Process of intercalation of C_{60} with molecular hydrogen from XRD data

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The process of normal hydrogen infusion into a C_{60} powder at 1 bar and room temperature was monitored using x-ray diffraction. The effect of the intercalation on the lattice proved to be rather weak: the volume expansion upon complete saturation does not exceed 0.13%. The characteristic saturation time was found to be 320 h; the corresponding diffusion coefficient amounts to $(2.8 \pm 0.8) \cdot 10^{-14}$ cm^2/s. The integrated reflection intensity calculations for completely saturated sample suggest that only octahedral voids are filled under the conditions of experiment. The effect of complete saturation on the rotational subsystem of the C_{60} fullerite is rather weak: the orientational phase transition shifts by 6 to 7 K to lower temperatures; no essential hysteresis is noticeable. The dopant shows reluctance to leave the sample under a vacuum of 10^{-3} Torr at room temperature.

Introduction

Fullerite C_{60} is still considered as a good candidate for gas separation or efficient storage of molecular hydrogen [1]. It is therefore necessary to understand the interaction of H_2 with carbon nanostructures of all types and the kinetics of penetration of hydrogen into fullerite C_{60}. At elevated pressure hydrogen is known to easily diffuse into the C_{60} lattice within two or three hours at room temperature [2,3]. At present, the spectrum of an isolated hydrogen molecule trapped in an octahedral void is well known [4]. The fcc lattice of fullerite C_{60} contains quite large interstitial octahedral (the size of about 2.3 Å) and tetrahedral (the size of about 1.1 Å) voids, which, under certain conditions, allow filling with various atoms and molecules. Hydrogen in tetrahedral sites has a higher ground state energy compared to octahedral ones. Nonetheless the tetrahedral sites appear

to be important *dynamically* [3,5] when loading or evacuating C_{60}. Intercalation brings about noticeable changes in the structural and other physical properties of fullerite crystals [3,6–9]. The orientational system is the most sensitive to intercalation [8,10]: even the lattice symmetry can change upon saturation [11].

There are solid grounds for the conclusion that loading of hydrogen into C_{60} under not too severe conditions does not entail chemical bonding of hydrogen with the carbon atoms in buckyballs. Only at high temperatures ($T > 620$ K) and pressures ($P > 100$ bar) hydrogen actively react with C_{60} [12–14]. Low-temperature studies of C_{60} doped with CO [15], NO [16], or H_2 [17] also yielded evidence that no chemical bonding was involved but a strong effect of doping on the orientational glass state occurred. The C_{60}–H_2 system was thoroughly studied using various tech-

niques (see the above references and others [2,18–21]. Based on the relevant experimental findings it has been concluded that the low-temperature dynamics of H_2 and D_2 molecules in the fullerite lattice is of quantum nature and the high-temperature mobility of these molecules is high enough. It is commonly considered that, because of the smaller dimensions of tetrahedral cavities, the hydrogen molecules occupy predominantly octahedral voids and that their interaction with the matrix particles becomes essential at sufficiently low ($T \leq 100$ K) temperatures.

The aim of this paper was to carry out powder x-ray diffraction studies of the process of intercalation of C_{60} with normal hydrogen as well as the effect of this intercalation on the structural and thermodynamic (rotational contribution) properties over a wide temperature interval from 10 to 296 K in order to solve a few questions. First, we planned to utilize accurate structural characteristics (reflection widths and intensities) to better understand the migration and dynamical behavior of the H_2 interstitial in the C_{60} lattice. Second, we needed to know details of the temporal dependence of the saturation process at comparatively low pressures in order to have reliable grounds for the assessment of the dopant concentration over the powder crystallite volume, which is important for the correct treatment of the ensuing photoluminescence experiments, part of which have been published elsewhere [17].

Experimental

In our investigations we used a high purity (99.98% Aldrich) polycrystalline fullerite C_{60}. Two types of powder samples were studied. Both were prepared from the same rather large-grain material: one (type I) was a result of manual grinding to an average grain size of about (1.8 ± 1.0) μ; the other (type II) was milled to smaller grain sizes. Preliminary XRD characterization of type II samples showed that they were polymerized to a substantial degree, most likely because of the prolonged milling. Mild annealing of these sample removed most of the features in the XRD patterns but not completely. Detailed x-ray measurements reported below have been carried out only on type I samples.

With the aim of preliminary degassing the samples were kept for five days at 200 °C in a vacuum of about 10^{-3} Torr. Then the sample was placed at room temperature into the working chamber of a x-ray cryostat and was kept there continuously at 1 bar for a quite long time. During the intercalation process, the powder sample was XRD characterized, the time between successive takes varying from 1 to 10 h initial stages to 100 h or more at longer intercalation times. The saturation complete, the structure characteristics of the saturated sample were studied as a function of temperature, both under cooldown and warmup. The temperature interval included the two critical points, viz., the orientational phase

transition at about 260 K and the orientational vitrification point at ≈ 95 K.

The x-ray studies were performed using an automated DRON x-ray diffractometers with a nickel anode ($\lambda = 1.6591$ Å). The temperature was stabilized within the whole 11 to 300 K range to ± 0.1 K. The characteristic lattice parameter error was about 0.02% if the complete x-ray pattern was recorded. High-accuracy measurements of that type have been performed at 11 K and at room temperature. The temperature dependence of the lattice parameter between these two reference points was evaluated from the positions of the three most intensive reflections (111), (220), and (311).

After the completely saturated sample was finally characterized as described above, the intercalant was evacuated from the fullerite lattice. To this end, the chamber was pumped down to 10^{-3} Torr and the lattice parameter was monitored in time until it came to a constant level. During both saturation and degassing we determined the widths and intensities of the above reference reflections, which allowed us to make certain conclusions concerning the diffusion process of H_2 in crystalline C_{60}.

Results and discussion

Our measurements of the lattice parameter a as a function of intercalation time showed that the properties of this C_{60}–H_2 system differ substantially from those found for He in C_{60}. As C_{60} was kept at room temperature in the hydrogen atmosphere, its lattice parameter a grew perceptibly but little during the initial 200 h from 14.161 to 14.167 Å and afterwards stayed virtually unchanged during a very long period of up to 2000 h to within experimental scatter. We also subjected an annealed type II sample to the same saturation procedure. The starting lattice parameter was somewhat smaller than in the type-I sample; upon saturation during about 300 h the lattice parameter increment was below 0.002 Å, which is barely above the experimental error. The smaller intercalation-related expansion of the type II sample can be due to the presence of the polymeric bonds, which are known to cause a sharp increase in the hardness and Young modulus [22].

We remind that the process of the intercalation of C_{60} with helium under the same conditions has two stages: during the first stage it is octahedral voids that are filled comparatively fast; the second, much slower stage corresponds to the filling of tetrahedral voids with He atoms. In the C_{60}–H_2 system the second stage is absent, which suggests that hydrogen molecules do not penetrate into tetrahedral voids, at least at the pressure of our experiment (around 1 bar). Otherwise, the lattice must have responded with a much larger expansion. Since the saturation in the case of hydrogen was completed at room temperature and taking into consideration [5] that the migration over octahedral voids proceeds through tetrahe-

dral cavities, it is clear that the intensive translational motion of C_{60} molecules at 300 K allows a hydrogen molecule to occupy only momentarily a neighboring tetrahedral site with subsequent jump to an octahedral void.

The second difference concerns the magnitude of the intercalation-related C_{60} lattice expansion. With He [5], the total expansion when octahedral voids are occupied to the full (at the end of stage 1) is much larger (by a factor of 3.5) compared to the case of hydrogen as intercalant. A possible explanation can be ascribed to the larger diameter of the H_2 molecule, which deprives it freedom to move in a gas-like fashion (as a He atom does) exerting a pressure on the octahedral cage from within. This is more so, considering a substantially stronger interaction between C_{60} and H_2 molecules.

In Fig. 1 we show the measured time dependence of the lattice parameter increment (empty circles) normalized to the maximum increment at complete saturation; the relevant parameters are $a_0 = 14.161$ Å and $a_{inf} = 14.167$ Å. Applying of the diffusion theory in the spherical geometry approximation (solid curve in Fig. 1), similar to that employed [5] for He–C_{60} system, we estimate the characteristic time to be 320 h. Knowing the average grain size (about 1.8 μ) we calculate the diffusion coefficient of H_2 in C_{60} at room temperature to be $D \approx (2.8 \pm 0.8) \cdot 10^{-14}$ cm^2/s, which is only 2.7 slower than for He atoms at the same conditions. The reason for that might be that as far as diffusion is concerned the stronger C_{60}–H_2 interaction is outbalanced by the lighter hydrogen mass.

The fact that the time dependence of the full widths at half-maximum (FWHM) for the C_{60}–H_2 system (Fig. 2) does not reveal a clear maximum, like in the C_{60}–He system, may be due to the insignificant lattice distortions in the case of hydrogen that could entail a line broadening detectable in our experiment.
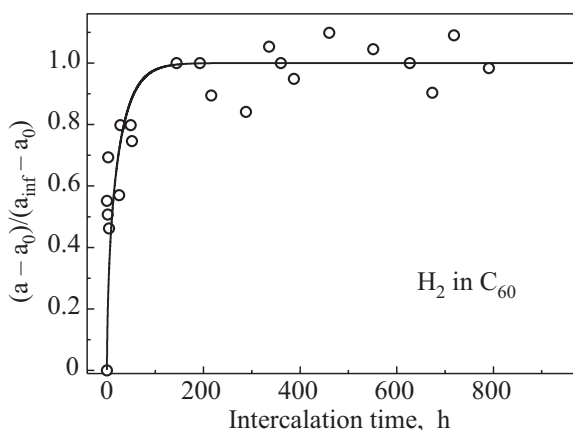

Fig. 2. The FWHM of the three bright reflections as a function of the hydrogen intercalation time.

In Fig. 3 we show the time dependence of the integrated intensities of the same three reflections during the initial stages of saturation; all three lines tend to become weaker with progressing saturation. According to evaluations similar to those for the C_{60}–He system [5], lines (111) and (220) were expected to weaken at complete saturation by roughly 4% and 5% whereas line (311) was to brighten by 6%, after which they must level off. As expected, during the initial stages of saturation the integrated intensities of lines (111) and (200) went down by, respectively, 4.4% and 5.2%. However, like in the case of the C_{60}–He system, the line (311) in Fig. 3 did not obey our predictions: although the intensity change was 6.3% but it diminished instead of growing. Nevertheless, these findings allow us to conclude that the saturation of powder was very close to complete. These inferences are at variance with the conclusions of Aleksandrovskii *et al.* [21] that a similar intercalation procedure results in a 12%

Fig. 1. The reduced cubic lattice parameter increment as a function of the normal hydrogen intercalation time at a pressure of 1 bar and room temperature. The circles are experimental data, the curve is the diffusion theory for spherical particles (see also text).
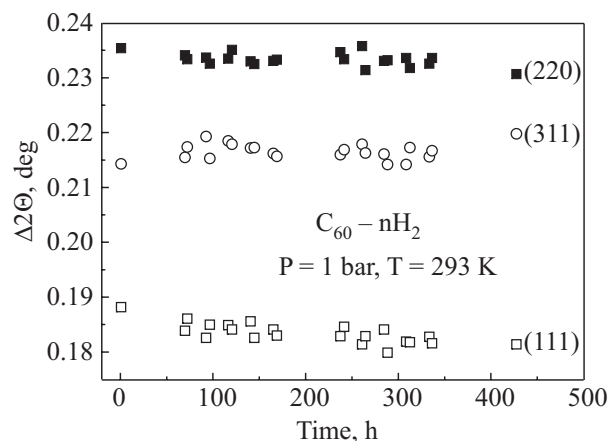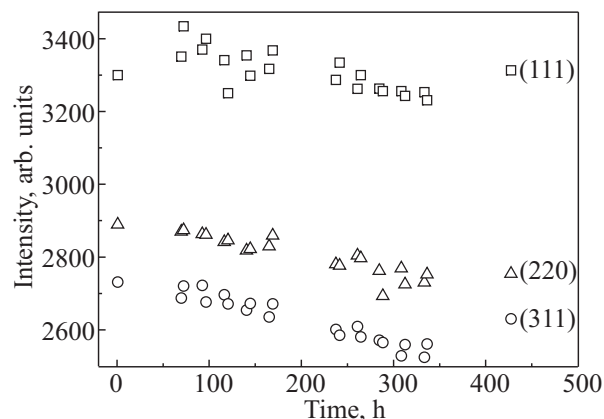

Fig. 3. Variations of the integrated intensities of the three bright reflections during intercalation.

occupancy. This striking discrepancy is most likely due to the capital difference in the samples studied: our sample was a loose set of separate small grains of a ten micron size whereas the sample in the low-temperature thermal expansion experiments [21] was a large block of compressed C_{60} of a few centimeters. Therefore, in the latter case the characteristic diffusion time must be roughly $(1 \text{ cm}/ 1 \mu)^2$ times longer than our value of 320 h and, thus, their estimated occupancy of 12% does not seem unrealistic.

Stuffing crystalline C_{60} with hydrogen must affect the intermolecular interactions and thermodynamic characteristics. Usually, orientational transition points are sensitive to various impurities. In order to establish how intercalated hydrogen influences the processes of orientational ordering and glassification, we studied the temperature dependence of the lattice parameter of the ultimately saturated sample from 11 to 293 K both in the cooldown and warmup regimes. These data are presented in Fig. 4 together with our results for high-purity fullerite C_{60} [23]. It should be noted that notwithstanding the very small saturation-related expansion the orientational phase transition is shifted appreciably (by 6 to 7 K) to lower temperatures. The very phase transition is understandable less acute than in ideal crystals owing to remaining irregularities of the distribution of the hydrogen molecules over the volume of crystallites. As a result, the lattice parameter jump across the transition is understandably smaller than in pure samples. At any temperature the lattice parameter in saturated samples exceeds that in pure C_{60}; at room temperature the relative lattice parameter increase is about $4.3 \cdot 10^{-4}$, which is only twice the experimental error.
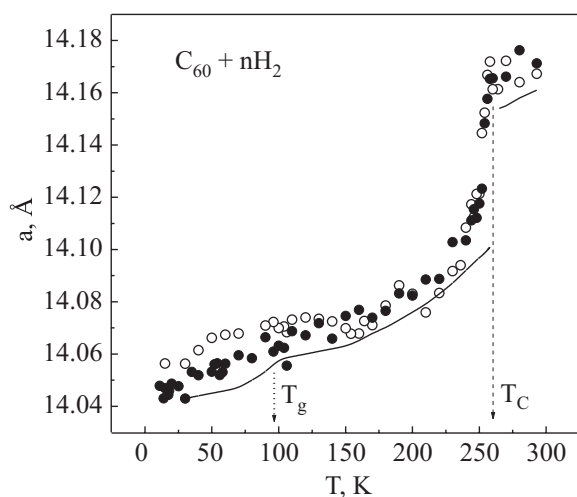
Down to 130 K no clearly detectable hysteresis is observed. At lower temperatures, close and below the orientational glassification point, a hysteresis is clearly detectable. This hysteresis, which is by far less pronounced than with other neutral intercalants, especially Xe [24], could be possibly due to the so called polyamorphic transformations [25].

We also measured the temperature dependence of the standard structure characteristics (widths and intensities) for the three bright reflections in the completely saturated sample. To speed up the procedure, only a short region where the set of closely spaced reflections (220, 222, 311) are situated, was recorded. From Fig. 5 one can see that the integrated intensities do not change appreciably (only due to changes brought about by thermal expansion); the temperature dependence is rather smooth, if not for weak phantom disturbances around the critical points. The FWHM of the same reflections (Fig. 6) do not show large anomalies. However, in the region of the transition to the orientational glass state all traces reveal a surge which suggests freezing-in of static strains in this disordered state. These strains are not related with the presence of the intercalant but appear owing to the (partial) disorder in the mutual orientations of neighboring C_{60} molecules.

Degassing undertaken within the same procedure as in the case with He [5] (evacuation in a vacuum of 10^{-3} Torr at room temperature) showed that, unlike helium, hydrogen is very reluctant to leave C_{60}. Even after more than 50 days the lattice parameter, though having somewhat diminished, remained above the value characteristic for pure fullerite beyond experimental error. A similar effect has been documented by Aleksandrovskii *et al.* [23] in dilatometry experiments.
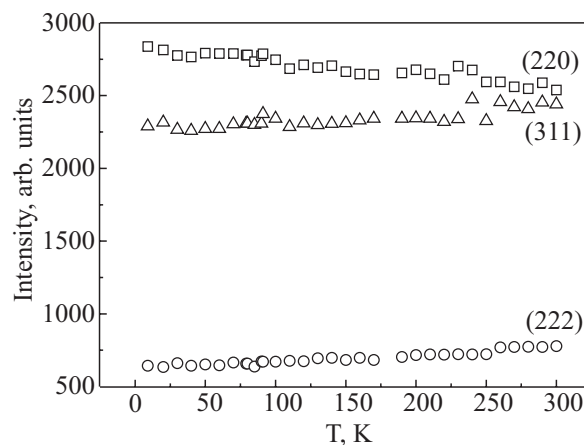

Fig. 4. Temperature dependence of the cubic lattice parameter of C_{60} fullerite with octahedral voids completely occupied by hydrogen molecules. The symbols ($\bigcirc$) and ($\bullet$) denote respectively cooldown and warmup data; the solid line is for pure C_{60} [23].

Fig. 5. The integrated intensity of three closely spaced lines of the saturated sample as a function of temperature.
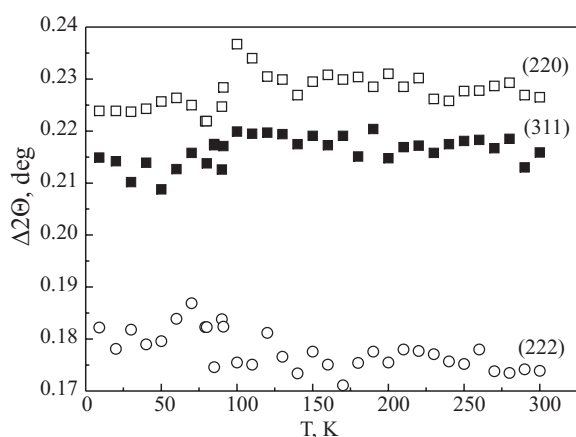
Fig. 6. The full widths at half-maximum as a function of temperature for the three closely spaced lines of the saturated sample.

Conclusions

The process of loading C$_{60}$ with normal hydrogen at room temperature and a pressure of 1 bar was studied by monitoring the XRD characteristics (Bragg angles as well as the intensities and widths of reflections). Our experimental data together with integrated intensities calculations allowed us to conclude that only octahedral voids are filled under the above conditions. The characteristic hydrogen infusion time was evaluated to be 320 h, which corresponds to the diffusion coefficient about $3 \cdot 10^{-14}$ cm^2/s.

The temperature dependence of the lattice parameter of a completely saturated C$_{60}$ powder sample show insignificant changes compared to pristine C$_{60}$; a 6–7 K shift of the orientational transition point to lower temperatures; at all temperatures the lattice parameter is slightly higher than in pure samples (at room temperature the intercalation-related volume expansion does not exceed 0.13%); no essential hysteresis was observed in the temperature range studied.

1. M.M. Calbi and M.W. Cole, *Rev. Mod. Phys.* **73**, 857 (2001).
2. S.A. FitzGerald, T. Yildirim, L.J. Santodonato, D. A. Neumann, J.R.D. Copley, J.J. Rush, and F. Trouw, *Phys. Rev.* B**60**, 6439 (1999).
3. S.A. FitzGerald, R. Hannachi, D. Sethna, M. Rinkoski, K.K. Sieber, and D.S. Sholl, *Phys. Rev.* B**71**, 045415 (2005).
4. S.A. FitzGerald, S. Forth, and M. Rinkoski, *Phys. Rev.* B**65**, 140302 (R) (2002).
5. K.A. Yagotintsev, M.A. Strzhemechny, Yu.E. Stetsenko, I.V. Legchenkova, and A.I. Prokhvatilov, *Physica* B**381**, 224 (2006).
6. B. Renker, G. Roth, H. Schober, P. Nagel, R. Lortz, C. Meingast, D. Ernst, M.T. Fernandez-Diaz, and M. Koza, *Phys. Rev.* B**64**, 205416 (2001).
7. B. Morosin, Z. Hu, J.D. Jorgensen, S. Short, J.E. Schirber, and G.H. Kwei, *Phys. Rev.* B**59**, 6051 (1999).
8. G.E. Gadd, S. Moricca, S.J. Kennedy, M.M. Elcombe, P.J. Evans, M. Blackford, D. Cassidy, C.J. Howard, P. Prasad, J.V. Hanna, A. Burchwood, and D. Levy, *J. Chem. Phys. Solids* **58**, 1823 (1997).
9. I.V. Legchenkova, A.I. Prokhvatilov, Yu.E. Stetsenko, M.A. Strzhemechny, K.A. Yagotintsev, A.A. Avdeenko, V.V. Eremenko, P.V. Zinoviev, V.N. Zioryanski, N.B. Silaeva, and R.S. Ruoff, *Fiz. Nizk. Temp.* **28**, 1320 (2002) [*Low Temp. Phys.* **28**, 942 (2002)].
10. B. Renker, H. Schober, M.T. Femandez-Diaz, and R. Heid, *Phys. Rev.* **B61**, 13960 (2000)
11. M. James, S.J. Kennedy, M.M. Elcombe, and G.E. Gadd, *Phys. Rev.* **B58,** 14780 (1998).
12. A.V. Talyzin and S. Klyamkin, *Chem. Phys. Lett.* **397**, 77 (2004).
13. A.N. Lommen, P.A. Heiney, G.B.M. Vaughan, P.W. Stephens, D. Liu, D. Li, A.L. Smith, and A.R. McGhie, *Phys. Rev.* **B49,** 12572 (1994).
14. A.I. Kolesnikov, V.E. Antonov, I.O. Bashkin, G. Grosse, A.P. Moravsky, A.Yu. Muzychaka, EG. Ponyatovsky, and F.E. Wagner, *J. Phys: Condens. Matter.* **9**, 2831 (1997).
15. S. van Smaalen and R. Dinnebier, *Phys. Rev.* **B57**, 6321 (1998).
16. M. Gu, T.B. Tang, and D. Feng, *Phys. Rev.* **B66**, 073404 (2002).
17. P.V. Zinoviev, V.N. Zoryansky, and N.B. Silaeva, *Fiz. Nizk. Temp.* **34**, 609 (2008) [*Low Temp. Phys.* **34**, 484 (2008)].
18. B.P. Uberuaga, A.F. Voter, K.K. Sieber, and D.S Sholl, *Phys. Rev. Lett.* **91**, 105901 (2003).
19. Y. Ye, C.C. Ahn, B. Fultz, J.J. Vajo, and J.J. Zinck, *Phys. Rev. Lett.* **77**, 2171 (2000).
20. A. FitzGerald, H.O.H. Churchill, P.M. Korngut, C.B. Simmons, and Y.E. Strangas, *Phys. Rev.* **B73**, 155409 (2006).
21. A.N. Aleksandrovskii, M.A. Vinnikov, V.G. Gavrilko, A.V. Dolbin, V.B. Esel'son, and V.P. Maletskii, *Ukr. Phys. Zhurn.* **51**, 1152 (2006) [in Ukrainian].
22. A.P. Isakina, S.V. Lubenets, V.D. Natsik, A.I Prokhvatilov, M.A. Strzhemechny, L.S. Fomenko, N.A. Aksenova, and A.V. Soldatov, *Fiz. Nizk. Temp.* **24**, 1192 (1998) [*Low Temp. Phys.* **25**, 896 (1998)].
23. L.S. Fomenko, V.D. Natsik, S.V. Lubenets, V.G. Lirtsman, N.A. Aksenova, A.P. Isakina, A.I. Prokhvatilov, M.A. Strzhemechny, and R.S. Ruoff, *Fiz. Nizk. Temp.* **21**, 465 (1995) [*Low Temp. Phys.* **21**, 364 (1995)].
24. A.I. Prokhvatilov, N.N. Galtsov, I.V. Legchenkova, M.A. Strzhemechny, D. Cassidy, G.E. Gadd, S. Moricca, B. Sundqvist, and N.A. Aksenova, *Fiz. Nizk. Temp.* **31**, 585 (2005) [*Low Temp. Phys.* **31**, 445 (2005)].
25. A.N. Aleksandrovskii, A.S. Bakai, D. Cassidy, A.V. Dolbin, V.B. Esel'son, G.E. Gadd, V.G. Gavrilko, V.G. Manzhelii, S. Moricca, and B. Sundqvist, *Fiz. Nizk. Temp.* **31**, 565 (2005) [*Low Temp. Phys.* **31**, 429 (2005)].