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Elastic properties of superhard amorphous carbon pressure-synthesized from C_{60} by surface Brillouin scattering

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Surface Brillouin scattering technique has been used to study the elastic properties of superhard amorphous carbon, synthesized from C_{60} under high pressure (13–13.5 GPa) and temperature ($900\pm100\,°\mathrm{C}$). This is the first reliable determination of bulk and shear elastic moduli for this type of amorphous carbon material, to the best of our knowledge. The measured moduli are found to be close to those of diamond in agreement with the general trend for elasticity, hardness, and density among the carbon phases, demonstrating as well the efficiency of high-pressure fullerene technique for synthesis of sp^3-based amorphous carbon materials.

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A recent interest in new superhard materials triggered by the discovery of the fullerene molecule C_{60} has led to a series of extensive experimental studies of amorphous and nanocrystalline carbon phases and their properties.[1–7] Subjected to high pressures and temperatures fullerite C_{60}, a metastable phase of carbon, undergoes transformations to the more stable diamond and graphite through a sequence of previously unknown intermediate phases. In particular, heating at relatively low pressures ($P<8$ GPa) has revealed one-dimensional (1D) and 2D polymerization[8] of C_{60} and subsequent collapse of the fullerene structure into graphitelike disordered carbon.[9] Whereas, heating at $P>8$ GPa has resulted in formation of 3D polymerized amorphous phases of C_{60}, with a large number of sp^3 atomic sites[3,4] and nanocrystalline composites (nanoceramics) of diamond and graphite,[5,6] fueling the most recent debates on existence of ultrahard fullerene-based phases with hardness higher than diamond.[10–12]

The covalent bonds between carbon atoms are among the shortest and strongest, and this stimulates the development and search of new carbon superhard materials alongside with the understanding of the correlations between structure and physical properties of such phases. Since hardness and strength depend on the method of measurements and sample morphology, elastic moduli, which can be measured by ultrasonic techniques[1,12] and acoustic microscopy,[13–16] are of greater importance for comparative characterization of carbon materials. Even though first measurements of elastic properties[1,12] have shown rather high Young's modulus values for superhard carbons (~400 GPa for the 3D polymerized phases and ~700 GPa for the amorphous sp^3-based structures) (Refs. 1 and 12) and an extremely high value of the longitudinal velocity (26 km/s) in a specimen formed under high pressure (13 GPa),[15,16] more experimental work is necessary to unambiguously characterize the elastic properties of superhard C_{60}-based materials and to understand their structural nature. In addition, previous studies[1,12,15,16] did not take into account the effect of possible directional anisotropy and, moreover, theoretical calculations produced a wide range of values for adiabatic bulk modulus K_s (from 34 GPa (Ref. 17) to 270 GPa (Ref. 18) for the 3D polymerized phases.).

Fullerite materials obtained under high pressure are often not homogeneous and consist of several phases with different elastic properties.[3] Even in one specimen, the dimensions of the different phases vary from a few tens to hundreds of microns. The surface Brillouin scattering (SBS) spectroscopy, which provides high resolution in the elastic property measurements ($\approx 5\ \mu$m on a focal plane), is ideally suited for characterizing such specimens. The first experimental Brillouin scattering study of the fullerene product resulted from laser irradiation of a C_{60} single crystal[19] revealed that its sound velocities (280–700 m/s that are typical for slow polymers or carbon gels) are substantially lower than the previously reported values for solid C_{60}.

In this paper, we report the first successful measurements by SBS of the elastic properties of the superhard amorphous carbon synthesized from C_{60} under high pressure (13 GPa) and high temperature (800–900 °C). The results of these measurements demonstrate the effectiveness of the SBS method in accurate characterization of small superhard specimens and provide further insight into the interplay among bonding nature, density, and elasticity of numerous carbon phases.

Two bulk amorphous carbon (a-C) samples, macroscopically homogeneous with glossy black color, were synthesized[12] from C_{60} fullerite powder at 13 to 13.5 GPa, $800\pm100\,°\mathrm{C}$ (sample A) and $900\pm100\,°\mathrm{C}$ (sample B). The pristine fullerite powder had C_{60} content not less than 99.9% and consisted of 50–100 μm crystalline grains. The powder of C_{60} microcrystals was pressed into 2-mm high and 2-mm-diam cylinders. A new version of the large volume "toroid" chamber (up to 30 mm^3) (Ref. 1) was used for high-pressure–high-temperature generation up to 13.5 GPa in the temperature range of 20–1700 °C. The samples were placed into Pd or Pt cells and heated by passing electric current through the outer graphite container. The hardness was measured by an indentation technique with the load on the indenter equal to ≈5 N. To investigate anisotropic properties of the synthesized specimens two faces normal to each other were polished in both samples: top face (where pressure was applied) and side face (normal to top face).

A detailed description of the SBS experimental setup has been published elsewhere.[20,21] In brief, light from an argon

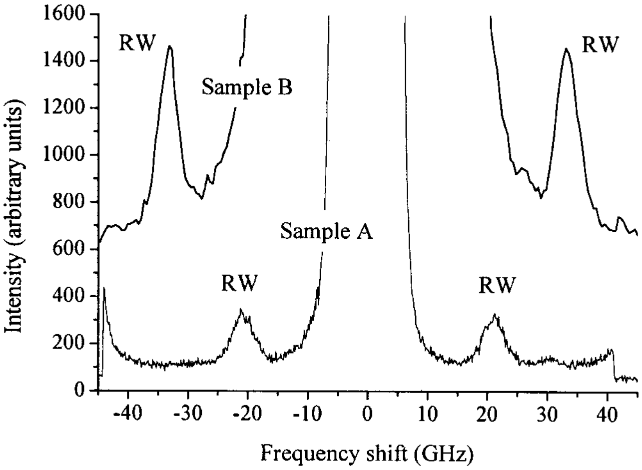

FIG. 1. Experimental SBS spectrum of samples A and B at $\theta = 60°$.

ion laser ($\lambda = 514.5$ nm and beam power of 60 mW) was focused onto the film with a 1:1.4 lens ($f = 50$ mm). The scattered light was collected with the same lens in a back-scattering geometry and analyzed using a high contrast and high-resolution Brillouin spectrometer, which incorporated a tandem six-pass Fabry-Perot interferometer.[22] The light was detected by a single photon counting module and its output was stored in a multichannel scaler card for further analysis. Each spectrum was accumulated for 1–2 h. The frequencies corresponding to each of the peaks were determined by a curve-fitting routine.

The frequency shift ν from the SBS spectra obtained for samples A and B (Fig. 1) is related to the surface acoustic wave (SAW) velocity V_{SAW} as

$$V_{\mathrm{SAW}} = \frac{\lambda \nu}{2 \sin \theta}, \qquad (1)$$

where θ is the scattering angle. The values of the Rayleigh wave (RW) velocity V_{RW} deduced from the spectra are compared (Table I) to those for bulk polycrystalline cBN specimen,[23] tetrahedral amorphous carbon films (ta-C),[24] and calculated values for polycrystalline diamond from single-crystal data.[25]

The SBS measurements on the side face of the sample A reveal strong heterogeneity in the elastic properties across the sample surface. It is reflected in the high value (4%) of the standard deviation of the measured Rayleigh wave velocity, which is well above the accuracy of the SBS measurements (1%). The highest measured value of the Rayleigh wave was 7.21 km/s, and the lowest was 6.41 km/s. The variation of the elastic properties determined by SBS spectroscopy along the top face of the sample B (Fig. 1) is significantly less than that on the side face of the sample A. The value of the standard deviation (Table I) of the RW velocity in sample B is ten times smaller than in sample A.

Brillouin scattering results for tetrahedral amorphous carbon films (ta-C) (Ref. 26) and diamondlike carbon films[24] suggested the possibility of detecting the longitudinal leaky wave or longitudinal mode (LM) (Ref. 27) in hard amorphous carbon samples. Indeed, the investigation of sample B revealed [Fig. 2(a)] a clear presence of symmetric (approximately, −60 GHz and 60 GHz for 70° incident angle) Brillouin peaks. The LM wave has not been detected in sample A. As a result of extremely high intensity of elastic scattering of the sample and consequent saturation of the system, an appearance of an asymmetric peak at about −60 GHz was detected during experimental runs as well. Since overlapping of the useful signal with the asymmetric component had occurred at higher incident angles, an accurate determination of the Brillouin shifts for the symmetric peaks was performed using nonlinear least-squares fitting (Microcal™Origin™, Version 5.0). The asymmetric peak (BG) was treated as a single peak with a Lorentzian shape and was assigned by curve fitting procedure at -62.92 ± 0.06 GHz, making an excellent fit [Fig. 2(b)] to data (thick solid line) with the less than 1% standard deviation for the peak positions.

Curve fitting described above was applied to extract positions of Brillouin peaks associated with inelastic scattering on LM. This measurement provides bulk longitudinal velocities (Table I) independently from refractive index.[27] Knowing the velocity of the longitudinal wave V_L and the velocity of the Rayleigh surface wave, it is possible to derive transverse velocity V_T, which happened to be very close to that of a polycrystalline diamond (Table I), from a Rayleigh dispersion equation for SAW in isotropic half-space.[28]

TABLE I. Measured and calculated velocities and moduli of a-C samples and related superhard materials.

Specimen	ρ (g/cm^3)	V_{RW} (km/s)	V_T (km/s)	V_L (km/s)	ν (Poisson's ratio)
A (Top face)	3.0 ± 0.1	6.49			
A (Side face)	3.0 ± 0.1	6.68 ± 0.27			
B (Top face)	3.15 ± 0.1	9.79 ± 0.07	10.920[a]	16.6 ± 0.5	0.121
B (Side face)	3.15 ± 0.1	9.99 ± 0.06			
ta-C[a]	3.26	9.129[d]	10.175	15.508	0.122
cBN[b]	3500	9.317[d]	10.388	15.818	0.128
Diamond[c]	3.515	10.944[d]	12.329	18.144	0.071

[a] Reference 24.
[b] Reference 23.
[c] Isotropic (Voigt-Reuss-Hill) average (Ref. 26).
[d] Calculated from Rayleigh equation (Ref. 28).

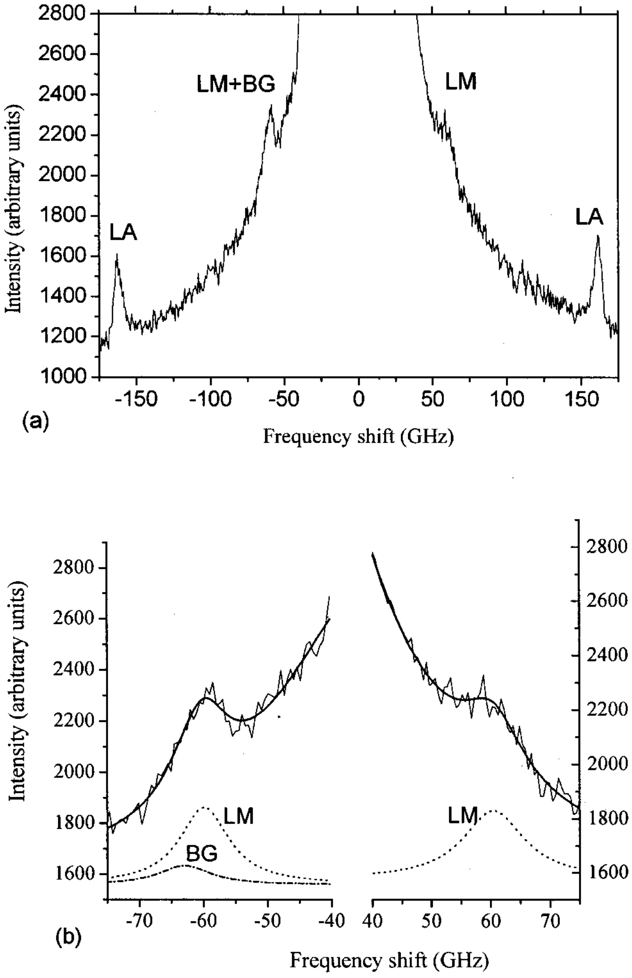

FIG. 2. (a) Experimental Brillouin spectrum of the sample B at $\theta = 70°$. (b) Curve fitting analysis: symmetric SBS peaks (LM), asymmetric peak (BG) and resulting peaks are represented by dashed, dotted, and thick solid lines, correspondingly.

The second peak present at a higher frequency [Fig. 2(a)] corresponds to the bulk longitudinal-acoustic wave (LA). In the backscattering geometry, sound velocity relates to the frequency shift as: $V_L = \lambda v/(2n)$, where n is the refractive index of the scattering medium. For sample B, the frequency shift is nearly the same as that in a diamond along the [100] direction, making $nV_L = 42.04 \pm 0.12$ km/s. Inelastic scattering from the bulk longitudinal wave (LA) can only be observed in sample B, implying that this specimen is not completely opaque with dominant sp^3 bonds in contrast to sample A with, presumably, sp^2 dominant bonds. Assuming the refractive index to be close to that of a diamond ($n = 2.42$), the longitudinal velocity in sample B can be as high as 17.4 km/s. On the other hand, taking into account the velocity of the LM, the refractive index of sample B should be about 2.53, which is close to the refractive index of pristine C_{60} single crystal (2.52).[19]

Recently, it was found that structural anisotropy of the 3D polymers has a memory sign of nonhydrostatic loading.[29] Our experimental setup allowed us to test the existence of elastic anisotropy in the synthesized samples. We carried out measurements of the anisotropic properties of the samples A and B by fixing the scattering angle θ at 60° for A and 50° for B with subsequent rotation of the samples about the normal to their side surfaces in steps of 20°. Since the side face of the sample A has well pronounced elastic heterogeneity, a cluster ($\approx 10-20\ \mu$m in diameter), with the lowest value of SAW velocity at 0° (when the top face of the sample is perpendicular to the horizontal surface), was chosen to perform an anisotropy test. A noticeable increase in value of the SAW velocity with the maximum at about 100° and subsequent decrease, confirmed by measurements at 140°, contrasts to the almost invariable angular behavior of sample B (Fig. 3).

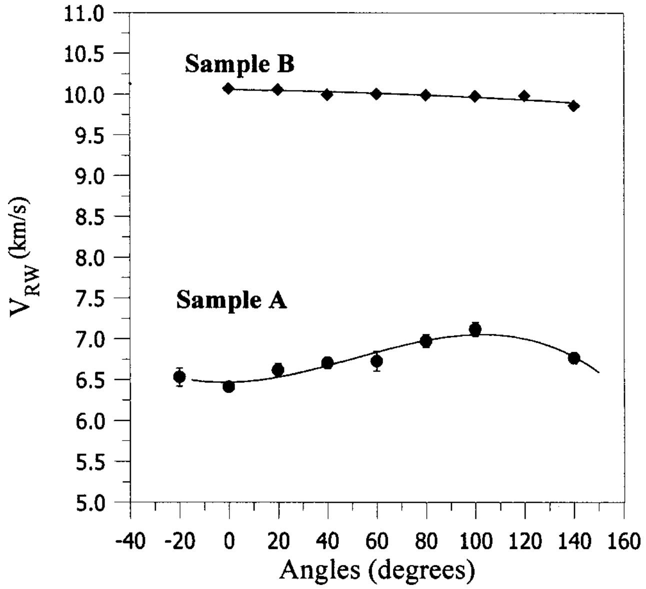

FIG. 3. RW velocity as a function of the angle for side faces of samples A (solid circles) and B (diamonds). Polynomial fit was done just as a guide for the eye (solid lines). Error bars are visible only if they exceed the size of the symbols.

Surprisingly, the spatial variation of the RW velocity (a direct evidence of the mentioned elastic heterogeneity) on the top surface of the sample A has the same range of values as the angular variation of that on the side face (Fig. 3). This indicates that the spatial variation of the RW velocity along the surface of the samples can be explained by the anisotropy of the roughly homogeneous elastic clusters randomly distributed in the sample.

Longitudinal velocities obtained from Brillouin measurements are close to those of diamond (Table I). The longitudinal velocity (V_L) in sample B (16.6 km/s) is higher than that in cBN (15.8 km/s) (Ref. 23) and in ta-C films (15.5 km/s);[24] in both cases the velocities are slightly lower than longitudinal wave velocity (18.6 km/s) in diamond in the [110] direction.[30]

For sample B all elastic constants can be deduced from SBS measurements: $G = 375$ GPa (adiabatic shear modulus), and $K_s = 368$ GPa (adiabatic bulk modulus), while an assumption that $V_{RW} = 0.9V_T$ is used to obtain $G = 171$ GPa for sample A. The difference in shear moduli of samples A and B may result from a temperature-induced crossover between

sp^2- and sp^3-based atomic bonding and, possibly, reflect a complex density-elasticity relation in carbon phases with basically 2D covalent ordering (2D C_{60} polymers and graphitelike phases).[32] However, this hypothesis needs to be further confirmed because of the large uncertainties in synthesis conditions.

The obtained Vicker's hardness (H_v) values (68 ± 4 GPa and 122 ± 9 GPa for samples A and B, respectively) correlate with the measured shear moduli and fit well in the general density-hardness relationship for carbon phases,[6,12,31] in which density appears to be directly related to the sp^2/sp^3 ratio. The elastic moduli of sample B are also in accordance with theoretical calculation for amorphous carbon with the varied sp^2/sp^3 ratio.[33]

Summing up, we carried out the first accurate measurements of the elastic properties of superhard bulk amorphous carbon synthesized from C_{60} at a pressure of 13–13.5 GPa and temperature $900\pm100\,^\circ$C and presented the first direct observation of directional elastic anisotropy in amorphous carbon materials. The unusually high values of bulk modulus (e.g., 1700 GPa) reported previously[15,16] were not confirmed by our measurements and resulted, probably, from strong anisotropy and heterogeneity of the samples, unaccounted for in those studies. Our experimental values of sound velocity, refractive index, bulk, and shear moduli are close to those for diamond, indicating, basically, sp^3 diamondlike bonding in these amorphous phases and demonstrating the efficiency of high-pressure technique for the synthesis of diamondlike (sp^3-based) amorphous carbon. The measured density, hardness and elastic moduli are in agreement with a previoulsy discussed relationship among these physical properties for carbon materials.[3]

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