Ultrasonic Study of Monomeric Fullerite C$_{60}$ under Pressure

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Abstract. The ultrasonic study of the elastic moduli of polycrystalline fullerite C$_{60}$ was carried out in the temperature range from liquid nitrogen to room temperature at pressures up to 1.4 GPa, including the regions of the orientational fcc-to-sc and glass transitions. The temperature dependencies of the elastic moduli at ambient pressure are in good agreement with previous studies. For the first time the pressure dependencies of the shear modulus and Poisson’s ratio were determined. Particularly, the Poisson’s ratio was found to increase from $\approx 0.3$ at ambient pressures to $\approx 0.38$ at $p = 1$ GPa. The observed high values of the Poisson’s ratio, as well as the high values of pressure derivatives of the bulk modulus $\approx 23-25$ are discussed in terms of the central $m-n$ power potential and contribution of the non-central intermolecular forces due to intramolecular deformations.

1. Introduction

Fullerene C$_{60}$ is the most stable molecule among other fullerenes, and fullerite C$_{60}$ is an archetype among all-carbon molecular solids bonded by the van der Waals forces. For the past two decades, the physical and chemical properties of fullerenes have been a fruitful subject of study. The measurements of the elastic properties are an important tool to study any material. The knowledge of the elastic constants is crucial to verify and develop the force potentials for an intermolecular interaction in C$_{60}$. Many experimental techniques have been applied to study the bulk modulus $B$: the measurements of the lattice constant by the use of the X-ray and neutron diffraction methods and the direct measurement of compressibility. Some experiments have involved the use of an ultrasonic technique [1,2]. A comprehensive review on physical and elastic properties of molecular C$_{60}$ is given in Ref. [3]. More recent results are presented in Refs. [2,4-6]. Although all these methods are comparably accurate, it is surprising that the results from different groups often vary by significant amounts [3]. Therefore, the issue of the C$_{60}$ bulk modulus $B$ still remains open. Also there is little information on the shear modulus $G$ of C$_{60}$ under pressure. Ref. [1] presented only the temperature dependence of $G$ at atmospheric pressure.

At room temperature the C$_{60}$ crystal structure is a face centered cubic one with space group $Fm3m$ [7]. The studies on this structure [8-10] show that the molecular rotation is not completely free. On cooling, the rotation slows down and, below an orientational transition temperature $T=260$ K [11,12], the rotational motion is replaced by a combination of a rapid jumping motion between a number of well-defined orientational states and librational motion about the equilibrium orientation in each such state. The basic structure of the low-temperature phase is identical with that of the fcc phase except...
that the four molecules in the cubic unit cell have different orientations, changing the fcc symmetry to a simple cubic (sc) structure. In such ordered structures, electron-rich double bonds on one molecule face the electron-poor centres of hexagons and pentagons. Below the glass transition temperature $T_g = 90\,\text{K}$ [12] the remaining orientational disorder becomes frozen in creating orientational glass with the crystalline order of molecular centers.

In this work we present an ultrasonic and volumetric study of $\text{C}_6\text{O}$ on compression and heating, including fcc, sc and glass phases. The study provides accurate data on the elastic characteristics of these phases under pressure and their changes during transitions.

2. Experimental details
The measurements were carried out using an ultrasonic piezometer in the pressure and temperature ranges up to $1.4\,\text{GPa}$ and $80 - 290\,\text{K}$, respectively, in accordance with the procedure described in Ref. [13]. The direct measurement of an ultrasonic wave was directly measured by the “Akustomer-1” device designed in the Institute for High Pressure Physics RAS. The measurements provided pressure and temperature dependencies of the longitudinal and transversal wave velocities in $\text{C}_6\text{O}$. The height of the sample and, subsequently, the density were determined independently. We estimated the accuracy in the determination of the bulk and shear moduli as $2\%$.

The studied samples of $\text{C}_6\text{O}$ were cylinders of $7-10\,\text{mm}$ in height and $16\,\text{mm}$ in diameter. The initial compaction of the $\text{C}_6\text{O}$ powder into a polycrystalline sample was made under air-free conditions. The pressure cell used in the experiments was of a piston-cylinder type.

For the experiments to be accurate, it was very important that hydrostatic loading could be provided. We hope our experiments adequately met this condition, because $\text{C}_6\text{O}$ is a soft and plastic molecular material. Additionally, we tried to increase the hydrostaticity by placing a lead pad between the sample and cell walls. It was also important, that the ultrasonic wave length we used was smaller than the sample height by a factor of 5-10. When measuring the bulk modulus it is important that both the $\text{C}_6\text{O}$ phases have the cubic symmetry, which diminishes the role of a possible sample texture during compression.

3. Results and discussion
First, we determined the elastic properties of $\text{C}_6\text{O}$ at room temperature ($293\,\text{K}$) and atmospheric pressure. Precise direct measurements of ultrasound velocities allow the determination of the bulk modulus $B_0$, shear modulus $G_0$, Poisson’s ratio $\sigma_0$, and Young's modulus $E_0$. The comparison of the $B_0$, $G_0$, and $E_0$ values is presented in Table 1. The moduli were obtained by the use of different techniques that gave adiabatic or isothermal values. However, it is known that the differences between adiabatic and isothermal elastic constants and moduli are less than $1\%$ [14], thus, comparing the data of different experiments, including our adiabatic ultrasound ones, seems correct.

| References | This work | Ref. [3] | Ref. [1] | Ref. [4] | Ref. [15] |
|------------|-----------|----------|----------|----------|----------|
| $G_0$, GPa | 4.14      | 4.85     | 3.75     |          |          |
| $B_0$, GPa | 10.02     | from 6.4 to 14.8 | 10.8 | 15.6 | 8.4 |
| $E_0$, GPa | 10.93     | 12.6     |          |          | 9.8      |

The most important results are the dependencies of the shear and bulk moduli on pressure and temperature. The ultrasonic wave travel time and sample length in isothermal experiments were measured on compression and in isobaric experiments – on heating (the heating rate was $\approx 1\,\text{K/min}$). As a result, the pressure and temperature dependencies of the ultrasound velocity were found (see, e.g., the inset in Fig. 3).

The pressure dependencies $B(p)$ and $G(p)$ are presented in Fig. 1. The anomalies in changes in the above characteristics were identified as phase transition points in $\text{C}_6\text{O}$. The high values of pressure derivatives of the bulk modulus ($B'_p \approx 23-25$) indicate that this molecular system may be rather...
sensitive to environmental conditions, and, hence, to non-hydrostaticity, presence of impurities, texture, and so on. This can explain the lack of coincidence of the data from different experiments on the bulk modulus. The values of both the bulk and shear modulus pressure derivatives are very slightly temperature-dependent. The pressure derivative of the bulk modulus for the fcc phase is very close to that for the sc phase. On the contrary, the pressure derivative of the shear modulus for the fcc structure is lower than that for the sc structure. From the data in Fig. 1 it is possible to calculate the Poisson’s ratio $\sigma$, which at room temperature varies from $\approx 0.3$ at atmospheric pressure to $\approx 0.38$ at $p=1$ GPa. A very similar picture is observed for the change of $\sigma$ at other temperatures for the sc phase.

![Figure 1. Pressure dependencies of shear and bulk moduli of C$_{60}$ at different temperatures.](image1)

![Figure 2. Temperature dependencies of shear and bulk moduli of C$_{60}$ at different pressures.](image2)

The temperature dependencies $B(T)$ and $G(T)$ are presented in Fig. 2. It is interesting that the $G$ modulus is almost insensitive to the sc-to-fcc structure transition, whereas the $B$ modulus changes dramatically. For the glassy state the temperature derivatives of both $G$ and $B$ are lower than those for the sc structure. The picture of the change of $B$ during the sc-to-fcc transition at $p=0.05$ GPa (close to atmospheric pressure) is qualitatively similar to the dependence from Ref. [2] for normal pressure.

Figure 3 shows our points of phase transitions established from the anomalies in the pressure and temperature dependencies of ultrasonic wave velocities. One can see a good agreement with the phase diagram previously proposed [3]. Typical anomalies of the ultrasound wave velocities at fcc-to-sc phase transition are shown in the inset in Fig. 3. In Figs. 1 and 2 one can see the examples of the corresponding anomalies for the elastic moduli, where for the bulk modulus the effects are much more pronounced. The hysteresis value of the pressure dependencies of ultrasound velocities (under compression and following decompression) was certainly lower than the transition width (see the inset in Fig. 3 and horizontal bars in the main part of Fig. 3). Also the anomalies at higher pressures were found. The points near the dashed line in Fig. 3 correspond to jumps in the pressure derivatives of sound velocities and volume. For example, the value of $(\partial V / \partial p)_{T=285K}$ derivative changes from $\approx 0.64$ (before the transition) to $\approx 0.45$ (after the transition). As regards the “isobaric points” at low temperatures ($\approx 100$ K), the temperatures correspond to the upper boundary of transition from the
glassy state to sc-phase. These points were determined as points of finalization of derivative changes of sound velocities and/or volume (see examples in Figs. 1 and 2).

The C\textsubscript{60} elastic moduli can be analyzed with respect to a simple central intermolecular potential (see, e.g., Ref. [14]). For the case of the \(m-n\) power potential \(U(V)=A/V^m-B/V^n\) (here, \(A, B, m, \) and \(n\) are constants), it is well known that the pressure derivative of the bulk modulus equals \(B'_p=m+n+2\) [16]. For the Lennard-Jones form of this potential, \(U(r)=\alpha/r^6-\beta/r^12\) (\(r\) is the intermolecular distance), we have \(B'_p=(a+b)/3+2\). For different sets of the \(a-b\) parameters approximated for molecular C\textsubscript{60} [14,17], we can obtain \(B'_p\approx19–21\), which is somewhat lower than the observed values in the current work. One can suppose that the difference between experimental and calculated values results from non-central contributions to the intermolecular potential and possibly from a stronger contribution of the repulsion part to the central potential under pressure. The first assumption can be easily verified. For the pure central interatomic (intermolecular in our case) potential, the Cauchy relation for the elastic constants under pressure [18] gives the following relation for the elastic moduli [19], \(G=(3B–6p)/5\), where \(G\) is the shear modulus calculated by the Voigt’s method. For cubically symmetric crystals the Voigt’s and real shear moduli are usually quite close.

![Figure 3](image_url). Phase diagram of C\textsubscript{60}. Inset: typical dependencies of longitudinal (\(v_l\)) and transverse (\(v_t\)) wave velocities.

For our experimental data, the experimental values of the shear modulus near room pressure are by \(\approx1.5\) times lower than those calculated from the bulk modulus for the central potential (for different temperatures). Moreover, the relation between the pressure derivatives of the elastic moduli for the central potential, \(G'_p=(3B'_p–6)/5\), is not valid for our experimental data either. Indeed, \(G'_p=3.2–4.3\) for the sc phase at different temperatures and pressures up to 1 GPa, while \((3B'_p–6)/5\approx15\) (or 9 if \(B'_p\) is calculated from the \(m-n\) potential). This means that the negative contribution of non-central forces to the shear modulus significantly increases with pressure. We suppose that this negative non-central contribution is associated with mutual intramolecular deformations due to their interaction. These deformations make easier any elastic shear deformation that provides additional ways for energy relaxations of the intramolecular deformations.

4. Conclusions
We present the study of the elastic moduli of polycrystalline fullerite C\textsubscript{60} at pressures up to 1.4 GPa and at temperatures from \(\approx80\) K to room temperature by an ultrasonic technique, which ensures quite
accurate direct determination of the elastic properties. The obtained values of the bulk and shear moduli and their pressure derivatives allow us to determine a considerable contribution of non-central intermolecular forces increasing with pressure.

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