'Magnetic properties of nano- and heterostructures' Joint scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences and of the Joint Physical Society of the Russian Federation (27 February 2002)

A joint scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) and of the Joint Physical Society of the Russian Federation devoted to studies of the magnetic properties of nano- and heterostructures was held on 27 February 2002 in the conference hall of the P N Lebedev Physics Institute of the RAS. The following reports were presented at the session.

(1) **Davydov V A** (L F Vereshchagin Institute of High-Pressure Physics, RAS, Troitsk, Russia) "A magnetically ordered state based on polymerized fullerene C_{60}";

(2) **Stetsenko P N, Antipov S D, Goryunov G E, Smirnitskaya G V, Surikov V V, Kolumbaev A L** (Physics Department, M V Lomonosov Moscow State University, Moscow, Russia) "Local magnetic states and hyperfine interactions in magnetic superlattices and spin-tunnel junctions";

(3) **Zvezdin A K** (General Physics Institute, RAS, Moscow, Russia), **Kostyuchenko V V** (Microelectronics and Information Science Institute, RAS, Yaroslavl', Russia), **Platonov V V** (All-Russia Research Institute of Experimental Physics, Sarov, Russia), **Plis V I, Popov A I** (Moscow State Institute of Electronic Engineering, Moscow, Russia), **Selemir V D, Tatsenko O M** (All-Russia Research Institute of Experimental Physics, Sarov, Russia) "Magnetic molecular nanoclusters in strong magnetic fields";

(4) **Mukhin A A, Prokhorov A S, Gorshunov B P, Zvezdin A K, Travkin V D** (General Physics Institute, RAS, Moscow, Russia), **Dressel M** (Stuttgart University, Stuttgart, Germany) "Submillimeter spectroscopy of electron transitions and the macroscopic quantum tunneling of magnetization in molecular nanoclusters";

(5) **Smirnov A I, Glazkov V N** (P L Kapitza Institute of for Physical Problems, RAS, Moscow, Russia) "Defects in spin-gap magnets: multispin clusters".

Abridged versions of the reports are given below.

A magnetically ordered state of carbon based on polymerized fullerene C_{60}

V A Davydov

It was discovered in studying the evolution of carbon states that arise as a result of subjecting fullerite C_{60} to different pressures and temperatures that some high-pressure states realized near the thermal stability limit of the rhombohedral polymer phase of C_{60} at 6.0 GPa exhibit a behavior typical of ferromagnets. The present report discusses the results of measurements of the magnetic properties of such materials, whose Curie temperature is about 500 K. Since the content of magnetic impurities in the samples investigated is insufficient to explain the observed value of saturation magnetization, it is assumed that the ferromagnetic behavior of the samples is caused by a magnetically ordered structure of carbon itself. Some of the possible types of such structures are discussed below.

The discovery of fullerenes and the subsequent discovery of superconductivity [1] and ferromagnetism [2] in systems based on fullerene C_{60} has attracted the attention of researchers to new molecular forms of carbon. It soon became obvious that new types of carbon materials could be produced on the basis of molecular forms of carbon. Pressure proved to be an effective instrument for such production.

The point is that, thermodynamically, the production of C_{60} fullerite (the crystalline phase of fullerene C_{60} [3]) meant the detection of a new metastable state of solid carbon, which was also the highest point of metastability in the carbon system. As the energy diagram (Fig. 1) built on the basis of the works of Vereshchagin [4] and Yakovlev and Voronov [5] implies, before the discovery of fullerenes the energy range of existence of the known forms of solid carbon amounted to about 10 kJ mol^{-1} under normal conditions. After the discovery of fullerite C_{60}, the upper boundary of this range became roughly 40 kJ mol^{-1}. The diagram clearly shows that the use of fullerite C_{60} as the initial state of the system raises hopes for producing a whole family of new carbon materials whose energy levels are within a range unattainable before the discovery of fullerenes. Such materials can be obtained as intermediate states in the process of the system passing from the highly metastable initial state (fullerite C_{60}) to states corresponding to the absolute minima of the system's energy (graphite or diamond). Since fullerite C_{60} is a modification of
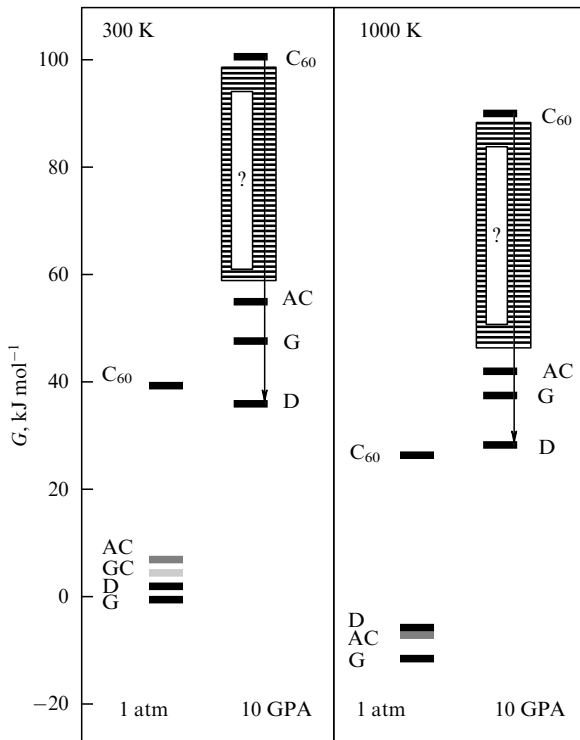
Figure 1. Gibbs energies of graphite (G), diamond (D), glassy carbon (GC), amorphous carbon (AC), and fullerite C_{60} at pressures of 1 atm and 10 GPa and temperatures of 300 and 1000 K.

Figure 2. The (p, T) diagram of molecular, M (fcc, sc), polymolecular, Mp (O, T, R, 3D), and atomic, A, carbon structures that form as a result of quasi-hydrostatic compression of fullerite C_{60}. The white lozenges indicate the p, T parameters of sample synthesis for isobaric cross sections at 2.5 and 6.5 GPa. The black lozenges, indicated by an arrow, correspond to the temperature interval within which the samples were found to exhibit ferromagnetic properties. D stands for the region where diamond forms, gc stands for the glassy state of the system, and DS for the dimerized state of the system [6 – 9].

carbon with a density ($\rho = 1.68$ g cm^{-3}) lower than that of graphite (2.26 g cm^{-3}) or diamond (3.52 g cm^{-3}), it is obvious that pressure becomes the crucial factor initiating the transition of the system to its equilibrium states.

Systematic studies of the behavior of fullerite C_{60} at high pressures and temperatures (a detailed review of such studies can be found in Ref. [6]) have shown that the transformations of fullerite C_{60} under these conditions are indeed accompanied by the formation of a whole series of new carbon states.

The variety of carbon modifications that form as a result of subjecting fullerite C_{60} to pressures up to 10 GPa and temperatures up to 1800 K is illustrated in Fig. 2, which represents in a generalized form the results of our experiments [7] and the data of other researchers [8]. This diagram is not a classical phase diagram referring to equilibrium existence of phases; rather, it is a generalized picture of the experimental data on the products of fullerite C_{60} treatment at different pressures and temperatures under conditions of quasi-hydrostatic compression and treatment times not exceeding 50 000 s. Using the structure-forming element (atom, molecule, or polymolecular cluster) as the classification criterion, we can single out at least four types of carbon compounds in the system [6]:

(1) molecular phases based on monomer molecules C_{60}, including the face-centered cubic (fcc) phase and the simple cubic (sc) phase with the glassy carbon (gc) region, i.e., phases that form region M in the diagram;

(2) polymolecular (Mp) states of the system, which are packings of different polyfullerenes that are formed as a result of $2 + 2$ cycloaddition reactions of C_{60} molecules [10]. Among these are the orthorhombic (O), tetragonal (T), and rhombohedral (R) crystalline phases, which are packings of linear (1D) and two types of two-dimensional (2D, with tetragonal
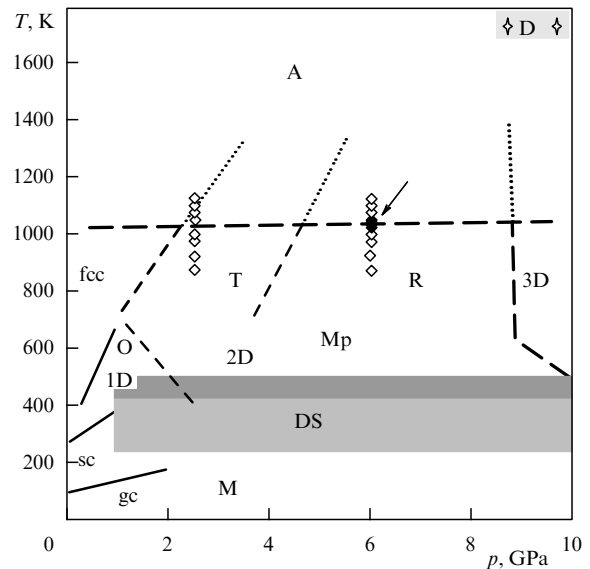
and hexagonal topologies of the layer) C_{60} polymers, and packings of low-molecular-weight polymers, such as dimers $(C_{60})_2$ (the DS region in the diagram), trimers, tetramers, and some other higher-molecular-weight polymers existing in the heavily shaded region of the diagram;

(3) polymolecular three-dimensional (3D) structures, which are observed at pressures higher than 8.5 – 9 GPa and comprise the high-pressure phases in which the molecular C_{60} cluster is still the structure-forming element, although the nature of bonding between C_{60} clusters differs from that observed in 1D and 2D polymers;

(4) various atomic carbon states (region A) existing at temperatures higher than the thermal stability limit of the molecular C_{60} cluster and 'ascending' to graphite and diamond as the treatment temperature grows.

Since the high-pressure states produced at different values of the p, T parameters are fairly stable under normal conditions, they are of real interest from the viewpoint of studying their band structure and optical, photoelectric, transport, and magnetic properties [11].

Here, I discuss the recent results of Makarova et al. [12] obtained in their study of the magnetic properties of these high-pressure states. In our investigations of the evolution of the entire set of physical properties of the initial fullerite C_{60}, depending on the treatment temperature in different isobaric cross sections of the (p, T) diagram, it was unexpectedly found that some of the samples of the rhombohedral polymer phase of C_{60} produced at the limit of thermal stability of that phase at 6.0 GPa (in the range of 1010 – 1050 K) clearly exhibit ferromagnetic properties.

Note that the above temperature interval is of special interest from the viewpoint of studying the evolution of the properties of the system, since it corresponds to the limit of

thermal stability of the carbon cluster C_{60}, depicted in Fig. 2 by a heavy dashed horizontal line separating the Mp and A regions in the diagram; when this line is crossed, the system's structure undergoes the most radical transformation. It is in this temperature range that C_{60} molecules, two-dimensional polymer molecules, and three-dimensional polymolecular C_{60} clusters, which are the structure-forming elements of mono-mer fcc, two-dimensional tetragonal, rhombohedral, and three-dimensional polymer phases, are transformed into various atomic states of carbon.

Makarova et al. [12] studied in great detail the isobaric cross sections of the (p, T) diagram at 2.5 and 6.0 GPa, which correspond to transformations into the atomic state of the tetragonal and rhombohedral polymer phases of C_{60}, respectively. The lozenges in Fig. 2 indicate the temperatures at which the various high-pressure states were synthesized in these isobaric cross sections. The synthesis process was carried out at the Institute of High-Pressure Physics of RAS in a high-pressure chamber of the Toroid type described in Ref. [13]. The initial material was a doubly sublimated finely crystalline fullerite C_{60} fabricated in the United States by Term Co., with a C_{60} content of up to 99.98%. Cylindrical samples of precompacted fullerite powder (with a mass of 14 mg each) were wrapped up in niobium or tantalum foil, encased in hexagonal boron nitride, which screened the samples from the heater manufactured from high-purity graphite of the MG OSCh grade, and placed in the high-pressure chamber. The experiment amounted to loading, heating, and isothermal exposure of the samples in the course of 1000 s under the load at a fixed temperature. The samples were then quenched under pressure to room temperature.

A systematic study of the electric and magnetic properties of the sample prepared in this manner was conducted at the A F Ioffe Physicotechnical Institute, RAS (St. Petersburg, Russia) by T L Makarova and at the Umeå University (Umeå, Sweden), Leipzig University (Leipzig, Germany), Institute for Physics, TU Ilmenau (Ilmenau, Germany), São Paulo University (São Paulo, Brazil) in cooperation with researchers of those institutions [12]. Elemental analysis of the material was performed by atomic absorption spectro-scopy on a Perkin–Elmer SIMAA 6000 spectrometer. An Oxford MagLab 2000 System was used to measure the ac magnetic susceptibility, and a SQUID Quantum Design quantum magnetometer was used to measure the magnetic susceptibility in a dc magnetic field.

Figure 3 shows the hysteresis loops and magnetization curves at 10 and 300 K for one of the samples in fields of ± 2 and ± 50 kOe [12] (a relatively small diamagnetic contribution has been eliminated). Figure 3b clearly shows that the magnetization is saturated when the magnetic field strength is higher than 20 kOe. With allowance for a spin concentration of 5×10^{18} cm^{-3} (the value was obtained from EPR measurements), the magnetic moment per electron was estimated to be $0.4\,\mu_{\mathrm{B}}$, where μ_{B} is the Bohr magneton.

The temperature dependences of magnetization in a 0.2 T field and of the remanent magnetization (Fig. 4) in a zero field suggest that the Curie temperature of the investigated samples is approximately 500 K. Measurements of the temperature dependence of the magnetic susceptibility have shown that the magnetic susceptibility of the samples slowly increases with temperature, starting at 30 K. It was also found that the magnetic susceptibility is highly anisotropic: its values differed by a factor of 5.5 for different orientations of the
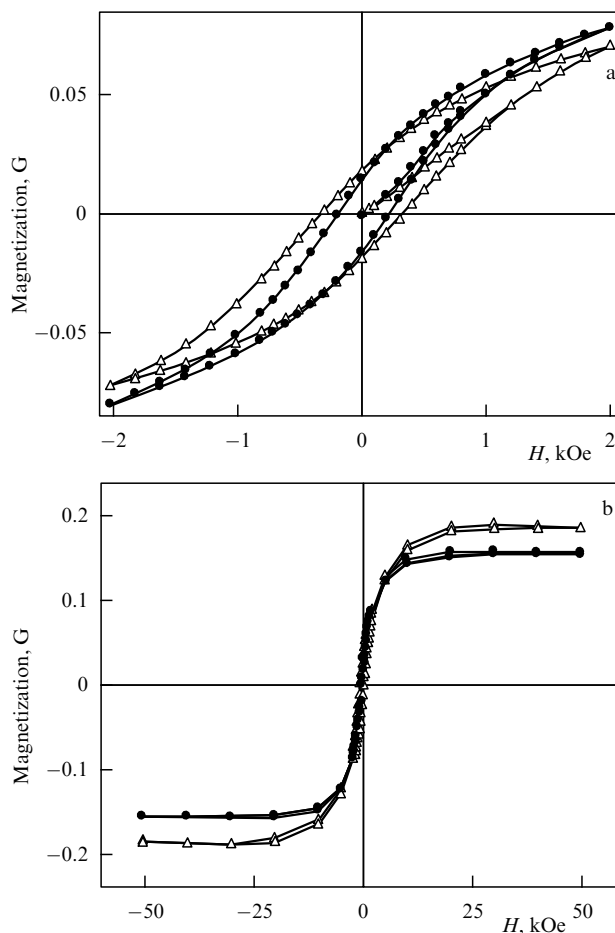

Figure 3. Hysteresis loops (a) and magnetization curves (b) of a magnetic sample at 10 K (white triangles) and 300 K (black circles) [12].
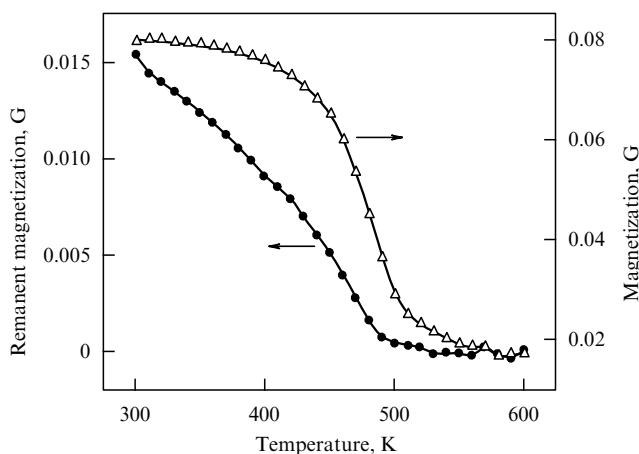

Figure 4. Temperature dependences of the magnetization of a magnetic sample in a 0.2 T magnetic field (upper curve, white triangles) and of the remanent magnetization in a zero magnetic field (lower curve, black circles) [12].

magnetic field — along and perpendicular to the polymerization plane of C_{60}.

Since the initial fullerite C_{60} is diamagnetic, the ferromagnetic behavior of the samples can be attributed either to the presence of a significant amount of a ferromagnetic impurity or to changes in the structure of the carbon material itself. A

survey elemental analysis of the initial fullerite C_{60} and of the samples subjected to high pressures and temperatures has shown that the general content of magnetic impurities in these materials does not exceed 0.003 at. %. According to the estimates done in Ref. [12], such an impurity content leads to a saturation magnetization value 30 times smaller than that observed in the experiment. It was also noted that pieces of ferromagnetic polymer samples that had undergone depolymerization as a result of heating to temperatures above 650 K completely give up their ferromagnetic properties. It was these two facts and the fact that the appearance of ferromagnetic states has been observed only in the isobaric cross section corresponding to the transformation of the rhombohedral phase and only within a narrow temperature range (outside this range such states have never been observed) that forced the researchers to search for an explanation of the ferromagnetism in the very nature of these high-pressure states. In Ref. [12], which summarized the results of the first stage of the investigations, it was suggested that the appearance of constant magnetic moments in the system is related to the presence of topological defects in the polymer C_{60} layers, which results in some of the electrons becoming unpaired. There it was also noted that only samples fabricated at the limit of thermal stability of the rhombohedral phase exhibited pronounced magnetic properties. Thus, although according to the results of X-ray phase analysis the rhombohedral phase is predominant in the ferromagnetic samples, the detected magnetic effects are, to all appearances, related to the deformation and partial destruction of C_{60} clusters, since in samples of a purely rhombohedral phase fabricated at lower temperatures, 873 or 973 K, ferromagnetic properties have never been observed. For the same reason, a defect structure based on the rhombohedral phase is, strictly speaking, not the only candidate for the role of the state that determines the ferromagnetic behavior of the samples. Other possible candidates are various ferromagnetic structures based on sp^2 and sp^3 hybridized states of carbon such as those proposed by Ovchinnikov and Shamovsky [14]. According to calculations of the band structure of some carbon materials and the related isostructural materials that are formed in a three-component $C - B - N$ system, magnetically ordered states can also arise when nanometer-sized fragments of graphene planes with 'zigzag' edges appear in the system [15, 16].

At the same time it is obvious that until the origin of the ferromagnetic behavior of samples obtained by subjecting fullerite C_{60} to high pressures has been established beyond all doubt, the possibility cannot be excluded that the observed phenomena are related to an uncontrolled inclusion of metallic impurities in the samples. The probability of such a situation occurring is finite, since we are speaking of monitoring an impurity content that amounts to several thousandths of one percent, which requires using special technological methods corresponding, in essence, to the requirements adopted in the semiconductor industry. This, strictly speaking, was not done in the process of producing the different high-pressure states.

At present, in order to independently verify the results of Makarova et al. [12], we are carrying out a detailed investigation of a new series of ferromagnetic samples together with researchers in a number of laboratories in Russia and in foreign countries. The results of these investigations show, among other things, that there is a significant inhomogeneity in the distribution of the ferromagnetic component over a sample, which is probably related to the gradients in the distribution of pressure and temperature that exist in modern high-pressure chambers. The presence of such inhomogeneities opens up the possibility to take a new look at the results of the measurements of spin concentrations in magnetic samples obtained by Makarova et al. [12]. Previously, the value of the spin concentration (5×10^{18} cm^{-3}), determined as the concentration averaged over the entire sample and corresponding to roughly one spin per three hundred C_{60} molecules, could hardly be explained within the scope of the usual notions about the structure of the exchange interaction, since it implied that the average distance between separate spins is extremely large. If inhomogeneities are present, the local spin concentration in the ferromagnetic regions of the sample may really be much higher than the average value.

The discovery of inhomogeneities in magnetic samples determined the main area of research in this field — local methods of studying the samples. We believe that in conjunction with cutting the samples into separate fragments and separating these fragments magnetically, with the purpose of extracting the ferromagnetic fragments in a more concentrated form, these studies will make it possible to determine without a doubt the nature of the emerging magnetically ordered states and will provide the final answer to a question that always arises in studies of the magnetic properties of organic or carbon compounds: is the observed ferromagnetism merely an artifact or is it indeed related to the specific features of the structure of pure carbon states?

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Local magnetic states and hyperfine interactions in magnetic superlattices and spin-tunnel junctions

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We have carried out a comprehensive study of the structure and magnetic and electrical properties of, and hyperfine magnetic fields in, the magnetic Fe/Al, Fe/Ti, Fe/Ta, Fe/Pd