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Structural and elastic anisotropy of carbon phases prepared from fullerite C_{60}

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We show 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 is induced by the uniaxial pressure component, in the case of disordered atomic-based phases, it may be governed by the uniform pressure magnitude.
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The synthesis of carbon phases attracts considerable attention in materials science, since many carbon materials combine a low density with superior mechanical characteristics (such as hardness and strength) and stability against thermal degradation. The discovery of fullerenes[1] and, in particular, the preparation of solid crystalline fullerite C_{60} in macroscopic amounts[2] have stimulated new efforts and provided new routes for synthesis of carbon-based materials. Pressure–temperature treatment of molecular carbon crystals of C_{60} provides the possibility of synthesizing engineered materials with a variable nanostructure, nanomorphology, type of bonding (sp^2/sp^3 ratio), dimension of covalent connectivity [one (1D)-, two (2D)-, or 3-dimensional (3D)], degree of polymerization (for molecular-type structures), and so on.[3–5]

Among pressure-synthesized C_{60}-based phases, several ordered and disordered modifications have been clearly identified to date, including crystalline 1D and 2D C_{60} polymers,[6–9] very hard graphite-type (sp^2-based) disordered phases,[7,10,11] 3D polymers with a varying degree of polymerization,[12–15] diamond-like (sp^3-based) amorphous phases,[14–16] and diamond–graphite nanocomposites.[14,15,17] Many of these phases are superhard materials[4,5,10–15,17] and are potentially interesting for practical applications.[5,15]

The recent observations of structural[18,19] and ultrasonic[20] directional anisotropy in samples synthesized from C_{60} under nonhydrostatic conditions, make possible a systematic study of the relationships between the high-pressure synthesis conditions, anisotropic structure, and corresponding nonuniform elasticity. This latter is of interest since the anisotropy of carbon materials may be an interesting property for certain applications; for example, as a method of increasing mechanical characteristics in particular directions.

Here, we report the systematic study of carbon phases obtained in nonhydrostatic conditions by heating fullerite C_{60} in the pressure range up to 8 GPa. In particular, we show that the samples produced in such a way display orientational anisotropy of structural and elastic properties that correlate across samples, and that this anisotropy can be an experimentally controlled parameter. The primary anisotropy of synthesis pressure, that is, the uniaxial component, occurs naturally in the quasihydrostatic conditions that occur in toroid-type chambers[21] with a single loading axis. Two-dimensional rhombohedral polymers of C_{60} and disordered graphite-type (sp^2) phases are among the materials under consideration.

The samples were synthesized from fullerite powder with C_{60} content not less than 99.9%. The C_{60} powder was pressed into cylinders with the 3 mm height and 4 mm diameter. Toroid-type chambers[21] were used for high-pressure–high-temperature (0–8 GPa and 600–1400 °C) generation in a large volume (up to 50 mm^3). The samples were synthesized in Pt or Cu cells with the outer graphite container serving simultaneously as a heater. The temperature was measured by chromel–alumel thermocouples. The structure of samples was examined by conventional x-ray diffraction (XRD, Cu K_α). The synthesized materials were obtained in the shape of cylinders, which were used to prepare samples in the shape of parallelepipeds with characteristic dimensions $1.5\times1.5\times1.2$ mm. Ultrasonic velocities were obtained from the determination of the time of flight of 10 MHz shear or compression ultrasonic pulses ($\sim 1\ \mu s$). The pulse flight times in the sound line with or without a sample were determined to an accuracy of a few nanoseconds.

In the first series of experiments, we synthesized samples of the 2D polymerized C_{60} rhombohedral phase in nonhydrostatic conditions at pressures from 3.5 to 7 GPa. The temperature interval chosen for the synthesis (from 600 to 800 °C) allowed us to avoid the effects of partial polymerization.[4,7] In addition, the chosen pressure interval and scheme of synthesis, that is, pressurizing and subsequent heating, prevented the formation of dominant amounts of tetragonal 2D polymerized C_{60}.[8] Figure 1(a) shows the lon-

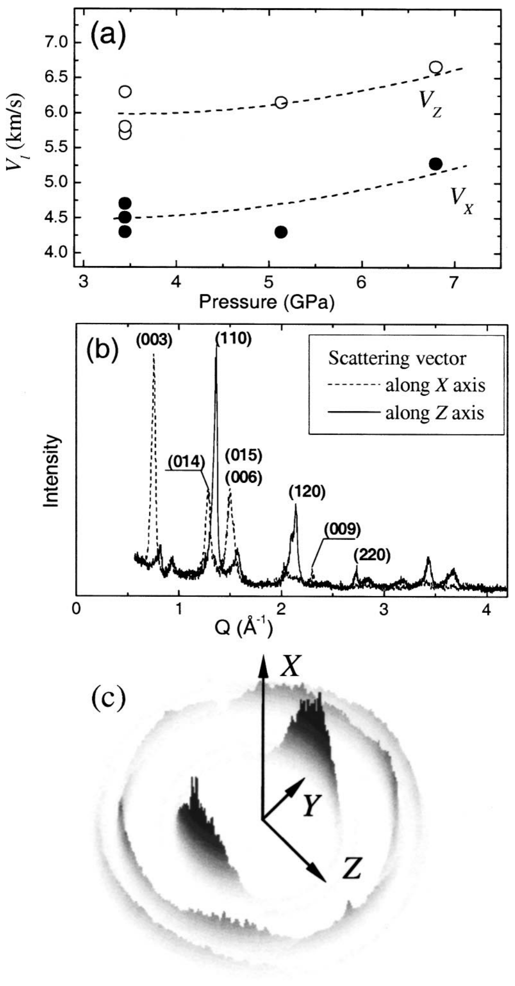

FIG. 1. Anisotropy of the 2D polymerized rhombohedral C_{60} phases revealed by (a) longitudinal ultrasonic velocities plotted as a function of the synthesis pressure, (b) XRD patterns (with the subtracted middle lines) recorded in reflection mode for different geometries of the scattering vector, and (c) 3D plot of intensity from the 2D diffraction image obtained in transmission mode with the x-ray beam along the X axis.

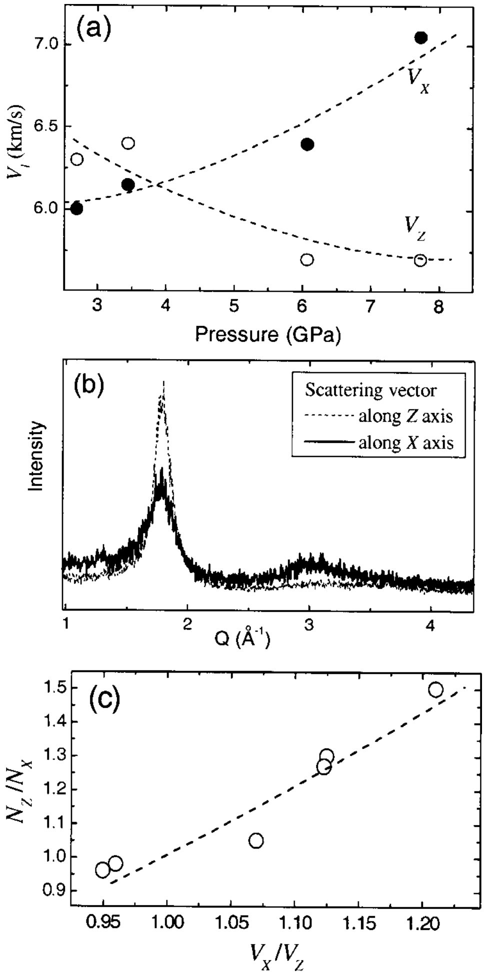

FIG. 2. Anisotropy of the superhard graphite-type (sp^2) atomic-based phases revealed by (a) longitudinal ultrasonic velocities plotted as a function of the synthesis pressure, (b) XRD patterns (with the subtracted middle lines) recorded in reflection mode for different geometries of the scattering vector. There is a direct correlation between the ratios of longitudinal velocities and the fractions of differently oriented graphite-like clusters (c).

gitudinal velocities of these samples, and typical diffraction patterns from these samples are presented in Fig. 1(b).

The ultrasound velocities along the Z axis [Fig. 1(a)], corresponding to the direction of load in high-pressure chambers, are systematically higher by ≈30% than those along the X axis for all experimental pressures (here, the X axis is perpendicular to Z and to the side facets chosen for the ultrasonic measurements). This observation is evidently related to a higher degree of polymerization along the loading axis, and this is directly confirmed by XRD [Fig. 1(b)]. All the reflections observed for the different geometries of recording diffraction can be attributed to the rhombohedral 2D polymers of C_{60}, whereas the behavior of peak intensities indicates a strongly textured structure of the material. In particular, the peaks identified as (110), (120), and (220) are the most intense in the diffraction patterns recorded with the x-ray scattering vector oriented along the Z axis, while the reflections (003), (014), and (006)/(015) are intense in the diffraction patterns recorded for the perpendicular geometry. Here, the plane (003) is parallel to the plane of polymerization of C_{60} molecules in the 2D polymer. This directly supports the conclusion about a higher degree of polymerization along the axis of loading; that is, along Z. The 3D image of diffraction intensity in Fig. 1(c) shows a more detailed picture of XRD from the anisotropic textured rhombohedral polymer, displaying both broad features and sharp maxima.

The second series of synthesized samples consisted of the disordered graphite-type (sp^2) phases of hard carbon[10,11] and was obtained upon heating to temperatures from 1000 to 1200 °C. A quite unexpected result [Fig. 2(a)] for the disordered sp^2 phases was that the ultrasonic velocities along the X axis proved to be higher than the corresponding velocities along the Z axis (for preparation pressures higher than 4 GPa); that is, the inverse relation with respect to those observed for the preceding 2D polymers of C_{60}. We assume that the differences in the sound velocity propagations along and across the Z axis are associated with a predominant orientation of graphite-like clusters in the nanometer-scale textured material. Indeed, the elastic anisotropy is directly confirmed by the difference in the corresponding XRD patterns [Fig. 2(b)]. XRD clearly shows the predominant orientation of graphite-like clusters with graphene-like sheets perpendicular to the Z axis.

The observed elastic anisotropy changes significantly with the uniform component of pressure, displaying an inversion of anisotropy at ≈4 GPa [Fig. 2(a)], and can be treated in terms of competition between the kinetic and thermodynamic contributions of the uniaxial pressure component to the mechanisms of atomic rearrangements. Indeed, an additional uniaxial pressure component should kinetically enhance the covalent bonding along its own directions, as in the 2D polymers of C_{60}. On the other hand, it is well known that graphite is much more compressible along the (002). That is, in the presence of an additional uniaxial pressure component along the Z axis, the orientation of clusters with (002) planes near the perpendicular to the Z axis proves to be thermodynamically preferred, because, in this case, the density of the cluster system is higher and the PV contribution to the Gibbs thermodynamic potential is less.

Suggesting that the first amorphous peak in the diffraction patterns [Fig. 2(b)] corresponds to the interference from the parallel graphene-like sheets, while the second one basically corresponds to the reflection along the graphene sheets, one can see that the double-intensity ratio $(I_Z^{(1)}/I_X^{(1)})/(I_Z^{(2)}/I_X^{(2)})$ provides a good evaluation for $(N_Z/N_X)^2$, where N_Z and N_X are the fraction of the graphite-like clusters with the graphene sheets perpendicular to Z and X, respectively. In the double ratio, the superscripts denote the numbers of peaks and the subscripts denote the scattering vector directions. The N_Z/N_X ratio estimated in this way correlates linearly with the elastic anisotropy for the longitudinal sound velocities in Fig. 2(c).

Summarizing, we have shown that nonhydrostatic pressure is indeed a powerful tool for the preparation of anisotropic carbon structures. The predominant orientation of the polymerized planes in 2D polymerized C_{60} phases can serve as a signature of an additional uniaxial pressure component. In contrast, the formation of anisotropic graphite-type (sp^2) atomic-based phases is of a more complicated nature, and the effect depends on both the uniaxial and uniform pressure components. In this case, the elastic anisotropy can be opposite to that observed for the 2D polymerized C_{60} phases, but it still correlates with the structural texture.

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[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).
[2] W. Krätschmer, L. D. Lamb, K. Fostiropolous, and D. Huffman, Nature (London) **347**, 354 (1990).
[3] B. Sundqvist, Adv. Phys. **48**, 1 (1999).
[4] A. G. Lyapin, V. V. Brazhkin, S. G. Lyapin, S. V. Popova, T. D. Varfolomeeva, R. N. Voloshin, A. A. Pronin, N. E. Sluchanko, A. G. Gavrilyuk, and I. A. Trojan, Phys. Status Solidi B **211**, 401 (1999).
[5] A. G. Lyapin, in *Perspectives of Fullerene Nanotechnology*, edited by E. Osawa (Kluwer, Dordrecht, 2002) p. 199.
[6] M. Núñez-Regueiro, L. Marques, J-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).
[7] L. Marques, J-L. Hodeau, M. Núñez-Regueiro, and M. Perroux, Phys. Rev. B **54**, R12633 (1996).
[8] V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. Agafonov, H. Allouchi, R. Céolin, A. V. Dzyabchenko, V. M. Senyavin, and H. Szwarc, Phys. Rev. B **58**, 14786 (1998).
[9] V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. M. Senyavin, R. Céolin, H. Szwarc, H. Allouchi, and V. Agafonov, Phys. Rev. **61**, 11937 (2000).
[10] M. E. Kozlov, M. Hirabayashi, K. Nozaki, M. Tokumoto, and H. Ihara, Appl. Phys. Lett. **66**, 1199 (1995).
[11] A. G. Lyapin, V. V. Brazhkin, E. L. Gromnitskaya, S. V. Popova, O. V. Stal'gorova, R. N. Voloshin, S. C. Bayliss, and A. V. Sapelkin, Appl. Phys. Lett. **76**, 712 (2000).
[12] V. V. Brazhkin, A. G. Lyapin, and S. V. Popova, JETP Lett. **64**, 802 (1996).
[13] V. D. Blank, S. G. Buga, N. R. Serebryanaya, G. A. Dubitsky, S. N. Sulyanov, M. Yu. Popov, V. N. Denisov, A. N. Ivlev, and B. N. Mavrin, Phys. Lett. A **220**, 149 (1996).
[14] V. V. Brazhkin, A. G. Lyapin, S. V. Popova, R. N. Voloshin, Yu. V. Antonov, S. G. Lyapin, Yu. A. Klyuev, A. M. Naletov, and N. N. Mel'nik, Phys. Rev. B **56**, 11465 (1997).
[15] V. V. Brazhkin, A. G. Lyapin, S. V. Popova, Yu. A. Klyuev, and A. M. Naletov, J. Appl. Phys. **84**, 219 (1998).
[16] H. Hirai, K. Kondo, N. Yoshizava, and M. Shiraishi, Appl. Phys. Lett. **64**, 1797 (1994).
[17] V. V. Brazhkin, A. G. Lyapin, R. N. Voloshin, S. V. Popova, Yu. A. Kluev, A. M. Naletov, S. C. Bayliss, and A. V. Sapelkin, JETP Lett. **69**, 869 (1999).
[18] L. Marques, M. Mezouar, J. L. Hodeau, M. Núñez-Regueiro, N. R. Serebryanaya, V. A. Ivdenko, V. D. Blank, and G. A. Dubitsky, Science **283**, 1720 (1999).
[19] L. Marques, M. Mezouar, J.-L. Hodeau, and M. Núñez-Regueiro, Phys. Rev. B **65**, 100101(R) (2002).
[20] V. V. Brazhkin, A. G. Glazov, V. V. Mukhamadiarov, E. L. Gromnitskaya, A. G. Lyapin, S. V. Popova, and O. V. Stal'gorova, J. Phys.: Condens. Matter **14**, 10911 (2002).
[21] L. G. Khvostantsev, L. F. Vereshchagin, and A. P. Novikov, High Temp. - High Press. **9**, 637 (1977).