

Unconventional and Exotic Magnetism in Carbon-Based Structures and Related Materials*

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Abstract

The detailed analysis of the problem of possible magnetic behavior of the carbon-based structures was fulfilled to elucidate and resolve (at least partially) some unclear issues. It was the purpose of the present paper to look somewhat more critically into some conjectures which have been made and to the peculiar and contradictory experimental results in this rather indistinct and disputable field. Firstly the basic physics of magnetism was briefly addressed. Then a few basic questions were thoroughly analyzed and critically reconsidered to elucidate the possible relevant mechanism (if any) which may be responsible for observed peculiarities of the "magnetic" behavior in these systems. The arguments supporting the existence of the intrinsic magnetism in carbon-based materials, including pure graphene were analyzed critically. It was concluded that recently published works have shown clearly that the results of the previous studies, where the "ferromagnetism" was detected in pure graphene, were incorrect. Rather, graphene is strongly diamagnetic, similar to graphite. Thus the possible traces of a quasi-magnetic behavior which some authors observed in their samples may be attributed rather to induced magnetism due to the impurities, defects, etc. On the basis of the present analysis the conclusion was made that the thorough and detailed experimental studies of these problems only may shed light on the very complicated problem of the magnetism of carbon-based materials. Lastly the peculiarities of the magnetic behavior of some related materials and the trends for future developments were mentioned.

Keywords: Nanostructures; nanomagnetism; carbon-based materials; pure graphene; magnetism of carbon-based materials; intrinsic magnetism; induced magnetism; exotic magnetic materials; ferromagnetism, paramagnetism, diamagnetism; quantum theory of magnetism.

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1 Introduction

Magnetism is a subject of great importance which has been studied intensely.^{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18} Many fundamental questions were clarified and answered and many applications were elaborated. Various magnetic materials,^{6, 7, 15, 18} e.g. *AlNiCo*, samarium-cobalt, neodymium-iron-boron, hard ferrites etc., were devised which found numerous technical applications. In particular *NdFeB* magnets are characterized by exceptionally strong magnetic properties and by exceptional resistance to demagnetization. This group of magnetic substances provides the highest available magnetic energies of any material. Moreover, *NdFeB* magnets allow small shapes and sizes and have multiple uses in science, engineering and industry.

In the last decades many new growth points in magnetism have appeared as well. The search for macroscopic magnetic ordering in exotic and artificial materials and devices has attracted big attention,^{13, 14, 15, 16, 17, 18, 19} forming a new branch in the condensed matter physics.

The development of experimental techniques and solid state chemistry²⁰ over the recent years opened the possibility for synthesis and investigations of a wide class of new substances and artificial magnetic structures with unusual combination of magnetic and electronic properties.^{14, 15, 16, 17, 18, 19, 21, 22}

This gave a new drive to the magnetic researches due to the finding of new magnetic materials for use as permanent magnets, sensors and in magnetic recording devices.^{23, 24, 25, 26, 27}

In particular, the carbon-based materials^{28, 29, 30, 31, 32, 33} like graphite, fullerenes and graphene were pushed into the first row of researches. Graphene is a monolayer of carbon atoms packed into a dense honeycomb crystal structure, which can be obtained by mechanical exfoliation from graphite.^{34, 35, 36, 37, 38, 39, 40, 41} Graphene has attracted a great interest in material science due to its novel electronic structure. Electrons in graphene possess many fascinating properties not seen in other materials. Graphene sample can be considered as an infinite molecule of carbon atoms with two-dimensional sp^2 network over a honeycomb lattice. Electrons in graphene are not governed by the Schrödinger equation with renormalized mass but should be described in terms of a relativistic theory using the Dirac equation with vanishing mass. Thus the electrons in graphene are, in a sense, "relativistic particles" in condensed matter.

The minimum unit cell of graphene contains two equivalent carbon sites A and B. Then it becomes a semiconductor but the energy gap vanishes at two momenta K and K' in the Brillouin zone, thus forming a zero-gap semiconductor. In contrast to a conventional semiconductor, the gap linearly vanishes and the energy bands form a cone structure (Dirac cone). The electronic structure of graphene has a topological singularity at the Dirac point where two bands cross each other, and it gives rise to anomalous behavior in the conductivity, dynamical transport, and the Hall effect.

Thus graphene can be viewed as the two-dimensional form of pure sp^2 hybridized carbon.⁴² In a sense it can be considered as a giant molecule of atomic thickness. In line with theoretical predictions, charge carriers in graphene behave like massless Dirac fermions, which is a direct consequence of the linear energy dispersion relation.

This results in the observation of a number of very peculiar electronic properties, from an anomalous quantum Hall effect to the absence of localization in this two-dimensional material. It also provides a bridge between condensed matter physics and quantum electrodynamics, and opens new perspectives for carbon-based electronics.⁴³ Such features are very much promising for the use of graphene for mechanical, thermal, electronic, magnetic, and optical applications, in spite that the absence of a band-gap in graphene seem makes it unsuitable for conventional field effect transistors. However recently the obstacle to the use of graphene as an alternative to silicon electronics (the absence of an energy gap between its conduction and valence bands, which makes it difficult to achieve low power dissipation in the off state) has been overcome. It was reported⁴⁴ about fabrication of a bipolar field-effect transistor that exploits the low density of states in

graphene and its one atomic layer thickness. The prototype devices are graphene heterostructures with atomically thin boron nitride or molybdenum disulfide acting as a vertical transport barrier. They exhibit high room temperature switching ratios. Thus such devices may have potential for high-frequency operation and large-scale integration.

It was conjectured in the last decade that in addition to its transport properties^{45, 46, 47, 48, 49, 50} a rich variety of magnetic behavior may be expected in carbon-based materials and graphene, including even a kind of intrinsic ferromagnetism. Some hypothesis were claimed that connected possible spin-ordering effects with the low-dimensionality and Dirac-like electron spectrum of graphene, thus inspiring a new kind of magnetism without magnetic ions. Indeed, the understanding and control of the potential magnetic properties of carbon-based materials may be of fundamental relevance in applications in nano- and biosciences. However the problem is not solved yet.

In spite of the fact that magnetism is not usually expected in simple *sp* oxides like *MgO* or in carbons like graphite it was speculated that basic intrinsic defects in these systems^{51, 52, 53} may be magnetic in ways that seem to be shared by more complex oxides. The possible magnetic nature of these intrinsic carbon defects may suggests that it is important to understand their role in the recently reported "magnetism" in some carbon-based systems. Moreover, a "room-temperature ferromagnetism of graphene" was claimed.⁵⁴ However, the mechanism responsible for that "ferromagnetism" in carbon-based materials, which contain only *s* and *p* electrons in contrast to traditional ferromagnets based on *3d* or *4f* electrons, is still rather unclear.

Thus the natural question arises: can carbon-based materials be magnetic in principle and what is the mechanism of the appearing of the magnetic state from the point of view of the quantum theory of magnetism? In addition, it should be emphasized strongly that almost all of the properties of these substances are affected by the imperfections and impurities of the nano-structures. In the present work, these questions were analyzed and reconsidered to elucidate the possible relevant mechanism (if any) which may be responsible for observed peculiarities of the "magnetic" behavior in these systems, having in mind the quantum theory of magnetism criteria.^{55, 56} Emphasis is placed on revealing key concepts and really measured magnetic phenomena on which such speculations rest.

2 Magnetism and Magnetic Materials

Before taking up the problem of the magnetic behavior of the carbon-based structures we must summarize briefly the most relevant of the fundamental concepts of the physics of magnetism. There are many examples of physical systems with a stable magnetic moment in the ground state.^{1, 3, 12, 17} These systems are the atoms, molecules and ions with an odd number of electrons, some molecules with an even number of electrons (*O*₂ and some organic compounds) and atoms (ions) with an unfilled (*3d*-, *4f*-, *5f*-) shells. Within each shell, electrons can be specified according to their orbital angular momenta, *s*-electron having no angular momentum, *p*-electrons having one quantum of angular momentum, *d*-electrons having two, and *f*-electrons having three. The *s*- and *p*-states tend to fill before *d*-states as the atomic number *Z* increased. Each electron carries with it as it moves a half quantum of intrinsic angular momentum or spin^{57, 58} with an associated magnetic moment. It have only two orientations relative to any given direction, parallel or antiparallel.

Magnetic materials,^{7, 14, 15, 16, 17, 18, 19} as a rule, can be metals, semiconductors or insulators which contain the ions of the transition metals or rare-earth metals with unfilled shells.^{1, 4, 8, 17, 55} Strong magnetic materials as a rule include *3d*- ions with unfilled shells.⁵⁵ The question of formulation of the universal criterion for *ferromagnetism* is a difficult problem, because of the existence of the huge variety of the magnetic substances and structures.

According to Pauli exclusion principle,⁵⁹ the electrons with parallel spins tend to avoid each other

Table 1. Magnetic behavior of materials.

Types of magnetism	Net magnetic moment	Order/disorder
Diamagnetism	absent	no long-range magnetic order
Paramagnetism	absent	no long-range magnetic order
Ferromagnetism	strong	long-range magnetic order for $T < T_c$
Ferrimagnetism	strong	long-range magnetic order for $T < T_c$
Antiferromagnetism	absent	long-range magnetic order for $T < T_N$
Weak ferromagnetism	weak	long-range magnetic order for $T < T_{DM}$

spatially. One can say that the Pauli exclusion principle lies in the foundation of the quantum theory of magnetic phenomena. It is worth noting that the magnetically active electrons which form the magnetic moment can be localized or itinerant (collectivized).^{55, 60, 61, 62, 63, 64, 65, 66}

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another.^{1, 2, 3, 4, 8, 17, 55} The basic object in the magnetism of condensed matter is the magnetic moment \mathbf{M} . It can be imagined as a magnetic dipole. Magnetic moment $\mathbf{M} = g\mu_B\mathbf{J}$ is proportional to the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where \mathbf{L} is orbital moment and \mathbf{S} is spin moment. In nature, magnetic moments are carried by magnetic minerals the most common of which are magnetite and hematite.^{1, 15, 17, 18} The magnetic moment in practice may depend on the detailed environment and additional interactions such as spin-orbit, screening effects and crystal fields. The magnetic behavior of materials can be classified into the six major groups as shown in Table 1.

All the materials respond to magnetic fields in essentially different way. The simplest magnetic systems to consider are insulators where electron-electron interactions are weak. If this is the case, the magnetic response of the solid to an applied field is given by the sum of the susceptibilities of the individual atoms. The magnetic susceptibility is defined by the the 2nd derivative of the free energy,

$$\chi = -\frac{\partial^2 F}{\partial H^2}. \quad (1)$$

With the aid of the analysis of the susceptibility one can understand (on the basis of an understanding of atomic structure) why some systems (e.g. some elements which are insulators) are paramagnetic ($\chi > 0$) and some diamagnetic ($\chi < 0$).

From the phenomenological point of view magnetic materials are characterized by the intrinsic magnetic susceptibility

$$\chi_{int} = \frac{M}{H_i}, \quad (2)$$

where M is the magnetization of a sample and H_i is the internal field. When external magnetic field H_{ext} is applied then the experimental susceptibility $\chi_{exp} \sim M/H_{ext}$ can be written as

$$\chi_{exp} \sim \frac{M}{H_i + \eta_d M} = \frac{\chi_{int}}{1 + \eta_d \chi_{int}}, \quad (3)$$

where η_d is the demagnetizing factor. In principle, a ferromagnetic material may have no net magnetic moment because it consists of magnetic domains.

In some materials there is no collective interaction of atomic magnetic moments; they belong to diamagnetic substances.² Diamagnetic behavior is characterized by repulsion of a substance out of an applied magnetic field. This behavior arises from the interaction of the applied magnetic field with molecular or atomic orbitals containing paired electrons. With the exception of the

hydrogen radical, all atomic or molecular materials exhibit some diamagnetic behavior. This magnetic behavior is temperature independent, and the strength of the interaction is roughly proportional to the molecular weight of the material.

Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms which have no net magnetic moments (ie., all the orbital shells are filled and there are no unpaired electrons). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative and weak. It does not depend on the temperature. Diamagnetic susceptibility χ_d is a part of the total susceptibility of a material χ . It can be represented in a very approximative form as²

$$\chi \cong \chi_p + \chi_d. \quad (4)$$

Here χ_p is the paramagnetic susceptibility. Diamagnetism of metallic systems^{1,2,4,8,15,17} is the diamagnetic response of the electron gas. The diamagnetic susceptibility is given by^{1,2}

$$\chi_d \sim -\frac{1}{3}\mu_0\mu_B^2 D(E_F) \quad (5)$$

and

$$\chi_d \sim -\frac{1}{3}\chi_p. \quad (6)$$

Here $D(E_F)$ is the density of states at the Fermi level E_F ; μ_B is the Bohr magneton. Majority of metallic systems are paramagnetic due to the fact that the (positive) χ_p is three times larger than the (negative) χ_d . The diamagnetic behavior of various molecules and complex compounds and its competition with paramagnetism is rather diverse. In some cases this interrelation can be estimated to give²

$$\bar{\chi}_p \cong \frac{2}{3} \frac{(\Delta\bar{\chi}_d)^2}{\bar{\chi}_d}. \quad (7)$$

For example, for methane molecule² $\chi_d \sim -13.906 \cdot 10^{-6}$ and $\chi_p \sim +0.189 \cdot 10^{-6}$.

Paramagnetism^{1,2,4,8,15,17} is characterized by the attraction of a substance into an applied magnetic field. This behavior arises as a result of an interaction between the applied magnetic field and unpaired electrons in atomic or molecular orbitals. Typically, paramagnetic materials contain one or more unpaired electrons, and the strength of paramagnetic interactions are temperature dependant. However, some substances exhibit temperature independent paramagnetism that arises as a result of a coupling between the magnetic ground state and non-thermally populated excited states. Temperature independent paramagnetism has been observed for materials with both paramagnetic and diamagnetic ground states, and it is usually associated with electrically conducting materials.

In paramagnetic materials, some of the atoms or ions have a net magnetic moment due to unpaired electrons in partially filled orbitals. One of the most important atoms with unpaired electrons is iron. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility. Paramagnetism is typically considerably stronger than the diamagnetism. In addition, the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility, termed by the Curie law^{1,2,4,5,8}

$$\chi \cong \frac{\mu_0 N m_0^2}{3k_B T} = \frac{C}{T} \quad (8)$$

or Curie-Weiss law^{1,2,4,5,8,15}

$$\frac{1}{\chi} \cong \frac{T - \theta_p}{C}, \quad \theta_p \geq T_c. \quad (9)$$

In summary, diamagnetism is characterized by negative susceptibility due to the fact that induced moment opposes applied field. Diamagnetic behavior is common for noble gas atoms and alkali halide ions (e.g., $He, Ne, F^-, Cl^-, Li^+, Na^+, \dots$). Paramagnetism has positive susceptibility because induced moments are favored by applied field (but are opposed by thermal disorder). In paramagnetic substance magnetization is immediately lost upon removal of field. Paramagnetism is observed for isolated rare earth ions, iron (group 3d) ions (e.g., $Fe^{3+}, Co^{2+}, Ni^{2+}, Sm^+, Er^+, \dots$). Ferromagnets and ferrimagnets are characterized by strong exchange interaction between localized atomic moments or strong electron correlation among itinerant (narrow band) electrons. The interaction arises from the electrostatic electron-electron interaction, and is called the *exchange interaction* or exchange force. Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field. Ferromagnets will tend to stay magnetized to some extent after being subjected to an external magnetic field. This tendency to remember their magnetic history is called hysteresis.⁵ The fraction of the saturation magnetization which is retained when the driving field is removed is called the remanence of the material, and is an important factor in permanent magnets.¹⁵ All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal motion. This temperature is called the Curie temperature T_c . Ferromagnetic materials are spontaneously magnetized below a temperature T_c and all local moments have a positive component along the direction of the spontaneous magnetization. In antiferromagnet individual local moments sum to zero total moment (no spontaneous magnetization) whereas in ferrimagnet local moments are not all oriented in the same direction, but there is a non-zero spontaneous magnetization.

In conventional magnetic materials the magnetic ions (magnetic moments) reside on a regular lattice. The interactions between moments is generally short-range, determined by overlap of the electron wave functions in conjunction with Pauli's exclusion principle. Thus the exchange interaction arises due to the Coulomb electrostatic interaction.^{3,55} The coupling, which is quantum mechanical in nature, is termed as the exchange interaction. As a rule only nearest neighbor interactions between magnetic moments are essential. The exchange interaction between the neighboring magnetic ions will force the individual moments into ferromagnetic parallel or antiferromagnetic antiparallel alignment with their neighbouring magnetic moments. Thus the important interactions responsible for ordering and magnetic dynamics in magnetic materials are the strong short-ranged correlations between electrons. Critical temperatures and magnetic excitation energies are therefore mainly determined by the short range interactions, and the weak long range dipolar interactions are significant only for long wavelength dynamic behavior and phenomena related to domain formation. Magnetic dipolar interaction

$$E_{dd} \sim \frac{\vec{\mu}_1 \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^3} \quad (10)$$

is too weak ($E_{dd} \sim 1 \text{ K}$ or $10^{-4} eV$) to account for the ordering of real magnetic materials.

There are various types of the exchange interaction: direct exchange, indirect exchange, superexchange.^{1,3,55,62} Direct exchange interaction is effective for moments, which are close enough to have sufficient overlap of their wave functions (atomic-like orbitals). It produces a strong but short range coupling which decreases rapidly as the ions are separated. For direct inter-atomic exchange the corresponding integral J_{ex} can be positive or negative depending on the balance between the Coulomb interaction and kinetic energy.

Indirect exchange interaction^{1,3,55,67} couples moments over relatively large distances. It is the dominant exchange interaction in metals, where there is little or no direct overlap between neighboring electrons. It therefore acts through an intermediary, which in metals are the conduction

electrons (itinerant electrons). This type of exchange is termed as the RKKY interaction. This type of interaction is especially relevant for the rare earth metals with the unfilled $4f$ shell. In these metals the direct exchange between the localized magnetic moments on the rare earth ions is negligible, but they are coupled through the medium of the conduction electrons by the indirect exchange interaction.^{1,3,55,67,68,69} This interaction is long range and oscillatory and, together with the strong anisotropy forces, which are a consequence of the anisotropic charge distribution in the $4f$ shell, lead to the complex magnetic structures.

Superexchange describes the interaction between moments on ions too far apart to be connected by direct exchange.^{1,70,71} This exchange is relevant, for example, for ferric-rare earth interaction in garnets. In these substances the coupling between the moments on a pair of metal cations separated by a diatomic anion is described by the superexchange interaction. In the P.W. Anderson theory of superexchange^{1,70,71} a set of magnetic orbitals, localized at the metal sites, defines the ground and excited state configurations. The main feature of his approach is that the covalent interaction between the metal and ligand orbitals is already included from the beginning while the on-site electron repulsion remains strong enough to keep the electrons mainly localized on the metals. The ion of Fe in a garnet has a half filled $3d$ shell and so has a spherically symmetric charge distribution. The rare-earth ion is not symmetric and has a strong spin-orbit coupling. As a consequence, its charge distribution is coupled to its moment. The ion's moments will be coupled by superexchange due to the ability of the Fe moment alters the overlap of the cation. This will lead to the changing of the magnitude of both the Coulomb and exchange interactions between the cations, leading to a coupling, which depends on the moment's orientation. The effective perturbation Hamiltonian reduces in every order of perturbation to the well-known effective spin-Hamiltonian of Heiseberg-Dirac type.

Anderson's theory has a few shortcomings. The ground state configurations may not be reasonable starting points for perturbation theory, due to the fact that the first-order energy of the singlet state is raised too much above the triplet energy. Moreover, it may be inadequate due to its perturbational description of covalency.

Transition and rare-earth metals and especially compounds containing transition and rare-earth elements possess a fairly diverse range of magnetic properties. The elements Fe , Ni , and Co and many of their alloys are typical ferromagnetic materials. The construction of a consistent microscopic theory explaining the magnetic properties of these substances encounters serious difficulties when trying to describe the collectivization-localization duality in the behavior of magneto-active electrons.^{55,60,61,62} This problem appears to be extremely important, since its solution gives us a key to understanding magnetic, electronic, and other properties of this diverse group of substances. Quantum theory of magnetism deals with variety of the schematic models of magnetic behavior of real magnetic materials. In papers^{55,61} we presented a comparative analysis of these models; in particular, we compared their applicability for description of complex magnetic materials.

Magnetic properties and the dynamic response of magnetic systems are strongly dependent on dimensionality⁵⁶ and on size.^{72,73} Saturation moments M_S of magnetic materials depart from their bulk values near a surface because of reduced symmetry and altered charge distribution, which is typical variation over a few Angstroms in metals. Another reason is the surface stress and/or surface segregation (about several tens of Angstroms). Surface magnetic effects are evident in studies of thin magnetic films and multilayers.^{23,24,25,26,27,72,74} The intrinsic magnetic properties - magnetization, critical temperature, anisotropy, magnetostriction - may differ substantially in thin films and bulk material. It is worth noting that sometimes the substrate influences the electronic structure and magnetic moment of the first atomic layers at the interface. Magnetic films with thickness ranging from a single monolayer to a few monolayers and bigger (up to $\sim 100\text{nm}$) may be grown on crystalline or amorphous substrates. In the transition ($3d$) metal films surface atoms have less of their neighbors. Thus the exchange interactions may be more weak. In terms

of the itinerant picture the corresponding bands may be more narrow at the surface. As a result the local density of states and the local magnetic moments may be enhanced. These effects as a rule are limited to the first one or two monolayers.

Magnetic multilayers^{75,76,77} typically consist of alternate stacks of ferromagnetic and nonferromagnetic spacer layers. The typical thickness of an individual layer ranges between a few atomic layers to a few tens of atomic layers. The magnetic layers usually consist of elemental metallic ferromagnets (*Fe, Co, Ni*) or alloys thereof (e. g. permalloy). The spacer layers can consist of any transition or noble metal; they are either paramagnetic (*Cu, Ag, Au, Ru, Pd, V, etc.*) or antiferromagnetic (*Cr, Mn*). Because of the spacer layers, the magnetic layers are, to first approximation, magnetically decoupled from each other, i. e. their basic magnetic properties such as magnetization, Curie temperature, magnetocrystalline anisotropy, magneto-optical response, *etc.*, are essentially those of an individual layer. This approximation, however, is not sufficient for accurate description of the magnetism of multilayers, and one must consider the magnetic interactions which couple successive magnetic layers through spacer layers.

The interactions which give rise to an interlayer magnetic interaction are essentially the dipolar interaction and the indirect exchange interaction of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type.^{1,3,55,67,68,69} For a homogeneously magnetized layer consisting of a continuous medium, there is no dipolar stray field, so that dipolar interlayer coupling can arise only as a result of departures from this idealized situation. This is the case when one considers the real crystalline structure of the layer. However, the dipolar stray field decays exponentially as a function of the distance from the magnetic layer, with a decay length of the order of the lattice parameter, so that this effect is completely negligible compared with the interaction as a result of exchange.^{75,76,77}

The indirect exchange interaction has a completely different physical origin. It is mediated by conduction electrons which are scattered successively by the magnetic layers. In metallic systems, exchange interactions are mediated by itinerant electrons and thus can be transmitted over relatively long distances. It follows that exchange interactions can couple magnetic layers through non-magnetic metallic layers. The interest of the exchange coupled multilayers has also been enhanced by the discovery of the giant magnetoresistance.^{75,76,77}

In order to understand the intrinsic properties of nanomagnets, much effort has been devoted to 3d ferromagnetic transition-metal clusters^{13,78,79,80} such as *Fe, Ni, Co* and *Pd, Pt* and rare earth 4f aggregates⁸¹ such as *Gd* and *Tb*. These studies provide insight into the electronic structure of the cluster and is fundamental for an understanding of how magnetism develops in small cluster. Intensive research on fullerenes, nanoparticles, and quantum dots led to interest in clusters, fullerenes, nanotubes and nanowires in last decades.^{82,83,84} The studies of nanophysics of materials, in particular clusters, fullerenes, nanotubes and nanowires posed many important problems of condensed matter physics in these nanoscale materials and structures.

It should be stressed that nanophysics^{13,79,30,31,33,82,83} brings together multiple disciplines to determine the structural, electronic, optical, and thermal behavior of nanomaterials. It includes also the electrical and thermal conductivity, the forces between nanoscale objects and the transition between classical and quantum behavior. These features are also the key aspects of carbon nanotubes, including quantum and electron transport, isotope engineering, and fluid flow, which are relevant also for inorganic nanotubes, such as spinel oxide nanotubes, magnetic nanotubes, and self-assembled peptide nanostructures.

3 Microscopic Models of Magnetic Substances

It is instructive to make a quick overview of the microscopic basis of the quantum physics of magnetism.^{3,55} It is well known that the quantum mechanics is the key to understanding magnetism. One of the first steps in this direction was the formulation of Hund's rules in atomic physics. In

Table 2. Energy scales for magnetic ordering

Energy scale	Order of magnitude
Coulomb interaction	\simeq eV
Magnetic ordering temperature	$T_c \sim 0.1$ meV - 100 meV
RKKY interaction	~ 0.1 meV - 1 meV
dipole-dipole interaction	~ 0.1 meV

rare-earth and transition metals elements the atomic shells are partially filled, and the ground state is determined by minimizing the atomic energy together with the intra-atomic Coulomb interaction needed to remove certain degeneracies.^{3,55,56} A physical analysis of the first Hund's rule leads us to the conclusion, that it is based on the fact, that the elements of the diagonal matrix of the electron-electron's Coulomb interaction contain the exchange's interaction terms, which are entirely negative. This is the case only for electrons with parallel spins. Therefore, the more electrons with parallel spins involved, the greater the negative contribution of the exchange to the diagonal elements of the energy matrix. Thus, the first Hund's rule implies that electrons with parallel spins tend to avoid each other spatially. Here, we have a direct connection between Hund's rules and the Pauli exclusion principle, which states that two electrons in the same orbit must move in opposite directions.

Thus it should be stressed once again that the origin of strong ferromagnetism is the electron-electron's Coulomb interaction $V(r_i - r_j) \sim e^2/(r_i - r_j)$. The corresponding energy scales are presented in Table 2. A schematic realization of the above principles gives the method of model Hamiltonians which has proved to be very efficient in the theory of magnetism.^{3,55} Without any exaggeration one can say, that the tremendous successes in the physics of magnetic phenomena were achieved, largely, as a result of exploiting a few simple and schematic model concepts for "the theoretical interpretation of ferromagnetism".^{55,62,85}

One can regard (with some reservation) the Ising model^{1,3,55} as the first model of the quantum theory of magnetism. In this model it was assumed that the spins are arranged at the sites of a regular one-dimensional lattice. Each spin S^z can obtain the values $\pm\hbar/2$:

$$\mathcal{H} \sim - \sum_{\langle ij \rangle} I_{ij} S_i^z S_j^z. \quad (11)$$

Here I_{ij} is the parameter of the spin-spin interaction. This was one of the first attempts to describe the magnetism as a cooperative effect.

However, the Ising model oversimplifies the situation in real crystals. Works of W. Heisenberg, P. Dirac and van Vleck have lead to devising of a more general theory which attributed the ferromagnetic state to an alignment of electron spins in atoms due to exchange forces. The Heisenberg model describes schematically the interaction between spins at different sites of a lattice by the following isotropic scalar function

$$\mathcal{H} = - \sum_{ij} J(i-j) \mathbf{S}_i \mathbf{S}_j - g\mu_B H_{ext} \sum_i S_i^z. \quad (12)$$

Here \mathbf{S}_i is the spin angular momentum operator of the atom at site i ; μ_B is the Bohr magneton and g is the gyromagnetic factor (the magnetic moment μ_0 is defined as $\mu_0 = 1/2g\mu_B$); H_{ext} is the intensity of a static magnetic field directed along the z axis; for the case $H_{ext} > 0$ the magnetic moments line up along the positive z axis when the system is in the ground state. The quantity $J(i-j)$ (the "exchange integral") is the strength of the exchange interaction between

the spins^{3,85,86,87} located at the lattice sites i and j . The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electron. Exchange force depends on relative orientation of spins of two electrons due to Pauli's exclusion principle. It is usually assumed that $J(i-j) = J(j-i)$ and $J(i-j=0) = 0$, which means that only the inter-site interaction is present (there is no self-interaction).

The Heisenberg Hamiltonian (12) can be rewritten in the following form:

$$\mathcal{H} = - \sum_{ij} J(i-j)(S_i^z S_j^z + S_i^+ S_j^-). \quad (13)$$

Here, $S^\pm = S^x \pm iS^y$ are the spin raising and lowering operators. Note that in the isotropic Heisenberg model the z -component of the total spin $S_{tot}^z = \sum_i S_i^z$ is a constant of motion, that is $[H, S_{tot}^z] = 0$.

Exchange forces are very large, equivalent to a field on the order of $\sim 10^3$ Tesla. In real substances direct exchange is driven by minimizing potential energy, by reducing wave functions overlap. To clarify this let us consider the Coulomb interaction V . For two-electron antisymmetric wave function

$$\psi(r_i, \sigma; r_j, \sigma) = \frac{1}{\sqrt{2}} \left(\varphi_\alpha(r_i) \varphi_\beta(r_j) - \varphi_\beta(r_i) \varphi_\alpha(r_j) \right) \chi_\sigma \chi_\sigma, \quad (14)$$

matrix element $\langle \psi | V | \psi \rangle$ will take the form

$$\begin{aligned} E_C &\sim \langle \psi(i, j) | V | \psi(i, j) \rangle = \\ &\int d^3 r_i d^3 r_j V(r_i - r_j) |\varphi_\alpha(r_i)|^2 |\varphi_\beta(r_j)|^2 - \\ &\int d^3 r_i d^3 r_j V(r_i - r_j) \varphi_\alpha^*(r_i) \varphi_\beta^*(r_j) \varphi_\alpha(r_j) \varphi_\beta(r_i) \\ &= U_{\alpha\beta} - J_{\alpha\beta}. \end{aligned} \quad (15)$$

Here U is the Coulomb interaction energy and J is the effective exchange integral. In real material the calculation of the effective exchange integral $J_{\alpha\beta}$ is very difficult task;^{55,63,87,70} it depends substantially on the proper choice of the many-electron wave functions for the system. In the work by Mattheiss⁸⁸ the magnetic properties of a linear chain of monovalent atoms were investigated from the point of view of perturbation theory. The many-electron wave functions for the system were expanded as linear combinations of determinantal functions which were eigenfunctions of S^2 and S_{tot}^z . These determinantal functions were constructed from orthonormal one-electron orbitals of the Wannier type so that the nearest neighbor exchange integral is positive definite and approaches zero at large lattice spacing. The analytic expression was found for an effective nearest neighbor exchange integral J . The main conclusion which follows from this consideration is that the Heisenberg type model is not a reasonable workable model at all internuclear separations. Rather, it implies that there is a gradual transition from the energy band to the orthonormalized atomic orbitals approximations which are valid at small and large lattice spacing respectively. The magnetic interaction is not **exactly** described by the Heisenberg exchange operator.

Thus, in the framework of the Heisenberg-Dirac-van Vleck model,^{1,3,55} describing the interaction of localized spins, the necessary conditions for the existence of ferromagnetism involve the following two factors. Atoms of a "ferromagnet to be" must have a magnetic moment, arising due to unfilled electron d - or f -shells. This is related simply to the fact that both the $3d$ and $4f$ wave functions are strongly localized and have no nodes in radial wave functions. Contrary to this the $4p$ and $4s$ wave functions are delocalized and have nodes in radial wave functions. The exchange integral J_{ij} related to the electron exchange between neighboring atoms must be positive. Upon fulfillment of these conditions the most energetically favorable configurations in the absence of an

external magnetic field correspond to parallel alignment of magnetic moments of atoms in small areas of the sample (domains).

Of course, this simplified picture is a scheme only. A detail derivation of the Heisenberg-Dirac-van Vleck model describing the interaction of localized spins is quite complicated.^{55,63,87,70} An important point to keep in mind here is that magnetic properties of substances are born by quantum effects, the forces of exchange interaction.

As was already mentioned above, the states with antiparallel alignment of neighboring atomic magnetic moments are realized in a fairly wide class of substances. As a rule, these are various compounds of transition and rare-earth elements, where the exchange integral J_{ij} for neighboring atoms is negative. Such a magnetically ordered state is called **antiferromagnetism**^{1,3,55} which was explained by L. Neel. For example, the transition-metal compound MnF_2 (manganese fluoride) have the antiferromagnetic behavior at low temperatures ($T_N \sim 66K$). In this compound Mn ion becomes Mn^{2+} ($3d^5$ configuration) and fluorine ion - F^- .

In 1948, L. Neel introduced also the notion of **ferrimagnetism**^{1,3,55} to describe the properties of substances in which spontaneous magnetization appears below a certain critical temperature due to nonparallel alignment of the atomic magnetic moments. These substances differ from antiferromagnets where sublattice magnetizations m_A and m_B usually have identical absolute values, but opposite orientations. Therefore, the sublattice magnetizations compensate for each other and do not result in a macroscopically observable value for magnetization. In ferrimagnetics the magnetic atoms occupying the sites in sublattices A and B differ both in the type and in the number. Therefore, although the magnetizations in the sublattices A and B are antiparallel to each other, there exists a macroscopic overall spontaneous magnetization. The antiferromagnetics and ferrimagnetics constitute a very wide group of various substances.

Later, substances possessing weak ferromagnetism were investigated.^{1,3,55} It is interesting that originally Neel used the term *parasitic ferromagnetism* when referring to a small ferromagnetic moment, which was superimposed on a typical antiferromagnetic state of the α -iron oxide Fe_2O_3 (hematite). Later, this phenomenon was called canted antiferromagnetism, or weak ferromagnetism. The weak ferromagnetism appears due to antisymmetric interaction between the spins \vec{S}_1 and \vec{S}_2 and which is proportional to the vector product $\vec{S}_1 \times \vec{S}_2$. This interaction is written in the following form

$$\mathcal{H}_{DM} \sim \vec{D} \vec{S}_1 \times \vec{S}_2. \quad (16)$$

The interaction (16) is called the Dzyaloshinsky-Moriya interaction.^{1,3,55,89}

Thus, there exist a large number of substances and materials that possess different types of magnetic behavior: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, ferrimagnetism, and weak ferromagnetism. We would like to note that the variety of magnetism is not exhausted by the above types of magnetic behavior; the complete list of magnetism types is substantially longer.⁹⁰ As was already stressed, many aspects of this behavior can be reasonably well described in the framework of a very crude Heisenberg-Dirac-van Vleck model of localized spins. This model, however, admits various modifications. Therefore, various nontrivial generalizations of the localized spin models were studied.^{1,3,55}

The Heisenberg model describing localized spins is mostly applicable to substances where the ground state's energy is separated from the energies of excited current-type states by a gap of a finite width. That is, the model is mostly applicable to semiconductors and dielectrics. However, the main strongly magnetic substances, nickel, iron, and cobalt, are metals, belonging to the transition group.^{1,3,55} In many cases inter-electron interaction is very strong and the description in terms of the conventional band theory is no longer applicable. Special properties of transition metals and of their alloys and compounds are largely determined by the dominant role of d -electrons.^{55,63,65,66} In contrast to simple metals, where one can apply the approximation of quasi-free electrons, the wave functions of d -electrons are much more localized, and, as a rule,

have to be described by the tight-binding approximation. The main aim of the band theory of magnetism is to describe in the framework of a unified approach both the phenomena revealing the localized character of magnetically active electrons, and the phenomena where electrons behave as collectivized band entities.⁵⁵

The quantum statistical theory of systems with strong inter-electron correlations began to develop intensively when the main features of early semi-phenomenological theories were formulated in the language of simple model Hamiltonians.^{55,63,65,66,85} The most known models are the Anderson model⁹¹ and Hubbard model.^{61,62} Both the Anderson model,⁵⁵ and the Hubbard model^{55,62} equally stress the role of inter-electron correlations. The Hubbard Hamiltonian and the Anderson Hamiltonian (which can be considered as the local version of the Hubbard Hamiltonian) play an important role in the electron's solid-state theory.^{55,61,62}

The Hamiltonian of the Hubbard model is given by:

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \quad (17)$$

The above Hamiltonian includes the one-site intra-atomic Coulomb repulsion U , and t_{ij} , the one-electron hopping energy describing jumps from a j site to an i site. As a consequence of correlations electrons tend to "avoid one another". Their states are best modeled^{55,61,62} by orthonormal atomic-like Wannier wave functions $[\phi(\vec{r} - \vec{R}_j)]$. The Hubbard model's Hamiltonian can be characterized by two main parameters: U , and the effective band width of tightly bound electrons

$$\Delta = (N^{-1} \sum_{ij} |t_{ij}|^2)^{1/2}.$$

The band energy of Bloch electrons $\epsilon(\vec{k})$ is given by

$$\epsilon(\vec{k}) = N^{-1} \sum_{\vec{k}} t_{ij} \exp[-i\vec{k}(\vec{R}_i - \vec{R}_j)],$$

where N is the total number of lattice sites. Variations of the parameter $\gamma = \Delta/U$ allow one to study two interesting limiting cases, the band regime ($\gamma \gg 1$) and the atomic regime ($\gamma \rightarrow 0$). Note that the single-band Hubbard model (17) is a particular case of a more general model, which takes into account the degeneracy of d -electrons. It is necessary to stress that the Hubbard model is most closely connected with the **Pauli exclusion principle**, which prohibits the double occupancy at the same site. In this case it can be written as $n_{i\sigma}^2 = n_{i\sigma}$.

A generalized spin-fermion model, which is also called the Zener model, or the s - d - (d - f)-model is of importance in the solid-state theory. The Hamiltonian of the s - d exchange model^{1,3,92,93,94} is given by:

$$\mathcal{H} = H_s + H_{s-d}, \quad (18)$$

$$H_s = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma}, \quad (19)$$

$$H_{s-d} = J \vec{\sigma}_i \vec{S}_i = -JN^{-1/2} \sum_{kk'} \left(c_{k'\uparrow}^\dagger c_{k\downarrow} S^- + c_{k'\downarrow}^\dagger c_{k\uparrow} S^+ + (c_{k'\uparrow}^\dagger c_{k\uparrow} - c_{k'\downarrow}^\dagger c_{k\downarrow}) S^z \right). \quad (20)$$

Here, $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ are the second-quantized operators creating and annihilating conduction electrons. The Hamiltonian (20) describes the interaction of the localized spin of an impurity atom with a subsystem of the host-metal conduction's electrons. This model is used for description of the Kondo effect and other problems. Note that the Hamiltonian of the s - d model is a low-energy realization of the Anderson model.

Table 3. Magnetic interactions: localized and itinerant models

Interaction	Hamiltonian	Curie Temperature
1: Dipolar interaction	$E_{dd} \sim \mu^2/4\pi r^3$	$E \sim 1K$
2: Exchange direct	$H \sim \sum J_{ij}S_iS_j$	$T_c \sim zJ \sim 10 - 10^3K$
3: Exchange indirect	$H \sim I(r)S_iS_j$	$T_c \sim 1 - 10^2K$
4: RKKY	$I(r) \sim \cos(2k_F r)/r^3$	$T_c \sim 1 - 10^2K$
5: Itinerant electron magnet	$H \sim U \sum n_{i\uparrow}n_{i\downarrow}$	$T_c \sim 10 - 10^3K$

Thus, the Anderson, Hubbard and s - d - models take into account both the collectivized (band) and the localized behavior of electrons^{55,61,62,92,93,94} whereas Heisenberg model emphasizes the localized character of magneto-active electrons (see Table 3).

To summarize the studies of the previous sections, the term magnetism refers to substances that at the atomic level exhibit temperature dependent paramagnetic behavior as the most characteristic feature.^{1,90} The non-zero spin angular moment associated with an unpaired electron gives rise to a magnetic moment. As a rule, in condensed matter, bulk magnetic properties arise as a result of long-distance interactions between atomic-like electrons.

The control of bulk magnetic properties has proven to be very difficult.^{15,16,19,18,95} This is also due to the many different types of magnetic behaviors that should be characterized and identified.^{90,95} These different magnetic behaviors arise from the various types of electron and spin interactions observed in these materials leading to variety of different models for their interpretation.^{55,85} The temperature of magnetic ordering can be varied in a very broad interval of temperatures. Table 4 provides examples of different magnetic materials with big variety of ordering temperature.^{15,16,17,18,19,96,97} The complexity associated with controlling magnetic properties has arisen from difficulties in controlling the spatial arrangement of spin containing units.^{15,16,19,18,95} There are several strategies for controlling spin-spin organization; the most efficient one of these strategies is the neutron scattering technique.^{60,95,98,99}

Traditional magnetic materials are two- and three-dimensional arrays of inorganic atoms, composed of transition metal or lanthanide metal containing spin units. These materials are typically produced at very high temperatures using the best achievements of metallurgical sciences. In contrast to traditional magnetic materials, molecular and carbon-based materials are organic or hybrid (inorganic/organic) materials. Certain fraction of these materials may manifest some magnetic features. They comprised of either metal containing spin units or organic radical containing spin units. It has been conjectured that these materials will allow for the low temperature synthesis of magnetic materials, materials with better optical properties, the combination of magnetic properties with mechanical, electrical, and/or optical properties. In addition, they may provide a better control over a material's magnetic characteristics.^{15,16,19,18,95,82,83} However, in order to design materials with interesting bulk magnetic properties it is necessary to understand how bulk magnetism arises in samples. A complete resolution of this task has not yet been achieved in the full measure,¹⁰⁰ however many of the general principles of magnetic behavior are well established.^{13,14,15,16,17,18,19,55} Some of those principles may be used in discussion of the complicated problem of the possible magnetic properties of carbon-based structures.^{101,102,103}

4 Carbon and its Allotropes

Carbon materials are unique in many ways.^{28,29,30,31,32,33} They are characterized by the various allotropic forms that carbon materials can assume.^{104,105,106} Chemical properties of carbon are

Table 4. Magnetic properties of various compounds^{15, 16, 17, 18, 19, 96, 97}

Compound	Type of ordering	Critical Temperature
Mn_3N_2	AFM	$T_N \sim 925K$
Ni_3Fe	FM	$T_c \sim 620K$
FeS	AFM	$T_N \sim 305K$
CrN	AFM	$T_N \sim 273K$
$MnSi$	AFM	$T_N \sim 30K$
ZrZ_2	weak FM	$T_c \sim 28K$
$ZnCu_3(OH)_6Cl_2$	spin-1/2 kagome-lattice AFM	$T_N \sim 0.05K$

remarkably versatile. Carbon electronic structure is $1s^2 2s^2 2p^2$. Moreover, the outer shell $2s$ and $2p$ electrons can hybridize in triple ways, forming sp^1 , sp^2 and sp^3 orbital wave functions. Each type of hybridization is realized in a material with substantially different properties. The sp^1 hybridization provides the formation of 2σ and 2π orbitals. Thus this hybridization favours linear structures such as those observed in polymers. The sp^2 hybridization results in three strong σ bonds, with an unhybridized p electron forming a π bond. This case is appropriate for description of graphite and graphite-like materials with planar two-dimensional structures. The sp^3 hybridization leads to four identical σ bonds arranged tetrahedrally in three dimensions. This case is suitable for the strong bonding in crystalline diamond. Diamond is a nonconductor. Thus different bonding results in radically different physical properties. For systems consisting of a mixture of bonding types (e.g. evaporated carbon, tetrahedral amorphous carbon, glassy carbon, etc.) a dominant factor in determining their properties is the proportion of the carbon atoms which are four-fold coordinated, i.e. the so called sp^3 content.

The materials science of carbon has been a rich area of discovery and development in the past decades. Until relatively recently, the only known polymorphs of carbon were graphite, in which sp^2 hybridized carbon atoms form planar sheets in a two-layer hexagonal stacking, and diamond, in which sp^3 carbons form a three-dimensional framework of cubic symmetry. In graphite the three sp^2 hybrid orbitals of carbon form σ -bonds with its neighbors and establish the hexagonal lattice (two dimensional honeycomb plane). These σ -bonds are strong enough. The additional $2p$ orbital of each carbon atom forms π -bond with its neighbors. The sideways overlapping of $2p$ orbitals between neighboring carbon atoms form a diffusive distribution of electrons. This results in delocalization of electrons within the honeycomb plane and graphite is thus conducting. Its electrical conductivity is highly anisotropic. Graphite is metallic when current is flowing within the honeycomb plane and is semiconducting when current is flowing perpendicular to the honeycomb plane. From the point of view of his conduction properties graphite should be classified as semi-metal.

In graphene sheet the conduction and valence bands consisting of π orbitals cross at K and K' points of the Brillouin zone, where the Fermi level is located. Graphene is a reasonable good conductor.¹⁰⁷

The properties of graphene can be modified significantly by introducing defects and by saturating with hydrogen. Graphane is a two-dimensional polymer of carbon and hydrogen with the formula unit $(CH)_n$ where n is large. It can be considered as a two dimensional analog of cubic diamond. The carbon bonds of graphane are in sp^3 configuration, as opposed to graphene's sp^2 bond configuration.

So far, the only two-dimensional carbon allotrope that can be produced or synthesized is graphene. However, as it was noted in Ref.¹⁰⁸ in principle, infinitely many other two-dimensional periodic

Table 5. Carbon-based materials

Material	Structure	Bonding
Diamond	3D crystal	involving sp^3 hybridization
Graphite	3D crystal	involving sp^2 hybridization
Graphene	2D single graphite layer	involving sp^2 hybridization
Graphane	2D polymer	involving sp^3 hybridization
Carbolite	chain-like crystal	involving sp^1 hybridization
C_{60}	molecule	involving sp^2 hybridization
Carbon nanotube	-	-
Activated carbon	-	-

carbon allotropes, e.g., graphynes or graphdiynes, can be envisioned. Unlike graphene, which has single or double bonds, graphynes and graphdiynes may be built from triple- and double-bonded units of two carbon atoms and it is not restricted to just a hexagonal pattern. It was conjectured that the number of patterns that it can exist may be very big.

Thus, as it was long known, the different allotropic forms of carbon have essentially different structures. Due to the different bonding characteristics they have different chemical and physical properties (see Table 5).

During the last twenty years, the multiplicity of potential carbon structures has consistently posed a big challenge to theoretical and computational physicists. Several different methods are currently being used to study the structure and the properties of such systems.^{13, 79, 109, 110} These methods include simulations based on empirical potentials, tight-binding calculations and density functional theory. A combination of these methods is needed to make significant progress in the field of carbon-based structures, forming regular solids and clusters. Cluster-based solids⁸² illustrate the importance of local order in determining global properties in solids. These solids add a new dimension to material science. The stronger intra-cluster bonding in these materials allows them to keep their individual identity while forming part of the bulk material.

The most striking example of this is the C_{60} molecule.³⁰ Bulk carbon crystals made of C_{60} are highly stable and form a metastable phase of carbon in addition to the energetically most stable bulk graphite. Fullerene C_{60} is a molecular crystal formed by all-carbon molecules with a closed-cage structure and a nearly spherical shape. C_{60} molecules form a face-centered cubic crystal lattice at room temperature with weak van der Waals type bonding between the molecules. The solid forms of other fullerenes can also be expected to be stable when synthesized under optimal conditions. Indeed, successful synthesis of a solid form composed of C_{36} fullerene molecules has been reported.¹¹¹

The study of transformations of C_{60} fullerene at high pressures and temperatures has shown that the identification of the different carbon states formed in the system presents certain difficulties. V. A. Davydov and his group^{112, 113, 114, 115, 116, 117} have achieved big progress in the studies of transformations of C_{60} fullerene at high pressures and temperatures. In Ref.¹¹² they proposed a scheme for classifying the carbon states that form under nonhydrostatic compression of C_{60} fullerite at pressures up to 10 GPa and temperatures up to 1900 K . Using the character of the structure-forming element (atom, molecule, polymolecular cluster) as a criterion, different types of carbon states were distinguished in the system: molecular, polymolecular (polymerized and polycondensed), and atomic. They performed an x -ray phase analysis of the polymerized states on the basis of the phase identification made in Ref.¹¹⁸ It was established also by x -ray diffraction and Raman scattering that the polymerization of C_{60} fullerene at 1.5 GPa and 723 K leads to the formation of an orthorhombic phase that is different from the previously identified

high-pressure orthorhombic phase. The mechanisms leading to the formation of the polymerized phases was discussed on the basis of the results obtained. Thus in the works by V. A. Davydov and his group^{112, 113, 114, 115, 119, 116, 120, 117} the experimental and model computational results of big importance were obtained that made it possible to refine the previously obtained data on the identification of the polymerized states.

As it was shown in Ref.¹¹⁸ the heating under high pressure drives C_{60} to new distorted crystalline phases that are metastable at room temperature and pressure. Additional information was obtained in Ref.¹²¹ where it was shown that application of nonhydrostatic pressure to cluster-based molecular material, like fullerite C_{60} , provides an opportunity to create elastically and structurally anisotropic carbon materials, including two-dimensional polymerized rhombohedral C_{60} and superhard graphite-type (sp^2) disordered atomic-based phases. There is direct correlation between textured polymerized and/or textured covalent structure and anisotropic elasticity. Whereas this anisotropy was induced by the uniaxial pressure component, in the case of disordered atomic-based phases, it may be governed by the uniform pressure magnitude.

In recent paper¹²² by K. P. Meletov and G. A. Kourouklis, the great advantages of the C_{60} molecule and its potential for polymerization due to which the molecule can be the building block of new all carbon materials were reviewed. This substance contains, both (sp^2) and (sp^3) hybridized carbon atoms, which allows synthesizing new carbon materials with desired physicochemical properties using both types of carbon bonding. The one- and two-dimensional polymeric phases of C_{60} are prototype materials of this sort. Their properties, especially polymerization under pressure and room temperature via covalent bonding between molecules belonging to adjacent polymeric chains or polymeric layers, can be used for further development of new materials. The review¹²² was focused on the study of the pressure-induced polymerization and thermodynamic stability of these materials and their recovered new phases by in-situ high-pressure Raman and x -ray diffraction studies. The phonon spectra show that the fullerene molecular cage in the high-pressure phases is preserved, while these polymers decompose under heat treatment into the initial fullerene C_{60} monomer. In Ref.¹²³ the orthorhombic polymer have been studied by NMR method. Authors conjectured that there exist nine inequivalent carbons on a C_{60} molecule in the orthorhombic polymer.

It was shown recently in Ref.¹²⁴ by the methods synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments that graphene, a two-dimensional layer of (sp^2)-hybridized carbon atoms, can be viewed as a sheet of benzene rings fused together. Extension of this concept leads to an entire family of phenalenyl derivatives - 'open-shell graphene fragments'.

M. Koshino and E McCann¹²⁵ studied the electronic structure of multilayer graphenes with a mixture of Bernal and rhombohedral stacking and proposed a general scheme to understand the electronic band structure of an arbitrary configuration. The system can be viewed as a series of finite Bernal graphite sections connected by stacking faults. They found that the low-energy eigenstates are mostly localized in each Bernal section, and, thus, the whole spectrum is well approximated by a collection of the spectra of independent sections. The energy spectrum was categorized into linear, quadratic, and cubic bands corresponding to specific eigenstates of Bernal sections. The ensemble-averaged spectrum exhibits a number of characteristic discrete structures originating from finite Bernal sections or their combinations likely to appear in a random configuration. In the low-energy region, in particular, the spectrum is dominated by frequently appearing linear bands and quadratic bands with special band velocities or curvatures. In the higher-energy region, band edges frequently appear at some particular energies, giving optical absorption edges at the corresponding characteristic photon frequencies.

Thus molecule-based materials underlie promising next generation nanoscale electronic devices, machines and quantum information processing systems, by virtue of the wide diversity and flexibil-

ity in the design of molecular and electronic structures that can be attained by chemical syntheses. For example, the spins of unpaired electrons in tailor-made open shell species can afford control of quantum information in molecules and thus provide the potential for molecular electronics and information processing.

Carbon-based materials and nanostructured materials have huge number of applications.^{13, 79, 82, 83, 126, 127} The numerous applications were presented in the books,^{126, 127, 128, 129} which provides also further information on bioceramics specifically for medical applications.^{127, 128, 129} New materials for sensors were also reviewed. Nanostructured materials and coatings for biomedical and sensor applications contribute to the dissemination of state-of-the-art knowledge about the application of nanostructured materials and coatings in biotechnology and medicine, as well as that of sensors for the chemical and biomedical industries. The research presented in the books^{127, 128, 129} addresses the fundamental scientific problems that must be resolved in order to take advantage of the nanoscale approach to creating new materials.

There are various applications of nanoscale carbon-based materials in heavy metal sensing and detection.¹³⁰ These materials, including single-walled carbon nanotubes, multi-walled carbon nanotubes and carbon nanofibers among others, have unique and tunable properties enabling applications in various fields spanning from health, electronics and the environment sector. Specifically, there are the unique properties of these materials that enable their applications in the sorption and preconcentration of heavy metals ions prior to detection by spectroscopic, chromatographic and electrochemical techniques. Their unique distinct properties enable them to be used as novel electrode materials in sensing and detection. The fabrication and modification of these electrodes is very fine skill. Their applications in various electrochemical techniques such as voltammetric stripping analysis, potentiometric stripping analysis, field effect transistor-based devices and electrical impedance are numerous.

5 Carbon-Based Structures and Magnetism

Magnetic properties of carbone-based nanostructures have attracted a lot of recent interest. The permanent magnetic properties of materials such as iron, nickel, cobalt, gadolinium stem from an intrinsic mechanism of the quantum origin called ferromagnetism. Conventional wisdom has it that carbon (containing only s and p electrons) does not have a spontaneous magnetic moment in any of its allotropes. The possibility of ferromagnetism at room temperature in carbon-based materials as, e.g., doped graphite, synthetic fullerene C_{60} , graphene and carbon composites has recently gained a lot of attention of the experimentalists and theoreticians.^{52, 53, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149} The understanding and control of the magnetic properties of carbon-based materials is of fundamental relevance in their possible applications in nano- and biosciences.

Graphite^{150, 151} has been known as a typical diamagnetic material.² As such it can be levitated in the strong magnetic field. In addition magnetically levitating graphite can be moved with laser and a laser moves the disk in the direction of the light beam. This effect was demonstrated by Kobayashi and Abe.¹⁵² They showed that the magnetically levitating pyrolytic graphite can be moved in the arbitrary place by simple photoirradiation. It is notable that the optical motion control system described in their paper requires only $NdFeB$ permanent magnets and light source. The optical movement was driven by photothermally induced changes in the magnetic susceptibility of the graphite. Moreover, they demonstrated that light energy can be converted into rotational kinetic energy by means of the photothermal property. They found that the levitating graphite disk rotates at over 200 *rpm* under the sunlight, making it possible to develop a new class of light energy conversion system.

A physical property of particular interest regarding all the aforementioned carbon allotropes is

the magnetic susceptibility,^{153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164} χ_b , since this bulk probe is related to the low energy electronic spectrum. The relationship between the magnetization induced in a material \mathbf{M} and the external field \mathbf{H} is defined as:

$$\mathbf{M} = \chi_b \mathbf{H}. \quad (21)$$

The parameter χ_b is treated as the bulk magnetic susceptibility of the material. It can be a complicated function of orientation, temperature, state of stress, time scale of observation and applied field, but is often treated as a scalar. It is of use to consider the symbol \mathbf{M} for volume normalization (units of Am^{-1}). Volume normalized magnetization therefore has the same units as \mathbf{H} . Because M and H have the same units, χ_b will be dimensionless.

Graphite is known as one of the strongest diamagnetic materials among natural substances. This property is due to the large orbital diamagnetism related to the small effective mass in the band structure, i.e., narrow energy gap between conduction and valence bands. The diamagnetic effect becomes even greater in graphene monolayer which is truly a zero-gap system. R.C. Haddon³² showed that the difference in magnetic susceptibility of graphite and diamond prompted Raman to postulate the flow of currents around the ring system of graphite in response to an applied magnetic field. The discovery of new carbon allotropes, the fullerenes, has furthered our understanding of this phenomenon and its relationship to aromatic character. C_{60} and the other fullerenes exhibit both diamagnetic and paramagnetic ring currents, which exert subtle effects on the magnetic properties of these molecules and provide evidence for the existence of π -electrons mobile in three dimensions.

In general, all known carbon allotropes exhibit diamagnetic susceptibility^{153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164} with a few exceptions. The polymerized C_{60} prepared in a two-dimensional rhombohedral phase (depending on the orientation of the magnetic field relative to the polymerized planes) shows weak ferromagnetic signal in some experiments. Also the disordered glass-like magnetism was observed in activated carbon fibers possibly due to non-bonding p electrons located at edge states. The unusual magnetic behavior was observed as well in single wall carbon nanohorns which was ascribed to the Van Vleck paramagnetic contribution. Superparamagnetic and/or ferromagnetic-like behavior in carbon-based material has been previously observed in amorphous carbon materials obtained by chemical synthesis or pyrolysis. The origin of ferromagnetism was suggested to be attributed to the mixture of carbon atoms with sp^2 and sp^3 bonds and resulted ferromagnetic interaction of spins separated by sp^2 centers. An increase in saturated magnetization of amorphous-like carbon prepared from different hydrogen-rich materials indicated the importance of hydrogen in the formation of the magnetic ordering in graphite. The ferro- or ferrimagnetic ordering was reported in proton-irradiated spots in highly oriented pyrolytic graphite. It was demonstrated that protons implanted in highly oriented pyrolytic graphite triggered ferro- (or, ferri-) magnetic ordering with a Curie temperature above room temperature.

Previously, the "hybrid materials" known as molecular ferromagnets^{165, 166, 167} in which organic groups are combined with transition metal ions were prepared.^{166, 167} Here the organic groups were themselves not magnetic but were used to mediate the magnetism between transition metal ions. Organic ferromagnetism was first achieved using organic radicals called nitronyl nitroxides. Many organic radicals exist which have unpaired spins, but few are chemically stable enough to assemble into crystalline structures. Ferromagnetism in organic materials is rare because their atomic structure is fundamentally different from metals. One of the few examples identified to date is called TDAE- C_{60} : a compound comprising spherical carbon cages attached to an organic molecule known as tetrakis-dimethylamino-ethylene. Since its identification in 1991,¹⁶⁸ many theoretical and experimental studies have provided some insight into the mechanism driving this unexpected ferromagnetism,¹⁶⁹ but the explanation was not fully definitive.

It is also possible to prepare molecule based magnets in which transition metal ions are used

to provide the magnetic moment, but organic groups mediate the interactions. In 1998 the ferromagnetism in a cobaltocene-doped fullerene derivative was reported.¹⁷⁰ This strategy led to the fabrication of magnetic materials with a large variety of structures, including chains, layered systems and three-dimensional networks, some of which show ordering at room temperature and some of which have very high coercivity. Nevertheless, it was recognized that "reports of weak magnetization in organic materials have often proved to be wrong".

Magnetism in carbon allotropes has indeed been a fundamental and also controversial problem for a long time.^{29,32} It is of importance to examine this complicated problem thoroughly.

In spite of the fact that carbon is diamagnetic, in 2001 an "observation of strong magnetic signals in rhombohedral pristine C_{60} , indicating a Curie temperature T_C near 400-500 K" was reported.^{171,172} In short, it was speculated that the polymerization of C_{60} fullerenes at certain pressure and temperature conditions, as well as photopolymerization in the presence of oxygen may lead to appearance of magnetically ordered phases. "Ferromagnetic behavior" was reported which is close to the conditions where the fullerene cages are about to be destroyed, and the effect was presumably associated with the defects in intramolecular or intermolecular bonding. In the authors' opinion the observation of magnetic domain structure in impurity-free regions provides an evidence in favor of the *intrinsic nature* of fullerene ferromagnetism.

As was shown above, polymerization of fullerenes can be realized through various methods^{112,113,114,115,116,117,122} including the high-pressure and temperature treatments and through irradiation with *UV* light. It can also occur through reactions with alkali metals. The reported measurements^{171,172} were described as the "ferromagnetic fullerene".^{173,174} This new magnetic forms of C_{60} have been identified with the state which occur in the rhombohedral polymer phase. The existence of previously reported ferromagnetic rhombohedral C_{60} was confirmed. This property has been shown to occur over a range of preparation temperatures at 9 GPa. The structure was shown to be crystalline in nature containing whole undamaged buckyballs. Formation of radicals is most likely due to thermally activated shearing of the bridging bond resulting in dangling bond formation. With increasing temperatures this process occurs in great enough numbers to trigger cage collapse and graphitization. The magnetically strongest sample was formed at 800 K, and has a saturated magnetization at 10K.

Moreover, in paper¹⁷⁵ the observation of the ferromagnetically ordered state in a material obtained by high-pressure high-temperature treatment of the fullerene C_{60} was confirmed. It had a saturation magnetization more than four times larger than that reported previously. From their data the considerably higher value of $T_C \approx 820$ K was estimated.¹⁷⁵

The widely advertized "discovery" of a ferromagnetic form of carbon^{171,172,173} stimulated huge stream of the investigations of the carbon-based materials.^{171,172,173,175,176,177,178,179,180,148} However, difficulties to reproduce those results and the unclear role of impurities casted doubts on the existence of a ferromagnetic form of carbon.

And nevertheless, it was claimed that "the existence of carbon-based magnetic material requires a root-and-branch rework of magnetic theory". Moreover, "the existing theory for magnetism in elements with only *s* and *p* electron orbits (such as carbon)" should be reconsidered in the light of the fact that there are many publications "describing ferromagnetic structures containing either pure carbon or carbon combined with first row elements", in spite of the fact that "these reports were difficult to reproduce".

It is worth mentioning that in the publications^{171,175,176} the characterization of the samples was not made properly. This fact was recognized by the authors themselves.^{181,182,183} In paper¹⁸² a C_{60} polymer has been characterized for the first time with respect to impurity content and ferromagnetic properties by laterally resolved particle induced *x*-ray emission and magnetic force microscopy in order to prove the existence of intrinsic ferromagnetism in this material. In the sample studied the main ferromagnetic impurity found was iron with remarkable concentration.

In spite of that fact authors insisted that they were able "to separate between the intrinsic and extrinsic magnetic regions and to directly prove that intrinsic ferromagnetism exists in a C_{60} polymer".

In 2004 the band structure calculations of rhombohedral C_{60} performed in the local-spin-density approximation were presented.¹³² Rhombohedral $C_{60}(Rh - C_{60})$ is a two-dimensional polymer of C_{60} with trigonal topology. No magnetic solution exists for $Rh - C_{60}$ and energy bands with different spins were found to be identical and not split. The calculated carbon $2p$ partial density of states was compared to carbon K -edge x -ray emission and absorption spectra and showed good agreement. It was concluded that the rhombohedral distortion of C_{60} itself cannot induce magnetic ordering in the molecular carbon. The result of magnetization measurements performed on the same $Rh - C_{60}$ sample corroborates this conclusion.

It is worth noting that in majority publications on the possible ferromagnetism of carbon-based "magnetic" material the effects of the low dimensionality^{73,56} on the possible magnetic ordering were practically ignored.

In 2006 a retraction letter¹⁸⁴ has been published. Some of the authors (two of them decline to sign this retraction) recognized that reported high-temperature ferromagnetism in a polymeric phase of pure carbon that was purportedly free of ferromagnetic impurities was an artefact. Other measurements made on the same and similar samples using particle-induced x -ray emission with a proton micro-beam have indicated that these had considerable iron content. Also, polymerized C_{60} samples mixed with iron before polymerization had a similar Curie temperature (500 K) to those they described,¹⁷¹ owing to the presence of the compound Fe_3C (cementite). In addition, it has since been shown that the pure rhombohedral C_{60} phase is not ferromagnetic.¹³² Nevertheless, they concluded that "magnetic order in impurity-free graphitic structures at room temperature has been demonstrated independently (before and after publication of ref.¹⁷¹). Ferromagnetic properties may yet be found in polymerized states of C_{60} with different structural defects and light-element (H, O, B, N) content".

In spite of this dramatic development, the search for magnetic order at room temperature in a system without the usual $3d$ metallic magnetic elements continues. It was conjectured that the graphite structure with defects and/or hydrogen appears to be one of the most promising candidates to find this phenomenon.

The irradiation effects for the properties of carbon-based materials were found substantial. Some evidence that proton irradiation on highly oriented pyrolytic graphite samples may triggers ferro- or ferrimagnetism was reported.^{185,186} The possibility of a magnetism in graphene nanoislands was speculated and a defective graphene phase predicted to be a room temperature ferromagnetic semiconductor was conjectured as well.¹³⁸

O. V. Yazyev and L. Helm¹⁸⁷ studied from first principles the magnetism in graphene induced by single carbon atom defects. For two types of defects considered in their study, the hydrogen chemisorption defect and the vacancy defect, the possibility of the itinerant magnetism due to the defect-induced extended states has been concluded. The coupling between the magnetic moments is either ferromagnetic or antiferromagnetic, depending on whether the defects correspond to the same or to different hexagonal sublattices of the graphene lattice, respectively. The relevance of itinerant magnetism in graphene to the high- T_c magnetic ordering was discussed.

In Ref.¹⁸⁸ vacancies and vacancy clusters produced by carbon ion implantation in highly oriented pyrolytic graphite, and their annealing behavior associated with the ferromagnetism of the implanted sample were studied using positron annihilation in conjunction with ferromagnetic moment measurements using a superconducting quantum interferometer device magnetometer. Authors' results give some indication that the "magnetic moments" may be correlated to the existence of the vacancy defects in the samples and this is supported by theoretical calculations using density functional theory. The possible mechanism of magnetic order in the implanted sample was

discussed. Authors¹⁸⁸ claimed that "it has become evident ... that even pure carbon can show substantial paramagnetism and even ferromagnetism".

In paper¹⁸⁹ recently obtained data were discussed using different experimental methods including magnetoresistance measurements that indicate the existence of metal-free high-temperature magnetic order in graphite. Intrinsic as well as extrinsic difficulties to trigger magnetic order by irradiation of graphite were discussed. The introduction of defects in the graphite structure by irradiation may be in principle a relevant method to test any possible magnetic order in carbon since it allows to minimize sample handling and to estimate quantitatively the produced defect density in the structure. The main magnetic effects produced by proton irradiation have been reproduced in various further studies. *x*-ray magnetic circular dichroism studies on proton-irradiated spots on carbon films confirmed that the magnetic order is correlated to the π -electrons of carbon only, ruling out the existence of magnetic impurity contributions. The role of defects and vacancies continues to be under current intensive study.

In paper,⁵³ by means of near-edge *x*-ray-absorption fine-structure and bulk magnetization measurements, it was demonstrated that the origin of ferromagnetism in $^{12}\text{C}^+$ ion implanted highly oriented pyrolytic graphite is closely correlated with the defect electronic states near the Fermi level. The angle-dependent near-edge *x*-ray-absorption fine-structure spectra imply that these defect-induced electronic states are extended on the graphite basal plane. It was concluded that the origin of electronic states to the vacancy defects created under $^{12}\text{C}^+$ ion implantation. The intensity of the observed ferromagnetism in highly oriented pyrolytic graphite is sensitive to the defect density, and the narrow implantation dosage window that produces ferromagnetism should be optimized.

In paper,¹⁹⁰ electronic and structural characterization of divacancies in irradiated graphene was investigated. Authors provided a thorough study of a carbon divacancy, a point defect expected to have a large impact on the properties of graphene. Low-temperature scanning tunneling microscopy imaging of irradiated graphene on different substrates enabled them to identify a common twofold symmetry point defect. Authors performed first-principles calculations and found that the structure of this type of defect accommodates two adjacent missing atoms in a rearranged atomic network formed by two pentagons and one octagon, with no dangling bonds. Scanning tunneling spectroscopy measurements on divacancies generated in nearly ideal graphene showed an electronic spectrum dominated by an empty-states resonance, which was ascribed to a nearly flat, spin-degenerated band of π -electron nature. While the calculated electronic structure rules out the formation of a magnetic moment around the divacancy, the generation of an electronic resonance near the Fermi level reveals divacancies as key point defects for tuning electron transport properties in graphene systems. Thus the situation is still controversial.¹⁸⁹

High-temperature ferromagnetism in graphene and other graphite-derived materials reported by several workers^{54,148} has attracted considerable interest. Magnetism in graphene and graphene nanoribbons is ascribed to defects and edge states, the latter being an essential feature of these materials.^{52,191,187,190,192} Room-temperature ferromagnetism in graphene¹⁴⁸ is affected by the adsorption of molecules, especially hydrogen. Inorganic graphene analogues formed by some layered materials also show such ferromagnetic behavior.¹⁴⁸ Magnetoresistance observed in graphene and graphene nanoribbons is of significance because of the potential applications.

The problem of possible intrinsic magnetism of graphene-based materials was clarified in paper.¹⁹³ The authors have studied magnetization of graphene nanocrystals obtained by sonic exfoliation of graphite. No ferromagnetism was detected at any temperature down to 2 K. Neither do they found strong paramagnetism expected due to the massive amount of edge defects. Rather, graphene is strongly diamagnetic, similar to graphite. Their nanocrystals exhibited only a weak paramagnetic contribution noticeable below 50 K. The measurements yield a single species of defects responsible for the paramagnetism, with approximately one magnetic moment per typical graphene crystal-

lite.

It should be noted once again that finding the way to make graphite magnetic could be the first step to utilising it as a bio-compatible magnet for use in medicine and biology as effective biosensors. Thus the researchers¹⁹⁴ found a new way to interconnect spin and charge by applying a relatively weak magnetic field to graphene and found that this causes a flow of spins in the direction perpendicular to electric current, making a graphene sheet magnetized. The effect resembles the one caused by spin-orbit interaction but is larger and can be tuned by varying the external magnetic field. They also show that graphene placed on boron nitride is an ideal material for spintronics because the induced magnetism extends over macroscopic distances from the current path without decay.

Recently the Geim's team investigations shed an additional light on controversial magnetic behavior of carbon-based structures.^{195,196,197,198} It was shown^{195,196,197,198} that magnetism in many commercially available graphite crystals should be attributed to micron-sized clusters of predominantly iron. Those clusters would usually be difficult to find unless the right instruments were used in a particular way.

To arrive at their conclusions, a piece of commercially-available graphite was divided into four sections and the magnetization of each piece was measured. They found significant variations in the magnetism of each sample. Thus it was concluded that the magnetic response had to be caused by external factors, such as small amount of impurities of another material (the induced magnetism). To confirm that essential fact the structure of the samples was thoroughly investigated using a scanning electron microscope. It was found that there were unusually heavy particles positioned deep under the surface. The majority of these particles were confirmed to be iron and titanium, using a technique known as *x*-ray microanalysis. As oxygen was also present, the particles were likely to be either magnetite or titano-magnetite, both of which are magnetic.

The very ingenious craftsmanship was used to deduce how many magnetic particles would be needed, and how far apart they would need to be spaced in order to create the originally observed magnetism.^{195,196,198} The observations from their experiments agreed with their estimations, meaning the visualized magnetic particles could account for the whole magnetic signal in the sample.

6 Magnetic Properties of Graphene-Based Nanostructures

There has been increasing evidence that localized defect states (or surface or edge states) in *sp* materials may form local moments and exhibit collective magnetism.^{52,53,139,140,142,144,191,187,190,192} A special interest was connected with the magnetic properties of graphene-based nanostructures.^{199,200,201,202,203} Furthermore graphene is a promising candidate for graphene-based electronics.

Ferromagnetism in various carbon structures, mostly highly defective, has been observed and investigated theoretically. Edges of nano-structured graphene, or vacancies, cracks, *etc.*, may lead to localized states that increase density of states close to Dirac point.

First principles and mean-field theory calculations have shown that zero-dimensional graphene nanodots or nanoflakes, graphitic petal arrays, one-dimensional nanoribbons, nano and two-dimensional nanoholes that consist of zigzag edges can all exhibit magnetism, making them an interesting new class of nanomagnets. It was speculated that the magnetization in graphene-based nanostructures may be originated from the localized edge states that give rise to a high density of states at the Fermi level rendering a spin-polarization instability. However, the complete mechanism leading to the magnetic properties is still a matter of discussion. Despite the promise shown by the theoretical studies in magnetic graphene-based nanostructures, however, the experimental realization of these magnetic graphene-based nanostructures remains a big challenge because

synthesis of graphene is a difficult task before one further makes them into different forms of nanostructures.¹³⁶

Electronic and magnetic structure of graphene nanoribbons and semi-infinite ribbons made from graphene sheets is of especial interest.^{199, 200, 201, 202, 203, 204, 205, 206, 207, 208} It was shown, that the electronic structure of these ribbons is very sensitive to the edge geometry and to the width of the ribbon. The strong influence of the exact edge geometry is a typical feature for graphene, and will also be reflected in the conductance properties of the nanoribbon.^{199, 200, 201, 202, 203, 204, 205, 206, 207, 208} The review paper²⁰⁰ covers some of the basic theoretical aspects of the electronic and magnetic structure of graphene nanoribbons, starting from the simplest tight-binding models to the more sophisticated ones where the electron-electron interactions were considered at various levels of approximation. Nanoribbons can be classified into two basic categories, armchair and zigzag, according to their edge termination, which determines profoundly their electronic structure. Magnetism, as a result of the interactions, appears in perfect zigzag ribbons as well as in armchair ribbons with vacancies and defects of different types. Therefore, the effects of different edges on the transport properties of nanometer-sized graphene devices need to be investigated carefully. Especially, it is known, that the two basic edge shapes, namely zigzag and armchair, lead to different electronic spectra for graphene nanoribbons.

K. Harigaya²⁰³ analyzed theoretically the mechanism of magnetism in stacked nanographite. Nanographite systems, where graphene sheets of dimensions of the order of nanometres are stacked, show novel magnetic properties, such as spin-glasslike behaviors and change of electron spin-resonance linewidths in the course of gas adsorptions. Harigaya investigate stacking effects in zigzag nanographite sheets theoretically, by using a tight-binding model with Hubbard-like on-site interactions. He found a remarkable difference in magnetic properties between the simple A-A-type and A-B-type stackings. For the simple stacking, there were no magnetic solutions. For the A-B stacking, he found antiferromagnetic solutions for strong on-site repulsions. The local magnetic moments tend to exist at the edge sites in each layer due to the large amplitudes of the wavefunctions at these sites. Relations with experiments were discussed.

In Ref.¹³⁶ using first-principles calculations, it was shown that nanopatterned graphite films can exhibit magnetism in analogy to graphene-based nanostructures. In particular, graphite films with patterned nanoscale triangular holes and channels with zigzag edges all have ferromagnetic ground states. The magnetic moments are localized at the edges with a behavior similar to that of graphene-based nanostructures. Authors' findings suggest that the nanopatterned graphite films form a unique class of magnetic materials. In conclusion, they have demonstrated that graphite films can become an all-carbon intrinsic magnetic material when nanopatterned with zigzag edges, using first-principles calculations. The magnetism in nanopatterned graphite films may be localized within one patterned layer or extended throughout all the patterned layers. It is originated from the highly localized edge states in analogy to that in graphene-based nanostructures. Because graphite film is readily available while mass production of graphene remains difficult, it was argued that the nanopatterned graphite films can be superior for many applications that have been proposed for graphene-based nanostructures.

In Ref.¹⁴⁶ the so-called zigzag edge of graphenes has been studied. It was supposed theoretically that they has localized electrons due to the presence of flat energy bands near the Fermi level. The conjecture was that the localized electron spins are strongly polarized, resulting in ferromagnetism. The graphenes with honeycomb-like arrays of hydrogen-terminated and low-defect hexagonal nanopores were fabricated by a nonlithographic method using nanoporous alumina templates. Authors reported large-magnitude room-temperature ferromagnetism caused by electron spins localizing at the zigzag nanopore edges. This observation may be a realization of rare-element free, controllable, transparent, flexible, and mono-atomic layer magnets and novel spintronic devices.

In summary, edge atomic structures of graphene have been of great interest,^{199,200,201,202,203,204,205,206,207,208} due to its strongly localized electrons, which originate from the presence of flat energy bands near the Fermi level. The zigzag edge of graphene may have a high electronic density of states. The localized edge electron spins become stabilized and strongly polarized leading to possible "ferromagnetism" depending on the exchange interaction between the two edges, which forms a maximum spin ordering in these orbitals similar to the case of Hund's rule for atoms, e.g., the localized edge spins in a graphene nanoribbon and in graphene with hexagonal nanopore arrays. Moreover, spin ordering strongly depends on the termination of edge dangling bonds by foreign atoms (e.g., hydrogen (H)) and those numbers that result in the formation of edge π and σ orbitals. From another theoretical viewpoint, Lieb's theorem²⁰⁹ for bipartite lattices predicts that an increase in the difference between the number of removed A and B sites of the graphene bipartite lattice at zigzag edges may induce net magnetic moments and yields ferromagnetism, particularly in nano-size graphene flakes and nanopores.

It should be stressed that rigorous proof of the appearance of ferromagnetism in realistic model of itinerant electrons is extremely complicated problem.^{55,56,62,210,211} Lieb's theorem²⁰⁹ regards the total spin S of the exact ground state of the attractive and repulsive Hubbard model in bipartite lattices. Lieb²⁰⁹ obtains that independently of lattice structure, for N even the ground state is unique (and hence has $S = 0$) if $U < 0$. For $U > 0$ at half-filling on bipartite lattice the ground state is a $(2S + 1)$ -fold degenerate state with $S = 1/2||B| - |A||$. From the other hand, Rudin and Mattis²¹² calculated the ground state of the Hubbard model in two dimension approximately. They found ground state energies of paramagnetic and ferromagnetic states as well as the (Pauli) paramagnetic spin susceptibility. Their conclusion was that the conditions for ferromagnetism fail to be met in their (non-rigorous) approach. Moreover, the rigorous proof of the applicability of the Hubbard model to zigzag edges is still lacking as well. Thus the real reason of the strong polarization of electrons was not established definitely. The problem of magnetism due to edge states requires the additional careful investigations and separate thorough discussion.

7 Some Related Materials

The ferromagnetism is a macroscopic phenomena.²¹⁰ On the microscopic level it is a cooperative effect of the Coulomb interaction in many-electron systems and is a consequence of the Pauli exclusion principle. The term "ferromagnetism" has been used often in literature in too broad sense. According to Arrott, by definition, a material is ferromagnetic if there can exist regions within the material where a spontaneous magnetization exists. The temperature below which ferromagnetism occurs is called the Curie temperature and is a measure of the interaction energy associated with the ferromagnetism. As Arrott²¹³ showed there is *a criterion* for onset of ferromagnetism in a material as its temperature is lowering from a region in which the linearity of its magnetic moment versus field isotherm gives an indication of paramagnetism.

While magnetic order is most common in metallic materials containing narrow bands of d - or f -electrons, the magnetic polarization of p -electrons has been investigated only during recent years. Triggered by the growing interest in spintronics materials the search for magnetic semiconductors or for half-metals used for spin-injection has produced quite a number of new materials classes. The future of the spintronic technology requires the development of magnetic semiconductor materials.²¹⁴ The search for magnetic semiconductors has gathered the attention of researches for many years. They are rare in nature, and when they do occur, they possess low Curie temperatures, and their potential technological applications depend on their capacity to keep the ferromagnetic order up to room temperature. Most research groups have focused on diluted magnetic semiconductors because of the promising theoretical predictions and initial results. In the work,²¹⁴ the current experimental situation of ZnO based diluted magnetic semiconductors was considered.

Recent results on unexpected ferromagnetic-like behaviour in different nanostructures were also revised, focusing on the magnetic properties of *Au* and *ZnO* nanoparticles capped with organic molecules. These experimental observations of magnetism in nanostructures without the typical magnetic atoms are of great importance and were discussed thoroughly. The doubts around the intrinsic origin of ferromagnetism in diluted magnetic semiconductors along with the surprising magnetic properties in absence of the typical magnetic atoms of certain nanostructures should make us consider new approaches in the quest for room temperature magnetic semiconductors.

Magnetism in systems that do not contain transition metal or rare earth ions was recently attracted exceptionally big attention. There are numerous both the experimental and theoretical results in literature which treats the term "ferromagnetism" too broadly and without the proper carefulness. Magnetism is a cooperative phenomenon essentially and can be an *intrinsic* property of a crystalline state, or it can be *induced* by magnetic impurities in a non-magnetic system or by specific defects or vacancies. The main problem in this case is the fact that spin polarization is local. The possibility of the magnetically ordered state will depend on the delicate balance of the various interactions in the system. The non-vanishing stable spin polarization may arise in certain cases due to specific combination of peculiarities of the band structure of the system but as an exception. We summarize very briefly a few examples below.

Okada and Oshiyama²¹⁵ reported first-principles total-energy electronic-structure calculations in the density functional theory performed for hexagonally bonded honeycomb sheets consisting of *B*, *N*, and *C* atoms. They found that the ground state of *BNC* sheets with particular stoichiometry is ferromagnetic. Additional analysis of energy bands and spin densities leads them to conclusion that the nature of the ferromagnetic ordering is connected with the flat-band character of electronic structure. The flat-band ferromagnetism¹⁴¹ is one of the of the mechanisms which may play a role side by side with the high density of states at the Fermi level and strong electron correlation.

In paper²¹⁶ cation-vacancy induced intrinsic magnetism in *GaN* and *BN* was investigated by employing density functional theory based electronic structure methods. It was shown that the strong localization of defect states favors spontaneous spin polarization and local moment formation. A neutral cation vacancy in *GaN* or *BN* leads to the formation of a net moment of $3\mu_B$ with a spin-polarization energy of about 0.5 eV at the low density limit. The extended tails of defect wave functions, on the other hand, mediate surprisingly long-range magnetic interactions between the defect-induced moments. This duality of defect states suggests the existence of defect-induced or mediated collective magnetism in these otherwise nonmagnetic *sp* systems.

The *p*-electron magnetism in doped $BaTiO_{3-x}M_x$ ($M = C, N, B$) was investigated in Ref.²¹⁷ Authors presented Vienna *ab initio* simulation package (VASP) calculations using the the hybrid density functional for carbon, nitrogen, and boron-doped $BaTiO_{3-x}M_x$ ($M = C, N, B$). They calculated a 40-atom supercell and replaced one oxygen atom by *C*, *N*, or *B*. For all three substituents they found a magnetically ordered ground state which is insulating for *C* and *N* and half-metallic for *B*. The changes in the electronic structure between the undoped and the doped case are dominated by the strong crystal field effects together with the large band splitting for the impurity *p*-bands. Using an *MO* picture they proposed an explanation for the pronounced changes in the electronic structure between the insulating non-magnetic state and the as well insulating magnetic state for doped $BaTiO_3$. The conclusion was made that the *p*-element-doped perovskites could provide a new class of materials for various applications ranging from spin-electronics to magneto-optics.

In interesting paper by Upkong and Chetty²¹⁸ the study of substitutionally doped boronitride was carried out. They performed first-principles molecular dynamics simulations to investigate the magnetoelectronic response of substitutionally doped boronitrene to thermal excitation. Authors showed that the local geometry, size, and edge termination of the substitutional complexes of

boron, carbon, or nitrogen determine the thermodynamic stability of the monolayer. In addition, they found that hexagonal boron or triangular carbon clusters induce finite magnetic moments with 100% spin-polarized Fermi-level electrons in boronitrene. In such carbon substitutions, the spontaneous magnetic moment increases with the size of the embedded carbon cluster, and results in half-metallic ferrimagnetism above 750 K with a corresponding Curie point of 1250 K , above which the magnetization density vanishes. Authors predicted an ultrahigh temperature half-metallic ferromagnetic phase in impurity-free boronitrene, when any three nearest-neighbor nitrogen atoms are substituted with boron, with unquenched magnetic moment up to its melting point.

Unfortunately the form of the presentation of their results contains some delicate misleading features related to the precise definition of the term "ferromagnetism". The title "half-metallic ferromagnetism" suggests the long-range order, which it is not present really. What authors described were the local high-spin defects where a few spins interact by "ferromagnetic coupling". But there are another possibility which authors ignored. The nearly the same result would be obtained when the clusters were terminated by e.g. hydrogens. There is only a slight spin polarization which extends over the rim of the defect. Such things can hardly be termed by "ferromagnetism". Moreover, the authors even used term "ferrimagnetism". They found spin-polarized density of states (figure 8) for s and p orbitals of the four carbon atoms in the star-shaped carbon cluster. However the interpretation of the changes of bond length in their figure 8 may be simply Jahn-Teller type distortions which are common in open-shell systems. In this sense the paper treats the term "ferromagnetism" too broadly and without the proper carefulness. Nevertheless, the paper is rather stimulating and will promote further investigations in this direction.

8 Conclusions

In summary, in the present work, the problem of the existence of carbon-based magnetic material was analyzed and reconsidered to elucidate the possible relevant mechanism (if any) which may be responsible for observed peculiarities of the "magnetic" behavior in these systems, having in mind the quantum theory of magnetism criteria. Some theoretical conjectures and experimental results were re-examined critically. It is difficult to take into account and to summarize concisely the many important results covered in the numerous publications. But we hope that the present study shed some light on many complicated aspects of the controversial problem of magnetism of the carbon-based structures. However, it leaves many open questions which should be answered in additional publications.

In general, the origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another.^{55,56} The basic object in the magnetism of condensed matter is the magnetic moment. The magnetic moment in practice may depend on the detailed environment and additional interactions such as spin-orbit, screening effects and crystal fields. To understand the full connection between magnetism and chemical structure of a material, a detailed characterization of the samples studied is vital.

Characterization of magnetic materials by means of neutron scattering technique is highly desirable.^{60,95,98,99,219} Carbon-based structures should be investigated by neutron scattering and its spin density distribution should be measured in order to visualize the pathway of the magnetic interactions. The spin density of these complex structures should be measured by polarized neutron diffraction.

The similar problem was mentioned already in context of organic ferromagnets.^{220,221} Unpaired electrons in these compounds are usually valence electrons and are of great chemical interest. The polarized neutron diffraction experiments were usually analyzed in such a way as to produce the unpaired electron density or spin density. The spin density is, or should be, a positive quantity

because (i) there is a higher population of up-spin electrons than down-spin electrons (when an magnetic field is applied), and (ii) electrons tend to always be paired so that only the unpaired electrons contribute to the spin density (i.e. the spin density from the paired electrons cancels out).

Unfortunately the polarized neutron diffraction experiment does not directly determine the unpaired electron density. Instead, polarized neutrons are scattered from the magnetic field density in the crystal (they are also scattered from the nuclei, but this effect can usually be modelled). Therefore, one should examine the magnetic field density rather than the spin density itself.²²¹ It is of importance to obtain the fully information on the actual spin density in carbon-based materials. The full picture of the spin density distribution will clarify the problem of magnetism of the carbon-based materials greatly.

On the basis of the present analysis the conclusion can be made that the thorough and detailed experimental studies of this problem only may lead us to a better understanding of the very complicated problem of magnetism of carbon-based materials.

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