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# Elastic properties of carbon phases obtained from C<sub>60</sub> under pressure: the first example of anisotropic disordered carbon solid

V V Brazhkin, A G Glazov, V V Mukhamadiarov, E L Gromnitskaya,  
A G Lyapin, S V Popova and O V Stal'gorova

Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow Region,  
142190, Russia

E-mail: alyapin@hppi.troitsk.ru

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## Abstract

We observe an anisotropy of the propagation velocities of longitudinal and transverse ultrasonic waves, as well as of the hardness, for disordered graphite-like samples obtained from the C<sub>60</sub> fullerite, which is heated to different temperatures under a pressure of 7.5 GPa. The anisotropy of the elastic properties and the hardness is connected to the additional pressure component that occurs in the quasi-hydrostatic experimental conditions. The elastic characteristics of the samples are determined. We propose a model description relating the observed properties of superhard sp<sup>2</sup> carbon to its possible structural features and to the mechanism of its formation.

## 1. Introduction

The C<sub>60</sub> fullerite is an object of great interest for investigations, because the carbon phases obtained from it combine low densities with high mechanical and elastic characteristics [1–12]. Under the effects of temperature and pressure, the C<sub>60</sub> fullerite can transform to molecular polymer phases or to disordered or nanocrystalline modifications, depending on the experimental conditions [1–14].

The pressure anisotropy naturally occurs in quasi-hydrostatic conditions that occur, for example, in toroidal-type chambers with a single loading axis. The presence of a structural anisotropy has been observed for three-dimensional (3D) C<sub>60</sub> polymers obtained in such chambers [15]. One of the direct methods used to reveal the anisotropy is the ultrasonic technique.

Until now, in the studies of the elastic properties of materials obtained from C<sub>60</sub>, the bulk *B* and shear *G* moduli have been calculated using the isotropic medium approximation [8–12]. Such calculations have provided the values of the Poisson ratio that were anomalously high for

**Table 1.** The densities, as well as the longitudinal ( $l$ ) and transverse ( $t$ ) sound velocities, propagating along or perpendicular to  $z$  with different polarizations ( $V_{t,x}^y$  denotes, for example, the velocity of the transverse wave propagating along the  $x$ -axis with  $y$  polarizations), for disordered carbon phases prepared from  $C_{60}$  at 8 GPa.

$T$ (°C)	$\rho$ (g cm <sup>-3</sup> )	$V_{l,z}$ (km s <sup>-1</sup> )	$V_{l,x}$ (km s <sup>-1</sup> )	$V_{t,z}$ (km s <sup>-1</sup> )	$V_{t,x}^z$ (km s <sup>-1</sup> )	$V_{t,x}^y$ (km s <sup>-1</sup> )
1000	2.2	5.14	6.9	3.2	3.05	4.48
1000	2.21	6.44	6.55			
1150	2.3	6.78	7.3	3.7	3.6	4.5
1180	2.4	6.5	7.25	3.8	3.6	4.6
1190	2.05	5.05	6.42	2.75	2.7	3.3
1300	1.99	4.2	6.5	2.8	2.6	3.8
±100	±0.1	±0.15	±0.15	±0.15	±0.15	±0.15

covalent structures [8–11], and the values of the bulk modulus that were nonphysically high [8–10]. However, the possible orientational anisotropy and inhomogeneity (see the example in [11]) of materials were not taken into account in these calculations.

In this paper we describe the study of the orientational anisotropy of the elastic properties and the microhardness of superhard samples with a disordered graphite-like (i.e. mainly  $sp^2$ ) structure.

## 2. Experimental details

The disordered samples were synthesized from a fullerite with a  $C_{60}$  content of no less than 99.9% under the pressure  $P = 7.5$  GPa at temperatures from 1000 to 1300 °C. To study the possible effect of the substance surrounding the fullerite on the anisotropy of the synthesis conditions, two types of container, made of graphite and NaCl, were used. The synthesized material was obtained in the form of cylinders, which were used to prepare samples in the form of parallelepipeds with the characteristic dimensions  $1.5 \times 1.5 \times 1.2$  mm<sup>3</sup>. The ultrasonic measurements consisted of measuring the time of the longitudinal and transverse ultrasonic wave propagation through the sample at a frequency of 10 MHz. The microhardness was measured by the Vickers indentation method by a PMT-3 hardness tester with a load of 2 N.

## 3. Results and discussion

The experimental results are presented in table 1. The values obtained for the density and the microhardness,  $\rho = 1.9$ – $2.4$  g cm<sup>-3</sup> and  $H_V = 21$ – $32$  GPa, are in good agreement with the data reported for disordered phases in earlier publications [2, 6, 12]. The velocities of longitudinal and transverse ultrasonic waves also agree with the velocity values obtained earlier for similar phases [11, 12]. The x-ray diffraction curves obtained for the synthesized samples (see similar curves in [2, 12]) testify that the phases under study are strongly disordered and have a graphite-like ( $sp^2$ ) structure.

A fundamentally new result is the strong anisotropy observed for the velocities of transverse and, especially, longitudinal ultrasonic waves propagating parallel and perpendicular to the  $z$ -axis, which corresponds to the loading axis of the sample synthesis. The anisotropy of the velocities reaches 20–30%. For microhardness, the values obtained with the indentation parallel to the  $z$ -axis ( $H_z = 27$  and 21 GPa for samples prepared at 1000 and 1180 °C, respectively) and perpendicular to it ( $H_x = 32$  and 27 GPa for the same samples) are also different; the microhardness anisotropy is within ~15–20%.

**Table 2.** Components of the elastic constant tensor (according to the calculations by equations (1), the estimate for  $c_{13}$ , the bulk modulus and the Poisson ratio in different directions for the samples from table 1.

No	$c_{11}$ (ГПа)	$c_{33}$ (ГПа)	$c_{44}$ (ГПа)	$c_{12}$ (ГПа)	$c_{13}$ (ГПа)	$B$ (ГПа)	$\sigma_z$	$\sigma_x^y$	$\sigma_x^z$
1	104.7	58.1	22.5	16.4	9.1	37.4	0.08	0.15	0.13
2	94.8	91.7	—	—	—	—	—	—	—
3	122.6	105.7	31.5	29.4	25.4	56.8	0.17	0.20	0.19
4	126.2	101.4	34.7	24.6	19.8	53.5	0.13	0.17	0.16
5	84.5	52.3	15.5	39.8	24.7	44.4	0.20	0.38	0.29
6	84.1	35.1	15.6	26.6	11.1	33.4	0.10	0.28	0.23

From the point of view of the synthesis conditions, the material of the samples should exhibit an anisotropy in a single selected direction  $z$ , whereas all directions lying in the  $xy$  plane must be equivalent. The elastic constant tensor of such a material is similar to the corresponding tensor of a crystal with a hexagonal symmetry [16], i.e. it is characterized by five independent constants— $c_{11}$ ,  $c_{12}$ ,  $c_{33}$ ,  $c_{13}$  and  $c_{44}$ . In the experiment, we measured five ultrasonic velocities (see table 1): two longitudinal wave velocities along the  $x$ - and  $z$ -axes ( $V_{lx}$  and  $V_{lz}$ ) and three transverse wave velocities, one along the  $z$ -axis and two along the  $x$ -axis with  $y$  and  $z$  polarization directions ( $V_{tz}$ ,  $V_{tx}^y$  and  $V_{tx}^z$ ). The relations between these velocities and the components of the elastic constant tensor are well known [17]:

$$\rho V_{lx}^2 = c_{11}, \quad \rho V_{lz}^2 = c_{33} \quad (1a)$$

$$\rho V_{tx}^{y2} = \frac{1}{2}(c_{11} - c_{12}) \quad (1b)$$

$$\rho V_{tx}^{z2} = \rho V_{tz}^2 = c_{44}. \quad (1c)$$

The results obtained by calculating the components of the elastic constant tensor are presented in table 2. The bulk modulus  $B$  can be determined by averaging according to the Voigt–Reuss–Hill approach [18].

In the framework of the chosen approximation, we estimate the values of the Poisson ratio, which depend on the measurement orientation:

$$\sigma_z = c_{13}/(c_{11} + c_{12}) \quad (2a)$$

$$\sigma_x^y = \frac{c_{12}c_{33} - c_{13}^2}{c_{11}c_{33} - c_{13}^2} \quad (2b)$$

$$\sigma_x^z = \frac{(c_{11} - c_{12})c_{13}}{c_{11}c_{33} - c_{13}^2}. \quad (2c)$$

The calculated values of the Poisson ratio are also presented in table 2.

The presence of anisotropy should be naturally attributed to the uniaxial pressure anisotropy that occurs in the quasi-hydrostatic conditions of the experiment. In the case of the synthesis with the use of NaCl containers, which provide a higher degree of hydrostatics, the difference in the elastic characteristics corresponding to different directions is much smaller. An unexpected result is that the ultrasonic velocities along the  $x$ -axis prove to be higher than the corresponding velocities along the  $z$ -axis. The additional positive pressure component is directed along the  $z$ -axis, and this fact determines, for example, the higher degree of polymerization along the  $z$ -axis in 3D polymers [15]. From the data on the Brillouin scattering, it is also known that, in amorphous (mainly  $sp^3$ ) samples synthesized from C<sub>60</sub> under a pressure of about 13 GPa, the velocity of acoustic waves is higher when their propagation is along the  $z$ -axis [19].

The x-ray diffraction data suggest that the  $sp^2$  phases under consideration have a nanocluster structure in which the clusters can have the form of graphite-like crystallites with a parallel atomic packing or an amorphous conglomerate of partially ordered nanoregions, as in, for example,  $CN_x$  films [20]. The velocities of ultrasonic waves propagating along the graphite planes are known to be higher than the propagation velocities in the perpendicular directions. It is natural to attribute the anisotropy of the elastic properties observed in the experiment to the anisotropy of the spatial orientation of the structure-forming clusters, namely, to the presence of the preferred orientation of graphite-like planes that is normal to the  $z$ -axis. The deviation from the spherically symmetric distribution of the orientation of graphite-like clusters leads to the formation of a sort of texture in the disordered samples.

Let us consider a possible mechanism for the formation of an anisotropic cluster system under pressure in the process of the disruption of the fullerite structure. It is well known that graphite is much more compressible along the (001) direction; i.e. in the presence of the additional positive pressure component along the chamber axis ( $z$ -axis), the orientation of clusters with (001)  $\parallel z$  proves to be preferred because, in this case, the density of the cluster system is higher and the  $PV$  contribution to the Gibbs thermodynamic potential is smaller.

The observed anisotropy of the elastic properties is very significant for analysing the experimental data. If the elastic moduli are calculated in the framework of the isotropic medium model, considerable errors may occur. For example, for No. 6 (see table 1), the isotropic medium approximation, when applied separately to the data obtained for different directions, provides the values of the bulk modulus  $B \sim 15$  and 55 GPa for the  $z$ -axis and the  $x$ -axis; i.e. one obtains values that differ by a factor of more than three. The aforementioned values of the Poisson ratios that are anomalously high for covalent structures [8–11] are presumably related to the application of such an incorrect approach. In our case, the values of the Poisson ratios obtained allowing for the anisotropy are more adequate for carbon covalent structures.

#### 4. Conclusion

Thus, in analysing the elastic properties of the phases synthesized from  $C_{60}$  under pressure in quasi-hydrostatic conditions, it is necessary to take into account the anisotropy, for example, by using equations (1) and (2). The study of the anisotropy of polymerized phases is of special interest, because it can provide information on the mechanisms of their formation. The possibility of creating an anisotropy (a texture) in superhard samples can be of practical interest, for example, for increasing the hardness in certain directions.

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