

Elastic properties of a van der Waals solid: C_{60}

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The elastic response (Young's modulus and internal friction) of solid C_{60} has been measured in single-crystal specimens as a function of temperature. We determine a Debye temperature of ~ 100 K and a room-temperature Young's modulus of $2.0 \pm 0.5 \times 10^{11}$ dyn/cm². The elastic properties are strongly anharmonic and indicate phase transitions at ~ 150 and ~ 269 K.

The spectacular electronic and chemical properties of molecular and solid C_{60} have prompted intense interest in this material. Solid C_{60} is particularly intriguing because the nearly spherical molecules are only weakly bound by van der Waals (vdW) forces. In undoped material, the C_{60} molecules rotate^{1,2} for temperatures (T) greater than 100 K and are arranged on a face-centered-cubic (fcc) lattice at room temperature.³ At 259 K, a fcc to simple cubic (sc) transition occurs indicating that some of the orientations become correlated.⁴ Elastic properties are an important tool in investigating any material because they both probe the harmonic and anharmonic components of the intermolecular potential and are extremely sensitive to phase transitions. A bulk modulus study has confirmed the weak nature of the intermolecular bonding.⁵ Here, we present the results of our study of the effect of temperature on the elastic properties of crystalline C_{60} . We determine a Debye temperature θ_D , of ~ 100 K, a room-temperature Young's modulus $Y_{RT} = 2.0 \pm 0.5 \times 10^{11}$ dyn/cm², and see evidence for phase transitions and substantial anharmonicity in the intermolecular potentials. The anharmonicity is compared to that of the rare-gas solids.

We produce the C_{60} crystals using a process in which they crystallize as needlelike parallelepipeds (typical dimensions: $500 \mu\text{m} \times 100 \mu\text{m}^2$) in a saturated solution of toluene and hexane at room temperature. Our x-ray results confirm a fcc, though twinned, structure for these crystals. Raman studies find no residual solvent to ~ 0.5 mol %. For the elasticity experiments, we employ a vibrating reed technique⁶ in which the flexural resonant frequency f and damping δ of a crystal are monitored as a function of temperature T . The Young's modulus Y is proportional to f^2 and $\delta = \Delta/f$, where Δ is the full width at half maximum of the resonance. One end of the beam-like sample is rigidly affixed to a piezoelectric transducer which excites flexural vibrations. Movements of the free end of the sample are detected capacitively using a rf technique described elsewhere.⁷

Because undoped C_{60} is insulating, a thin film of gold was sputtered on one side of the crystal to allow transmission of the rf carrier signal. Film thicknesses were varied from 250 to 1000 Å with no substantial change in the magnitude or temperature dependence of

the Young's modulus. This technique can determine relative changes in $Y(T)$ to 1 ppm; however, because of sensitivity to sample geometry, it provides only an estimate of the absolute magnitude of Y . Using data from four samples, we find that the room-temperature Young's modulus $Y_{RT} = 2.0 \pm 0.5 \times 10^{11}$ dyn/cm². To provide good thermal contact, the sample is cooled in a He environment of ~ 1 Torr with typical warming and cooling rates of ~ 1 – 2 K/min. Piezoelectric drive amplitudes were varied from 1 to 12 Å with no noticeable change in the resonant frequencies or damping. To ensure that the beam oscillations occurred in the linear regime, we operated the piezoelectric drive at ~ 1 Å at room temperature and ~ 0.02 Å for $T < 70$ K.

In Fig. 1, we plot $Y(T)$ and $\delta(T)$ for one sample; similar $Y(T)$ and $\delta(T)$ are seen for each of the five samples tested. Changes in Y are referenced to $Y_0 = Y(6 \text{ K})$. The

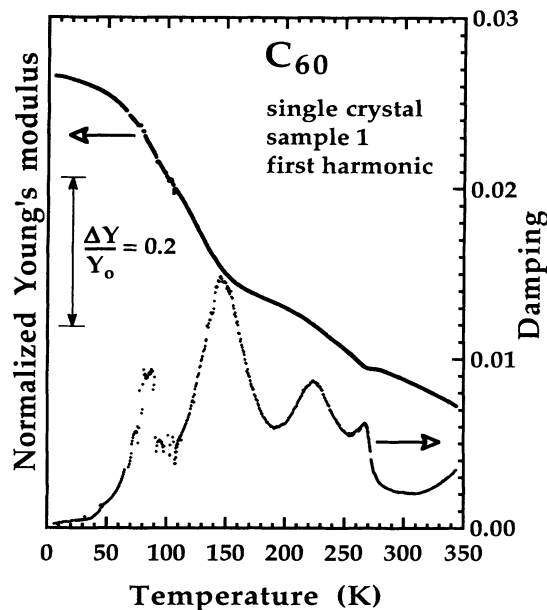


FIG. 1. The Young's modulus (Y) and damping (δ) are plotted as functions of temperature for the high-frequency mode of sample 1. Changes in Y are referenced to its low-temperature value $Y_0 = Y(6 \text{ K})$. $\Delta Y = Y - Y_0$.

43% change in Y from 6 to 300 K, a huge decrease, is much larger than for most elemental solids. Several additional features are striking. The critical softening in Y and increase in δ clearly indicate that the fcc-sc phase transition T_{fcc} couples to uniaxial strains. For our samples, the peaks in Y and δ occur at $269 \text{ K} \pm 1 \text{ K}$. An expanded view of this region is shown in Fig. 2. Upon cooling further, the damping increases with decreasing temperature with one peak at $\sim 225 \text{ K}$ and a second stronger peak at $\sim 150 \text{ K}$, suggesting that the sc phase has several relaxation mechanisms to which uniaxial strain can couple. In this same regime, Y is concave downward and a sharp upturn occurs at 150 K . The scatter in Y and δ seen from 85 to 110 K occurs in all samples and may indicate a structural instability. In particular, the size of the 85 K anomaly in δ is not reproducible from sample to sample or even for successive runs of a given sample. In all the samples, the warming and cooling curves for Y , except in the region $85\text{--}110 \text{ K}$, were identical within 100 ppm . Wachtman determined that for many oxides the Young's modulus is well fitted to $Y(T) = [1 - bT \exp(-T_0/T)]Y(0)$, where b depends on the strength of the anharmonic terms of the interatomic potential, $Y(0)$ is the Y at 0 K , and T_0 is the characteristic T of the phonon spectrum ($T_0 \approx \theta_D/2$).⁸ This expression⁹ arises naturally with the assumption that the effect of anharmonicity is small relative to the harmonic contribution to $Y(T)$, which holds for our data in the region $T < 120 \text{ K}$. Upon expanding the exponential for high T , we see that T_0 is the temperature where the high- T linear form of $Y(T)$ intercepts $Y = Y(0)$. Using the linear portion of $Y(T)$ between 120 and 80 K , we estimate a θ_D of $\sim 100 \text{ K}$. This represents the intermolecular phonon modes and agrees well with Debye temperatures calculated from specific heat and thermal conductivity measurements.^{10,11}

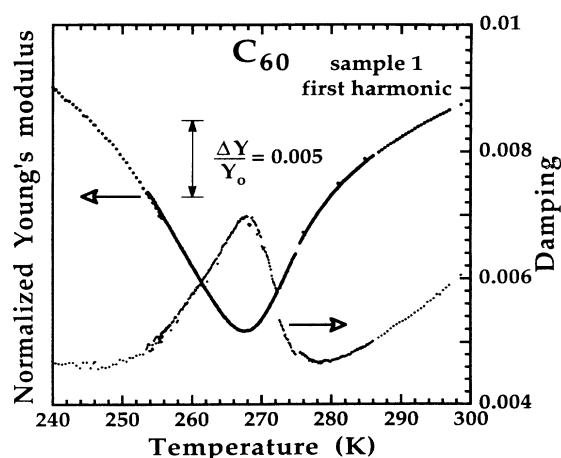


FIG. 2. Experimental data for the Young's modulus (Y) and damping (δ) are plotted as functions of temperature in the region of the fcc-sc phase transition for sample 1. Linear slopes have been subtracted from both curves to highlight their critical behavior. The slopes were fitted with points at 240 and 300 K for Y and at 240 and 280 K for δ . Changes in Y are referenced to its low-temperature value $Y_0 = Y(6 \text{ K})$. $\Delta Y = Y - Y_0$.

To distinguish between the various processes underlying the temperature dependence of Y and δ , we plot $Y(T)$ and $\delta(T)$ for three different flexural modes in Fig. 3. Comparing the first harmonic (No. 1, f_1) and fundamental (No. 1, f_0) damping curves for sample 1, we see that, as is expected for a phase transition, the position of the dissipation peak associated with T_{fcc} does not shift with frequency. The lower peaks, however, do show a frequency-dependent shift, suggesting that the axis of rotation of the C_{60} molecules or the correlation between lattice sites is strain dependent with characteristic frequencies which increase with temperature. Because of the scatter in the data, we were unable to determine the frequency dependence of the damping peak which occurs between 85 and 110 K .

An important question is whether the large anharmonicity evident in the 43% decrease in Y from 6 to 300 K can be explained within the framework of vdW bonding or whether it is necessary to include other mechanisms such as interactions between the π orbitals on the C_{60} surfaces. From x-ray studies, the thermal expansion of C_{60} is 1% between 4 and 300 K .⁴ Assuming that this contraction occurs predominantly in the weak intermolecular vdW bonds, the 1% change in the C_{60} -to- C_{60} spacing (10.1 \AA) (Ref. 12) translates to a 3.26% change in the vdW bond length, a_{vdW} (3.1 \AA).¹³ In rare-gas solids, the best examples of vdW solids with spherical constituent Y decreases by $\sim 12\%$ for each 1% change in the lattice constant caused by either changing T or pressure.¹⁴ Therefore, in terms of a_{vdW} , the 43% decrease in Y seems

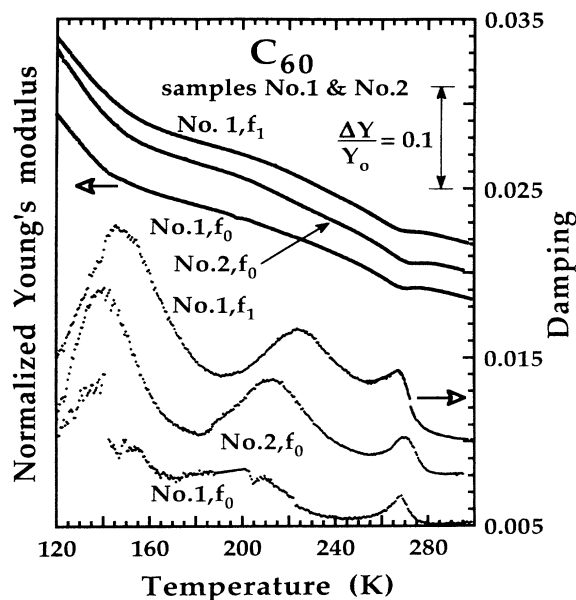


FIG. 3. The Young's modulus (Y) and damping (δ) are plotted as functions of temperature for three different modes, the fundamental (No. 1, f_0) and first harmonic (No. 1, f_1) of sample 1 and the fundamental (No. 2, f_0) of sample 2. At 300 K , the resonant frequencies for modes No. 1, f_0 ; No. 2, f_0 ; and No. 1, f_1 are $12\,344$, $18\,063$, and $77\,800 \text{ Hz}$, respectively. The damping curves No. 2, f_0 and No. 1, f_1 have been vertically offset by 0.005 and 0.008 , respectively.

reasonable. For the rare-gas solids, the elastic properties depend only on the intermolecular spacing.¹⁴ The large increase in Y for a 3.26% decrease in a_{vdw} indicates that an average bulk modulus K_{av} measured in another experiment⁵ at a 14% decrease in a_{vdw} may overestimate the ambient pressure bulk modulus.

This experiment has shown directly that anharmonic terms in the intermolecular potential dominate the room-temperature properties of solid C₆₀. A clear signature of the fcc-to-sc transition is seen near 270 K and additional frequency-dependent anomalies are seen near 150

and 200 K. These results are of great importance in determining both the dynamic properties of C₆₀ molecules imbedded in the solid and the appropriate bonding potentials between the molecules.

Note added. X.D. Shi *et al.*¹⁵ have submitted similar work that confirms the general features of our results.

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