also collinear, but their magnetic moments are directed oppositely, and they are totally self-compensated. The axis, on which all these moments are directed, is called antiferromagnetic axis. In collinear *ferrimagnetic* structure the neighbouring atoms also shows antiparallel orientation of magnetic moments, but total magnetic moment of elementary cell of crystal is nonzero. So these structures have *spontaneous magnetization*, inasmuch as magnetic moments of ions in different sublattices are non-compensated.

8. The carriers of ferromagnetism are uncompensated electronic spins, associated with electronic orbital moments in ions. In both cases the electrons have both spin and orbital moments. However, calculations show that only spin-type magnetic interaction *not able to provide spins parallel orientation* that is main characteristic of ferromagnetic at temperatures below Curie point. It is assumed (by Weiss) that stable orientation of spins can be caused by *molecular field* that has non-magnetic nature. Forces that coordinate ions magnetic moments orientation have *electrostatic nature*. They arise as a result of spin and orbital *exchange interaction* of electrons.

9. While cooling from high temperatures (i.e., cooling from disordered paramagnetic phase), permeability of ferromagnetic increases and reaches maximum at Curie temperature T_C. In paramagnetic phase, above phase transition point, *Curie-Weiss law* can be implemented: $\text{æ} \approx \mu = C(T - \theta)$, where C is Curie-Weiss constant and θ is Curie-Weiss temperature (latter is slightly different from phase transition temperature T_C).

10. Sharp maximum of *heat capacity* is observed at Curie temperature of ferromagnetic; it is caused by excess energy necessary for magnetic moments disordering. Moreover, in behaviour of heat capacity of ferromagnetic another significant anomaly is seen: pronounced increase of heat capacity in the ferromagnetic phase (differing from smooth curve of saturation, observed in non-magnetic metals). Thus, the spin ordering is inherent to ferromagnetic, and for its destruction it is necessary to add energy throughout temperature range.

11. It is seen that magnetic moment of bulk ferromagnetic materials at temperatures below Curie point is much lower than its theoretical determination that can be defined for the case, when all atomic moments are directed equally. This is due to the formation of *domains*: regions, in which all magnetic moments of atoms are directed equally, so in each domain magnetization corresponds to saturation, i.e., takes maximum value. However, in different domains of magnetic crystals (or polycrystal) vectors of magnetization are not parallel each other. Thus, total magnetization of ferromagnetic sample is lower than in case of complete ordering of atomic magnetic moments. Therefore, without external field ferromagnetic crystal is composed of many small individual plots, magnetized to saturation – domains. Domains are separated by layers – domain walls – in which spins gradually change orientation, inherent in one domain, to orientation, inherent in neighbouring domain.

12. At reversal operation (changing direction of external field H), magnetic moment M first increases to its maximum – to *spontaneous* magnetization M_s, With decrease of external field magnetization remains behind, so if magnetic field again becomes zero ($H = 0$) the induction is not zero, but its value gains to *residual* value M_r. Phenomenon of magnetization lateness while magnetic field changes is the *magnetic hysteresis*. For residual magnetism disappearance it is necessary to apply the counter field H_c that can reverse magnetization of ferromagnetic. This field is the *coercive field* (retentive force). Depending on shape and area of hysteresis loop, ferromagnetic materials are divided into the "soft" (low coercivity) and the "hard" (high coercivity).

13. Magnetization of ferromagnetic materials is accompanied by changes in the size and shape of magnetic sample. This phenomenon is *magnetostriction.* The reason for this effect (that is widely used in engineering) is large spin-orbital coupling in ferromagnetic materials. Magnetic properties change in case of ferromagnetic deformation is observed experimentally, and it is called the *magnetoelastic effect*. Some of ferromagnetic materials are so sensitive to internal stresses that this property is used for strain and tension measurement.

14. Magnetization makes essential influence on ferromagnetic deformation – the *magnetostriction*. Conditioned by exchange interaction, it depends not only on applied magnetic field, but also on temperature change (without any external field). The thermally induced magnetostriction (sometimes called as *thermostriction*) is the spontaneous effect (as it occurs when external field is not applied), and it is greatest in vicinity of Curie point, i.e., when transition to magnetically ordered phase occurs. Some ferromagnetic materials assume name the *invar alloys*: in them *negative*

(ferromagnetic) deposit to thermal expansion (α_f) compensates typical for all crystals *positive* (anharmonic) thermal expansion coefficient (α_a), so as total coefficient can be practically zero ($\alpha = \alpha_a + \alpha_f \approx 0$).

15. *Antiferromagnetic interaction* occurs in case of negative sign of exchange integral, so anti-parallel orientation of spins in lattice cells of crystal is energetically more profitable. Spins locations are ordered, but no spontaneous magnetization occurs, because neighboring moments are directed anti-parallel and cancel each other. In such a crystal two (or more) magnetically opposite sublattices are interpenetrated. The structure with anti-parallel arrangement of spins is formed lower than temperature called *Neel point* (T_N), when spins interaction surpasses chaotic thermal motion. If crystal is heated above this temperature, uncompensated spins form a kind of paramagnetic system that is characterized by very special temperature dependence of magnetic susceptibility: $æ = C(T + \theta)$, where C is Curie-Weiss constant. At that, θ is the characteristic temperature, which in contrast to paramagnetic phase of ferromagnetic is located in the *negative part* of Kelvin temperatures scale.

16. In addition to totally magnetically compensated antiferromagnetics, there are many crystals and polycrystals, in which magnetic moments of sublattices (although being directed opposite to each other) have significant difference in their size – the *ferrimagnetics*. They have complicated structures with varying nature of atoms location that forms some uncompensated electrons in 3*d*- or 4*f*-shells. Ferrimagnetics have properties similar to ferromagnetic materials because they have spontaneous magnetization due to total magnetic moment of sublattices is nonzero.

17. *Ferroelectrics* are characterized by spontaneous polarization, which direction can be changed by externally applied electrical field. Except ferroelectrics, the steady polarization is inherent to electrets as well as to pyroelectric crystals. But in contrast to non-equilibrium *residual* polarization of electrets, in pyroelectrics internal polarization is thermodynamically stable state. Ferroelectric differs from pyroelectric by its ability to re-polarization: switching of spontaneous polarization in external electrical field (dielectric hysteresis). Also definition of ferroelectrics may be such: ferroelectric is pyroelectric that divides on domains.

18. Ferroelectrics are characterized by strongly expressed *nonlinear properties*. At audio and radio frequencies nonlinear ferroelectric capacitors (*variable capacitors*) allow the modulation of signals and generation of higher harmonics. At microwave frequencies thin film of displace type ferroelectrics in

their paraelectric phase can be used for microwave phase modulation and for adjustable filters. Optical nonlinearity of ferroelectrics is applied in the electrooptics and nonlinear optics.

19. By analogy with magnetism (where ferromagnetics, antiferromagnetics and ferr*i*magnetics can exist), not only the ferroelectrics but *antiferroelectrics* and *ferrielectrics* are known. Spontaneous polarization of antiferroelectric is compensated already in a crystal unit cell, while in the ferr*i*electrics their antipolarization is not totally compensated. Mechanical analogue of ferromagnetics and ferroelectrics are the *ferroelastics*, in which phase transition occurs owing to *spontaneous deformation*. Coexistence of spontaneous deformation and spontaneous polarization is inherent to the *improper* ferroelectrics.

20. *Paraelectrics* are the crystals with peculiar temperature dependence of dielectric constant that is described by Curie-Weiss law: $\varepsilon(T) = \varepsilon_1 + C/(T - \theta)$. In most of these crystals at certain temperature called *critical temperature* ($T = T_C$) the phase transition to ferroelectric or antiferroelectric state occurs. Thus, properties of paraelectrics are closely related to ferroelectrics.

21. Most of paraelectrics (*displace type*) are ionic crystals, in which the *covalent bonding* of atoms also is very important. In this case temperature dependence of permittivity looks more flat: $C \approx 10^5$ K, and phase transition to ferroelectric (or antiferroelectric) state occurs at temperature $T_C > \theta$, having a pattern of first-order type transition. To describe properties of these paraelectric a dynamic theory of lattice vibrations and the model of "*soft phonon mode*" should be applied.

4.9 References

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4.10 Questions for self-examination

1. What physical phenomena can be combined in multiferoics?
2. What physical mechanisms lead to ferromagnetism?
3. What distinguishes and what unites paramagnetism and ferromagnetism?
4. Describe the magnetism of 3d and 4f materials.
5. What physical mechanisms lead to ferroelectricity?
6. How are magnetoelectric effects manifested and where are they applied?
7. Describe the differences between ferroelectricity and ferromagnetism.

Chapter 5. Magnetic nanostructures

Contents

Magnetic materials have long been widely used in the electrical engineering and electronics, and in recent years they have become increasingly important in the information technology. Magnets are the main materials of magneto-acoustics, microwave technology, magneto-optics and magneto-electronics (spintronics). Nanostructuring of bulk magnetic materials allows controlling their characteristics within wide limits. Nanotechnology can be used primarily to create materials with a given type of magnetization type – both for very soft magnetic materials and for extremely magnetically hard materials.

Apparently, the possibilities of volumetric materials used by engineers already reached their maximum. It is believed that it is hardly possible to get any significant improvement in their performance only through a more thorough technology or by changing in components. Therefore, it might be assumed that a subsequent creation of materials with *new properties* should be associated with fundamental changes in the *structure* of substances, affecting such properties that are necessary for contemporary applications. It is considered that one of most promising is new research area in field of material science is creation of materials which are condensed from *very small* crystals, clusters, fragments that consist of around 10^2–10^5 atoms.

Main reason of nanomaterials difference from conventional materials is that the *ratio of surface to volume* in nanomaterials is rather big. The smaller size of nanocluster, the greater is influence of its surface properties as compared to bulk properties. In a certain sense, the nanostructure transforms properties of crystal surface into the volumetric properties of condensed nano-material. In other words, properties of nano-formed substance depends on the ratio of number of atoms located on surface of nanocluster to number of atoms located in its volume, and this ratio might be quite different. Therefore, by controlling the size and the shape of clusters, the properties of nano-material can be purposefully changed.

Nano-structurization of *magnetic materials* enables to operate in a wide range of their characteristics. Nanotechnology can be used, primarily, to create material with adjusted type of magnetization curve: both for extremely magnetically-soft materials and for extremely magnetically-hard materials. Fundamental magnetic properties of a matter in their nano-state vary considerably due to correlation in the interaction of spin and orbital moments in lattice cells, located on the surface of nano-particle. The properties of ferromarnetics and ferrimagnetics in their nano-state can be changed especially strongly. In the magnetics formed from nano-clusters the nature of short-range ordering becomes different, that is why new properties appear (sometimes, very important for technical application).

5.1 Magnetism in nanoparticles

Along with electricity, the magnetism is one of electromagnetic interaction the manifestation. This interaction is manifested in the fact that electric charges interact with each other at a distance with the help of a magnetic field. If the sources of the *electric field* are the individual electric charges (electrons or protons), then the microscopic sources of the *magnetic field* are the orbital and spin magnetic moments of elementary particles, atoms and molecules, as well as on the macroscopic scale the magnetic field is created by electric current or permanent magnets.

All substances react to external magnetic fields to one degree or another, that is, they have a certain magnetic *susceptibility*. However, usually only those substances are called "magnetic", in which at least part of the atoms have *unpaired electronic spins* without application of external magnetic field,. The occurrence of spontaneous spin magnetic moments in some atoms or ions is due to the presence in them of partially filled *d*- or *f*-shells of atoms. This spontaneous magnetic moment of atoms is also preserved in crystals, if the *radius* of 3*d*- or 4*f*-orbitals is significantly smaller than the *constant* of crystal lattice.

In crystals, the magnetic moment of an atom can differ significantly from the magnetic moment of the same atom in the free state due to the spin-spin or spin-orbital interactions. These discrepancies are especially large for atoms of the third group (iron group), in which the shell of 3*d* electrons has a larger radius. However, in crystals of rare-earth elements, the magnetic moment of atoms is determined by the shell moments of strongly localized 4*f*-electrons, so it is approximately equal to the magnetic moment of a free atom of rare-earth elements. The interaction of magnetic electronic shells with their surroundings in crystal not only affects the value of atomic magnetic moment, but also causes the exchange bonds between all magnetic atoms of a crystal.

The value of the energy of magnetic interactions between atoms in crystals can be estimated by the Curie point for ferromagnetics or by the Néel point for antiferromagnetics, when the magnetic ordering is destroyed, and crystal acquires the disordered paramagnetic state. Curie and Néel temperatures usually do not exceed 1000 K, and therefore in most cases magnetic interactions are much weaker than electric interactions in crystals, which in free atoms can be roughly estimated by Coulomb energy of electrons, and in crystals by their melting temperature.

According to the nature of interaction with magnetic field and internal magnetic structure, the substances are divided into several types.

I. ***Magnetically disordered substances*****:**

- ***diamagnetics*****,** magnetically disordered substances, whose molecules do not have their own magnetic moment, and magnetic behavior of material is determined by Faraday's law of electromagnetic induction, according to which molecular currents in a substance change in such a way in order to partially compensate the change in magnetic flux through a substance;
- ***paramagnetics,*** having their own non-zero magnetic moment of the molecules which are oriented along externally applied magnetic field.

II. ***Substances with long-range magnetic order*** of various types of ordering:

- ***ferromagnetics***, in which, due to exchange interaction, the parallel orientation of magnetic moments of atoms or molecules in the macroscopic areas of a material (or domains) is energetically advantageous; the ferromagnets are usually good current conductors;
- ***antiferromagnets,*** in which exchange interaction is such that two or more antiparallel oriented sublattices are formed in a crystal, the magnetic moments of which add up to zero magnetization; the antiferromagnets have high resistivity;
- ***ferrimagnets*** (ferrites), which, unlike antiferromagnets, do not achieve full compensation of magnetic moments of crystal sublattices, so the material as a whole has the non-zero spontaneous magnetization; the ferrites combine properties of high electrical resistance and high magnetic activity.

III. ***Substances with short-range magnetic order (nano-magnetism)***:

- spin glasses;
- superparamagnetic ensembles of particles;
- molecular magnets and clusters.

Some examples of atomic magnetic moment dependence on the size of nanoparticles in main ferromagnetics are shown in Fig. 5.1. Magnetic moment of atoms in the *bulk* ferromagnetic usually is less than the number of uncompensated spins in atoms (which are 2μ_B for nickel, 3μ_B for cobalt and 4μ_B for iron). Due to *spin-orbital interaction,* the effective magnetic moment of atoms in bulk ferromagnetic is much smaller (0.6μ_B for nickel, 1.8μ_B for cobalt and 2.2μ_B for iron). Changing the number of atoms in the nanoparticles leads to significant *increase* of effective magnetic moment with particle size decrease (at last, it becomes very close to magnetic moment of single atom). This effect significantly increases permeability of magnetic nano-composites and causes a number of other effects.

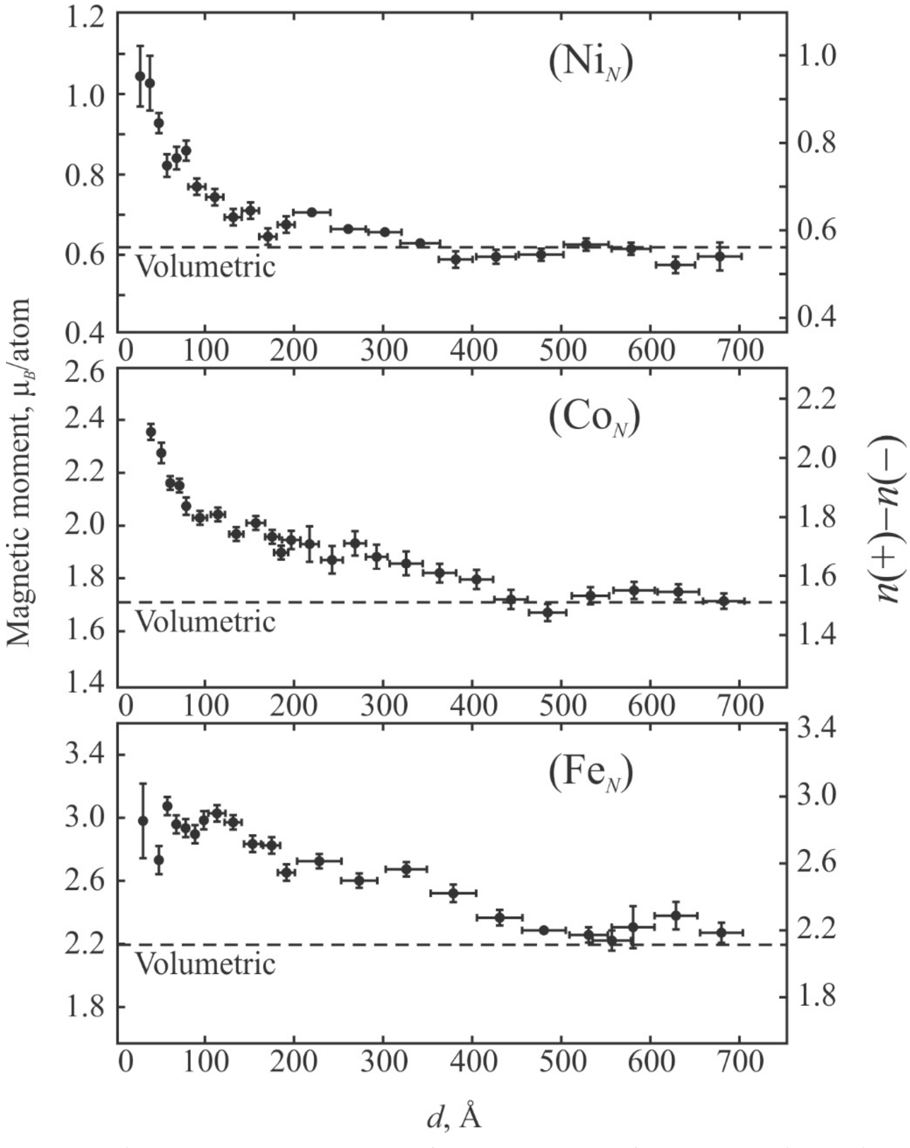


Fig. 5.1. Magnetic moment per atom for nano-state ferromagnetics Ni, Co and Fe depending on particle size in the Angstroem unit scale (1 A = 0.1 nm)

Thus, the effect of nano-structuring on the ferromagnetic properties is very significant, particularly, effect of nanoparticles size that is used in the composed from nano-particles magnetic materials. Therefore, in modern materials technology it is possible to "design" their properties particularized for various fields of technology by changing the size of grain structure.

5.2 Soft and hard magnetic nanomaterials

Soft magnetic nanomaterials. Change in the orientation of magnetic domains or clusters under externally applied magnetic field influence might be possible even in small magnetic fields: these are *soft magnetic* materials. For example, very soft magnetics are the films of amorphous alloys, made with compound $Fe_{70}Si_{13}Nb_3Cu_9$ and obtained by rapid cooling of melt that is poured on the cold copper rotating drum: prepared alloy consist of disordered 10 nm nanoparticles. Having large saturated induction (1.2 T), this alloy shows very small coercive force (0.5 A/m). One reason of magnetic softness increase and, therefore, the appearance of huge magnetic permeability ($\mu \sim 5{\cdot}10^5$) is lightly orientation of spins. The point is that concentration of structural defects in the nano-particles is small (in them any defects easily diffuse on the surface); as a result, the orientation of spins in external magnetic field becomes much easier. Nanomagnetic cluster can have its magnetic moments orientation such as shown in models on Fig. 5.2.

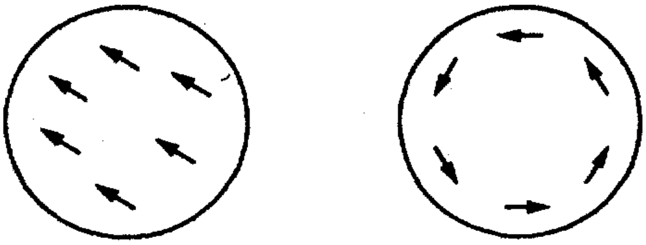
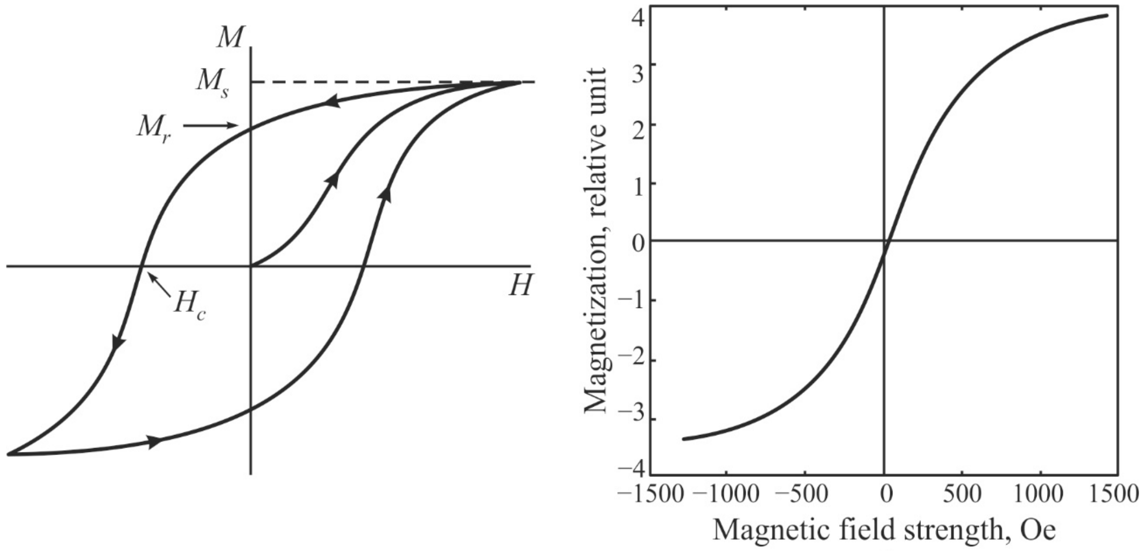


Fig. 5.2. Different orientation of magnetic moments in ferromagnetic nano-particles

As shown by experimental study with magnetically soft materials (nanosized powders of amorphous alloy of compound $Fe_{70}NiO_{10}CO_2$ with grain size of 10-15 nm), the coercivity in hysteresis loop is practically absent, Fig. 5.3*b*, because each of nanoscale grain constitutes of only one domain. (In common ferromagnetic hysteresis is caused by the big domains orientation). Magnetic materials of this type, showing no hysteresis, are the ***super-paramagnetics***. This term means that at temperatures below Curie point and in a wide temperature range the super-paramagnetics are similar to the paramagnetics. In the typical ferromagnetic (or in the ferrite), their spontaneous magnetization, occurred below Curie point, is accompanied by the internal force, which strongly keeps spins in their oriented state, so to the change their direction one need to overcome coercive field (H_c in Fig. 5.3

a). In this case, in the ferromagnetic, a sufficiently large energy of anisotropy exists that makes magnetic moment to choose one or other direction. However, in the nanoparticles, due to significant violations in structural bonds of atoms, the energy of anisotropy is practically absent, so the direction of orientation of electronic spins can be easily changed even in a very weak magnetic field. Therefore, during reversal of magnetization there is no hysteresis.



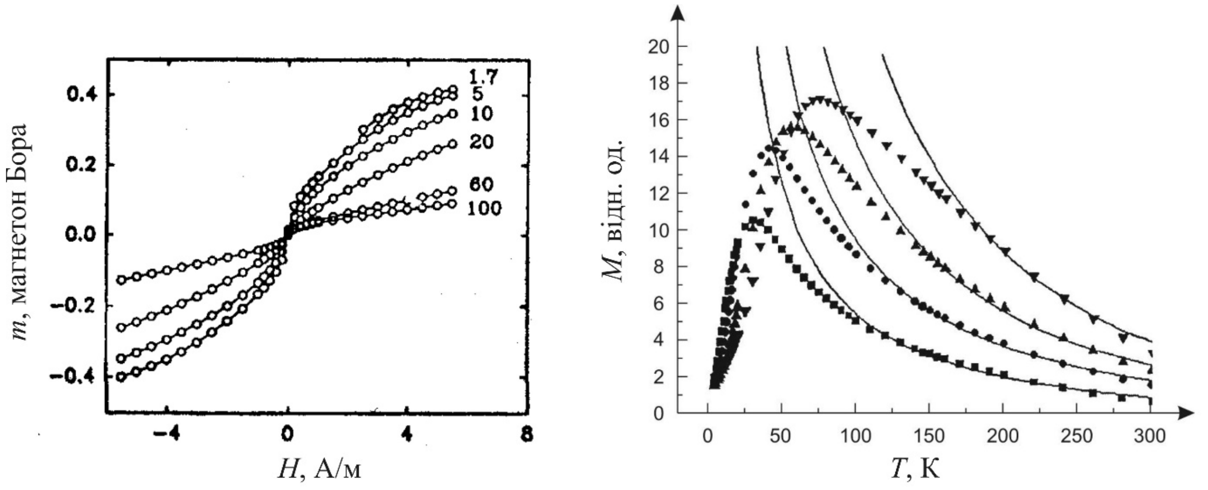
a *b*

Fig. 5.3. Typical magnetic hysteresis (*a*): magnetization *M* and coercive field H_c; *b* – non-hysteresis magnetization curve for nano-material Ni-Fe-Co

A change in the orientation of magnetic sites under the action of an externally applied magnetic field can occur both in very strong fields (magnetic hardness) and in extremely weak fields (magnetic softness). For example, ribbons of amorphous alloy with $Fe_{70}Si_{13}Nb_3Cu_9$ composition, created by the method of rapid cooling of the melt poured onto rotating cold copper drum, are quite magnetically soft. After heat treatment, such an alloy consists of particles with a size of the order of 10 nm. In the case of a large saturation induction (1.2 T), the coercive force of such an alloy is very small (0.5 A/m).

Magnetic hysteresis, observed in the volume ferromagnets, Fig. 5.3*a,* is caused by the orientation of many different magnetic regions – domains. During experimental study of one of soft-magnet materials (nanosized $Fe_{70}Ni_{10}CO_2$ alloy powder with grain size of 10–15 nm), the usual magnetization hysteresis is not observed, Fig. 5.3*b*, since there is only one domain in each nanosized grain.

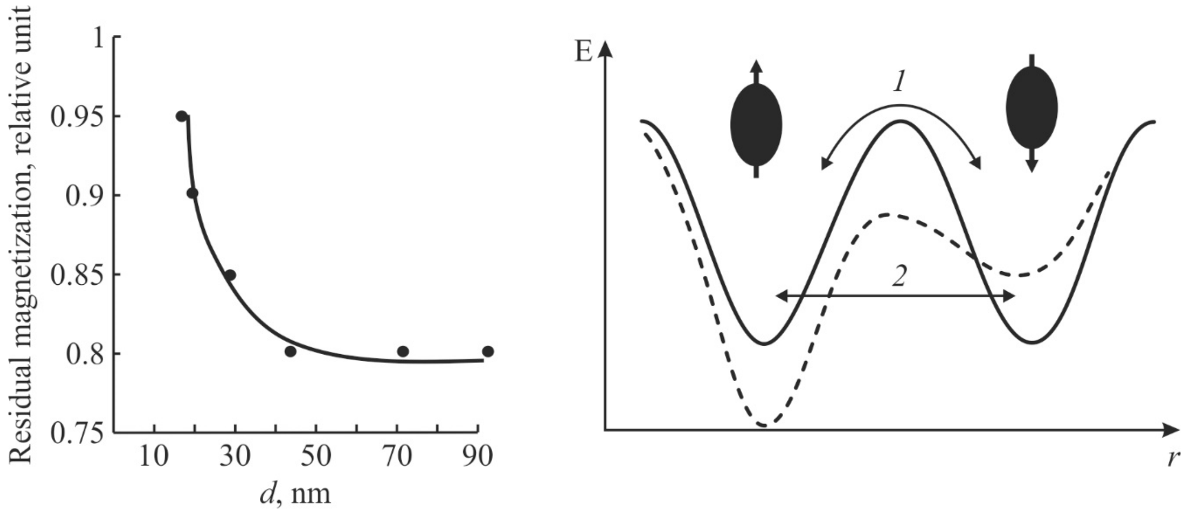
The magneto-softness becomes the more pronounced the smaller particles are, Fig. 5.4*a*. However, unlike ordinary paramagnets, in which Curie's law is fulfilled at arbitrarily low temperatures, for the superparamagnets there is a certain limiting temperature, below which the possibilities of soft, non-coercive orientation of magnetic moments cease. Fig. 5.4*b*. The reason for this limitation is that the orientation of magnetic moments is *supported by thermal chaotic motion* in crystals, which is insufficient at low temperatures. The value of which blocks this movement depends on the size of nanoparticles, Fig. 5.4.



a *б*

Fig. 5.4. Dependence of magnetic moment of cobalt nanoparticles on strength of magnetic field *H* for particles 1.7–100 nm in size (*a*) and temperature dependence of magnetization (*b*)

Magnetically hard nanomaterials. Nanotechnology allows also to control the *coercive field* that is very important to achieve great H_c. In traditional (bulk) materials some powerful permanent magnets are made from the alloys of neodymium, iron and boron. In them, a very big residual induction is reached (1.3 T) with coercive force value of 10^6 A/m, that is more than million times higher than in soft alloys.



a *b*

Fig. 5.5. Residual magnetization M_r dependence on particles of size (*a*); *b* – scheme of double potential well showing energy dependence on magnetic moment orientation when magnetic field absence (solid line) and presence (dotted line): *1* – thermally activated switching, *2* – tunneling

However, the nanotechnology can significantly improve even these data. Some results of grain size influence on alloy $Nd_2Fe_{14}B$ properties is shown in Fig. 5.5*a*. From this figure it follows that residual magnetization *increases* significantly, if grain size becomes smaller than 40 nm (at that, coercive field becomes three times more). Another approach how to change parameters of magnetization curve of this material is to create a mixture of nanoscale particles of magnetically hard compound $Nd_2Fe_{14}B$ and magnetically soft α-phase of iron.

The study of soft iron particles influence on magnetically hard matter confirms that coercive field can be further increased. This is due to exchange interaction between hard and soft nano-particles that turns magnetization of soft phase particles exactly in the direction of hard particles magnetization. By size reducing of nano-particles the granular magnetic material can be significantly improved.

5.3 Nanomagnetic films for computer memory devices

Study of magnetic materials, mainly, the films produced by nanotechnology, aims to increase the capacity of magnetic information drives (such as hard drive of computer). The unit of storage information is *bit*; to reach the density of 10 Gb (10^{10} bits) per square inch the single bit should have length of ~1 micron and width of ~70 nm. The thickness of magnetic layer in this case should be about 30 nm. Magnetic storage medium, such as hard drives, can be realized with using small crystals of chromium-cobalt alloy. Problem of bit size diminution less than 10 nm is the "self-erasing" of memory, because the magnetization vector of micro-area can change its direction under the influence of thermal fluctuations. Solving this problem requires the use of nanosized grains with large values of saturation magnetization, which are characterized by a stronger interaction between grains. For example, with the help of nanotechnology, the magnetic FePt nanograin compounds with the much higher magnetization value than in analogues were obtained. FePt particles were formed during heating of a solution of platinum acetylacetonate and iron carbonyl with the addition of reducing agent. After spraying the solution on the substrate, it evaporated, leaving passivated particles on it. The thin film formed as a result of this operation consists of a solid carbon layer containing FePt particles about 3 nm in size. This size of magnetic nanoparticles can provide a recording density of 150 GB per square inch, that is, 10 times greater than most existing media.

Another example: using nanotechnology, such magnetic FePt nanograins are obtained which have higher magnetization than their analogs. Particles of FePt are formed by heating of solution of platinum acetylacetonate and carbonyl iron with addition of reducing agent. After spraying this solution on substrate, it evaporates leaving passivating particles. Thin film, obtained as a result of these operations, consists of hard carbon layer, containing FePt particles with the size of about 3 nm. This kind of magnetic nano-particles allows reach density of 150 Gb per square inch, that is 10 times greater than most existing commercially available medium.

When the size of magnetic nano-particles is too small, magnetic vectors of atoms are oriented by magnetic field equally within a grain, avoiding difficulties that arise in other cases (when the adjacent domain walls exist with different directions of magnetization). The reason is a peculiarity of nano-clusters: the reducing defects concentration within cluster (defects easily diffuse to surface). Typically, magnetic medium uses elongated magnetic grains. Dynamic properties of such magnetic particles can be described by a model, which assumes that without magnetic field applying the ellipsoidal grains have only two possible directions of their magnetic moment: "up" or "down", relatively to long axis of magnetic elongated particles, such as shown in Fig. 5.5*b*.

Magnetic energy dependence on magnetic moment orientation is characterized by symmetric potential well with two minima, divided by potential barrier. Under the influence of thermal fluctuations the elongated particle can change orientation of its magnetic vector. This particle can also (but far less likely) change its magnetic orientation by means of quantum-mechanical *tunneling*. This occurs, when heat energy k_BT is much less than the height of barrier. Tunneling is a purely quantum-mechanical effect, which arises from the fact that there is a probability of magnetic state changing from the direction "up" to the direction "down". In the external magnetic field the potential, that divides minima, changes, as shown in Fig. 5.5*b* by dotted line; in case, when magnetic field equals to coercive force, one of levels becomes unstable.

This model explains many magnetic properties of small magnetic particles, for example, the shape of hysteresis loop. However, this model has a limitation with coercive field value, because it allows only one way for reorientation. Magnetic energy of particle is assumed as function of *collective orientation* of spins in magnetic atoms, as well as function of external magnetic field. This model takes into account only simple (linear) dependence of magnetic energy of particle on its size. However, when the size of particle becomes close to approximately 6 nm, most of atoms are located on the particle surface. This means that they can have such magnetic properties that significantly differ from parameters of larger particles.

It is shown that replacement of magnetically soft α-iron in variety of chemicals substances leads to change in coercive force up to 50%, indicating the importance of particle's surface in the magnetic properties formation of a grain. Thus, dynamic behavior of very small magnetic particles is more complicated than it follows from considered model.

5.4 Giant and colossal magnetoresistance

The magnetoresistance effect is caused by electrical conductivity change in the magnetic field. In metals and semiconductors this phenomenon is long time known: electrical resistance is caused by scattering of electrons during their collisions with lattice. In magnetic field conduction electrons should move on helical trajectories. The elongation of trajectory increases the number of collisions, and resistance *increases*. However, in *ordinary* metals, the effect of magnetoresistance is small: the *increase* of resistance happens only on a part of percent (that is why, this effect in ordinary metals is rarely used in practice). Nevertheless, this ***positive*** magneto-resistance effect is more noticeable in strong magnetic fields and at low temperatures, when electrons trajectory is characterized by much bigger free path.

In the *ferromagnetic* materials magnetoresistance effect is ***negative*** and reaches already several percents. The point is that at the absence of external magnetic field the ferromagnetic divides on magnetic domains, in which magnetic moments have different orientation; domains boundaries lead to *additional scattering* of conductive electrons. Under external magnetic field the influence, domains boundaries disappear, so the entire sample turns close to single domain that is completely magnetized, and its resistance *decreases*. It is noteworthy also that electrical resistance of magnetic materials depends on the angle between magnetic field and current. This phenomenon is *anisotropic magnetoresistance.* This effect, despite relatively small size, is used in some devices to measure magnetic field in automation systems and in alarm information devices.

Recently, the application of magnetoresistance effect becomes wider due to ***giant*** *magnetoresistance* (GMR) discovery. It is seen in materials created artificially by deposition on a substrate some alternating ferromagnetic and non-ferromagnetic layers of nanometer thickness. The scheme of such layered structure with the magnetization vector direction in layers is shown in Fig. 5.6*a*.

The GMR effect was first observed in the films with alternating layers of iron and chromium, but later many other combinations of layers are discovered. In films composed from cobalt and copper layers magnetoresistance is much larger than in the Fe-Cr films. Simplest device may consist of two parallel placed ferromagnetic layers, in which electrical resistance depends on relative orientation of spins in magnetic layers. If magnetic moments in ferromagnetic layers are found as parallel, device has *smaller* resistance; if magnetic moments are found as anti-parallel, the resistance *increases* greatly. Electrical current can flow both perpendicular and parallel to segments. In both cases, the change in resistance is sufficiently big (~ 40%).

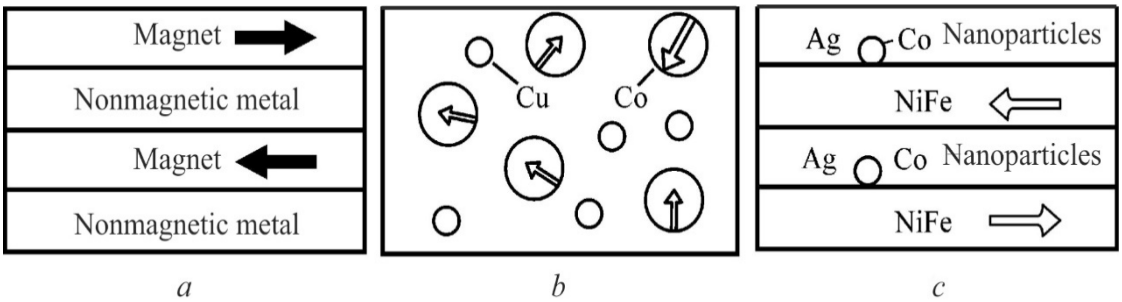
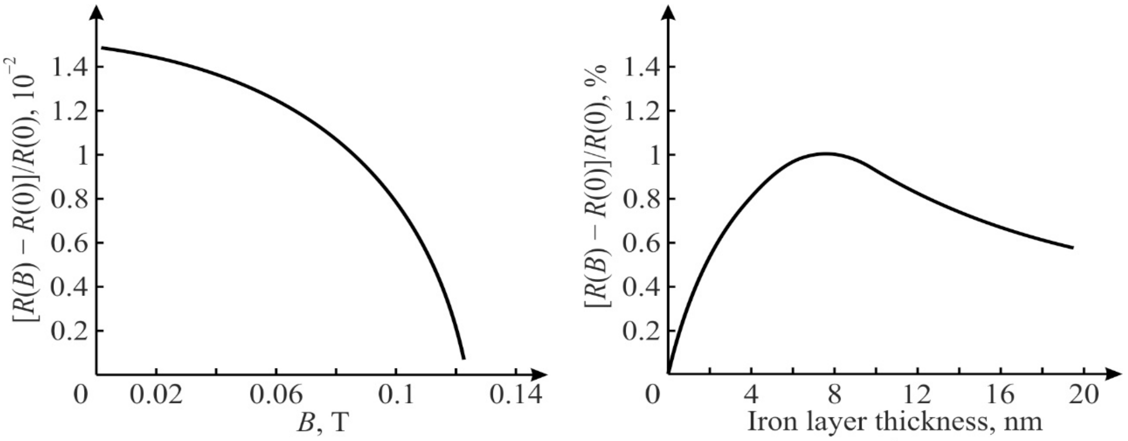


Fig. 5.6. Three structures that shows giant magnetoresistance: *a* – layers of nonmagnetic material with ferromagnetic layers, magnetized in opposite directions; *b* – randomly oriented ferromagnetic cobalt nanoparticles (large circles) in nonmagnetic copper matrix (small circles); *c* – mixed system consisting of silver layers with cobalt nanoparticles and magnetic layers of alloy Ni-Fe

Effect of constant magnetic field on the resistance of multilayer iron-chromium system is shown in Fig. 5.7*a*. Degree of resistance change depends on thickness of iron layers and reaches maximum at thickness of 7 nm, as shown in Fig. 5.6*b*. This effect arises from electrons scattering dependence on the direction of their spin relatively magnetization vector. The electrons, which spins are directed opposite to magnetization *B,* scatter more intense than electrons which spins are directed equally with *B*. Application of constant magnetic field along layers orients magnetization vector of all layers in one direction. Conduction electrons, which spins are directed opposite to magnetization, are scattered on the metal-ferromagnetic boundary more stronglym, than electrons which spins are oriented in the direction of magnetization. Since both channels operate in parallel, the channel with less resistance determines the impedance of a film.

Effect of magnetoresistance in layered materials is used in sensitive detectors of magnetic field, and this effect is a basis for creation new highly sensitive magnetic head (capping for disk) which read information. Until this effect discovery in magnetic storage devices the induction coil for operation with magnetic small cells was used: as in recording mode, so for information reading. Giant magnetoresistive reading head is much more sensitive than the induction one.



a *b*

Fig. 5.7. Magnetoresistance in Fe-Cr multilayered structure: *a* – magnetic field applied parallel to surface layers; *b* – dependence on magnetic layer thickness

Compound materials, consisting of single-domain ferromagnetic nanoparticles with randomly oriented magnetization, being placed in the nonmagnetic matrix also show GMR. A scheme of such system is shown in Fig. 5.6*b*. Unlike layered structures, magnetoresistance in this system is isotropic. Magnetization vectors of ferromagnetic nanoparticles aspire to be oriented in the magnetic field which *reduces* electrical resistance. The influence of magnetic field on the resistance increases with field strength rise and with decrease in the size of magnetic particles. Typical measurement results with film consisting cobalt nanoparticles in the copper matrix are shown in Fig. 5.7*a*. Hybrid system, composed of metallic nanoparticles in matrix placed between two ferromagnetic layers (Fig. 5.6*b*) demonstrates similar properties.

The GMR effect is used not only in the heads of hard disks. On the basis of such magnetic structures, many sensors, switches and nonreciprocal devices are elaborated. Low cost and low power consumption promote high competitive ability of these devices. Magnetic storage devices based on GMR devices can compete with conventional semiconductor storage devices by integration density, speed and cost.

Some materials have even much higher magnetoresistance effect than shown in Fig. 5.8, and this phenomenon is the *colossal magnetoresistance*. Correspondent materials also have many opportunities for use, for example in magnetic recording heads or sensitive magnetometer elements. This materials have perovskite structure, such as $LaMnO_3$, where manganese, like lanthanum, has valence of “+3”. If ions La^{+3} are partially replaced by bivalent ions, such as Ca, Ba, Sr, Pb or Cd; then, in accordance to electro-neutrality law, some of manganese ions should change their state from Mn^{+3} to Mn^{+4}. The result is a system with *mixed valences* of Mn^{+3}/Mn^{+4}, in which large number of mobile charge carriers exists. It is found that this system shows very large magnetoresistance. For example, the resistance of $La_{0,67}C_{0,33}MnO_x$ system at magnetic inductance of 6T can be changed in hundreds of times. The dependence of resistivity of thin film made of this material on applied magnetic field is shown in Fig. 5.8*b*.

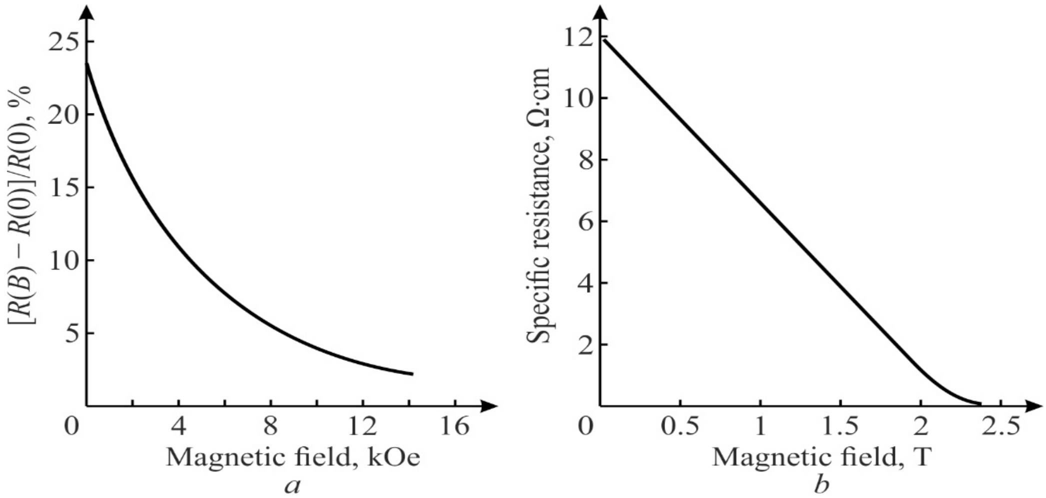


Fig. 5.8. Dependence of magnetoresistance change on applied magnetic field: *a* – for thin film of cobalt nanoparticles in copper matrix; *b* – for La-Ca-Mn-0 near Curie point (250 K)

Tunneling magnetoresistance is the effect of spin-dependent electrons tunneling through the nanometer layer of dielectric or semiconductor, located between two ferromagnetics. This structure has similar construction as in Fig. 5.6*b*, but instead of copper layer the dielectric layer ($A1_2O_3$) or semiconductor layer is used. As in case of giant magnetoresistance, electrons show tunneling, creating a current from one ferromagnetic to another, if they have parallel magnetization.

Because the magnetization of ferromagnetics is antiparallel, the probability of tunneling greatly reduces, and, hence, current through a structure decreases sharply due to significant increase of resistance. At room temperature the change of resistance is about 30% that allows apply this effect in devices. As in the case of giant magnetoresistance, the soft and hard ferromagnetics are used. The state of magnetization is stored up to new magnetic switching; that is why, the switching can be used as a transfer of bit of information in electronic memory. Based on tunnel magnetoresistance effect new computer memories are developed. Such devices use very small currents, so they have low power consumption. The imperfection of these devices is that currents are directed perpendicular to layers. As a result, decrease in the area of layers increases electrical resistance of device.

Development of spintronics significantly increases as the operation speed so the density of processed information. In magnetic carriers, elongated magnetic grains are usually used. The dynamic properties of the behavior of the system of elongated nano-sized magnetic particles are described by a model in which it is assumed that without a magnetic field, ellipsoidal grains have only two possible stable directions of the magnetic moment: "up" or "down" relative to the long axis of the magnetic particle, as shown in Fig. 2.47. The dependence of the magnetic energy on the orientation of the magnetic moment vector is a symmetric potential well with two minima separated by a potential barrier. Under the influence of thermal fluctuation, the particle can change the orientation of the magnetic vector.

A particle can also (but with a much lower probability) change its magnetic orientation through quantum mechanical tunneling. This can be observed when the thermal energy k_BT is much smaller than the height of the barrier. Tunneling is a purely quantum mechanical effect. It is explained by the fact that the solution of the wave equation of this system gives a small probability of changing the magnetic state from the "up" direction to the "down" direction. In an external magnetic field, the potential changes and if the field reaches a value equal to the coercive force, one of the levels becomes unstable.

The given model gives a simple explanation of many magnetic properties of small magnetic particles, for example, the shape of the hysteresis loop. However, this model has limitations. It overestimates the value of the coercive field, since only one way of reorientation is possible. The magnetic energy of the particles in the model is a function of the collective orientation of the spins of the magnetic atoms that make up the particle and the external magnetic field. The model assumes the simplest (linear) dependence of the magnetic energy of particles on their volume. However, when the particle size approaches 6 nm, most of the nanocluster atoms are on the surface. This means that they can have such magnetic properties that are very different from the parameters of large particles. It is shown that surface treatment of magnetically soft α-iron nanoparticles with a length of 600 nm and a width of 100 nm with various chemicals changes the coercive force by up to 50%, which indicates the important role of the surface of nanosized magnetic particles in the formation of the magnetic properties of the grain. Thus, dynamic behavior of very small magnetic particles turns out to be more complicated than it appears from the considered model.

5.5 Spin electronics

In recent years, a new scientific and technical field – magnetoelectronics, or, as it is now called – "*spintronics*", which is engaged in the study and practical applications of the effects and devices using electronic spins, has been actively developing. Spintronics studies magnetic and magneto-optical interactions in metal and semiconductor structures, as well as the quantum magnetic phenomena in nanometer-sized structures. In modern information technologies, information processing and calculations are carried out in integrated microelectronic circuits, and information is stored on magnetic disks. The use of magnetic semiconductors would make it possible to place the processor and memory on the same chip, eliminating relatively slow information "input-output" channels, which would significantly increase the speed of operation. Another advantage is that magnetic semiconductors, which would be capable of receiving and amplifying optical signals, would enable the direct conversion of information from optical form to electronic form, without the detection process.

Specific phenomena related to the spin-dependent transfer of charge carriers in solid-state structures and electronic devices based on them are united by the general scientific and technical direction of spintronics. Spintronics was formed as an independent direction only at the end of 20th century as a result of the accumulation of fundamental knowledge and the manufacture of the first electronic devices with spin-dependent transport of charge carriers using the methods of microelectronic technology and nanotechnology, which is rapidly developing. The interest in spintronic electronic devices is caused by the fact that, firstly, they are expected to have better properties compared to their conventional semiconductor counterparts. Second, they are believed to provide the basis for the implementation of quantum computing and quantum computers based on it.

Spin effects are clearly manifested due to the features of charge transfer by electrons in microelectronic and nanoelectronic structures under the influence of a magnetic field. Their main characteristic is magnetoresistance, which is defined as a change in the electrical resistance of a material or structure caused by the magnetic field. The value of magnetoresistance is defined as the ratio $\Delta R/R_0$ in percent, where ΔR is the change in resistance, and R_0 is the resistance in the absence of a magnetic field. Positive magnetoresistance corresponds to the increase in resistance under the influence of magnetic field, while negative magnetoresistance corresponds to the decrease in resistance. Magnetoresistance indirectly characterizes spin effects in conditions of diffusion and ballistic transport of charge carriers, as well as in conditions of tunneling of spin-polarized electrons.

Thus, spintronics is a direction of nanoelectronics in which, along with the charge, the spin of an electron is also used for information processing. In modern electronics, there are already devices that work on spin phenomena. These are, for example, heads that read information from magnetic disks (manufactured by IBM) and a new type of magnetic memory – MRAM (magnetic random access memory), magnetic memory with random sampling. These devices work using the giant magnetoresistance effect.

Spin-polarization current in magnetic nanostructures. During the last decade, the effects that occur when an electric current flows through magnetic transition - thr multi-layered nanoscale structure that includes ferromagnetic layers that influence each other – have been actively investigated. The greatest attention in experiments and theory is paid to structures of the spin valve type consisting of three layers:

- rigidly oriented ferromagnetic layer;
- non-magnetic layer or spacer;
- free ferromagnetic layer, the magnetization of which can change its direction under the action of an external magnetic field and/or current.

The ferromagnetic layers are separated by a thin non-magnetic spacer to prevent the occurrence of a direct exchange connection between the ferromagnetic layers. The passage of current through the spacer is ballistic, diffuse, or tunneling in nature. At the same time, the thickness of spacer is small compared to the length of electron's free path, so the spin states of electrons do not change when current passes through it.

A vivid example which illustrates the above is new method of remagnetization of magnetic bodies. This refers to a jump-like change in the orientation of the magnetization of free ferromagnetic layer relative to the magnetization of rigidly oriented layer under the influence of a current flowing perpendicular to the layers. This phenomenon occurs, if the current density exceeds a certain threshold value, which lies within 10^6–10^8 A·cm^{-2}. The original antiparallel configuration of spins is thus switched to a parallel configuration. The resulting parallel configuration is preserved when the current is reduced to zero and even when the direction of the current is reversed. However, when the reverse current density reaches the threshold value, reverse switching occurs with the restoration of the antiparallel spin configuration. Since the resistance of the magnetic junction depends on the relative orientation of the magnetic layers (effect of giant magnetoresistance is also related to this), the switching is accompanied by a change in the resistance of the junction, so that the dependence of the resistance on the current looks like hysteresis loop.

The reason for such remagnetization is determined by the physical process, the essence of which is that the current flowing through the magnetic system carries not only charge, but also spin, that is, the electric current is also the flow of the moment of magnetic pulse. The spin polarization (that is, the non-zero spin moment) of the current occurs as a result of the exchange interaction when the current flows through the ferromagnetic. If the current flows from the ferromagnetic into a non-magnetic metal, then its polarization is preserved for some length. If the polarized current flows through a magnetic system with inhomogeneous magnetization, then its spin moment is forced to adapt to the latter. Due to the local storage of spin, the change in the moment of the current pulse is transmitted to the ferromagnetic. As a result, the divergence of the spin flow leads to the generation of a torque acting on the magnetization.

This process is called *spin transfer*. Under certain conditions, the spin transfer can lead to the remagnetization of magnetic structures, as well as to the generation of spin waves or the motion of domains. This effect, quantum in nature, is also the fundamental in nature. Interest in the methods of excitation of magnetization described here is also stimulated by successes and problems in the field of creating magnetic memory elements, microwave devices, and magnetic logic elements.

Spin transfer processes are usually considered on planar structures in two configurations. In the first configuration, the current flows perpendicular to the magnetic layer of a structure, which contains layers with different directions of magnetization. In the second configuration, the current flows along the magnetic layer containing the domain wall. The most common is the first configuration, which is the nanocolumn containing magnetic multilayer with structure $N_1/F_1/N/F_2/N_2$, where F is the magnetic layers, N is the non-magnetic layers. The oval cross-section of the column has typical dimensions of about 100 nm. The size of a system is largely determined by the need to reduce parasitic effect of eddy magnetic field, generated by the current flowing in a system. Under certain conditions, the transfer of electric current through a magnetic transition is accompanied by the process of spin transfer, which leads, in particular, to remagnetization of multilayer nanoscale structures. The theoretical consideration of this phenomenon is based on the idea of exchange interaction between electrons – current carriers – and magnetic lattices of a ferro-, ferro- or antiferromagnet.

Semiconductor spintronics. Although devices based on the effects of giant magnetoresistance and tunneling magnetoresistance have already been created, these devices still use metals, while modern technologies are focused on semiconductors. A number of other spintronic devices requiring spin-polarized current have been developed, but creating an efficient injection of ferromagnetic metal into the semiconductor faces with great difficulties. Therefore, development of semiconductor spintronics compatible with modern chip technology is of great importance.

Semiconductor spintronics requires new type of materials – the magnetic semiconductors. As already noted above, it was found that ferromagnetic properties can be given to compounds $A^{III}B^{V}$ and $A^{II}B^{VI}$ by doping them with iron, cobalt, and manganese ions. However, the technology of such alloying faces difficulties due to the low limits of solubility of these impurities in $A^{III}B^{V}$ and $A^{II}B^{VI}$ crystals. In addition, such materials have acceptable characteristics only at low temperatures. Therefore, development and research of properties of new magnetic semiconductors is underway. Such materials are obtained with an operating temperature above room temperature, such as GaMn, GaCr, and others.

Existing spintronic devices are based on both the giant magnetoresistance effect and spin-dependent tunneling. Switching the direction of magnetization in them is carried out with the help of either their own (internal) magnetic field or with the help of an external magnetic field. The list of possible spintronic devices can be quite large, but most of the proposed and theoretically justified devices still await technological development and experimental research. Among the most famous spintronic devices, the read head on a giant magnetoresistor, a non-volatile memory on tunnel magnetoresistor, and spin-polarized field-effect transistor are considered. The literature also describes a ballistic spin-filtering transistor, a spin logic element, unipolar spin diodes and transistors, etc.

Magnetoresistive memory and a spin-valve transistor. Once switched, the magnetic element can retain its magnetization until a new switch, and so it can be used as a memory element. Such elements are used in MRAM magnetic memory. Spin-dependent tunneling provides significant efficiency of such a memory, schematically shown in Fig. 5.9.

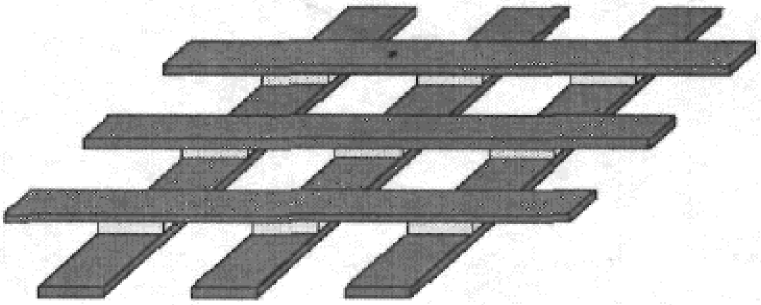


Fig. 5.9. Eragment of memory device with arbitrary sampling order, built from elements on tunnel magnetoresistor

The memory device with an arbitrary sampling order is formed from two arrays of parallel ferromagnetic tracks orthogonal in the plane, separated in space by a thin insulating layer. Each track crossing acts as a magnetic tunnel transition. When the magnetization directions of two opposite ferromagnetic regions are aligned by an external magnetic field, the tunneling resistance will be lower than when they are in opposite directions. Resistance change of at least 30% is required for practical use in memory devices.

An interesting device of spintronics is a ***spin field transistor***. The schematic diagram of the device is shown in Fig. 5.10. This is a three-electrode device similar to a transistor with a metal base. As in a traditional FET, a narrow channel is placed between drain 1 and drain 3. Above the channel is a third electrode, gate 2. Here, the drain and drain are ferromagnets magnetized in the same direction (horizontal arrows), and the channel is a semiconductor with a 2D electronic gas. The current entering the channel from the leak is spin-polarized. If there is no voltage on the gate, then the current flows freely into the drain (low resistance state).

If the voltage is applied to the gate, then the spin of the electrons of the current precesses (shown by inclined arrows in the channel). By adjusting the gate voltage, it is possible to adjust the change in the orientation of the electron spins during passage through the channel. If at the end of the channel the electron spins have the orientation shown in Fig. 5.10, and, then the electrons are reflected from the flow boundary. In this state, the transistor has a high resistance. Thus, the resistance of the spin field transistor can be controlled by the electric field of the gate. The version of the implementation of the spin-valve transistor is shown in Fig. 5.10*b*. The base region of the transistor contains a metal, multilayer spin gate between two regions of n-type silicon that act as emitter and collector. In such a structure, the "hot" electron passes through the spin-valve base to get from the emitter to the collector. The base is designed as the exchangeable soft spin-valve system, in which there are two ferromagnetic materials, namely NiFe and Co. They have different coercive forces and are separated by a layer of non-magnetic material (Au).

Due to the difference in coercive force, the layers of NiFe and Co make it possible to obtain clearly defined parallel and antiparallel orientation of their magnetization in a wide temperature range. They can be individually switched by a suitable magnetic field. Schottky barriers are formed at the interface between the metal base and semiconductors. In order to obtain the desired high-quality barrier with a rectifying effect, thin layers of Pt and Au are placed on the emitter and collector sides. In addition, they separate the magnetic layers from direct contact with silicon. Since the Si–Pt contact forms a high Schottky barrier, it is used as an emitter. The collector Schottky diode is designed to have a lower barrier height compared to the emitter diode. For the manufacture of such a spin-valve transistor, a specially developed technique is used, which includes the deposition of metal on two silicon plates and their subsequent connection in conditions of ultra-high vacuum.

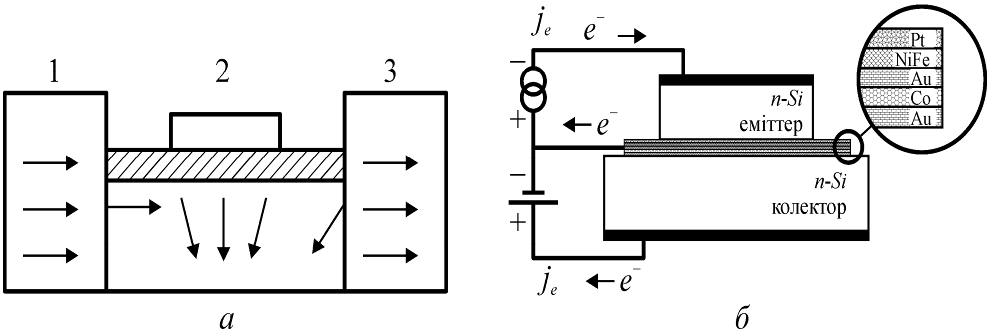


Fig. 5.10. Spin-valve transistor: *a* – schematic image, *b* – one of possible implementations with Si–Pt emitter, Si–Au collector and NiFe–Au–Co spin-valve base

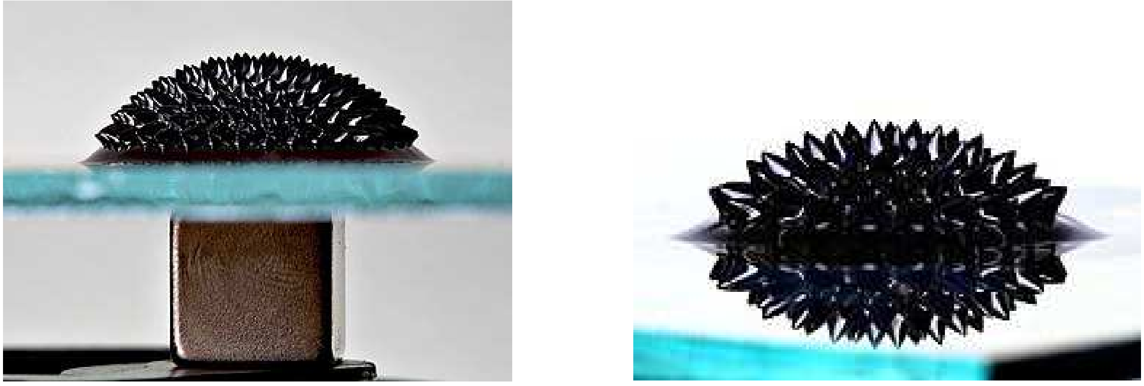
The transistor works in the following way. The current is established between the emitter and the base, at which electrons are injected into the base perpendicular to the spin gate layers. The injected electrons must pass through the Si–Pt Schottky barrier and therefore enter the base as non-equilibrium, "hot" electrons. The energy of hot electrons is determined by the height of the Schottky emitter barrier, which is usually between 0.5 and 1 eV depending on the metal-semiconductor combination. As soon as hot electrons cross the base, they are affected by both inelastic and elastic scattering, which changes both their energy and the distribution of their moments.

Electrons can enter the collector only when they have acquired enough energy to overcome the energy barrier on the collector side. The value of this barrier should be slightly lower than the emitter barrier. It is equally important that the moment of appearance of a hot electron is consistent with the available states in the collector. Part of the electrons collected in the collector and, therefore, the current of the collector depend significantly on the scattering in the base, which is spin-dependent. This is regulated by switching the base from the magnetization-matched low-resistance state to the anti-matched high-resistance state. The total dissipation is controlled by an external magnetic field that changes the alignment of the two ferromagnetic layers of the spin-valve. Such a spin-valve transistor is promising in magnetic memory devices and for magnetic field sensors.

5.6 Ferromagnetic liquid

The ferromagnetic liquid (ferrofluid) is a material which strongly polarizes in the presence of magnetic field. Ferromagnetic liquids are colloidal systems consisting of nanometer-sized ferromagnetic or ferrimagnetic particles suspended in a carrier liquid, which is usually the organic solvent. To ensure the stability of such a liquid, the ferromagnetic particles are connected to a special surface-active substance, which creates the protective shell around the particles and prevents them from sticking together due to van der Waals or magnetic forces.

In the ferrofluids, the magnetite particles Fe_3O_4 are usually used. In this case, such nanoparticles are single-domain "magnets", the orientation of their magnetic moments is random without external magnetic field application, and, therefore. total magnetization of such a "liquid" is zero. When the magnetic field is applied, the moments of individual particles are oriented in the direction of field, and the liquid is magnetized. Thus, ferromagnetic fluids are superparamagnetic soft magnet materials.



a *b*

Fig. 5.11. Ferromagnetic liquid: *a* – on glass under influence of magnet located under glass; *b* – the case of a vertical magnetic field

Figure 5.11 shows photograph of ferrofluid in the magnetic field. Suspensions of magnetic particles in liquids have long been used in magnetic vacuum valves, but relatively large (micron) sized particles were used. Placing such a suspension in the permanent magnetic field causes its viscosity to increase to a "solid state", so that in the magnetized state this material is not a liquid. Materials similar to ferrofluids are called the "magneto-rheological fluids". The difference between a ferromagnetic fluid and magneto-rheological fluid is in the size of particles. Particles in ferromagnetic liquid are nanometer-sized particles that are suspended due to Brownian motion and do not settle under normal conditions. Particles in magneto-rheological fluid are mostly micrometer in size (1–3 orders of magnitude larger), they are too heavy for Brownian motion to maintain them in the suspended state, and therefore they settle over time due to the natural difference in the density of particles and the carrier fluid. As a result, these two types of magnetic fluids have different applications.

Despite the name, ferrofluids do not exhibit typical ferromagnetic properties because they do not retain residual magnetization and coercive field after the external magnetic field disappears. In fact, ferromagnetic liquids are *paramagnetics*, or they are often called superparamagnetics, due to their high magnetic susceptibility. Ferrofluids consist of nanometer-sized particles (typical size 10 nm or less) of magnetite, hematite, or other magnetic material suspended in a carrier fluid. They are small enough that the thermal motion distributes them uniformly throughout the carrier fluid, and, therefore, they contribute to the response of the fluid as a whole to the magnetic field. Ferromagnetic liquids are colloidal solutions, that is, the substances which have the properties of more than one state of matter. The two states in this case are the solid metal and the liquid in which it is contained. It is the ability to change state under the influence of magnetic field that allows the use of ferromagnetic fluids as sealants and lubricants, and can also open up other applications in various nano-electromechanical systems.

In order to prevent nanoparticles from sticking together, preventing them from forming too heavy clusters that cannot be kept in suspension due to Brownian motion, the ferromagnetic liquids use surface-active substances which coat the particles of the ferromagnetic liquid. In an ideal ferromagnetic liquid, thr magnetic particles do not settle even in a very strong magnetic or gravitational field. Surfactant molecules have a polar "head" and a non-polar "tail" (or vice versa), one of these ends is adsorbed to the particle, and the other is attached to the carrier liquid molecules, forming, respectively, micelles around the particle.

As a result, spatial effects prevent particles from sticking together. A double electric layer appears on the surface of the particles, which leads to the emergence of Coulomb forces of repulsion between the particles and increases the stability of the liquid.

Ferromagnetic liquids are stable: their solid particles do not stick together and do not separate into a separate phase even in a very strong magnetic field. However, the surface-active substances present in the ferrofluids tend to break down over time (about a few years), so that eventually the magnetic particles will stick together, separate from the liquid and cease to affect the liquid's response to the magnetic field. Also, ferromagnetic liquids lose their magnetic properties at their Curie temperature, which for them depends on the specific material of the ferromagnetic particles.

Under the influence of a sufficiently strong vertically directed magnetic field, the surface of a liquid with paramagnetic properties involuntarily forms a regular structure of folds, Fig. 5.11*b*. This effect is known as "instability in a normally directed field". The formation of folds increases the free energy of the surface and the gravitational energy of the fluid, but decreases the energy of the magnetic field. Such a configuration occurs only when the critical value of the magnetic field is exceeded, when the decrease in its energy exceeds the contribution from the increase in the free energy of the surface and the gravitational energy of the liquid. Ferromagnetic liquids have a very high magnetic susceptibility, and a small bar magnet may be enough for folds to appear on the surface (for a critical magnetic field).

Ferromagnetic fluids are commercially used in some devices as a sealant that prevents dust from penetrating inside the case of hard drives of personal computers and vacuum seals designed to introduce high-speed axes into a high-vacuum zone. Here, the liquid is used to seal the gap between the rotating roller and the support that supports it. The seal consists of several drops of ferromagnetic fluid in the gap between the shaft and the sleeve and is controlled by a cylindrical permanent magnet. The liquid forms an impenetrable ring around the axis, which, however, does not cause noticeable friction. Seals of this type are used in engineering. Ferromagnetic fluids are also used in acoustic speakers for membrane damping.

Ferromagnetic fluid is also used in acoustics in high-frequency speakers - to remove heat from the voice coil. At the same time, it works as a mechanical damper, suppressing unwanted resonance. The ferromagnetic fluid is held in the gap around the voice coil by a strong magnetic field, being in contact with both magnetic surfaces and the coil at the same time.

Since ferromagnetic liquids have paramagnetic properties, they obey the Curie-Weiss law, becoming less magnetic at elevated temperatures. A strong magnet near the heat-generating voice coil attracts the cold fluid more strongly than the hot fluid, drawing the hot fluid away from the coil and into the cooler. This is an effective cooling method that does not require additional energy consumption.

The ferromagnetic fluid can reduce friction. Applied to the surface of a sufficiently strong magnet, such as neodymium, it allows the magnet to slide on a smooth surface with minimal resistance. Ferromagnetic fluids have many applications in optics due to their refractive properties. Among these applications, one should note the measurement of the specific viscosity of the liquid placed between the polarizer and the analyzer, illuminated by a helium-neon laser.

To study controlled birefringence, a magnetic fluid is placed in a closed glass cell several microns thick. Applying a magnetic field parallel to the surface using an optical microscope, one can observe how some magnetic particles in the liquid assemble into needle-like chains oriented along the field. As the magnetic field increases, more and more particles join these chains, which become thicker and longer. The distance between the chains also decreases.

If the field acts perpendicular to the surface of a film, the chains are arranged in a structure, usually hexagonal. This behavior is analogous to the formation of a lattice of vortices in a superconductor of the second kind. The formation of chains in a ferrofluid in a magnetic field makes it optically anisotropic. With the propagation of light or an electromagnetic wave, the electric and magnetic field intensity vectors oscillate in planes perpendicular to the direction of wave propagation. Light is called linearly polarized if the vector oscillations of the same type occur in one plane perpendicular to the beam, and not in a random transverse direction.

If linearly polarized light falls on a film of a ferromagnetic liquid placed in a magnetic field, it emerges from the other side of the film elliptically polarized (Cotton–Mouton effect). The intensity of transmitted light strongly depends on the angle of incidence. This effect may form the basis of optical switches, in which the intensity of transmitted light changes with changes in the magnetic field or direction of the polaroid.

With the help of a ferromagnetic liquid, it is possible to create diffraction gratings that are rebuilt by a magnetic field. Diffraction occurs as a result of the superimposition of two or more light waves of the same length arriving at the detector (for example, photographic film) along trajectories of slightly different lengths. If the lengths of the trajectories differ by half the wavelength, then such waves cancel each other, and a dark area is formed on the film. If the lengths of the trajectories differ by a wavelength, the intensities of the waves add up, forming a bright area on the detector. Diffraction gratings consist of thin slits spaced apart by the wavelength of the incident light.

If a magnetic field is applied to the ferromagnetic liquid with different susceptibility (which arises, for example, due to a temperature gradient), a non-uniform magnetic volume force arises, which leads to a specific form of heat transfer (so-called thermomagnetic convection). This form of heat transfer can be used where conventional convection is not suitable, for example, in microdevices, or in conditions of reduced gravity.

A frozen or polymerized ferromagnetic liquid, which is under the combined effect of a permanent field (which is magnetizing) and an alternating magnetic field, can serve as the source of elastic oscillations with the frequency of an alternating field, which can be used to generate ultrasound.

5.7 Nanobiomagnetism

Nanobiomagnetism is an important scientific field at the intersection of nanomagnetism and medicine, focusing on biological systems or processes. Magnetism is an integral part of life – from the presence of magnetic iron in the blood to the orientation mechanisms of birds and bees, which are able to navigate the Earth's magnetic field. Magnetic components containing iron play an important role in many aspects of human physiology. The ability of magnets to act on objects at a distance makes them a valuable medical tool. For example, there is a well-known procedure for removing iron shavings from the eye using a magnet. Pins, bullets and grenade fragments are also removed with the help of magnets. The invention of stronger and smaller permanent magnets makes possible more delicate applications, such as the temporary fixation of prostheses in dentistry, the control of catheters moving within the brain or through the body.

Nanoscale materials are of particular importance for biomedical applications, because their size is comparable to the size of cells (10–100 μm), viruses (20–450 nm), proteins (5–50 nm) and genes (2 nm wide and 10–100 nm long). Nanoparticles are small enough to move inside the body without disrupting its normal functioning, and can access places unreachable by other methods.

Magnetic biomaterials. The use of magnetic biomaterials is limited, as their use in vivo (inside the body) requires strict biocompatibility. The requirements for materials used in vitro (outside the body) are less strict, but in any case, the methods of studying living cells must take into account the impact of materials on the sample under study. In addition to biocompatibility, materials must be able to interact with one or several molecules, must retain their magnetic properties for the required period of time in water environments with different *pH* levels, and must not be excreted from the body too quickly.

The vast majority of research in this area uses iron oxide particles because they are highly biocompatible and can be made in a variety of ways and sizes, and they can be superparamagnetic or ferromagnetic. In addition, iron oxide can be assimilated by the body to elemental iron and oxygen with the help of hydrolytic enzymes of the body. Intravenous injections of up to 250 mg of iron per kilogram of body weight have been shown in animals to produce no chronic or acute toxic effects, and doses of 1 to 3 mg of iron per kilogram of body weight have been clinically tested in humans.

The disadvantage of iron oxides, however, is their relatively low magnetic susceptibility. Iron nanoparticles have an order of magnitude higher susceptibility than microscopic iron oxide particles, but nanoparticles are easily oxidized and are not as biocompatible as oxides. Particles of the FeC compound, which are produced by mechanical grinding or chemical reduction, are used in clinical trials to create hyperthermia and drug delivery. These particles are biocompatible, and the carbon in their composition can help neutralize drug toxicity through physical adsorption.

Coating particles with a polymer can increase their resistance to oxidation and phagocytosis, colloidal stability, ability to function, mechanical stability, and biocompatibility. Many polymers are biocompatible and can be used as coatings for metal or ceramic particles. Particles introduced into the bloodstream are quickly coated by circulating components such as plasma proteins. After that, the body's defense system captures and removes these particles from the body. Most nanoparticles can be removed from the bloodstream in just 15 minutes. The time of particle removal depends on the size, charge, number and nature of functional groups on the surface of the particle.

For targeted transport of nanoparticles in the human body, it is necessary that they be in a state of suspension in a water-based solution. In vitro applications also typically require an aqueous medium. Magnetic nanoparticles must remain in the state of suspensions in the liquid and not form clusters due to magnetic interaction.

Magnetic particles in solution undergo two types of relaxation: Brownian relaxation and Néel relaxation.

The Brownian relaxation time is equal to $\tau_{\beta} = \frac{3\eta V_H}{k_B T}$, where V_H, is the hydrodynamic volume of the particle, k_B is the Boltzmann constant, T is the temperature, and η is the dynamic viscosity of the liquid.

The Néel relaxation time is $\tau_N = \tau_0 e^{\frac{\Delta E}{k_B T}}$, where ΔE is the energy barrier, $\tau_0 \sim 10^{-9}$ s. The ΔE parameter is usually determined by the product of the anisotropy K and the magnetic volume V: $\Delta E = KV$. The rate of relaxation has different effects on reducing the mobility of nanoparticles. The Brownian relaxation time can be varied by changing the viscosity of the carrier, while the Néel relaxation must be independent of the carrier fluid. Ferritin is one of the most important magnetic biomaterials that support human life.

Features of ferritin. In nature, there are materials with molecular cavities filled with nanosized magnetic particles. An example is naturally occurring iron in the body, which is usually found in the form of ferritin, i.e., nano-magnetic particles in interstices. Interesting research in the field of nanomagnetism is to create porous material crowded by magnetic nano-particles. In the nature there are some substances with molecular cavities filled with nanoscale magnetic particles. One example is the ferritin – biological molecule that contains 25% iron by weight, while its shape is symmetrical protein shell. It has hollow sphere with inner diameter of 7.5 nm and 12.5 nm in outer diameter. In biological systems this molecule plays a part of "repository" of iron Fe^{+3} in organism. One quarter of iron in human organism is contained in molecules of ferritin and 70% in hemoglobin.

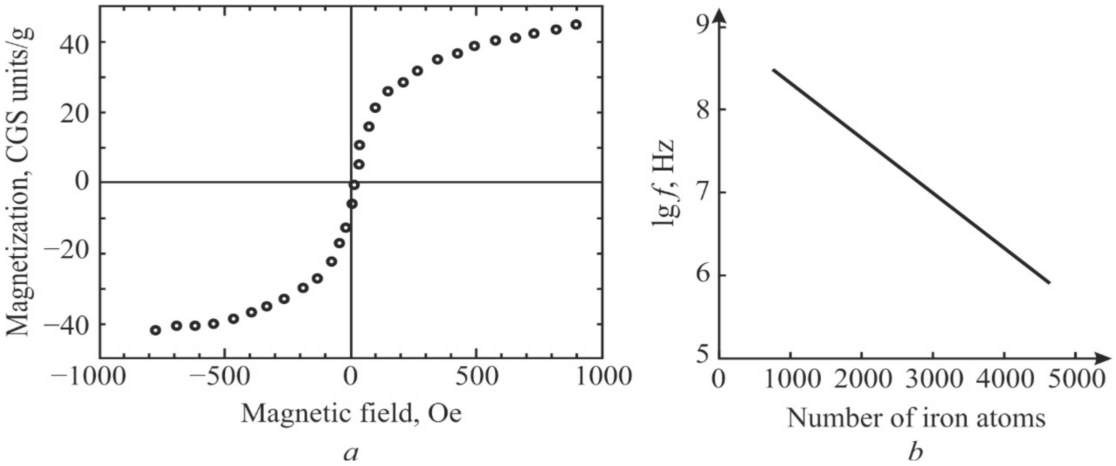


Fig. 5.12. Magnetic properties of ferritin: *a* – magnetization curve; *b* – resonant frequency dependence on number of iron atoms in the cavity of molecule

At normal conditions the cavity of ferritin is filled by the quasi-crystalline iron oxide: $5Fe_2O_3{\cdot}9H_2O$. This iron-oxide solution can enter from outside into a cavity, in which the number of iron atoms can vary from a few to several thousand. Magnetic properties of this molecule depend on number and type of particles in a cavity. It can be both ferromagnetic and antiferromagnetic. At low temperature the quantum tunnelling can be observed ferritin. At that even when magnetic field is absent the magnetization demonstrates tunnelling between two minimal positions. Resonant frequency of this tunnelling depends on total magnetic moment; frequency dependence on number of iron atoms in the ferritin molecule are shown in Fig. 5.12*b*. It is seen that resonant frequency decreases with the increase of atoms quantity in a cluster. Under external magnetic field this resonance disappears, because symmetry of double-well potential becomes broken.

Biocapture and separation of magnetic biomaterials. Some magnetic materials are readily attached to all cell types, while other materials are preferentially attached to specific cell types. The disadvantage of systemic treatment is that the drugs can have a negative effect on healthy cells, for example, as happens during chemotherapy in oncology. Often a certain type of molecule must be separated from other types for further study, and therefore the ability to distinguish between different cell types is a very important property. Nanoparticles can be classified by their physical, chemical, or magnetic capture ability.

Particles with a certain capture capacity have specific surface features, such as hydrophobicity, electrical charge, or *pH*. These properties cause reactions that allow the nanoparticle to "stick" to or enter the cell. Such a mechanism can be used for self-cleansing of certain organs or the body as a whole. Nanoparticles can target specific pathologies, such as tumor or tissue inflammation. Chemical capture particles use features that increase binding selectivity. Particles with magnetic capture ability are used for such therapy when the chemical properties of binding to a certain type of cells are limited. The magnetic orientation force opposes the force associated with linear blood flow, which is about 0.05 cm/s in capillaries, about 10 cm/s in arteries, and 50 cm/s in the aorta.

The accuracy of magnetic binding orientation also depends on the depth of the target tissue in the body: for organs such as the liver and lungs, it is lower than for target organs located closer to the surface. The biggest challenge is creating a focusing field of the required amplitude and gradient with a sufficiently large moment. Magnetic direction of particles significantly reduces their movement to unwanted organs and tissues during application of a magnetic field. Nanoparticles, for example, FeC with sizes up to one micrometer, can be directed to various organs, such as the liver, lungs, brain. But the complication is that these particles are retained mainly only during the time of the magnetic field.

One of the new approaches to magnetic steering is the so-called ferromagnetic seeding. Nanosized ferromagnetic particles (dockers) are introduced into the body using a catheter. Docker increases the magnetic gradient of the external magnetic field, which allows you to significantly reduce the intensity of this field. This method is now widely used for stenting during the treatment of vascular diseases (stenting - installation of a stent - a special wire frame that keeps the lumen of the artery free and passable) in the place of a narrowed section of the artery.

Identification of specific molecules is crucial for diagnosis, treatment and prevention of diseases. The development of fast, portable electronic analyzers capable of detecting some types of substances becomes very urgent due to the threat of biological and chemical terrorism. Magnetic separation is used in various fields of technology, starting with the separation of tin from stainless steel during metal processing to the separation of pure natural diamonds from diamonds with inclusions of other (magnetic) minerals.

Only a small number of cells have sufficient natural magnetic properties to be separated by their own magnetism, so cells must be attached to magnetic nanoparticles or microparticles with a detectable magnetic moment. For the first time, magnetic cell sorting was proposed to be used for surface markers of cell receptors. Magnetic separation of cells allows you to isolate target cells directly from blood, bone marrow and other fluids in a short time due to fast reaction kinetics. The limiting factor for magnetic separation is finding molecules with high specificity to the desired target cells. *Magnetic sorting* is capable of separating micro- or nano-sized particles.

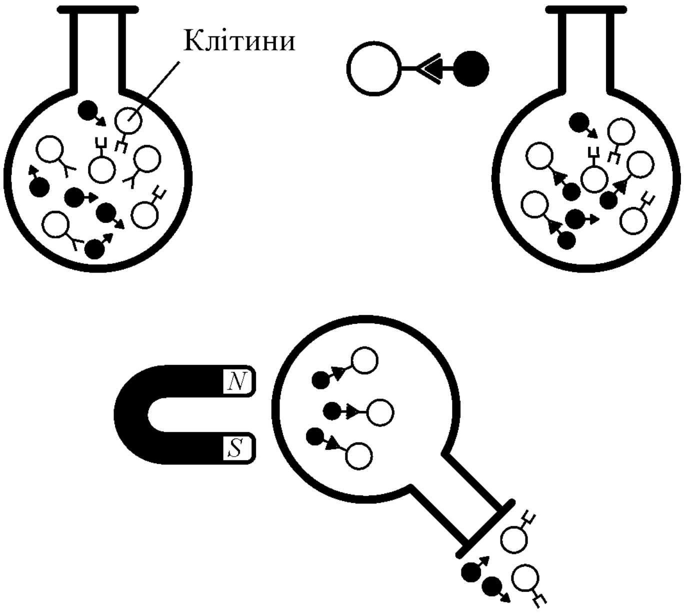


Fig. 5.13. Schematic representation of the process of magnetic separation of cells

Magnetic separation consists of three steps: marking or labeling the desired cells with magnetic markers, separating the magnetically labeled cells from unlabeled cells, and measuring the magnetic properties of the substance to determine the number of labeled cells. A magnet is used to separate cells marked with a magnetic marker from unmarked cells. Most often, as a material for marking, polymers are used, in which magnetic materials are embedded. The permanent magnet can be used to either repel or attract magnetically labeled cells. The magnetic force acting on the magnetic carriers is equal to $F_b = \frac{1}{2\mu_0}\Delta\chi V_H \nabla B^2$, where F_b is the force acting on one carrier, ∇B is the gradient of the magnetic field, $\Delta\chi$ is the hydrodynamic volume of the magnetic carrier, Δ□ is the difference in the magnetic susceptibility of the magnetic carriers and the medium. This repulsive force opposes the drag force F_d of the particle in the liquid. The pulling force is equal to $F_d = 3\pi\upsilon_m D_H\eta$, where D_H is the hydrodynamic diameter of the magnetic carrier, υm is the speed of the magnetic carrier, and η is the viscosity of the liquid. Magnetic sorting methods have a high probability of detecting and monitoring bacterial, viral and other pathogenic contaminants in real time.

Detection of several types of molecules with the help of one chip can be carried out by installing the studied molecules (usually DNA molecules) on a polymer layer that covers the sensor, Fig. 5.14. The DNA sample under study is attached to the polymer layer on the chip (1), then the sample DNA labeled with molecules such as biotin is introduced and bound (2). The excess is removed, and molecules bound to biotin (or streptavidin) attach magnetic markers (3).

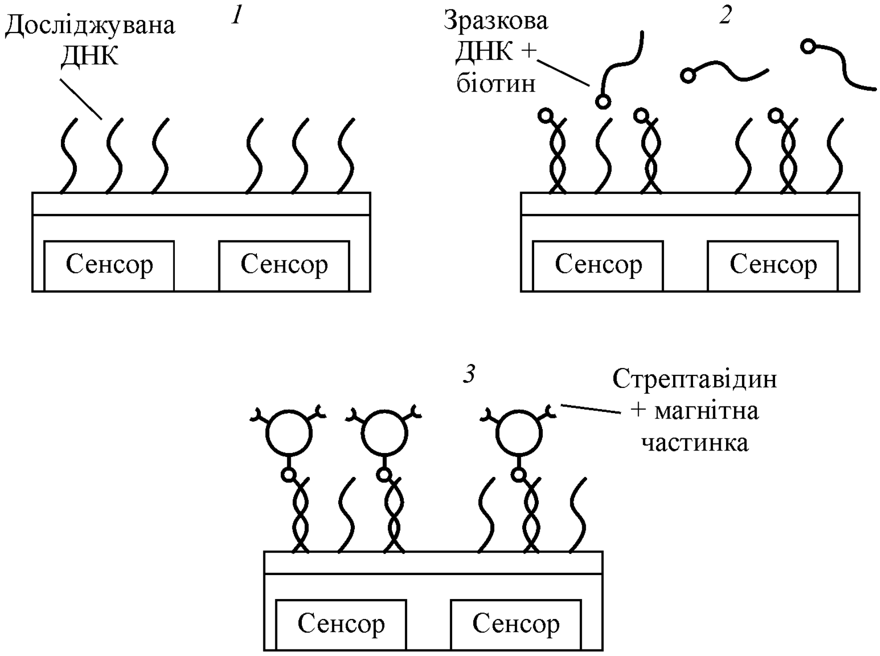


Fig. 5.14. The process of DNA detection using a magnetoresistive device

The sample DNA is complementary to the DNA molecules under study and is labeled, most often, with biotin. Magnetic microspheres bound to streptavidin attached to biotin; therefore, the microspheres bind to biotin, which is present only on successfully captured DNA. The signal measured by the sensor can be used to determine the number of studied molecules at the present time. The feedback on the sensor determines the tangential component of the scattering field induced by the magnetized microspheres. Such sensors have detected concentrations as low as 3 pg/ml. The introduction of sensor elements on the tunnel magnetoresistor and smaller magnetic markers will increase the sensitivity of the method.

The alternative method for detecting biological molecules is based on the change in Brownian relaxation during binding. The relaxation frequency of nanoparticles changes when they bind to other molecules because binding increases their hydrodynamic size. The frequency shift should be proportional to the hydrodynamic dimensions of the nanoparticles, which allows to recognize the studied molecules with different sizes. The advantage of this method is that the signal is present both before and after binding, which is taken into account in the case of robustness testing.

Delivery of medicines. Controlled drug delivery is of great importance to improve drug efficacy as well as patient convenience. Control of delivery allows to reduce the total dose of drugs by 50–80%, at the same time, the dosage in the target organ increases, and the systemic absorption of drugs decreases. Protecting drugs before they reach the target organ increases the effectiveness of drugs that have a short half-life in the body.

Nanoparticles have been used for drug delivery since around 1970, when they were developed as carriers for vaccines and anticancer drugs, and this method is now widely used in medicine. Ideally, nanoparticles for drug delivery should effectively bind a sufficiently large mass fraction (load) of the drug, should form stable suspensions in an aqueous environment, should be biocompatible and biodegradable, and should not be cleared too quickly from the bloodstream. The main advantage of magnetic nanoparticles from the point of view of drug delivery is the possibility of using magnetic properties either to limit the area of drug delivery by magnetic positioning or for remote drug release. The drug can be contained in nanoparticles, can be associated with them or adsorbed on their surface. Most magnetic nanoparticles used for drug delivery are based on iron oxide or iron-carbon compounds. Chemotherapy drugs in oncology, such as mitoxantrone, doxorubicin, and others, are bound to iron oxide or FeC solution using magnetic targeting. Magnetic fields can be used for remote activation of drugs and control of their release rate.

Polymer spheres filled with magnetic nanoparticles and drugs are exposed to an alternating magnetic field, which creates small stress-induced cracks in the polymer. The cracks allow fluids to enter the sphere and release the medicine. Using magnetism as a release-on-demand mechanism may be beneficial for insulin-dependent diabetics. Currently, magnetic capsules of two or more parts that are held together magnetically have been developed. Demagnetization of magnetic capsules using pulses of opposite magnetic polarity allows the capsule to open. The constituent parts of the capsule are quite small and therefore easily removed from the patient's body. Capsules smaller than those currently used for endoscopy could be used to deliver drugs in the gastrointestinal tract.

Nanospheres are solid polymer matrices on which the active substance is distributed. Nanocapsules consist of a polymer shell surrounding a cavity filled with a substance. These types of nanoparticles differ in the release of the active substance:

from nanospheres, the release is exponential (the dependence of the volume of the released substance on time), and from nanocapsules, it is constant for some time.

Magnetic hyperthermia. Currently, a number of methods of treatment of various diseases using local and general controlled hyperthermia are proposed. In the case of overheating of the human body above 42°C, serious disturbances in life support systems occur and heat stroke develops. During the further increase in temperature, there is the irreversible violation of the structure and function of protein molecules in the body, which is incompatible with life. In this regard, methods of local (local) hyperthermia attract the most attention, although most of them are still at the stage of development or clinical trials.

The simplest option for local hyperthermia is heating with a metal needle inserted into the affected area; concentration of focused microwave radiation on it is also possible. Different variants of local magnetic hyperthermia are actively developing, in which the magnetic material introduced into the affected area is heated from the outside with the help of electromagnetic radiation in the range of 100–800 kHz, which is practically not absorbed by body tissues, but intensively interacts with ferro- and superparamagnets. Nanoparticles of iron oxides and various alloys, potentially able to penetrate inside cells, and larger submicron particles of biocompatible ferromagnets located in the intercellular space can act as mediators. Since it is difficult to control the distribution of such particles between healthy and affected tissues in some cases, this can lead to overheating of healthy areas. To solve this problem, it is proposed to use mediators with low Curie temperature values, which automatically stop heating after reaching a set temperature value. The second solution is vectorization of nanoparticles (for example, with antibodies) for targeted delivery to affected cells.

Hyperthermia is implemented due to capacitive or inductive connections of the radio wave field (10 –100 MHz), microwave field (with a frequency higher than 300 MHz), ultrasound, laser or external heat. A macroscopic implant made of Cu or other highly conductive metal is used for eddy current heating. The use of magnetic nanoparticles (magnetic monodomains) is better than the use of microparticles (magnetic multidomains), because magnetic nanoparticles more effectively absorb the energy of the external magnetic field.

The connection of the external radio-frequency magnetic field with magnetic particles in the body allows energy to be transferred to tissues by various mechanisms: eddy current heating; hysteresis heating (heat is generated when the state of the magnetic material is forced to pass part or all of the hysteresis loop); heat of internal friction (heat of kinetic movement of a particle in a viscous liquid);

magnetic resonance. The loss of efficiency of the magnetic particles should be as large as possible to allow lower doses. In order to avoid neuromuscular electrical stimulation, the frequency of the alternating field must be higher than 50 kHz. Limitations imposed by the depth of field penetration mean that the field frequency cannot exceed 5–10 MHz, eliminating the effect of magnetic resonance. When iron oxide nanoparticles are used, typical field frequency values are in the range of 50–500 kHz, and typical field amplitudes are 1 –15 kA/m.

Modeling magnetic hyperthermia is a difficult task due to the complex mechanisms of remagnetization in nanoparticles. Optimizing the properties of the nanoparticles is important to limit the amount of material that must be injected. Hyperthermia, which is achieved in a certain combination of field, frequency and type of particles, as a rule, is determined experimentally. Hyperthermia depends on many factors, including the effect of surface properties on Brownian relaxation, size, and other factors.

Magnets with a large loop area have been found to be best for hysteresis hyperthermia, however the magnitude of the magnetic field at the location of the nanoparticle may be limited, making only small loops available. In macroscopic implants, shape anisotropy can be used to increase the area of the loop, however, local heating should be avoided.

The properties of the hysteresis loop in nanoparticles are determined by overcoming the energy barrier for magnetization rotation. For ferromagnetic particles with dimensions much larger than the limiting dimensions of superparamagnetic particles, there is no clear dependence on hysteresis in the considered frequency range. The physical basis of heating with superparamagnetic particles shows that the frequency dependence is more significant than for their ferromagnetic counterparts.

Nanoparticles for the treatment of neoplasms can be injected into the body once and then used repeatedly during treatment. One approach to temperature control is to use materials with a Curie temperature between 42°C and 50°C, as these materials automatically "turn off" when temperature gets too high. Ferrites such as $(Co_{1-x}Zn_x)Fe_2O_4$, manganates such as $La_{1-x}Me_xMnO_3$ [Me = Sr, Ba, Pb, Ag, Na] and Y_3Fe_5 are used for these purposes.

5.8 Summary

1. Nanophysics is a scientific direction in the field of physical materials science, which is considered one of the most promising. This is the creation and

study of the structure and properties of materials condensed from very small crystals, clusters, fragments that have only 10^3–10^6 atoms. The nanophysics dedicates the creation and study of structures and properties of materials, condensed in form of very small crystals, clusters, fragments that have around of $10^3 \ldots 10^5$ atoms. Main reason of nanomaterials differences from customary materials is that in these substances the *ratio of surface to volume is rather big*.

2. The main reason for the difference of nanomaterials from ordinary materials is that these substances have a very large surface-to-volume ratio. The smaller the size of the nanocluster, the greater the influence of surface properties over bulk properties. In some sense, nanostructures allow to transform the surface properties of the crystal into bulk properties.

3. Nanotechnology is a scientific and technical direction for the creation of materials, functional structures and devices of nanometer size. Due to the small size of the blocks (particles, granules, phases) from which they are built, nanomaterials demonstrate unique mechanical, optical, electrical, and magnetic properties. Just because of small size of units (particles, granules, phases) the nanomaterials exhibit unique mechanical, optical, electrical and magnetic properties. The nanostructured *magnetic materials* can operate with wide range of characteristics. Moreover, nanotechnology can be used to create materials with prescribed type of magnetization curve – both for record magnetically soft materials and for extremely magnetically hard materials.

4. Nanostructuring of volumetric magnetic materials allows controlling their characteristics within wide limits. Nanotechnology can be used to create materials with a given type of magnetization curve - both for record-breaking magnetically soft materials and for extremely magnetically hard materials.

5. Magnetic materials of this type, which demonstrate the ability for large magnetization and at the same time the absence of hysteresis, are called superparamagnets. The essence of this name is that at temperatures lower than the Curie point and in a wide temperature range, they remain, as it were, in a paramagnetic phase.

6. Magnetoresistance is the effect caused by a change in the electrical conductivity of a solid body when it is moved into a magnetic field. Multilayer structures composed of layers of nonmagnetic material alternating between oppositely magnetized ferromagnetic materials show a significant change in resistance when they are placed in a magnetic field. This phenomenon is called the giant magnetoresistance effect.

The effect can be both longitudinal, if the electric current flows in the plane of layers, and transverse - if the current is perpendicular to layers. Multilayered structures composed of layers of nonmagnetic material alternating between oppositely magnetized ferromagnetic materials show significant change in their resistance when putting them in magnetic field. This phenomenon is called as effect of *giant magneto-resistance* (GMR). This effect can be either *longitudinal*, when electrical current flows in plane of layers, or *transversal*, if current is perpendicular to layers.

7. In recent years, a new scientific and technical field has been actively developing - magnetoelectronics, or, as it is now called - "spintronics", which is engaged in the study and practical applications of effects and devices using electron spins. Spintronics studies magnetic and magneto-optical interactions in metal and semiconductor structures, as well as quantum magnetic phenomena in nanometer-sized structures.

8. Spintronics deals with study and practical application such effects and devices that use electronic spin. Electrical current, passing through magnetic crossing, under a certain conditions can be accompanied by the transfer of polarised spins, leading, in particular, to switching of magnetization in layered nanoscale structures. Theoretical examination of this phenomenon is based on conception of exchange interaction between electrons – carriers – and magnetic lattices in ferro-, ferri- or antiferromagnetics

9. The transfer of electric current through the magnetic transition under certain conditions is accompanied by the process of spin transfer, which leads, in particular, to remagnetization of layered nanoscale structures. The theoretical consideration of this phenomenon is based on the concept of the exchange interaction between electrons - current carriers - and magnetic lattices of ferro-, ferro- or antiferromagnets.

10. Materials and structures of spin electronics are a part of semiconductor microelectronics. More complex heterostructures such as semiconductor-ferromagnet-semiconductor and ferromagnet -semiconductor-ferromagnet have been grown using molecular beam epitaxy.

Spintronics is a relatively new, but quite promising field, the focus of which is the use of electron spins. The main focus of scientists is on the possibility of manipulating the quantum spin states of an individual electron to create spintronic quantum logic gates and – in the future – fully functional quantum computers.

15. The relaxation frequency of nanoparticles changes when they bind to other molecules, as binding increases their hydrodynamic size. The frequency shift should

be proportional to the hydrodynamic dimensions of the nanoparticles, which allows to recognize the studied molecules with different sizes.

16. Currently, many different technologies for obtaining an image of the internal structure of the body are used in medicine, including magnetic resonance imaging (MRI). This technology allows medicine to make significant progress in the field of diagnostics and therapy.

17. In a magnetic field, magnetic nanoparticles are magnetized and create an induced magnetic field, which disturbs the process of magnetic relaxation of protons in the water molecules surrounding the magnetic nanoparticles. In turn, this leads to a reduction in the spin-spin relaxation time of protons, and, as a result, is registered as contrast in MRI.

18. Nanoparticles are used for controlled drug delivery, which is of great importance for improving the effectiveness of drugs, as well as for the convenience of patients. Protecting drugs before they reach the target organ increases the convenience of using drugs that have a short half-life in the body.

19. Treatment with heat is called hyperthermia. The use of magnetic nanoparticles in hyperthermia is due to the fact that magnetic nanoparticles more effectively absorb the energy of an external magnetic field.

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5.10 Questions for self-examination

1. Physical nature of magnetism in nanoparticles
2. Soft and hard magnetic nanomaterials (comparison)
3. Nanomagnetic films for computer memory devices
4. Giant and colossal magnetoresistance
5. How and where spin electronics are applied
6. Ferromagnetic liquids physics and application
7. Magnetic hyperthermia and magnetic biomaterials
8. Features of ferritin and its meaning in biology
9. Biocapture and separation of magnetic biomaterials

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