Elastic properties of fullerites $C_{60}$ and $C_{70}$ under pressure

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Abstract. Here we present a study of the elastic moduli of polycrystalline fullerites $C_{60}$ and $C_{70}$ in the temperature range 77–340 K at pressures up to 2.5 GPa using an improved ultrasonic technique. The comparison of the isothermal (quasistatic) and adiabatic (ultrasonic) bulk moduli has been realized for these fullerites. We have also shown the considerable difference in elasticity under pressure for fullerites $C_{60}$ and $C_{70}$.

1. Introduction
Elastic properties of the most stable quasi-spherical fullerites $C_{60}$ and $C_{70}$ are subjects of numerous studies. Specificity of fullerite compressibility and complexity of a high pressure experiments hinder complete understanding of fullerites behavior under pressure and as a result, the data on elastic properties under pressure are scanty or contradictory [1]. Using an improved high pressure ultrasonic technique we have enhanced the experimental data on elastic properties of fullerite $C_{60}$ that have been reported earlier as a preliminary [2]. Scant information on elastic properties of fullerite $C_{70}$ has been supplemented with new data. The pressure range was expanded up to 2.5 GPa. The present work deals with the elastic characteristics of $C_{60}$ and $C_{70}$ under pressure and the changes in these characteristics during phase transitions.

2. Experimental details
The studied samples were cylinders of 6-10 mm in height and 16 mm in diameter. Initial compaction of the fullerite powder to obtain polycrystalline samples was made at air-free conditions. The pressure cell used in the experiments was of a piston-cylinder type. The measurements were carried out using an ultrasonic piezometer in the pressure–temperature range up to 2.5 GPa and 77–340 K [3]. The measurements of the travel time of ultrasonic wave using up-to-date equipment and data processing methods (including the correlation analysis of sound pulses [4]) resulted in accurate pressure and temperature dependencies of the longitudinal and transversal wave velocities in $C_{60}$ and $C_{70}$. The bulk and shear moduli were determined in the approximation of isotropic medium.

3. Results and discussion
Novel direct measurements of ultrasonic wave traveltime and the sample compressibility have resulted in an extension of the pressure range for the data on ultrasound velocities $v_l(p)$ and $v_t(p)$. Anomalies in the dependencies were identified as the fcc-to-sc and sc-to-glass phase transitions and are in good agreement with the known phase diagram of the fullerite $C_{60}$ [1].

Pressure dependencies of the bulk $B(p)$ and shear $G(p)$ moduli of fullerite $C_{60}$ are presented in Fig. 1. Values of bulk and shear moduli and their derivatives were analyzed with regard to the simple
central intermolecular potential. In the case of the \( m-n \) power potential, the pressure derivative of the bulk modulus for the fcc phase \((B'_p\approx19–21\text{ for different sets of parameters [5]})\) is lower than the observed values in the current work \((B'_p\approx29)\). However, for simple cubic (sc) modification of \( \text{C}_{60} \) the experimental value \( B'_p\approx29\) is quite close to the theoretical prediction. The difference between experimental and calculated values can be caused by non-central contributions to the intermolecular potential and possibly by a stronger contribution of the repulsion part to the central potential under pressure. The non-central features of the intermolecular potential in \( \text{C}_{60} \) can be verified using the fundamental Cauchy relation under pressure [6]. Particularly, from these relations one can find for the elastic constants of a system with only central interparticle forces and for pressure derivatives of the elastic constants [7]:

\[
G = \frac{3B - 6p}{5} \quad \text{and} \quad G' = \frac{3B'_p - 6}{5},
\]

respectively. At normal pressure a theoretical shear modulus is 50% larger. Moreover, the relation between pressure derivatives for the central potential \(-G'_p = \frac{3B'_p - 6}{5}\) does not coincide with the experimental one. In fact, the experimental derivatives \(B'_p\approx21.5\) and \(G'_p\approx3.6÷7.6\) for the sc phase at different temperatures and pressures up to 1 GPa (see Fig. 1), whereas the expression \(\frac{3B'_p - 6}{5}\) gives \(\approx11.7\) (or 10 calculated for the \( m-n \) power potential). Thereby, a significant increase of the negative contribution of the non-central forces to the shear modulus under pressure is determined from the quantitative analysis of experimental data (Fig. 1). This negative non-central contribution is associated with intramolecular deformations caused by molecular interactions under pressure. The distortions of the molecules relieve shear deformations as they make possible the relaxation of the intramolecular deformation energy.

![Figure 1. Pressure dependencies of the bulk \( B(p) \) and shear \( G(p) \) moduli of \( \text{C}_{60} \) at different temperatures.](image)

![Figure 2. Experimental isothermal and adiabatic bulk moduli for \( \text{C}_{60} \) at 295 K compared to previous data [8,9].](image)

The independent measurements of the ultrasonic velocity and sample volume allowed the comparison of ultrasonic adiabatic \((B_{\text{adi}})\) and isothermal quasistatic \((B_{\text{iso}})\) bulk moduli:

\[
B_{\text{adi}} = \rho V_o^2 \quad \text{and} \quad B_{\text{iso}} = -\frac{V}{V_o} \left( \frac{\partial(V/V_o)}{\partial p} \right)^{-1}.
\]

Behavior of \(B_{\text{adi}}(p)\) and \(B_{\text{iso}}(p)\) dependencies for fullerite \( \text{C}_{60} \) differ appreciably (Fig. 2), although the thermodynamic difference calculated from the empirical intermolecular central potential is less than
Dependence $B_T(p)$ is in good agreement with data of previous studies [8,9], while pressure derivative of $B_S(p)$ is very close to the calculation based on the empirical potential [5]. For comparison, $B'_T(p)\approx 7-9$, while $B'_S(p)\approx 17-22$ at room temperature. This discrepancy of bulk moduli is observed for simple cubic phase at every temperature in the experimental range. Values of $B(p)$ for the fcc phase are close and pressure derivatives nearly coincide in contrast to sc phase. The nature of this difference should be related to some structural process (relaxation). We assume that orientational relation between molecules and the corresponding formation of orientational clusters in the simple cubic phase, as well as molecular deformations in the compressed polycrystalline C$_{60}$ can be responsible for the observed phenomenon.

![Figure 3](image1.png) **Figure 3.** Pressure dependencies of the shear and bulk moduli for C$_{60}$ at 295 K.

![Figure 4](image2.png) **Figure 4.** Pressure dependencies of the Poisson’s ratio for fullerites C$_{60}$ and C$_{70}$ at 295 K.

The preliminary ultrasonic study of fullerite C$_{70}$ reveals that its elasticity behaviour is different from that of C$_{60}$. The dependencies $B(p)$ and $G(p)$ for fullerite C$_{70}$ at 295 K are presented in Fig. 3. Fullerite C$_{70}$ is slightly more compressible than C$_{60}$ and the shear modulus $G_0$ is smaller for C$_{70}$. Figure 3 gives the comparison of the adiabatic bulk modulus under pressure with the isothermal modulus obtained in this work for C$_{70}$. Dependence $B_T(p)$ from the preceding paper [10] is presented as well. These dependencies $B(p)$ show quite similar behaviour and the approximated values of the bulk modulus at normal conditions ($B_0=8.8$ GPa, $B'_0 =18.3$) are close to those known from Ref. [10-12]. In our experiments we did not observe a large initial rise of the bulk modulus reported in Ref. [10] explained by a drop in the volume. The Poisson’s coefficient calculated for a homogeneous medium decreases under pressure from 0.43 to 0.39 at 1.7 GPa (Fig. 4). These values of the Poisson’s coefficient point to a significant contribution of the non-central forces, which decreases under pressure. On the contrary, as stated above for C$_{60}$ contribution of the non-central forces increases with pressure.

4. Conclusions
We present an extended study of the elastic moduli of polycrystalline fullerites C$_{60}$ and C$_{70}$ by a new ultrasonic technique, which provides an accurate direct determination of the elastic properties. The obtained values of the bulk and shear moduli and their pressure derivatives allow us to reveal a considerable contribution of non-central intermolecular forces, which increases for C$_{60}$ and decreases...
for C\textsubscript{70} under compression. Application of an ultrasonic method allowed the comparison of the adiabatic and isothermal bulk moduli, which discrepancy in C\textsubscript{60} is the evidence of complexity of these carbon molecular systems.

**Acknowledgements**

Financial support from The Russian Foundation for Basic Research (Project No. 07-02-01275-a; No. 08-02-00014-a), The Russian Science Support Foundation, and the Programs of the Presidium of Russian Academy of Sciences is gratefully acknowledged.

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