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High-Pressure Hydrofullerites

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Abstract—This paper is a brief summary of the results of long-term experimental studies of $C_{60}H_x$ hydrofullerites with a hydrogen content of up to $x \sim 60$ or more, obtained by loading C_{60} fullerites with hydrogen at pressures up to 9 GPa and temperatures up to 500°C. Basically, this is an overview of already published data. Some results for hydrofullerites with compositions of $x \sim 60$ and $x \sim 90$ are presented for the first time.

Keywords: fullerene, hydrofullerite, hydrogen, high pressures, X-ray diffraction, infrared spectroscopy, inelastic neutron scattering

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INTRODUCTION

The techniques for synthesis of hydrides in a hydrogen-gas atmosphere under pressures of up to 9 GPa and temperatures of up to 800°C with subsequent quenching the samples under pressure to a temperature of 80 K, which were developed at the Institute of Solid State Physics, Russian Academy of Sciences, provide the opportunity to obtain relatively large single-phase and homogeneous samples with the minimum number of defects and to save them for subsequent study in a metastable state under atmospheric pressure [1, 2]. The amount of the substance synthesized in one experiment varies from 30 to 500 mm^3 depending on the pressure, which is sufficient for measurements using most physical methods.

These techniques were used for the saturation of various forms of carbon with hydrogen, more specifically, nanofibers and nanotubes, graphite, and fullerite C_{60}. New compounds with compositions of up to $CH_{0.88}$ stable in vacuum at temperatures up to 450°C were prepared on the basis of carbon nanofibers and nanotubes [3]. A new compound with a composition close to CH was synthesized on the basis of graphite [4]. The compound is a crystal consisting of corrugated layers of graphane in chair conformation, which are perpendicular to the hexagonal axis of the initial graphite. The formation of this multilayer graphane is accompanied by an increase in the distance between graphite layers by 42% from 3.36 to 4.77 Å.

In this work, we consider the most significant results obtained for hydrofullerites $C_{60}H_x$. In particular, crystalline hydrofullerite $C_{60}H_{60}$ was synthesized under high hydrogen pressure [5, 6], while other methods afford compositions of no higher than $C_{60}H_{36}$. Room-temperature ferromagnetism was discovered in hydrofullerite $C_{60}H_x$ with $x = 24$ [2]. Amorphous hydrofullerite $C_{60}H_x$ with $x \approx 90$ has been synthesized.

EXPERIMENTAL

The initial material for hydrogenation was a powder of C_{60} with a purity of 99.99% with respect to C_{70}, which was extracted from fullerene-containing soot using a standard procedure [7, 8] and transformed into a polycrystal through sublimation in an evacuated quartz tube at 600–650°C. The fullerite was hydrogenated under various pressures from 0.6 to 9 GPa and temperatures from 350 to 500°C in quasi-hydrostatic high-pressure chambers of the Toroid type [9]. A weighed portion of fullerite with a mass of about 100 mg was encased in a sealed copper or lead cell together with a powder of AlH_3, which was separated from the fullerite by a thin palladium foil and used as an internal source of molecular hydrogen (the procedure is described in more detail in [2]). At the end of hydrogenation, which proceeded from several hours to several days, the high-pressure chamber was rapidly (within 10–20 s) cooled to room temperature and then more slowly to liquid-nitrogen temperature. The pressure was lowered to atmospheric; the sample was released from the cell and stored in liquid nitrogen until the studies.

The hydrogen content of the synthesized hydrides was determined in two stages. Firstly, the sample was heated from the boiling point of nitrogen to room temperature in a preliminarily evacuated container of known volume and the amount of evolved hydrogen was determined from its pressure. Not much hydrogen was evolved; the atomic ratio was of the order of $H/C_{60} = 3$. The evolution completely ceased in less than 1 h at room temperature and no losses of hydrogen were observed over several years when the samples were stored under normal conditions. The significant destruction of hydrofullerites began upon heating in vacuum to 500°C. The second stage of determining the hydrogen content of the samples consisted of combustion of a weighted portion of nearly 2 mg of hydride in an oxygen flow at 1400°C and weighing the products of combustion: H_2O and CO_2. The relative measurement error was 3%.

Both the kinetics of hydrogenation and the achieved hydrogen content of the $C_{60}H_x$ samples prepared under identical conditions varied significantly from one experiment to another; therefore, the baric dependences of the equilibrium concentration of hydrogen in fullerite at temperatures from 350 to 500°C were not constructed. It could only be stated that the hydrogen content of the samples of $C_{60}H_x$ increased from $x \approx 24$ to $x \approx 60$ with an increase in the hydrogen pressure from 0.6 to 5 GPa [5, 6]. The initial fullerite C_{60} was black; the samples of $C_{60}H_x$ with $x = 24$ were yellowish or brownish and the samples with $x \geq 36$ were white.

The investigation of hydrofullerites by inelastic neutron scattering was carried out on a KDSOG-M spectrometer at the Joint Institute for Nuclear Research (Dubna). X-ray measurements were performed at room temperature on a SIEMENS D500 diffractometer using $\mathrm{Cu}K_{\alpha 1}$ monochromatic radiation. The IR spectra of the powder samples were measured using an IFS-113v Fourier spectrometer at room temperature in the spectral range 400 cm$^{-1} \leq \nu \leq 5000$ cm^{-1} (62–620 meV) with a resolution of 4 cm^{-1} (0.5 meV). The obtained transmittance spectra $T(\nu)$ were then transformed into optical density spectra $A(\nu) = -\ln(T)$; to do this, we first constructed the spectrum $A^* = -\ln(T)$, and then subtracted from it a monotonous “baseline” resulting predominantly from the light scattering on the powder particles. However, it should be noted that the spectrum $A(\nu) = kd$ differs from that of the absorption coefficient $k(\nu)$, because the thickness d is unknown in the case of powder samples.

RESULTS AND DISCUSSION

Crystal Structure of $C_{60}H_x$

Under normal conditions, fullerite possesses a face-centered cubic (fcc) lattice composed of C_{60} molecules [10]. In the case of hydrofullerites, “molecules” of $C_{60}H_x$ form either a fcc or body-centered cubic (bcc) lattice. For example, the sample of hydrofullerite $C_{60}H_{36}$ synthesized in [11] possessed a fcc lattice (personal communication from [11]), whereas in [12], a hydrofullerite sample with a similar composition possessed a bcc lattice. A total of 12 syntheses were carried out for samples of $C_{60}H_x$ with compositions of $x = 24$–32 obtained by exposing C_{60} powder for 24 h at $T = 350$°C and a hydrogen pressure from 0.6 to 3 GPa [2]. It turned out that about half of these samples possessed a fcc lattice, while the other half possessed a bcc lattice. There was no dependence of the structure on the conditions of synthesis. Typical diffraction patterns of the initial C_{60} and hydrofullerites with fcc and bcc lattices are given in Fig. 1.

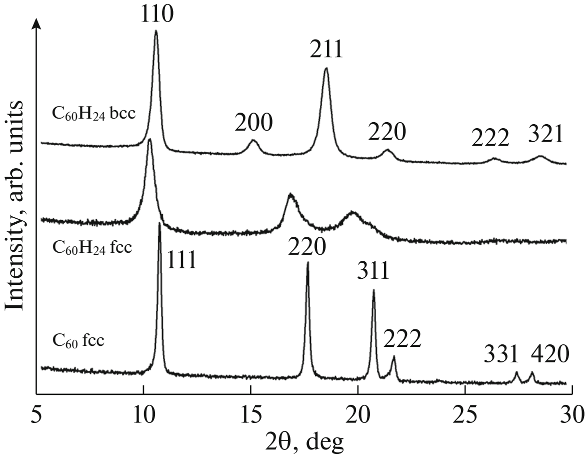

Fig. 1. Powder diffraction patterns of the initial fullerite C_{60} with a fcc lattice and hydrofullerites $C_{60}H_{24}$ with fcc and bcc lattices [2]. The hydrofullerite samples were synthesized by a 24 h exposure to a hydrogen pressure of 0.6 GPa and a temperature of 350°C and, then, were kept under normal conditions for one day. The diffraction patterns were recorded at room temperature using a SIEMENS D500 diffractometer with $\mathrm{Cu}K_{\alpha 1}$ monochromatic radiation.

In the case of hydrofullerites $C_{60}H_x$ with $x > 36$, which were obtained under hydrogen pressures higher than 3 GPa, an increase in the time of synthesis resulted in a transition from the fcc to bcc phase without a noticiable change in the hydrogen content of the samples. Figure 2 shows the concentration dependences of the specific volume of fcc and bcc hydrofullerites. As one can see, the volume of the bcc samples practically ceases to change at $x > 36$. The smaller specific volume of the bcc phase increases its thermodynamic stability relative to the fcc phase due to a decrease in the PV term in the Gibbs energy of the C_{60}–H_2 system. This is presumably the main reason for the observed fcc → bcc transition in high-pressure hydrofullerites.

The temperature 500°C is close to the upper limit of the thermal stability of hydrofullerites. Hydrogenation of C_{60} for 1–3 h at temperatures of 550°C and 600°C gives heterogeneous samples composed of two fcc phases with lower lattice parameters. After treatment at 700°C for 1 h, the reflections of the crystal lattice almost disappear and after 1 h at 800°C the sample completely transforms to a nanocrystalline state with the short-range order of graphite.

Two States of Hydrogen in Hydrofullerites

It was mentioned above that two states of hydrogen were observed in $C_{60}H_x$ hydride. Hydrogen of the first type was evolved from the samples upon heating from 80 K to room temperature. Its content did not exceed an atomic ratio of $H/C_{60} = 3$. The low temperature of desorption indicates that this hydrogen was loosely bound to the carbon framework of fullerite. The temperature of about 500°C, at which hydrogen of the second type is evolved, indicates a chemical bond of this hydrogen with C_{60}. These statements are confirmed by the results of studying inelastic neutron scattering.

In [13], a sample of $C_{60}H_{27}$ synthesized at $P = 0.6$ GPa and $T = 350$°C was studied by inelastic neutron scattering at 85 K firstly in the quenched state and, then, after annealing at 300 K for 35 h. The annealing decreased the hydrogen content of the sample by $\Delta x = 2.8 \pm 0.2$. The composition of the annealed sample was $x = 23.5 \pm 2.5$. X-ray diffraction study at $T = 85$ K showed that the quenched sample possessed a bcc lattice with the parameter $a = 12.00$ Å and this parameter decreased to $a = 11.72$ Å after the annealing at 300 K.

The total neutron scattering cross section of hydrogen atoms is much higher than that of carbon atoms ($\sigma^H = 82.02$ barn, $\sigma^C = 5.551$ barn [14]); therefore, the spectra of inelastic neutron scattering on hydrofullerites are mainly determined by scattering on hydrogen. The difference in these spectra measured on the hydrofullerite sample before and after its annealing at 300 K (Fig. 3) represents the spectrum of hydrogen removed from the sample by annealing. It is seen that the difference spectrum has a low intensity at energies in the range of intermolecular vibrations of fullerite at $E < 4$ meV and in the range of bending vibrations of C–H bond in hydrocarbons at $E > 100$ meV. This suggests that the "excess" hydrogen was not chemically bound to the molecules of C_{60}. This excess hydrogen in the form of H_2 molecules presumably occupied the voids in the bcc lattice of hydrofullerite. The conclusion was made in [13] based on the presence of peaks near 12, 18, 30, and 45 meV in the difference spectrum of inelastic neutron scattering (Fig. 3), which is close to the energies of transitions in the spectrum of rotational vibrations of a free H_2 molecule [15] (vertical arrows in Fig. 3).

The positions of the experimental peaks at 30 and 45 meV agree with the energies $\Delta E_{1\to2} = 29.4$ meV and $\Delta E_{0\to2} = 44.1$ meV for molecular hydrogen. The low intensity of the peak at 45 meV is caused by the fact that it corresponds to the transition between rotational states in para-hydrogen molecules, which scatter neutrons coherently [15]. The mean peak energy at 12 and

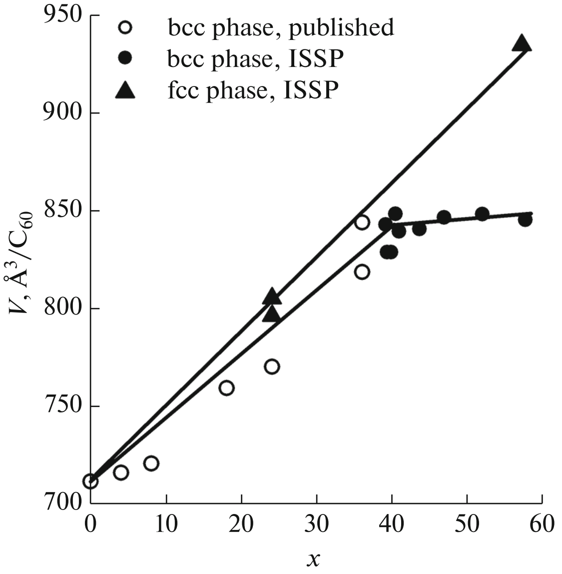

Fig. 2. Specific volumes V of hydrofullerites $C_{60}H_x$ and $C_{60}D_x$ as a function of the mean hydrogen content, $x = H(D)/C_{60}$. AlD_3 was used to synthesize the deuterated samples. The specific volume of the hydrofullerites did not change within the experimental error with the replacement of protium with deuterium.

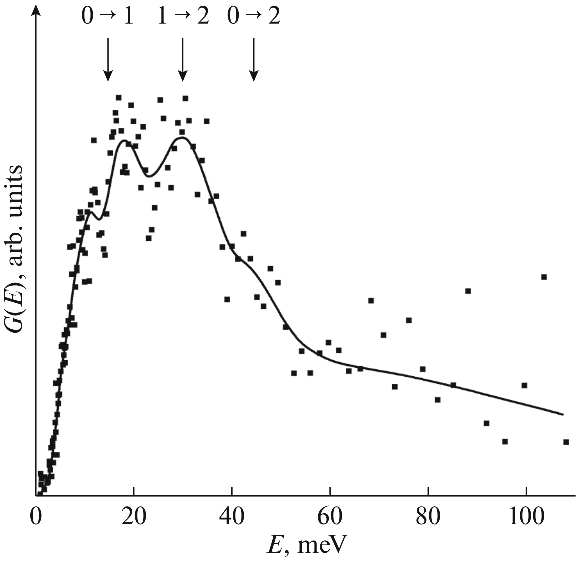

Fig. 3. Difference between the spectra of the generalized density of vibrational states $G(E)$ of the sample of $C_{60}H_x$ quenched to 77 K and measured before and after annealing for 35 h at 300 K, which resulted in a decrease in the hydrogen content by $H/C_{60} \approx 2.8$, corresponding to 1.4 molecules of H_2 per molecule of C_{60} [13]. Arrows indicate the positions of rotational transitions in a free molecule of H_2. The measurements were performed at 85 K on a KDSOG-M neutron spectrometer at the Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna.

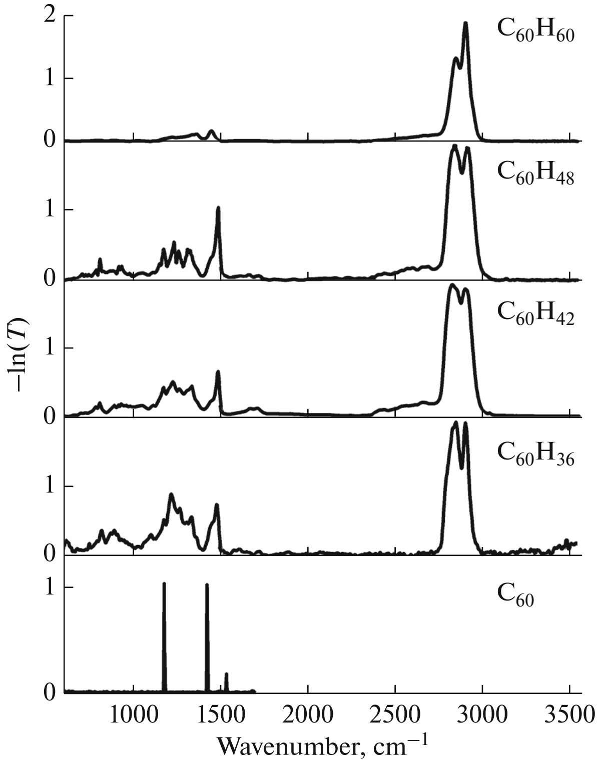

Fig. 4. Optical density spectra of fullerite C_{60} (normalized to unity) and hydrofullerites $C_{60}H_x$ with x = 36, 42, 48, and 60 (normalized to 1.96) at T = 300 K [4].

18 meV is 15 meV, which is close to the value $\Delta E_{0\to 1}$ = 14.7 meV for the para–ortho transition in free H_2 molecules. The appearance of these two peaks can be attributed to splitting of the peak (0 → 1) due to the interaction of H_2 molecules located at the interstices of the bcc lattice of hydrofullerite with the neighboring molecules of $C_{60}H_x$. Similar splitting of the peak (0 → 1) into two peaks at 12.5 and 18 meV was previously observed in the spectra of inelastic neutron scattering of H_2 molecules in amorphous carbon [16, 17].

In the inelastic neutron scattering spectra of the quenched and annealed samples of hydrofullerite, a broad and intense peak was observed at 155 meV, or 1250 cm^{-1}, whose presence and position are characteristic of bending vibrations in hydrofullerites with chemically bound hydrogen, which are studied in more detail and with a higher resolution using IR spectroscopy [6]. Therefore, it is reasonable to assume that it was the chemically bound hydrogen that remained in the hydrofullerite after heating the sample to 300 K.

Hydrofullerites with chemically bound hydrogen and compositions of up to $C_{60}H_{60}$ were studied at room temperature using IR spectroscopy [6]. The optical density spectra $A(\nu) = -\ln(T)$, where $T(\nu)$ is the transmittance spectrum of the powder samples of $C_{60}H_x$ with x = 36, 42, 48, and 60, as well as the spectrum of the initial fullerite C_{60} for comparison are given in Fig. 4. No absorption bands were observed in the spectral range 3000–5000 cm^{-1}. The spectra of the hydrides are dominated by lines close to ν = 2900 cm^{-1}, which are absent in the spectra of C_{60}. This unambiguously indicates the presence of strong chemical C–H bonds. The bending vibrations of C–H bonds are observed near 1450 cm^{-1}. This result agrees with quantum-chemical calculations for $C_{60}H_{36}$ (e.g., [18, 19]), which showed that the bending and stretching vibrations of C–H-bonds are near 1450 and 2900 cm^{-1}, respectively. Due to the lower molecular symmetry and the presence of various isomers, hydrofullerites with x = 36, 42, and 48 had more dipole-active modes than fullerite C_{60}. As follows from Fig. 4, the number of dipole-active modes decreases again for $C_{60}H_{60}$. This indicates a higher symmetry of the molecule of $C_{60}H_x$ with x = 60 than that of the molecules with x = 36, 42, and 48.

Thus, hydrogen exists in two states in the hydrofullerite samples synthesized under high pressures. Most of the hydrogen is chemically bound to molecules of C_{60}, while its small fraction (approximately 1.4 H_2/C_{60}) penetrates into the sample in the form of molecules of H_2 and occupies intersices in the bcc lattice built of $C_{60}H_x$ molecules. The intersticial hydrogen does not form strong chemical bonds with the molecules of $C_{60}H_x$ and leaves the samples when heated to room temperature.

Magnetic Ordering in Hydrofullerite $C_{60}H_{24}$

While pure fullerite C_{60} is a diamagnetic material [20], hydrofullerite $C_{60}H_{36}$ with the bcc lattice prepared through the reduction of C_{60} in the melt of 9,10-dihydroanthracene demonstrated ferromagnetic behavior at room temperature [11]. At the same time, its magnetization amounted only to $\sigma_{\max} \approx 0.005\ \mu_B/C_{60}$ (where μ_B is the Bohr magneton) in a field of H = 10 kOe, so it cannot be excluded that it was caused by ferromagnetic impurities.

As mentioned above, a total of 12 samples of $C_{60}H_x$ with compositions of x = 24–32 were obtained in [2] under a hydrogen pressure from 0.6 to 3 GPa and a temperature of 350°C. About half of them had a fcc lattice, while the other half had a bcc lattice and they all behaved as ferromagnetics with a Curie point much higher than 300 K. Namely, magnetization dependences $\sigma(H)$ measured upon a change in the magnetic field H in the range from −10 to +10 kOe demonstrated a distinct hysteresis with a coercive force of about 100 Oe. Within the experimental error, neither the coercive force, nor magnetization value in the maximum field changed with an increase in the temperature from 80 to 300 K. At the same time, the magnetization value changed significantly from sample to sample. Most of the samples had $\sigma_{\max} \approx 0.001–0.003\ \mu_B/C_{60}$ at H = 10 kOe, i.e. even less than hydrofullerite in [11].

However, two samples had $\sigma_{max} \approx 0.046$ and 0.054 μ_B/C_{60}, and the magnetization of one sample reached σ_{max} = 0.16 μ_B/C_{60}.

All three samples with maximum magnetization values were synthesized from diamagnetic powder of fullerite C_{60} under the same hydrogen pressure of 0.6 GPa and a temperature of 350°C, had the same yellowish color, a fcc lattice, and the same compositions close to $C_{60}H_{24}$. The dependences $\sigma(H)$ for the two samples with the maximum magnetization values are shown in Fig. 5. The concentrations of metallic impurities in the sample with σ_{max} = 0.16 μ_B/C_{60} (Fig. 5a) are given in Table 1. The relatively high value σ_{max} of the sample $C_{60}H_{24}$ along with the results of its chemical analysis show that ferromagnetic ordering is a property of the hydrofullerite itself, and not of the impurities present in it. For example, in order to acquire the observed magnetization, the sample should have contained at least 0.5 wt % Fe with a spontaneous magnetization of σ_S = 2.2 μ_B/atom or 0.7 wt % Co with σ_S = 1.7 μ_B/atom or 1.7 wt % Ni with σ_S = 0.6 μ_B/atom.

Figure 5 also demonstrates another interesting feature of the hydrofullerites under study. Long-term storage of the samples with high magnetization values at room temperature results in a remarkable decrease in σ_{max} to values of the order of 0.001 μ_B/C_{60} (Fig. 5a) and further to diamagnetic behavior of the magnetization (Fig. 5b). With an arbitrarily small but still positive value of σ_{max}, both this value and the coercive-force value do not depend on the temperature in the range from 80 to 300 K; the coercive force also retains its value of about 100 Oe.

The observed decrease and disappearance of spontaneous magnetization additionally confirms that the ferromagnetism of hydrofullerties cannot be attributed to the impurities of ferromagnetic metals, because these impurities could not disappear from the samples upon their storage at room temperature. The most plausible explanation of the observed effects is that [2] the synthesized hydrofullerite samples were not single-phase and consisted of a mixture of diamagnetic and ferromagnetic phases with a relatively high magnetization. The ferromagnetic phase gradually transformed into the diamagnetic phase upon the long-term exposure of the samples at room temperature. The poor reproducibility of the σ_{max} values for the samples synthesized under identical conditions could then be rationalized by the different amounts of the ferromagnetic phase formed at some intermediate stages of hydrogenation.

Regarding the reasons for the appearance of magnetic order in hydrofullerenes, they are still under debate. Moreover, even the predominant type of magnetic ordering is still unclear; one example is that hydrofullerenes should be collinear ferromagnetics according to the theoretical work [21], while the antiferromagnetic state is more stable according to [22]. It should finally be noted that hydrofullerite is the first example of a ferromagnetic consisting only of carbon and hydrogen. This is also the first example of an organic ferromagnetic with a Curie point higher than 16 K (such a value of T_C is found for tetrakis-dimethylaminoethylene compound TDAE-C_{60} [23, 24], which is also a fullerene-based material).

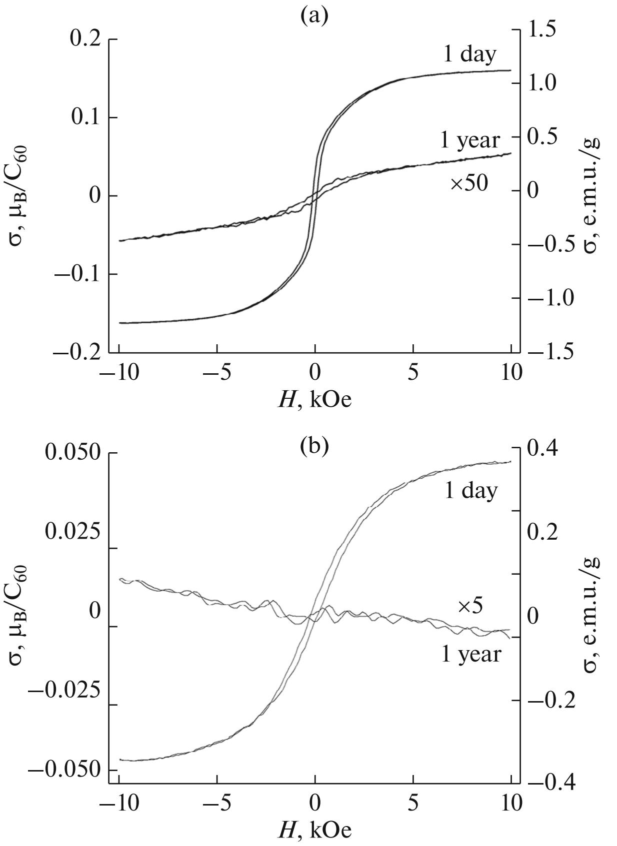

Fig. 5. Dependence of the magnetization σ on the magnetic field H at room temperature for two samples of $C_{60}H_{24}$ with a fcc lattice and magnetization at H = 10 kOe: (a) 0.16 and (b) 0.046 μ_B/C_{60}. The samples were synthesized at P_{H_2} = 0.6 GPa and T = 350°C and then kept under normal conditions for one day and one year [2].

Amorphous Deuterofullerite with a Formal Composition of $C_{60}D_{92}$

An unusual result was obtained in one of the experiments on the synthesis of deuterated fullerite C_{60}. Together with 66 mg C_{60}, some 135 mg of AlD_3 was

Table 1. Concentration of impurities in the sample of $C_{60}H_{24}$ with σ_{max} = 0.16 μ_B/C_{60} according to the results of atom-emission analysis (the sensitivity threshold was 0.001 wt %)

Metal	Fe	Co	Ni	Pd	Ga	Al	Cu
wt %	0.01	–	0.002	0.01	–	0.005	0.1

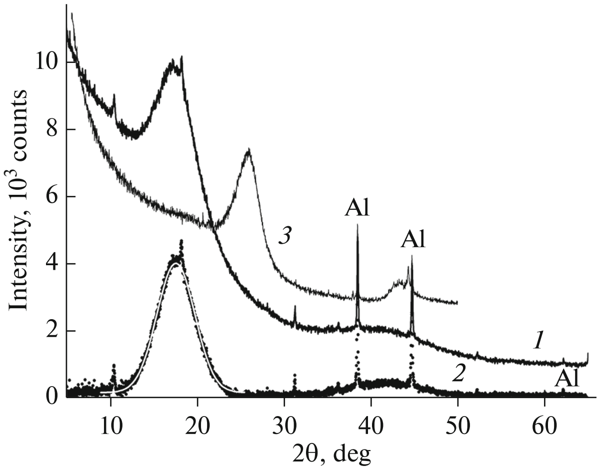

Fig. 6. Diffraction patterns of amorphous $C_{60}D_{92}$ ((*1*) experimental; (*2*) with a subtracted smooth background from an amorphous silicon substrate) and (*3*) amorphous graphite. The symbols "Al" mark three reference lines of aluminum powder deposited onto the sample of $C_{60}D_{92}$. Other narrow peaks represent the contribution of microcrystals of $C_{60}D_x$ with a bcc lattice and the parameter a = 11.91 Å, which were present in amorphous $C_{60}D_{92}$. Room temperature, a SIEMENS D500 diffractometer, $CuK_{\alpha1}$ radiation.

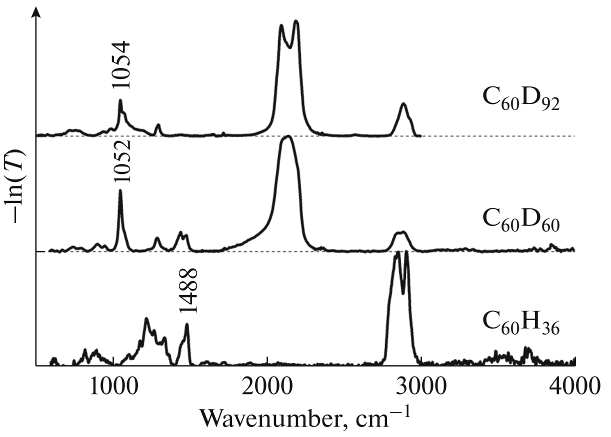

Fig. 7. Optical density spectra at room temperature for the crystalline hydrofullerites $C_{60}H_{36}$ and $C_{60}D_{60}$ with a bcc lattice and for the liquid deuterofullerite $C_{60}D_{92}$. The spectrum for $C_{60}H_{36}$ is the same as in Fig. 4.

charged to a standard lead cell as a deuterium source and its further thermal decomposition gave molecular deuterium at an amount of D/C = 2.2. Deuteration of the sample was carried out under a pressure of 3 GPa in two stages: first, it was kept for 19 h at 350°C and, then, for another 6 h at 450°C. After that, the high-pressure chamber was cooled to the temperature of liquid nitrogen, the pressure was lowered to atmospheric, the lead cell was removed from the chamber and heated to room temperature. When the cell was opened, a thick and sticky white bubbling substance immediately began to hiss out of the opening. After the sample stopped releasing the gas (presumably dissolved in it in the form of H_2 molecules as in solid hydrofullerites), the substance became colorless and transparent. The liquid deuterofullerite thus obtained was studied by elemental analysis, X-ray diffraction, and IR spectroscopy.

Elemental analysis, which was performed via a combustion of two 2-mg portions of the sample in oxygen at 1400°C gave an averaged composition of $D/C_{60} = 91.8 \pm 1.1$. To carry out X-ray diffraction analysis, the liquid sample was deposited as a thin layer onto an amorphous silicon substrate and sprinkled with fine Al powder as a reference material. The recorded diffraction pattern before and after subtraction of the monotonous background is shown in Fig. 6. Narrow peaks at angles $2\theta < 40°$ correspond to microcrystals of $C_{60}D_x$ with a bcc lattice and the parameter $a = 11.91$ Å; the minimum intermolecular distance is $a\sqrt{3}/2 = 10.31$ Å. As seen from Fig. 6, the diffraction pattern of this sample is dominated by a broad intense peak (halo) at $2\theta = 17.6°$ and a second halo at $2\theta \approx 42°$. The first peak is symmetric and well described by a Gaussian centered at $2\theta = 17.63°$ (white curve on the lower spectrum). In amorphous substances, the radius R_1 of the first coordination sphere can be estimated from the position of the first halo using the relationship $2R_1 = 1.23\lambda/\sin\theta$ (see, for example, [25]). In the case of the amorphous (liquid) sample with the average composition $C_{60}D_{92}$, this equation yields $R_1 = 6.18$ Å, which is approximately 0.6 of the minimum intermolecular distance in crystalline $C_{60}D_{60}$. It follows from here that the liquid "$C_{60}D_{92}$" mainly consists of particles with a significantly smaller size than the molecules of deuterated fullerene.

Figure 6 also shows a diffraction pattern of amorphous graphite. The first halo in this diffraction pattern is located at an angle of $2\theta \approx 26°$, which is close to the position of the reflection 002 of crystalline graphite and is far from the first halo of the liquid "$C_{60}D_{92}$". Comparison of the results for crystalline $C_{60}D_{60}$ and amorphous graphite thus indicates that the liquid "$C_{60}D_{92}$" consists of particles, which are much smaller than the molecules of $C_{60}D_{60}$, though larger than those in amorphous graphite.

The IR absorption spectra of crystalline powders of $C_{60}D_{60}$, $C_{60}H_{36}$, and of the liquid "$C_{60}D_{92}$" are presented in Fig. 7. Liquid "$C_{60}D_{92}$" was deposited as a thin layer onto a single-crystal substrate. The stretching vibration bands of the C–D bond both in $C_{60}D_{60}$ and "$C_{60}D_{92}$" are located at approximately 2100 cm^{-1}. As follows from Fig. 7, there is a much smaller number of vibrational modes in the low-energy part of the spectra of $C_{60}D_{60}$ and "$C_{60}D_{92}$" than in the spectrum of $C_{60}H_{36}$. In fact, the number of such modes in the deuterated samples is even lower than that in Fig. 7, because the peaks at 1488 and 2900 cm^{-1} should be attributed to the bending and stretching vibrations of C–H bonds formed by protium impurity atoms. Peaks at 1488 and near 2900 cm^{-1} were also observed in the spectrum of $C_{60}H_{36}$. The presence of these peaks is due to the fact that the deuteride AlD_3, which was used as a source of molecular deuterium for the synthesis of deuterofullerites under high pressure, contained $H/(D + H) = 2.9$ at % of impurity protium [26].

The smaller number of vibrational modes indicates a higher symmetry of molecules in the samples $C_{60}D_{60}$ and "$C_{60}D_{92}$" compared to $C_{60}H_{36}$. The absorption spectra of $C_{60}D_{60}$ and "$C_{60}D_{92}$" are very similar. The main difference between them lies in the significantly higher intensity of the absorption line at 2188 cm^{-1} in the spectrum of "$C_{60}D_{92}$" in comparison with the spectrum of $C_{60}D_{60}$. Therefore, the line at 2188 cm^{-1} can reasonably be attributed to the stretching vibrations of molecules, of which the liquid sample "$C_{60}D_{92}$" was mainly composed. The identity of these molecules is yet unknown. It could only be stated with a fairly high degree of confidence that their intrinsic size was 6.18 Å (the radius of the first coordination sphere of the liquid phase in the "$C_{60}D_{92}$" sample) and that the molecules were highly symmetric and thus most likely had an identical and strictly stoichiometric composition $C_{2n}D_{3n}$, where n is a natural number.

CONCLUSIONS

Thus, exposing the powder of C_{60} to a hydrogen-gas atmosphere under a pressure of 0.6–9 GPa and temperatures of up to 500°C provides bulk single-phase homogeneous hydrofullerite samples with a broad composition range from $C_{60}H_{24}$ to $C_{60}H_{60}$ [2, 5, 6], while other methods give compositions no higher than $C_{60}H_{36}$.

It should be noted that the specific properties of high-pressure hydrofullerites are far from being exhausted by what is described in this work. One example is that studying inelastic neutron scattering has revealed the polymerization of $C_{60}H_{32}$ molecules in hydrofullerite synthesized under a hydrogen pressure of 3 GPa and a temperature of 350°C [27], in complete analogy with the behavior of pure (without hydrogen) C_{60} fullerite, which polymerizes at this temperature under pressures higher than 0.7 GPa [28]. Mass spectrometric study has shown that the polymerization of $C_{60}H_{32}$ is partially retained even during laser desorption and the released gas mainly consists of dimers $(C_{60}H_x)_2$ and also of trimers $(C_{60}H_x)_3$ and tetramers $(C_{60}H_x)_4$, which quickly decompose into monomers $C_{60}H_x$ [28].

Studying the properties of high-pressure hydrofullerites often appears valuable for a wide variety of fields of knowledge. One example is that a combination of vibrational modes of $C_{60}H_{60}$ and hydrofullerite with a low hydrogen content allows one to rationalize the main features of the emission and absorption spectra of some interstellar and circumstellar nebulae [6]. The investigation and comparative analysis of these spectra initiated in 2001 [29, 30], are still in progress [31, 32].

At the same time, the most unexpected result of many years of research is not what was discovered, but what remained controversial—what is the atomic structure of the molecule of $C_{60}H_{60}$? Calculations of some authors show that some of the hydrogen atoms in this molecule should be located inside the carbon framework with decreased symmetry. According to some other works, the molecules of $C_{60}H_x$ become completely unstable at $x > 36$ due to strong spatial deformations. The theoretical work [33] should be noted in particular, since its results agree with the experimental IR spectrum of $C_{60}H_{60}$ [6], indicating high symmetry of the molecules from which this hydrofullerite is built. In [33], published long before the experimental preparation of $C_{60}H_{60}$ [5, 6], it was assumed that the $C_{60}H_{60}$ molecule should have the I_h symmetry (inverted icosahedron group) similar to the symmetry of the molecule of C_{60}. As for the high symmetry molecules, which form the "$C_{60}D_{92}$" liquid discussed in this paper, their structure is still a complete mystery.

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