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# Nanoparticles Surface as a Spheroidal Defect in the Parent Material

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**Abstract:** The review considers a general theoretical model of nanoparticles similar to the structure of a "green walnut", consisting of a core, a surface, and a layer of ligands. Due to the peculiarities of such surface defect structure in nanoparticles, the phenomenon of high-temperature ferromagnetism in the nonmagnetic parent structure is possible (it is considered by the example of semiconductor metal oxides, noble metals, and carbon nanostructures). It is shown that this phenomenon is not of an artifact nature, but it is possible for any materials in a highly dispersed state. The main reasons are proposed which can determine the cooperative magnetic effect in the system of defect-induced magnetic moments. The review also discusses the ferron model, which is successfully used to analyze the properties of modern magnetic nanomaterials.

**Keywords:** carbon materials, nanoparticles, defects, defect-induced magnetism, magnetism, ferromagnetism

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## 1. INTRODUCTION

Nanostructuring made possible to reveal a number of fundamentally new properties of materials; this was most clearly manifested by the example of various types of nanomaterials (NM), consisting

of isolated (by various methods) nanoparticles (NPs) with an average diameter of 2-10 nm [1-6].

Numerous examples [7-12] have shown that a "simple" reduction of a material up to nano sizes (2-10 nm) makes them highly defective, which radically changes their physical and chemical properties and the range of applications.

Most real materials are defective to some extent. Such defects are well-studied as vacancies - anionic and cationic; impurity atoms of substitution or insertion; dangling bonds, altered crystal lattice parameters; element-wise or structural separation (internal nanoclusters), etc. [13] In a number of cases, a relationship has been established between structural defects and material properties. Obviously, materials consisting of nanoparticles (NPs) 2-10 nm in size are unconditionally defective, but it is difficult to use the above types

of defects for describing their properties. NPs and NMs based on them contain specific defects characteristic only of them, which determine their unique properties [14,15].

## 2. NANOPARTICLES SURFACE AS A DEFECT

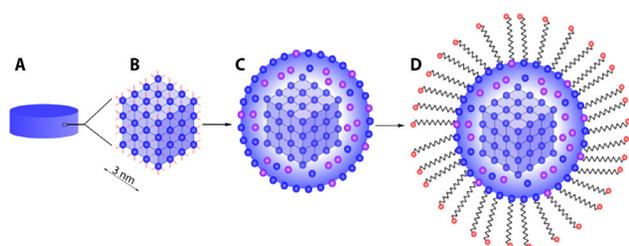
Let us consider the NP surface as an extended defect in the structure of the “parent” nanomaterial, which determines its behavior under the action of external electromagnetic radiation or a magnetic field, which differs from the properties of the initial parent material. Thus, let us assume that the surface of nanoparticles is a special type of defects in nanomaterials.

In order to understand how the physical properties of a material (including magnetic) can (should) change during the transition from a compact (for example, basically diamagnetic) material to a NP system of the same composition, we will conduct a mental experiment.

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Let's take a sample with an arbitrary crystal structure (**Fig. 1A**) (in this case, for simplicity,



**Fig. 1.** Diagram of NP formation from compact material.

a simple cubic lattice was chosen). The sample is in equilibrium at room temperature, normal atmospheric pressure. If you remove a cube with an edge of 3 nm from the middle of this crystal, you will get an object (**Fig. 1B**) along the edges, vertices and sides of which there are exposed atoms (ions) that were previously included in the crystal lattice of the parent material. The broken ties sticking out are clearly visible. These can be vacant or filled orbitals (a pair of electrons can be in an orbital, and a vacancy in a matrix). When they interact with each other, an electron cloud appears on the surface - a plasmon, which is easily polarized under the influence of electromagnetic radiation [16].

But, for example, for the occurrence of magnetism when removing a cube from a "non-magnetic" matrix, the most important is the homolytic breaking of bonds inside the crystal, as a result of which orthogonal surfaces appear on the surface of the removed cube - orbitals with unpaired electrons (spins). As a result of exchange interactions between them, a magnetic domain appears, covering the NP surface, and it becomes magnetic [17,18]. At the band approach, it is assumed that an electron from the valence or conduction band gets to the surface level appearing due to the broken bond (ie, a defect). The electron captured by the defect, first, stabilizes the ferromagnetic state closed to itself, and, second, it self-traps in this cavity. Thus, a ferromagnetic region appears on the surface near the defect, called ferron [19–22].

Plasmon is located along, ferron - orthogonal to the NP surface. This orbital configuration usually does not hinder spin-spin exchange.

Extracting the cube from the matrix will remove the external pressure of the crystal structure of the compact sample, which leads to the transformation of the cube into a spheroid - NP (**Fig. 1C**), consisting of a core, in which the crystal structure of the parent material and its physical properties are mainly preserved, and consisting of a shell of 1-2 atomic layers, in which the crystal structure of the parent sample is significantly distorted-destroyed [23,24]. Due to

surface decompensation of metal polyhedra, the structure degraded, bond lengths, bond angles, and coordination polyhedra changed. A significant number of vacancies - structural defects and impurities - are concentrated in such a shell; there is often structural disorder and similar changes. Thus, the surface (1–2 atomic layers) of spheroidal NPs (2–10 nm) is a specific defect in the structure of the parent material, which is responsible for the appearance of properties uncharacteristic of a compact material [25,26].

As the size decreases, the curvature of the NP surface arises, which leads not only to an increase in the distance between surface atoms and a weakening of electron – electron interactions, but also enhances the exchange interactions between the spins of dangling bonds [27,28]. The system of such exchange interactions covering the entire NP surface determines the behavior of the NP in a magnetic field.

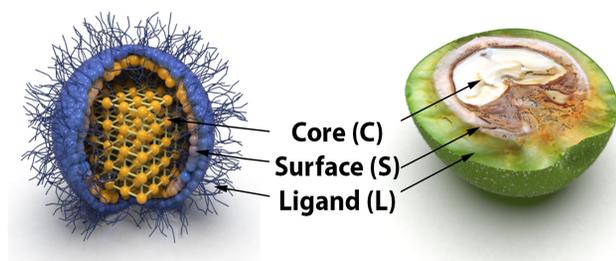
It is generally accepted that NPs consist of a core and two shells (Fig. 1D) (a “green walnut” structure) [28,29]. Each of the 3 parts of a NP (**Fig. 2**) behaves in its own way in an external magnetic field, so that the actually measured magnetic quantities are always a superposition of at least three components.

For small particles, the contribution of the surface layer to the determination of physical properties can be more than 50%, but with an increase in the NP size, the effect of the surface layer begins to rapidly decrease, and for particles > 100 nm, its contribution is usually neglected [30,31]. The set of such NPs is the most

rigorous and well-studied part of the entire huge array of objects which are considered today as nanomaterials.

NPs can be isolated from each other in gaseous, liquid, or solid media; in powders consisting ONLY of NPs and composite materials, where individual NPs are dispersed in matrices - inorganic or polymer [32,33]. Methods for obtaining NPs are well developed; they are obtained both by dispersing compact materials by various methods [34,35] and using various chemical reactions in solutions [36]. In the first case, at the destruction of the sample in the core (but not in the shell) of the formed NPs, the structure of the initial material is mainly retained, while in the second case, the composition and structure of NPs are reconstructed from individual atoms or ions [37]. Such materials based on NPs are universal among other disperse systems, in the sense that a highly defect state can be created in them not only by dispersing macrosamples, but also "construct" them from subatomic fragments, i.e. to one degree or another to manage the defectiveness of the created materials [38,39]. Methods for the synthesis of NPs of a certain size, composition, and structure, with a narrow size distribution, covered with a certain type of ligands, are well developed [40]. In other words, the type of defects and the degree of defectiveness (and hence the physical properties) of such materials can be finely controlled. However, when NPs are compacted, nanomaterials are obtained in which the idealized structure considered above can be distorted: the shells are deformed, penetrate into each other, are destroyed, the cores become larger, etc.

NPs have high surface energy. In a real medium - gas, liquid or solid - the NP surface (2-10 nm) is ALWAYS covered with a layer of light atoms (L in Fig. 2) - specially introduced ligands. The components of the real environment are also potential ligands for the nanoparticle surface. [41] Interaction with ligands makes it possible to partially or completely fill vacant coordination sites (structural defects) and makes the particle significantly more stable. However, such



**Fig. 2.** NP model representing the structure of a "green walnut".

coordination can hinder the spin exchange in the surface layer up to complete destruction.

Thus, any NP with a size of 2-10 nm consists of at least three parts: 1 - a core with a slightly changed structure of the parent sample; 2 - the first shell (1-2 nm), which has the same composition as the particle core, but a significantly distorted structure; 3 - ligand shell, usually consisting of light atoms (O, N, S, etc.). Each of the three components behaves differently under the action of electromagnetic radiation or an external magnetic field and contributes to the observed physicochemical parameters of NPs.

NPs and NMs based on them are a typical example of defective materials, the physical properties of which, along with chemical reactivity, are determined not so much by the composition and crystal structure as by the type and number of defects in the surface layer of NPs.

### 3. LIGAND SHELL

The NPs of the sizes considered in this article are never "naked"; on their surface there are always either individual atoms from the environment, or specially introduced molecules (CO, P(Ph)<sub>3</sub>, etc.). Polymers – organic or inorganic – are in use as specific stabilizers. [42] All these groups are called ligands, meaning that their main function is to interact with dangling surface bonds and fill vacant positions in the coordination sphere of surface atoms of NPs. The ligand shell is an integral part of NPs and has a significant effect both on the magnetic interactions in the particle itself and between them. [43-46] Interaction with the environment also often leads to a change in the chemical composition of the surface (in the most common variant – to oxidation), which inevitably affects the magnetic properties.

As a successful application of the above approach, let us consider NPs of "nonmagnetic" materials, the features of magnetism of which are described in detail in the review [47]. Magnetism still remains one of the most mysterious properties of matter. No less mysterious gravity differs in that its manifestations are universal – gravitational forces do not show any selectivity at the acting

on a material, regardless of its composition and electronic structure. [48,49] In contrast to this, the result of the action of a magnetic field on a material is highly dependent on its composition, structure, shape and other factors. Materials due to their behavior in an external magnetic field are roughly divided into two unequal groups: magnetic (their minority) and all the rest – "non-magnetic". [50,51] The latter, being as a rule diamagnets, are not completely indifferent to the action of an external magnetic field, although the general physical theory of magnetism does not contain reasons for differences.

Modern theoretical concepts of the nature of magnetism, as a rule, describe quite successfully the properties of most traditional magnetic materials, leaving aside "non-magnetic" materials [52,53].

However, as it often happened before, "the experiment turned out to be ahead of theory": it turned out quite unexpectedly that ferromagnetism is found in some samples of semiconductor nanomaterials which do not contain magnetic dopants [54,55]. The number of examples grew rapidly, it became clear that these are not isolated artifacts. In 2005, the term "d<sup>0</sup> magnetism" was introduced to determine this class of phenomena [56]. Later, systematic studies, reviews [57-61] appeared. Later, reports appeared devoted to high-temperature ferromagnetism (HTFM) of carbon NPs (quantum dots), graphene, and other highly defect structures [59,62-64]. It became clear that the observed phenomenon is of a general nature and requires consideration of the entire set of facts from a unified standpoint before it will be possible to start developing the theory of HTFM "nonmagnetic nanomaterials".

Various types of structural inhomogeneity, for example, vacancies and impurity atoms, can contribute to the appearance of HTFM in nanoparticles of materials whose volume analogs do not exhibit such magnetic properties [11,12,58,60,65].

In compact semiconductor NMs, a continuous layer L is usually absent on each NP; its role is most often played by the surface of adjacent neighboring NPs. The interactions arising here

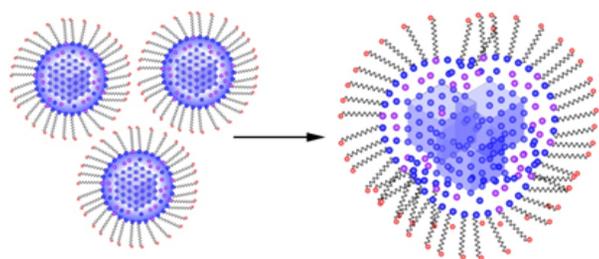
are random and difficult to formalize. To stabilize semiconductor NPs as ligands, mercaptans with long hydrocarbon radicals are most often used [28,66]. It has been shown that the covering of ZnO NPs with mercapto ligands can significantly change their magnetic properties: they can be diamagnetic, have Pauli paramagnetism, or become ferromagnetic [27]. It is believed that although the surface is covered with mercapto ligands, the main contribution to magnetism comes from Zn-O, not Zn-S bonds [67].

The brief review given in Ref. [68] clearly indicates that the behavior of “nonmagnetic” materials in a magnetic field directly depends on the degree of their dispersion and other types of defectiveness. The listed experimental results cover a wide range of materials and make it possible to assert *that a ferro (antiferro) magnetic state can be realized in any material by converting it into a nanodispersed state with a sharp increase in the degree of structural imperfection.*

Based on the above, it is now necessary to expand this conclusion.

SURFACE FERROMAGNETISM AT ROOM TEMPERATURE PRESENTS TO ANY MATERIALS IN A HIGH-DISPERSION NANOSTATE. The exception is organic, polymer and biomaterials.

This is most clearly manifested in nanomaterials, namely, nanopowders consisting of nanoparticles isolated from each other. Defective structures responsible for the appearance of magnetism in such NMs can be regulated within certain limits. Their characteristics are reproducible and can work as a basis for theoretical developments. However,



**Fig. 3.** Violation of the “ideal” structure of NPs when they are compacted.

there are still few such materials [69]. The bulk of nanopowders are formed by simple compaction of nanopowders. In this case, the “ideal” structure of individual NPs in them is violated (**Fig. 3**). In addition, for the implementation of collective magnetic effects, it is necessary to ensure the interaction between the magnetic shells (often severely destroyed) of individual NPs. All this is difficult to control. Therefore, the magnetic characteristics of such materials are generally poorly reproducible. Despite this, the general trends can be traced quite clearly.

At the first stage of the development of these works, it was believed that the surface HTFM is a characteristic of only macroform diamagnetic nanomaterials of a certain type, such as ZnO, Al<sub>2</sub>O<sub>3</sub>, MgO, GaN, and CdSe semiconductors [66,70-73]. Within this type of objects, models were built and calculations were carried out. For example, in [74-77], Thus, for the first time, the following proposition appears, which later became generally accepted for some time: for the manifestation of cooperative magnetic phenomena in some materials, it is necessary (but not sufficient) that uncompensated magnetic moments (spins) exist in them in a significant amount (this is a requirement of cooperative effects), and so that between these moments there were so-called “exchange” interactions, thanks to which their ordered spatial arrangement would be energetically favorable. The proposed model of “localized magnetic moments” well (at least qualitatively) explained the fact that in the overwhelming majority of materials known at that time (including important from a practical point of view), exhibiting collective forms of magnetism, uncompensated magnetic moments are due *to empty electrons d and f of the inner shells of transition metal atoms. The electrons of the outer valence s and p shells, as a rule, participate in the formation of a chemical bond and therefore their magnetic moments are compensated.* It was this phenomenon that later became known as “d<sup>0</sup> magnetism” [56], i.e. magnetism in the absence of d-metals.

The physical models proposed to explain the HTFM of NPs of “nonmagnetic” materials were based on the above-mentioned

well-known concepts. In addition, the concept of uncompensated magnetic sublattices, various types of spin subsystems, the emergence of a new crystal structure that promotes magnetism, etc. [78-82] were attracted. These approaches were suitable for describing the properties of a narrow range of materials and were difficult to use when considering systems other than those based on such approaches. This situation could not satisfy anyone.

It was noted that the realization of  $d^0$  magnetism requires a substantial defectiveness of the structure, which is more often found in low-dimensional systems of NPs or thin (only a few nm) films [83-86].

Gradually, an opinion began to form about the critical importance of structural defects (of various types) for obtaining HTFM in systems exhibiting  $d^0$  magnetism. This fact was reflected in the appearance in 2008 of the term “defect-induced” magnetism [56,83,87].

However, there are many defects, and it was not obvious which ones and how they determine magnetism. Many types of defects in NM did not lead to the appearance of HTFM. Often talked about artifact in such experiments, but this idea was quickly refuted in a number of works [27,85,88,89].

Each of these studies has been fairly successful in describing the properties (magnetic behavior) of a selected narrow set of materials. For example, when discussing the HTFM of a hafnium oxide nanofilm, the authors noted that, taking into account the conditions of sample preparation, a significant number of oxygen vacancies can be expected. In such oxides, which have a high dielectric constant, unpaired electrons tend to form an impurity band, where they can be localized due to correlation effects and local potential fluctuations [90]. Such an impurity band mixes with vacant  $5d$  states, which in turn polarizes the impurity band and provides the necessary ferromagnetic coupling. The observed anisotropy suggests a large  $5d$ -orbital contribution to the spin-orbit coupling. However, such approaches are

hardly suitable for describing the phenomenon as a whole.

It became clear that the existing understanding of magnetism in solids is insufficient to explain these results. However, there are no attempts to consider the entire set of available facts from a unified standpoint.

The clearly expressed HTFM of individual “pure” carbon nanostructures that have nothing other than  $s$  and  $p$  orbitals has received a definite theoretical consideration [62,91-93]. But the question arises, what is common between a 2D nanofilm of hafnium oxide and graphene, if they behave identically in a magnetic field? Realizing this, a number of authors began to consider structural disturbances – defects as a possible universal reason for the manifestation of HTFM in such materials. [94-98] Gradually they began to pay attention to edge effects, distorted surface states, various structural defects [99].

Initially, it looks paradoxical that in order to obtain the required magnetic properties in the systems under consideration, it is necessary not to get rid of defects, but to learn how to control them, *to turn a defect into an effect*. In this case, magnetism remains an intrinsic property of the system, as well as a significant degree of defectiveness, which is fundamentally unavoidable, as, for example, for NPs [14]. A well-developed system of defects (with the exception of defects arising during the growth of crystals – dislocations, disclinations, etc., which are rigidly embedded in the crystal structure – they are not considered here) can provide a sufficiently large number of exchange magnetic bonds necessary for the emergence of a cooperative magnetic effect. However, it immediately became clear that not every defect creates uncompensated magnetic moments. And not every system of defect-induced magnetic moments can turn into a cooperative state.

In review [100], an attempt was made not only to analyze and systematize the experimental results, but also to generalize the methods which make it possible to control the intensity of ferromagnetic exchange interaction in systems of NPs of nonmagnetic (in the volume state) materials. It

should be noted that the introduction of 3D metal ions, which is often used in the creation of magnetic semiconductors, is nothing more than one of the methods for realizing defect structures [83,101]. Such defect centers can act as mediators of magnetic exchange [102].

#### 4. IS IT POSSIBLE TO DIRECTLY INFLUENCE THE SURFACE MAGNETIC EXCHANGE, TO ENHANCE IT?

The reasons which can determine the cooperative magnetic effect in the system of defect-induced magnetic moments can be reduced to the following:

- 1) it is believed that a decrease in the distances between magnetic centers by careful compaction of NPs enhances exchange. On the other hand, compaction destroys the integrity of the surface layer of NPs, which can lead to unpredictable changes in the magnetic characteristics. [86,103];
- 2) surface modification by removing (replacing) adsorbents (ligands) that hinder the magnetic exchange [44,46,104];
- 3) adsorption of ligands – mediators of magnetic exchange [105].

From the data presented, it follows without doubt that the described phenomenon is of a general nature. A distinctive feature of all considered objects is the presence in them of a large number of defects of various nature. Purely phenomenologically, it is reasonable, in the first approximation, to associate the appearance of this or that type of magnetic ordering with the presence of defects of one nature or another in the object. But a number of difficult questions immediately arise, exhaustive answers to which have not yet been found.

There are direct, indirect, double indirect exchange, the interaction of Ruderman-Kittel-Kasuya-Yosida (RKKY) and some others [106]. The concept of exchange interactions is of a model nature (in fact, the form of the Hamiltonian is postulated), this explains its limitations [107]. But what about those cases when there are no d or f electrons, and exchange interactions are present and cooperative effects take place?

HTFM of NPs of “nonmagnetic” materials is a widespread phenomenon, for which there are still no unified phenomenological approaches, the role of defects is recognized, but which defects and how they affect HTFM is not specified.

It is believed that the surface of spheroidal nanoparticles is a defect that determines and causes HTFM. NPs isolated from each other in the matrix behave like pseudo-atoms with large (often giant) collective magnetic moments. As the distance between particles decreases, exchange interactions arise and intensify. The results of intraparticle exchanges are summed up with interparticle ones and together determine the behavior of an NM in a magnetic field.

Based on the thought experiment proposed at the beginning, as a result of the rupture of the structure of the original crystal, three types of orbitals can appear on the surface of the removed cube. (Fig. 4): two (A and B) as a result of heterolytic rupture of bonds and C - after homolysis of bonds. This is a simplified diagram designed to demonstrate the electronic consequences of bond breaking using the p-orbital as an example. In the case of d or f orbitals, the picture is more complicated, but in the end the electronic result of bond breaking is the same as in the diagram.

During the transformation of a cube into a spheroidal NP, these orbitals behave differently: orbitals with unpaired electrons remain directed orthogonally to the NP surface and cannot participate in the formation of direct valence bonds with each other in the surface layer. At the

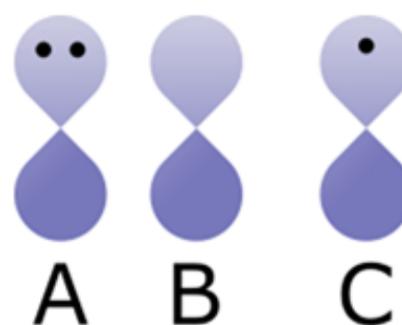


Fig. 4. Three types of bond breaking in NM.

same time, such a configuration does not prevent exchange interactions between parallel spins; as a result, a "magnetic layer" is formed, covering the entire surface of the NP and determining its behavior in a magnetic field.

The rest of the electrons and vacant orbitals formed as a result of breaking bonds in the macrostructure form an "electronic layer" also located on the NP surface and determining its behavior in an electromagnetic field, the interaction with which manifests itself in the spectra in the form of plasmon resonance [108].

These two subsystems "magnetic" and "electronic" coexist in the surface layer of the NP and determine its properties. The model considers idealized spheroidal NPs located separately from each other.

In real powders and other NMs, individual NPs behave like giant magnetic pseudo-atoms. In this case, interparticle magnetic interactions (exchange) occur along with intraparticle interactions. The convergence of NPs over short distances destroys the ideal picture, which often affects the reproducibility of the measurement results and complicates their interpretation.

The above "ideal" scheme stops working. In such materials (and there are most of them), intraparticle and interparticle exchange interactions, as a rule, cannot be separated and formalized. In the case of non-spheroidal morphology of planar 2D nanosystems (in nanofilms, graphene, etc.), "linear" defects are added to a spheroidal defect (shell) that has become flat – end and along internal breaks in the structure.

Orbitals with unpaired spins lie in the plane and their exchange interactions can occur only with neighbors at the edge of the plane.

There are two subsystems: electronic, due to the overlap of orbitals filled with electrons, and spin, due to exchange interactions between unpaired electrons. These two subsystems are orthogonal to each other. The electronic subsystem is polarized by an external electromagnetic field (light quanta); spin – by an external magnetic field. The model conceptually reflects the presence of

two subsystems, as exemplified by spheroidal and flat defects. [100]

## 5. THE ROLE OF BASS SIZE

When NPs grow larger, surface ferromagnetism does not disappear anywhere, just the fraction of surface atoms sharply decreases with increasing NP size, and their contribution to the magnetic behavior of the sample is beyond the sensitivity limit of the method [103].

The proposed model makes it possible to qualitatively generalize and classify the available information on the HTFM of NPs of "nonmagnetic" materials. Thus, as a result of the above-described virtual operation, the diamagnetic material is transformed into a system of NPs with uncompensated surface spins; their exchange interactions can lead to the manifestation of various forms of magnetic ordering, from para up to ferro (less often antiferro) magnetism.

## 6. THEORETICAL MODELS OF HTFM IN LF AND NM

The experimental detection of the HTFM phenomenon in NPs and other nanostructures was accompanied by attempts to interpret it theoretically (see reviews [100,107,109] and references therein). Ferromagnetism is more common in metal-containing compounds; therefore, the band approach dominates in the theory of magnetism as a whole. At the same time, the HTFM phenomenon is observed both in metals and in dielectrics and semiconductors, i.e. claims to be universal [110]. Therefore, it is not surprising that there is currently no unified explanation of this phenomenon for all materials where it was observed.

Attempts to theoretically explain HTFM in carbon nanostructures, with the exception of graphene, on the whole, do not go beyond the model of defect-induced band or localized magnetism used for most inorganic nanoparticles [62]. A theoretical study of HTFM in graphene "nanoislands" of triangular and hexagonal shape with zigzag edges was carried out in the Hubbard mean field model and using the DFT methods [111]. It is shown that electronic states with

nonzero spin actually appear in the structures. Attention was drawn to the dimensional features of HTFM in graphene in review [112]. Thus, carbon nanomaterials are an integral part of the family of materials with HTFM.

## 7. CONCLUSION

The nanostate of matter presented us with another surprise – the fundamental possibility of obtaining magnetic materials from almost any substance by fairly simple, sometimes (as in the case of ZnO) primitive methods. At the same time, theoretical concepts and deep understanding of this phenomenon (as often happened before) are still far from complete. The task of the authors of the review was to show that the material presented is not a collection of individual random facts taken from numerous experimental and theoretical studies, but is a phenomenon (a general pattern) that requires deep and theoretical analysis from a unified standpoint. The future will show to what extent we have managed to do this. Summarizing the state of the problem of the theoretical description of HTFM, we can say that, on the one hand, its satisfactory solution is still hampered by the diversity and incompleteness of experimental studies. On the other hand, the unusualness of the detected magnetic properties, apparently, should stimulate theorists to critically analyze the existing ideas about the magnetic properties of materials, model approaches, and computational techniques.

The discovery of the HTFM phenomenon occurred in the process of searching for materials in which the electrical and magnetic properties are closely interrelated. Such materials are necessary for spintronics which is a modern branch of electronics, which uses not only the electric charge of current carriers, but also their spin, i.e. magnetic properties [113,114]. In the theoretical models of HTFM, in particular, in the ferron theory of E.L. Nagaev, the electrical and magnetic properties of the material are closely interrelated on the NP surface. Therefore, there is no doubt that with further study of HTFM, it, in addition to undoubted fundamental scientific interest, will find important practical applications [115]. The most probable closest practical use of the HTFM

phenomenon is a magnetoresistance-based device. Although the magnitude of the magnetoresistance in magnetized materials is not too high [22,116], targeted control of the defect structure of the NP surface [117] can correct this drawback.

It can be assumed that the widespread involvement of magnetic methods in the study of NPs and NMs will not only lead to the discovery of new examples of the manifestation of magnetism in materials, but will also expand our understanding of magnetism as a fundamental property of matter. The authors hope that the approach presented in the article will become a reason not only for discussions, but also serve as a basis for a deeper consideration of the HTFM problem by specialists.

## REFERENCES

1. Gubin SP, Kataeva NA, Khomutov GB. Promising areas of nanoscience: chemistry of nanoparticles of semiconductor materials. *Izv. akad. nauk. Ser. Khim.*, 2005, 4:811-836 (in Russ.).
2. Jung DR, Kim J, Nahm C, Choi H, Nam S., Park B. Review paper: Semiconductor nanoparticles with surface passivation and surface plasmon. *Electronic Materials Letters*, 2011, 7 (3):185-194.
3. Gubin SP, Koksharov YA, Khomutov GB, Yurkov GYu. Magnetic nanoparticles: methods of preparation, structure and properties. *Advances in Chemistry*, 2005, 74 (6):539-574.
4. Faivre D, Bennet M. Magnetic nanoparticles line up. *Nature*, 2016, 535 (7611):235-236.
5. Gawande MB, Goswami A, Felpin F-X, Asefa T, Huang X, Silva R, Zou X, Zboril R, Varma RS. Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chem. Rev.*, 2016, 116:3722-3811.
6. Chaudhuri RG, Paria S. Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. *Chem. Rev.*, 2012, 112:2373-2433.
7. Ilka M, Bera S, Kwon S-H. Influence of Surface Defects and Size on Photochemical Properties of SnO<sub>2</sub> Nanoparticles. *Materials*, 2018, 11 (6):904.

8. Bera S, Khan H, Biswas I, Jana S. Polyaniline hybridized surface defective ZnO nanorods with long-term stable photoelectrochemical activity. *Appl. Surf. Sci.*, 2016, 383:165-176.
9. Anuchai S, Phanichphant S, Tantraviwat D, Pluengphon P, Bovornratanaraks T, Inceesungvorn B. Low temperature preparation of oxygen-deficient tin dioxide nanocrystals and a role of oxygen vacancy in photocatalytic activity improvement. *J. Colloid Interface Sci.*, 2018, 512:105-114.
10. Martínez B, Roig A, Molins E, González-Carreño T, Serna CJ. Magnetic Characterization of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles Fabricated by Aerosol Pyrolysis. *J. Appl. Phys.*, 1998 83:3256-3262.
11. Singh R. Unexpected magnetism in nanomaterials. *JMMM*, 2013, 346:58-73.
12. Crespo P, de la Presa P, Marín P, Multigner M, Alonso JM, Rivero G, Yndurain F, González-Calbet JM, Hernando A. Magnetism in nanoparticles: tuning properties with coatings. *J. Phys.: Condens. Matter.*, 2013, 25:484006-4840027.
13. Tilley RD. *Defects in solids*. Wiley, Weinheim, 2008, 552 p.
14. Gubicza J. *Defect Structure and Properties of Nanomaterials: Second and Extended Edition*. Cambridge, Woodhead Publishing, 2017, 410 p.
15. Wu Z, Cao S, Zhang C, Piao L. Effects of bulk and surface defects on the photocatalytic performance of size-controlled TiO<sub>2</sub> nanoparticles. *Nanotechnology*, 2017, 28:275706.
16. Pi X, Delerue C. Tight-binding calculations of the optical response of optimally P-doped Si nanocrystals: a model for localized surface plasmon resonance. *Phys. Rev. Lett.*, 2013, 111 (17):177402-5.
17. Schnack J. Large magnetic molecules and what we learn from them. *Contemp. Physics*, 2019, 60:127-145.
18. Gómez Vitoria M, Weick G, Wienmann D, Jalabert RA. Orbital magnetism in ensembles of gold nanoparticles. *Phys. Rev.B.*, 2018, 98 (19):195417-38.
19. Nagaev EL. Ground state and anomalous magnetic moment of conduction electrons in an antiferromagnetic semiconductor. *JETP Letters*, 1967, 6:484.
20. Nagaev EL. Ferromagnetic microregions in a semiconductor antiferromagnet. *JETP*, 1968, 54: 228.
21. Kasuya T. Mobility of the antiferromagnetic large polaron. *Solid State Commun.*, 1970, 8:1635.
22. Nagaev EL. Magnetic polarons (ferrons) of complicated structure. *JETP Letters*, 2001, 74:431.
23. Hamdy Makhlof AS, Barhoum A. *Fundamentals of Nanoparticles: Classifications, Synthesis Methods, Properties and Characterization*. Elsevier, 2018, 666 p.
24. de Mello Donega C. *Nanoparticles*. Springer-Verlag Berlin Heidelberg, 2014, 299 p.
25. Nealon GL, Donnio B, Greget R, Kappler J-P, Terazzi E, Gallani JL. Magnetism in gold nanoparticles. *Nanoscale*, 2012, 4:5244-52258.
26. Agrachev M, Antonello S, Dainese T, Ruzzi M, Zoleo A, Aprá E, Govind N, Fortunelli A, Sementa L, Maran F. Magnetic Ordering in Gold Nanoclusters. *ACS Omega*, 2017, 2(6):2607-2617
27. Garcia MA, Merino JM, Pinel EF, Quesada A, de la Venta J, Gonzalez MLR, Castro GR, Crespo P, Llopis J, Gonzalez-Calbet JM, Hernando A. Magnetic Properties of ZnO Nanoparticles. *Nano Lett.*, 2007,7(6):1489-1494.
28. Guglieri C, Laguna-Marco MA, García MA, Carmona N., Céspedes, Garsia-Hernández M., Espinosa A., Chaboy J. XMCD Proof of Ferromagnetic Behavior in ZnO Nanoparticles. *J. Phys. Chem. C.*, 2012, 116 (11):6608-6614.
29. Gubin SP, Koksharov YA. Preparation, structure and properties of magnetic materials based on Co-containing nanoparticles. *Neorg. Mat.*, 2002, 38(11):1287-1304.
30. Yamamoto Y, Hori H. Direct Observation of the Ferromagnetic Spin Polarization in Gold Nanoparticles: A Review. *Rev. Adv. Mater. Sci.*, 2006, 12:23-32.

31. Fiorani D. *Surface Effects in Magnetic Nanoparticles*. New York, Springer, 2005, 300 p.
32. Wang XQ, Mujumdar AS. A review on nanofluids — part I: theoretical and numerical investigations. *Brazilian J of Chem. Eng.*, 2008, 25(4):613-630.
33. Yu W, Xie H. A Review on Nanofluids: Preparation, Stability Mechanisms, and Applications. *J.Nanomaterials*, 2012, Article ID 435873, 1 p.
34. Merkel TJ, Herlihy KP, Nunes J, Orgel RM, Rolland JP, DeSimone JM. Scalable, Shape-specific, Top-down Fabrication Methods for the Synthesis of Engineered Colloidal Particles. *Langmuir*, 2010, 26(16):13086-13096.
35. Bulychev NA, Kazaryan MA, Kirichenko MN, Ivanov AV Study of Acoustoplasma Discharge as a Technique for Synthesis of Optically Active Materials. *Int. J. Nanotec.*, 2019, 16(1/2/3):34-41.
36. Lo CH, Tsung TT, Chen LC. Shape-controlled synthesis of Cu-based nanofluid using submerged arc nanoparticle synthesis system (SANSS). *J. Crystal. Growth*, 2005, 277(1-4):636-642.
37. Sato-Berrú R, Redón R, Vázquez-Olmos A, Saniger J. Silver nanoparticles synthesized by direct photoreduction of metal salts. Application in surface-enhanced Raman spectroscopy. *J. Raman Spectrosc.*, 2009, 40:376-380.
38. Jin R, Cao YC, Hao E, Metraux GS, Schatz GC, Mirkin C. Controlling anisotropic nanoparticle growth through plasmon excitation. *Nature* 2003, 425:487-490.
39. Kim S, Yoo B, Chun K, Kang W, Choo J, Gong M-S, Joo SW. Catalytic effect of laser ablated Ni nanoparticles in the oxidative addition reaction for a coupling reagent of benzylchloride and bromoacetonitrile. *J. Mol. Catal. A: Chem.*, 2005, 226(2):231-234.
40. Heuer-Jungemann A, Feliu N, Bakaimi I, Hamaly M, Alkilany A, Chakraborty I, Masood A, Casula MF, Kostopoulou A, Oh E, Susumu K, Stewart MH, Medintz IL, Stratakis E, Parak WJ, Kanaras AG. The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chem. Rev.*, 2019, 119(8):4819-4880.
41. Ling D, Hackett MJ, Hyeon T. Surface ligands in synthesis, modification, assembly and biomedical applications of nanoparticles. *Nano Today*, 2014, 9(4):457-477.
42. Kate K, Singh K, Khanna PK. Microwave formation of Polypyrrole/Ag nano-composite based on interfacial polymerization by use of AgNO<sub>3</sub>. *Synth. React. Inorg Met-Org Chem.*, 2011, 41:199-202.
43. Angappane S, Park J, Jang Y, Hyeon T, Park JG. Magnetic Pd nanoparticles: Effects of surface atoms. *J.Phys.: Condens. Matter.*, 2008, 20:295209-295215.
44. Guerrero E, Muñoz-Márquez MA, García MA, Crespo P, Fernández-Pinel E, Hernando A, Fernández A. Surface plasmon resonance and magnetism of thiol-capped gold nanoparticles. *Nanotechnology*, 2008, 19:175701-175706.
45. Ionita P, Caragheorgheopo A, Gilbert B, Chechik V. Dipole-Dipole Interactions in Spin-Labeled Au Nanoparticles as a Measure of Interspin Distances. *J. Phys. Chem. B*, 2005, 109:3734-3742.
46. Tu W, Fukui K, Miyazaki A, Enoki T. Magnetic and Electronic Properties of Palladium Nanoparticles Coated with  $\pi$ -Conjugated Tetrathiafulvalenes Derivative. *J. Phys. Chem. B*, 2006, 110:20895-20900.
47. Gubin SP, Koksharov YA, Ioni YV. Magnetism of nanoparticles of "non-magnetic" materials; the role of defects. *Zhurnal neorg. khimii*, 2021, 66(1):1-27 (in Russ.).
48. Cai L, Zhu J, Hou Y, Tong M, Kim H. Influence of gravity on transport and retention of representative engineered nanoparticles in quartz sand. *J. of Cont. Hydr.*, 2015, 181:153-160.
49. Palma-Jiménez M, Corrales Ureña Y, Villalobos Bermúdez C, Vega Baudrit JR. Microgravity and Nanomaterials. *Int. J of Biophysics*, 2017, 7(4):60-68.

50. Vonsovsky SV. *Magnetism. Magnetic properties of dia-, para-, ferro-, antiferro- and ferrimagnets.* Moscow, Nauka Publ., 1971, 1032 p.
51. Hurd CM. Varieties of Magnetic Order in Solids. *Contempt. Phys.*, 1982, 23:469-493.
52. Veciana J.  *$\pi$ -Electron Magnetism from Molecules to Magnetic Materials.* Springer, 2001, 208 p.
53. Mattis D.C. *The theory of magnetism made simple: an introduction to physical concepts and to some useful mathematical methods.* L.: World Scientific, 2006, 580 p.
54. Norberg NS, Kittilstved KR, Amonette JE, Kukkadapu RK, Schwartz DA, Gamelin DR. Synthesis of Colloidal Mn<sup>2+</sup>: ZnO Quantum Dots and High-TC Ferromagnetic Nanocrystalline Thin Films. *JACS*, 2004, 126(30):9387-9398.
55. Kittilstved KR, Norberg NS, Gamelin DR. Chemical Manipulation of High-TC Ferromagnetism in ZnO Diluted Magnetic Semiconductors. *Phys. Rev. Lett.*, 2005, 94(14):147209-147213.
56. Coey JMD. d<sup>0</sup> ferromagnetism. *Solid State Sciences*, 2005, 7:660-667.
57. Droghetti A, Pemmaraju CD, Sanvito S. Predicting d<sup>0</sup> magnetism: Self-interaction correction scheme. *Phys.Rev.B*, 2008, 78:140404 (R)-4.
58. Sundaresan A, Rao CNR. Ferromagnetism as universal feature of inorganic nanoparticles. *Nano today*, 2009, 4:96-106.
59. Hernando A, Crespo P, García MA, Coey M, Ayuela A, Echenique PM. Revisiting magnetism of capped Au and ZnO nanoparticles: Surface band structure and atomic orbital with giant magnetic moment. *Phys. Status Solidi B*, 248:2352-2360.
60. Trudel S. Unexpected magnetism in gold nanostructures: making gold even more attractive. *Gold Bull.*, 2011, 44:3-13.
61. Ackland K, Coey JMD. Room temperature magnetism in CeO<sub>2</sub> — A review. *Physics Rep.*, 2018, 746:1-39.
62. Makarova T, Palacio F. *Carbon-based Magnetism. An Overview of the Magnetism of Metal Free Carbon-Based Compounds and Materials.* Amsterdam, Elsevier, 2006, 576 p.
63. Wang Y, Huang Y, Song Y, Zhang X, Ma Y, Liang J, Chen Y. Room-Temperature Ferromagnetism of Graphene. *Nano Lett.*, 2009,9:220-224.
64. Matte HSSR, Subrahmanyam KS, Rao CNR. Novel Magnetic Properties of Graphene: Presence of Both Ferromagnetic and Antiferromagnetic Features and Other Aspects. *J. Phys. Chem. C*, 2009, 113:9982-9985.
65. Morozavska AN, Eliseev EA, Glinchuk MD, Blink R. Surface-induced magnetism in the solids with impurities and vacancies. *Physics B*, 2011, 406:1673-1688.
66. Singh SB, Limaye MV, Date SK, Kulkarni SK. Room temperature ferromagnetism in thiol-capped CdSe and CdSe: Cu nanoparticles. *Chem. Phys. Lett.*, 2008, 464(4-6):208-210.
67. Chaboy J, Boada R, Piquer C, Laguna-Marco MA, García-Hernández M, Carmona N, Llopis J, Ruíz-González ML, González-Calbet J, Fernández JF, García MA. Evidence of intrinsic magnetism in capped ZnO nanoparticles. *Phys. Rev. B.*, 2010, 82:064411-9.
68. Dietl T. A ten-year perspective on dilute magnetic semiconductors and oxides. *Nature Materials*, 2010, 9:965-974.
69. Sundaresan A, Bhargavi R, Rangarajan N, Siddesh U, Rao CNR. Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides. *Phys. Rev. B*, 2006, 74:161306 (R)-6.
70. Sharma P, Gupta A, Rao KV, Owens FJ, Sharma R, Ahuja R, Guillen JMO, Johansson B, Gehring GA. Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO. *Nat. Mater.*, 2003, 2:673-679.
71. Hong NH, Sakai J, Huong NT, Brizé V. Room temperature ferromagnetism in laser ablated Ni-doped In<sub>2</sub>O<sub>3</sub> thin films. *Appl Phys. Lett.*, 2005, 87(10):102505-102507.
72. Hong NH, Sakai J, Poirot N, Brizé V. Room-temperature ferromagnetism observed in

- undoped semiconducting and insulating oxide thin films. *Phys. Rev. B*, 2006, 73(13):132404-132407.
73. Seehra MS, Dutta P, Neeleshwar S, Chen Y-Y, Chen CL, Chou SW, Chen CC, Dong C-L, Chang C-L. Size-Controlled Ex-nihilo Ferromagnetism in Capped CdSe Quantum Dots. *Adv. Mater.*, 2008, 20:1656-1660.
74. Moriah T. Recent advances in the theory of magnetism of itinerant electrons. *UFN*, 1981, 135:117-170.
75. Moriah T. *Spin fluctuations in magnets with itinerant electrons*. Moscow, Mir Publ., 1988, 287 p.
76. Izyumov YA, Katsnelson MI, Skryabin YUN. *The magnetism of collectivized electrons*. Moscow, Fizmatlit Publ., 1994, 368 p.
77. Donath M., Nolting W. *Local-Moment Ferromagnets*. Springer, Berlin-Heidelberg, 2005, 329 p.
78. Aguilera-Granja F, Rodríguez-López JL, Michaelian K, Berlanga-Ramírez EO, Vega A. Structure and magnetism of small rhodium clusters. *Phys. Rev. B*, 2002, 66(22):224410-224419.
79. Gómez Vitoria M, Weick G, Wienmann D, Jalabert R. Orbital magnetism in ensembles of gold nanoparticles. *Phys. Rev. B*, 2018, 98:195417-195425.
80. Grèget R, Nealon GL, Vilenó B, Turek P, Mèny C, Ott F, Derory A, Voirin E, Rivière E, Rogalev A, Wilhelm F, Joly L, Knafo W, Ballon G, Terazzi E, Kappler JP, Donnio B, Gallani JL. Magnetic Properties of Gold Nanoparticles: A Room-Temperature Quantum Effect. *Chem. Phys. Chem.*, 2012, 13:3092-3097.
81. Hernando A, Crespo P, García MA. Origin of Orbital Ferromagnetism and Giant Magnetic Anisotropy at the Nanoscale. *Phys. Rev. Lett.*, 2006, 96(17):057206-057209.
82. Jeon YT, Lee GH. Magnetism of the fcc Rh and Pd nanoparticles. *J. Appl. Phys. B*, 2008, 103:094313-094317.
83. Coey JMD, Chambers SA. Oxide Dilute Magnetic Semiconductors - Fact or Fiction? *MRS Bull.*, 2008, 33:1053-1058.
84. Ivanovskiy AL. Magnetic effects in nonmagnetic sp-materials, induced by sp-impurities and defects. *UFN*, 2007, 177:1083-1105.
85. Tuboltsev V, Savin A, Pirojenko A, Räisänen J. Twist of Magnetism in Nanocrystalline Gold. *ACS Nano*, 2013, 7:6691-6699.
86. Suda M, Kameyama N, Ikegami A, Suzuki M, Kawamura N, Einaga Y. Size-reduction induced ferromagnetism and photo-magnetic effects in azobenzene-thiol-passivated gold nanoparticles. *Polyhedron*, 2009, 28:1868-1874.
87. Esquinazi P, Hergert W, Spemann D, Setzer A, Ernst A. Defect-induced magnetism in solids. *IEEE Transactions on Magnetics*, 2013, 49:4668-4674.
88. Abraham DW, Frank MM, Guha S. Abraham, D. W., Frank, M. M., & Guha, S. (2005). Absence of magnetism in hafnium oxide films. *Applied Physics Letters*, 2005, 87(25):252502-252504.
89. Coey JMD, Ackland K, Venkatesan M, Sen S. Collective magnetic response of CeO<sub>2</sub> nanoparticles. *Nat. Phys.*, 2016, 12: 694-699.
90. Venkatesan M, Fitzgerald CB, Coey JMD. Unexpected magnetism in a dielectric oxide. *Nature*, 2004, 430:630.
91. Sheka EF. Odd Electrons in Molecular Chemistry, Surface Science, and Solid State Magnetism. *Int. J. Quant. Chem.*, 2007, 107:2935-2955.
92. Ray S.C. *Magnetism and Spintronics in Carbon and Carbon Nanostructured Materials*, 1st Ed. Elsevier, 2020, 240 p.
93. Yaziev O. Emergence of magnetism in graphene materials and nanostructures. *Rep. Prog. Phys.*, 2010, 73:056601-056616.
94. Lee H, Son Y-W, Park N, Han S, Yu J. Magnetic ordering at the edges of graphitic fragments: Magnetic tail interactions between the edge-localized states. *Phys. Rev. B*, 2005, 72(17):174431-174438.
95. Okada S, Oshiyama A. Magnetic Ordering in Hexagonally Bonded Sheets with First-Row Elements. *Phys. Rev. B*, 2001, 64(14):146803-146806.

96. Scopel WL, Paz WS, Freitas JCC. Interaction between single vacancies in graphene sheet: An ab initio calculation. *Solid State Commun.*, 2016, 250:5-10.
97. Urita K, Suenaga K, Sugai T, Shinohara H, Iijima S. In Situ Observation of Thermal Relaxation of Interstitial-Vacancy Pair Defects in a Graphite Gap. *Phys. Rev. Lett.*, 2005, 94(15):155502-155505.
98. Zhou Q, Fu Z, Wang C, Tang Y, Zhang H, Yuan L, Yang X. The electronic and magnetic properties of B-doping Stone – Wales defected graphene decorated with transition-metal atoms. *Physica E*, 2015, 73:257-261.
99. Shukla V. Observation of critical magnetic behavior in 2D carbon based composites. *Nanoscale Adv.*, 2020, 2:962-995.
100. Coey JMD. Magnetism in d<sup>0</sup> oxides. *Nat. Mater.*, 2019, 18:770.
101. Coey JMD. Dilute magnetic oxides. *Current Opinion in Solid State and Materials Science*, 2006, 10:83-92.
102. Kikoin K. Ferromagnetic ordering in dilute magnetic dielectrics with and without free carriers. *J. Magn. Magn. Mater.*, 2009, 321:702-705.
103. Hori H, Yamamoto Y, Iwamoto T, Miura T, Teranishi T, Miyake M. *Phys. Rev. B.*, 2004, 16:174411-174415.
104. Crespo P, Litrán R, Rojas TC, Multigner M, de la Fuente JM, Sánchez-López JC, García MA, Hernando A, Penadés S, Fernández A. Permanent Magnetism, Magnetic Anisotropy, and Hysteresis of Niol -pped Gold Capped. *Phys. Rev. B*, 2004, 93(8):087204-087207.
105. Tang N. *In Spintronic 2D Materials: Fundamentals and Applications*. (Eds. Liu W, Xu Y). Amsterdam, Elsevier, 2005, pp. 137-161.
106. Rakitin YuV, Kalinnikov TV. *Sovremennaya magnetokhimiya* [Modern magnetochemistry]. Sankt-Petersburg, Nauka Publ., 1994, 287 p.
107. Zunger A, Lany S, Raebiger H. The quest for dilute ferromagnetism in semiconductors. *Guides and misguides for theory. Physics*, 2010 3:53-62.
108. Boken J, Khurana P, Thatai S, Kumar D, Prasad S. Plasmonic nanoparticles and their analytical applications: A review. *Applied Spectroscopy Reviews*, 2017, 52(9):774-820.
109. Stoneham M. The strange magnetism of oxides and carbons. *J. Phys.: Condens. Matter*, 2010, 22(7):074211-074217.
110. Sundaresan A, Rao CNR. Ferromagnetism as universal feature of inorganic nanoparticles. *Nano today*, 2009, 4:96-106.
111. Fernández-Rossier J, Palacios JJ. Magnetism in Graphene Nanoislands. *Physical Review Letters*, 2007, 99(17):177204-177207.
112. Sheka EA, Popova NA, Popova VA. Physics and chemistry of graphene. Emergence, magnetism, mechanophysics and mechanochemistry. *UFN*, 2018, 188:720-772.
113. Wolf SA, Treger D. Spintronics: a new paradigm for electronics for the new millennium. *IEEE Trans. On Magn.*, 2000, 36:2748-2751.
114. Saha SK, Baskey M, Majumdar D. Graphene Quantum Sheets: A New Material for Spintronic Applications. *Adv. Matter*, 2010, 22:5531-5536.
115. Hu J, Li W, Hou Y. Two-Dimensional Magnetic Nanostructures. *Trends in Chemistry*, 2020, 2:163-174.
116. Nagaev EL. *Izbrannyye proizvedeniya* [Selected Works]. Moscow, Fizmatlit Publ., 2004, 320 p.
117. Ziese M. Extrinsic magnetotransport phenomena in ferromagnetic oxides. *Rep.Prog. Phys.*, 2002, 65(2):143-249.