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Elastic and Dissipative Properties of Solid C₆₀

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Abstract. Elastic and dissipative properties of solid C₆₀ in the face centered cubic (fcc) and high pressure induced phases were measured on the same specimens. The high pressure phase was synthesized in our experiments by the thermobaric treatment of specimens at temperature of 350 °C and under pressure of 2 GPa. The structure investigations revealed the origination of the chemical bonding between C₆₀ molecules in that phase. The measurements of attenuation and velocities of longitudinal and transverse sound waves were carried out in the temperature range from 4.2 to 300 K at the frequencies of 5 and 10 MHz by echo pulse and high frequency resonance methods. It was found that the values of elastic moduli of the new phase, measured at room temperature, appeared two times higher and their temperature dependences two times weaker than corresponding ones of the pristine C₆₀. The internal friction spectrum of fcc phase differs significantly from that of hpp phase. The phenomena observed are discussed in terms of model taking into account the formation of polymer chains in the structure of the new pressure-induced phase of solid C₆₀.

1. INTRODUCTION

The experimental study of solid C₆₀ has shown that it normally forms in the face-centered cubic (fcc) phase at ambient conditions which transforms to the simple cubic (sc) phase on cooling below 260 K [1,2,3]. However although C₆₀ molecules are extremely stable at ambient conditions, quasihydrostatic pressure induces transformations to other phases. The new high pressure phases (hpp) are suggested to originate from a different kind of C₆₀ polymerization, that is an origination of sp³ bondings [4,5]. The lowest reported pressure for occurrence of such C₆₀ transformation is about 7 kbar at 620 K. This new phase was retained to ambient conditions and therefore could be investigated by different techniques. The phase was more dense than the pristine solid C₆₀ by at least 8.5% and less compressible. The main feature of the structure which was determined with certainty is the value of the nearest distance between the centers of C₆₀ molecules. It proved to be equal 9.2 Å, that according to calculations [6] means that along this direction the chemical bonding between C₆₀ molecules should occur. This conclusion is confirmed by the fact that this phase is absolutely insoluble in toluene.

This paper presents the results of the experimental studies of elastic and dissipative properties of the solid C₆₀ in the (fcc) and high pressure induced phases measured on the same samples but in the different structural states.

2. EXPERIMENTAL

The measurements were performed on the cylindrical samples of 8 mm diameter and from 2 to 3 mm thick compacted at room temperature by uniaxial compression to ≈1 GPa. A high purity powder obtained by a procedure described elsewhere [4,5,7] was used. The fcc crystal structure (a=14.17 Å) was determined by X-ray diffraction. The grain size was about 1 μm and the sample density was ≈1.62 g/mm³. To obtain a new phase the samples were subjected to a thermobaric treatment at the temperature of 620 K and pressure of 2 GPa followed by quenching under pressure to room temperature. The X-ray diffraction patterns of all specimens thus obtained corresponded to the new high pressure phase [5,8]. The grain size was ≈1 μm and the sample density was about 1.76 g/cm³.

Two acoustic techniques were used to determine the elastic moduli. The longitudinal and transverse sound velocities, v_L and v_S , were measured at room temperature with the accuracy of

$\approx 2\%$ using echo-pulse method modified for the small specimens. A high-frequency resonance method [7] was applied to measure an attenuation and the relative sound velocity change in dependence on temperature. The measurements were performed with LiNbO_3 transducers at frequencies of ≈ 5 and ≈ 10 MHz.

The longitudinal and shear moduli, C_L and G , were calculated from the sound velocities according to the well-known relations: $C_L = \rho v_L^2$ and $G = \rho v_S^2$. Other moduli, i.e. bulk modulus K , Young's modulus E and Poisson's ratio ν , were obtained from relations between the elastic moduli of an isotropic medium: $K = C_L - (4/3)G$, $\nu = (C_L - 2G)/(2C_L - 2G)$ and $E = 2G(1 + \nu)$.

3. RESULTS

In the Table the experimentally determined elastic moduli for the fcc phase and for the hpp of C_{60} are presented. These results were obtained on the same samples in different structural states. Here the elastic moduli of solid C_{60} calculated [9] on the basis of a modified Buckingham potential also are given. The theoretical values of K , E and G were obtained by Hill's averaging [10] for the elastic constants calculated for fcc structure of C_{60} [9].

Table

The experimentally measured and calculated elastic moduli of solid C_{60} (300 K).

	E, GPa	K, GPa	G, GPa	
fcc phase	13.4	9.0	5.4	theory [9]
fcc phase	9.8	8.4	3.8	experiment
new phase	25.2	23.8	9.5	experiment

The temperature dependences of the velocity $V_L(T)$ and internal friction $Q^{-1}(T)$ in the sample with fcc structure measured at 5 and 10 MHz are shown in the Fig.1. Two internal friction peaks at 250 K and 210 K at 5 MHz and corresponding changes in velocities are observed.

The temperature dependences of the internal friction Q^{-1} and the longitudinal sound wave velocity for pressure-induced phase are presented in Fig.2. There are no noticeable changes in $V_L(T)$ and $Q^{-1}(T)$ near the temperature of 250 K where orientational ordering transition occurs in the case of pristine phase of solid C_{60} . Some peculiarities of internal friction spectrum and corresponding velocity changes at ≈ 180 and ≈ 220 K are observed. One can see an influence of the measurement frequency on the high temperature part of the internal friction spectrum.

There is also a broad internal friction peak near 80 K.

The full change of sound velocity between 300 and 4.2 K for the new phase was about 12% for longitudinal and about 17% for transverse sound wave. Thus the temperature dependence of elastic moduli for the new phase is about two times weaker than that is for the fcc-sc phase.

4. DISCUSSION

Let us consider the results obtained taking into account the preliminary data on structure of the hpp-phase [8]. As one can see from the Table the elastic moduli of the C_{60} fcc phase are in a good agreement with the theoretical ones, which were calculated on the basis of the intermolecular potentials. However the elastic moduli of the C_{60} hpp phase are two and a half times higher than corresponding ones for the pristine fcc phase. It means that the new hpp phase lattice of solid C_{60} is much stiffer than fcc phase lattice which agrees well with the suggestion as to the origination of sp^3 bonding. This conclusion is confirmed also by the comparison of the temperature dependences of elastic moduli of fcc and hpp phase. The temperature dependence is about two times weaker in hpp phase than in fcc one which is also in favour of the assumption made.

The temperature dependences of internal friction and sound velocity variation in the fcc phase specimens are very similar to those obtained for fcc single crystals [10,12]. The peak at $T = 250$ K does not depend on the frequency and its temperature coincides with the temperature of the ordering phase transition from fcc to sc described elsewhere [1,2,3].

The second peak observed at $T = 210$ K depends strongly on the frequency and the $V(T)$ curves manifest distinctive variations near the peak temperature. This peak can be described by the Debye relaxation process with the activation parameters: $U \approx 0.3$ eV and $\tau_0 \approx 10^{-14}$ s, where U is the activation energy of the process and τ is the relaxation time. It is considered that this relaxation process is due to the reorientation jumping of the C_{60} molecules between different orientations in the sc lattice.

Fig.1: Temperature dependences of internal friction in fcc-sc phase of C_{60} at the frequencies of 5 MHz (circles) and 10 MHz (full triangles) and the corresponding variation of sound wave velocity (5 MHz). Longitudinal waves.

Fig.2: Temperature dependences of internal friction and the corresponding sound velocity variation in the pressure-induced phase of C_{60} . Longitudinal waves. Circles and squares - 5 MHz, full and empty triangles - 10 MHz.

The temperature dependences of internal friction and sound wave changes for hpp phase differ significantly from those for fcc phase. There are no distinctive peaks; nevertheless one can consider the internal friction spectrum $Q^{-1}(T)$ as a superposition of a number of the separate peaks. The fact that the variation of frequency influences part of the internal friction spectra (a shift to high temperature when frequency increases, Fig.2) allows us to assume a relaxation nature of some internal friction peaks which are components of the spectrum. A rough estimation of the possible relaxations parameters give the energy activation U values from 0.2 to 0.3 eV and the relaxation time τ_0 from 10^{-13} to 10^{-14} s.

One of the probable explanations of the internal friction found in C_{60} hpp samples is most likely to be connected with those changes in the lattice structure that have occurred under high pressure. X-ray and neutron diffraction measurements show that high pressure transforms C_{60} fcc lattice to an orthorhombic one where each molecule is bonded to the two nearest neighbours along a [100] fcc direction forming parallel chains. By analogy with crystalline polymers one can propose that in such structure different kinds of temperature dependent rotation mobility of the polymer chains are possible that can lead to relaxation phenomena and internal friction peaks correspondingly. However the relaxation times of relaxation processes in conventional crystalline polymers are much larger than those found in the present experiments. To overcome this discrepancy one has to assume the existence of a number of short (less than 10 nm) freely rotating (around polymer axis) polymer segments. Such assumption does not seem unrealistic taking into account imperfect conditions of the polymerization process that can lead to terminated polymer chains. Thus the polymer structure formed will differ from an ideal one by a great number of uncorrelated ruptures of chemical bonds. In that case the structure will consist of polymer segments of different lengths having the ability for rotation movement. One of the way to examine the assumption made is to study the samples subjected to different kinds of the heat treatments.

As to the low temperature (below 100 K) acoustic anomalies, if the approach given above is valid, they can be connected to the orientational "glass-like" transition due to the "freezing" of the rotation motion.

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