Sound Velocity and Attenuation in Single-Crystal C_{60}

X. D. Shi,(1),(2),(a) A. R. Kortan,(4) J. M. Williams,(3) A. M. Kini,(3) B. M. Savall,(3)
and P. M. Chaikin(2)

(1)*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
(2)*Department of Physics, Princeton University, Princeton, New Jersey 08544*
(3)*Argonne National Laboratory, Argonne, Illinois 60439*
(4)*AT&T Bell Laboratory, 600 Mountain Avenue, Murray Hill, New Jersey 07974*

(Received 20 November 1991)

We report the studies of the elasticity of C_{60} single crystals. For sublimed fcc crystals, Young's modulus has an 8% jump at the first-order transition at 260 K. At ~160 K there is a frequency-dependent elastic anomaly resulting from time-dependent stress relaxation. Comparison with rotation rates seen in NMR suggests that the dynamics below 260 K is more complex than jumps between equivalent molecular configurations. Solvent grown monoclinic crystals have a second-order transition at 242 K, while the 160-K glass transition remains unchanged.

PACS numbers: 62.20.Dc, 61.65.+d, 62.80.+f, 64.70.Kb

The success in efficiently synthesizing C_{60} [1,2] has generated much interest in the physical properties of this new class of molecular crystals. Spectroscopic studies on C_{60} crystals using techniques such as x-ray, NMR, and neutron diffraction have revealed that an orientational-ordering-induced face-centered-cubic (fcc) to simple-cubic (sc) transition occurs at temperatures around 260 K and rotational motions of C_{60} molecules persist to much lower temperatures [3-6]. In this paper we present the first elastic constant measurement on C_{60} single crystals which confirms the first-order nature of the 260-K transition, and shows a dramatic discontinuous change (an 8% stiffening) in the moduli at the transition temperature. Moreover, a frequency-dependent elastic anomaly at 160 K demonstrates that stress relaxation is related to rotational motions of the C_{60} molecules in the orientationally ordered phase. This necessitates a more complex dynamics than envisioned in the NMR experiments with the C_{60} molecules jumping between inequivalent configurations or undergoing collective rotations at low temperatures.

In Fig. 1 we show the temperature dependences of the sound velocity and attenuation in one sublimation-grown C_{60} crystal. The samples, shaped as platelets with typical dimensions of 0.6 mm×0.3 mm×0.2 mm, were grown from slow vaporization of solid C_{60} over a temperature gradient [7]. Their room-temperature structure is pure fcc [8]. We used a modified vibrating-reed technique [9,10] to measure the Young's sound velocity and attenuation. Because of the small physical dimensions of the fcc samples, metal blocks were clamped on the platelet ends. The Young's modulus of the crystal provides the restoring force for the resonance of the block mass. The resonant frequency is proportional to the Young's sound velocity, so that relative changes of the velocity with varying temperatures can be directly measured, but the absolute value depends sensitively on the geometries.

Around room temperature, the sound velocity shows a small maximum at ~290 K. The most dramatic feature in the velocity is the discontinuous jump at 260 K, shown in more detail in Fig. 2. The sharp increase in the velocity v corresponds to a Young's modulus E $(=\rho v^2)$ enhancement of about 8%. (The change in the density of the crystal at the transition has been measured to be less than 1% [11,12]. Therefore, the dominant contribution to the elastic modulus increase comes from the sound velocity.) The first-order nature of the transition is evident both from the abruptness of the transition and from the hysteretic behaviors of the temperature dependences which show a 2.5-K difference between sweeping the temperature up and down across the transition. Another dominant feature is the "anomaly" at about 160 K which does not appear in other measurements such as NMR and x-ray diffraction. At T~160 K, the sound attenua-

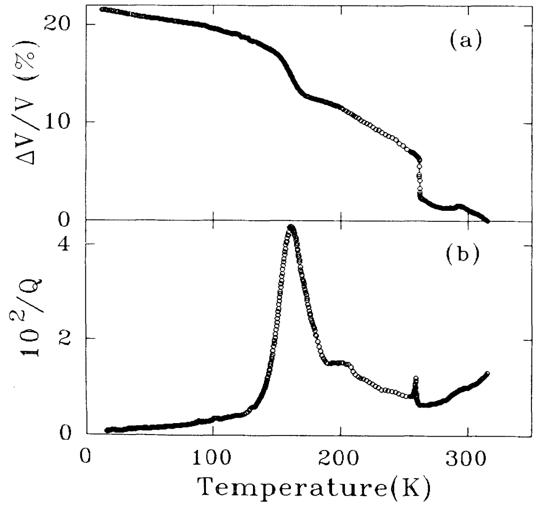

FIG. 1. The temperature dependences of (a) Young's sound velocity and (b) relative sound attenuation in a fcc C_{60} single crystal grown from sublimation. $\Delta V/V$ stands for relative change in velocity normalized to 315 K and Q is the quality of the resonance.

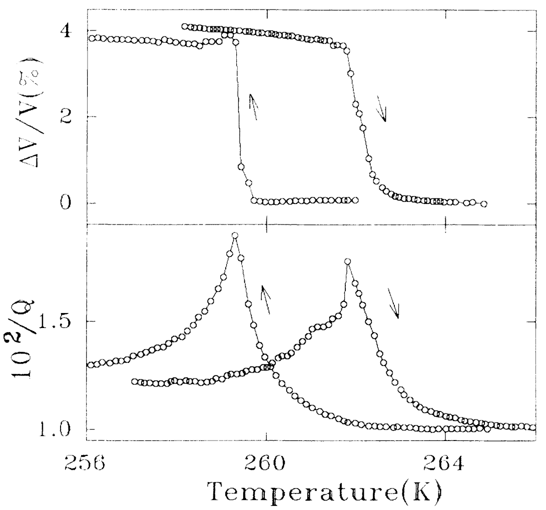

FIG. 2. The sound velocity and attenuation in the fcc C_{60} crystal in the vicinity of the orientational ordering transition at 260 K. The arrows indicate the directions of temperature sweeps.

tion shows a peak 10 times more intense than that at the 260-K transition, and the velocity shows a gradual enhancement upon cooling amounting to about a 7% increase in the elastic modulus. Most significantly, we found that the temperatures where the attenuation maxima occur are frequency dependent—the peak shifted to a 5-K lower temperature as the measurement frequency was changed from about 20 to 10 kHz.

The 8% increase in the Young's modulus at 260 K is a very dramatic value for the orientational ordering of C_{60} molecules which have such extremely high symmetry. It is very difficult for the van der Waals interaction alone to account for a modulus change of such magnitude. As has been suggested [6], the "donor-acceptor-like" interaction plays a very important role for the C_{60} molecules to choose the preferred configurations in the lattice. Since the elastic modulus effectively measures the interaction energy of the crystalline system, our finding indicates a very significant change in the strength of the interactions with the onset of the C_{60} molecules' orientational ordering. The result should provide a guide to theoretical studies and molecular-dynamics simulations of the interactions in the C_{60} crystalline lattice.

Frequency dependences of sound velocity and attenuation are very typical in systems with strong dynamical relaxations. A system is less rigid when probed on time scales that are longer compared to a stress relaxation time τ than on short time scales. Similarly the dissipation is maximum when the probing frequency is close to $1/\tau$ [13]. The 160-K anomaly resembles such a relaxation process in many aspects. If the stress relaxation rate is temperature dependent and slows through our measurement frequency with decreasing temperature, then we should observe a peak in attenuation and a crossover to a higher sound velocity. This is the characteristic behavior observed in traversing a glass transition. Assuming an activated behavior for $1/\tau$,

$$1/\tau=(1/\tau_0)e^{-U/kT}, \tag{1}$$

we can use the positions of the attenuation peaks at $T\sim 160$ K with respect to different measurement frequencies to estimate U and τ_0. For two fcc crystals, attenuation peaks occurred at $T=154\pm 1$ and 160 ± 1 K for $f=10.73$ and 21.40 kHz, respectively. Using Eq. (1), we obtain $U/k\sim 2800$ K and $1/\tau_0\sim 1.4\times 10^{13}\ \text{sec}^{-1}$.

For this relaxational model the frequency dependence of the sound velocity is [13]

$$\frac{1}{v^2}=\frac{1}{v_0^2}+\left(\frac{1}{v_\infty^2}-\frac{1}{v_0^2}\right)\frac{(\omega\tau)^2}{(\omega\tau)^2+1}, \tag{2}$$

where ω is the measurement frequency; v_0 denotes the zero-frequency ("equilibrium") velocity, which results when the system has time to relax to its equilibrium state, and v_∞ is the infinite-frequency ("frozen") velocity, which describes any stress that varies too fast for the system to follow. Our experiments are carried out with the measurement frequency fixed, while the relaxation rates of the system change with temperatures according to Eq. (1). For temperature $T>170$ K where the molecules respond to any stress at very high frequencies, we have $\omega\tau\ll 1$; therefore the measured v is equivalent to v_0. For $T<150$ K, the slowing down of the relaxation makes $\omega\tau\gg 1$; thus we effectively measure v_∞. In the relatively narrow temperature range between 150 and 170 K, where $\omega\tau$ falls in the vicinity of unity, we expect to see the most significant enhancement in the sound velocity as v crosses over from v_0 to v_∞. Equation (2) can be rewritten as

$$(\omega\tau)^2=\frac{v^2/v_0^2-1}{1-v^2/v_\infty^2}. \tag{3}$$

Fitting the high-temperature data (between 170 and 260 K) to $v_0^2(T)=a+bT^2+cT^4+\cdots$ and the low-temperature data to $v_\infty^2(T)=a'+b'T^2+c'T^4+\cdots$, we can experimentally determine $\omega\tau$. In Fig. 3 we plot $\ln[(v^2/v_0^2-1)/(1-v_\infty^2/v^2)]^{1/2}$ vs $1/T$, which gives us $U/k=3400$ K and $1/\tau_0=2.3\times 10^{14}\ \text{sec}^{-1}$. These values are consistent with those given by the attenuation peaks within experiment uncertainty and comparable to the NMR results [4].

One of the most widely adopted microscopic pictures for the C_{60} molecules below the orientational transition has been that the first-order transition at 260 K removes all of the rotational degrees of freedom of the molecules except for those jump rotations between symmetry equivalent orientations [4]. The frequency of the rotational motion was found to obey an activated form with typical values on the order of 10–100 kHz at about 160 K [4,5], which coincides with our measurement frequencies. Now that we can conclude that the observed 160-K anomaly bears the same origin as the phenomena causing

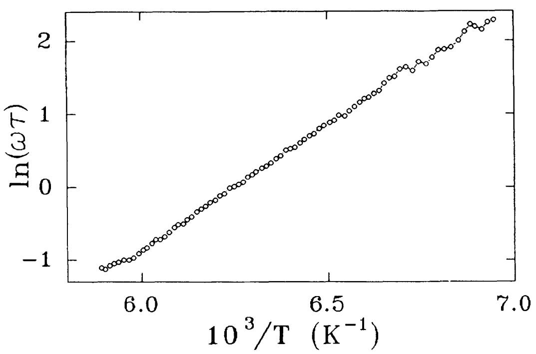

FIG. 3. ln(ωτ), given by Eq. (3), vs $1/T$ for temperature near 160 K. The slope gives the activation energy $U/k = 3400$ K.

the motional narrowing in NMR experiments, we find that the physical picture given for the C_{60} molecules below 260 K, that they jump only between symmetry equivalent configurations, would not explain the frequency dependence in the sound velocity and attenuation. The essence of the elastic relaxational model is that τ is the time to relax from a higher to a lower stress configuration. The instantaneous rotations from one orientation to another completely equivalent orientation will not give rise to any change in the interaction energy between the C_{60} molecules. Therefore, the stress before and after the jump is the same. In order for the stress induced by the propagating sound in the lattice to be relieved and the free energy of the system upon stress minimized, the system must be able to relax to *inequivalent* configurations. An interesting possibility is that collective effects such as the motion of a domain wall separating two of the four equivalent simple-cubic domains are responsible for both the molecular rotations and the stress relaxation. However, a more straightforward interpretation would be that there is more than one energetically favorable orientation for the C_{60} molecules below the 260-K transition. Thus at $T > 0$, C_{60} molecules are tunneling between both energy equivalent and nearly energy equivalent states with transition rates following an activated temperature dependence. There is a recent neutron experiment that suggests the possible existence of multilocal energy minimums at different orientational angles for the C_{60} molecules at low temperatures [12]. These may be the inequivalent states required for the elastic anomaly.

It is important to understand the C_{60} crystals with different structures since the superconductivity in the doped fullerenes are greatly affected by the lattice symmetries. It would also be very interesting to see how the orientational ordering takes place in the crystals with much lower symmetry than the fcc. C_{60} crystals can be grown from slow diffusion of solvent vapors such as carbon disulfide (CS_2) or pentane into C_{60} solutions [14]. Crystals thus grown are needle shaped with typical dimensions of about 1.5 mm×0.05 mm×0.05 mm. While it has been shown that crystals grown from pentane have a non-close-packed structure of a twinned-monoclinic cell with three-dimensional long-range translational order [7,14], it was also suggested that it may be possible to stabilize the fcc symmetry in the CS_2-grown crystals by heating the samples to above 200 °C [15]. In Fig. 4 we show the temperature dependences of the sound velocity and attenuation in one CS_2-solvated C_{60} crystal both prior to and after being heated to above 200 °C. C_{60} crystals grown from pentane, without any heat treatment, show almost identical temperature dependences both in velocity and attenuation to that of the *heated* CS_2-grown crystals, suggesting that they share the same twinned-monoclinic structure.

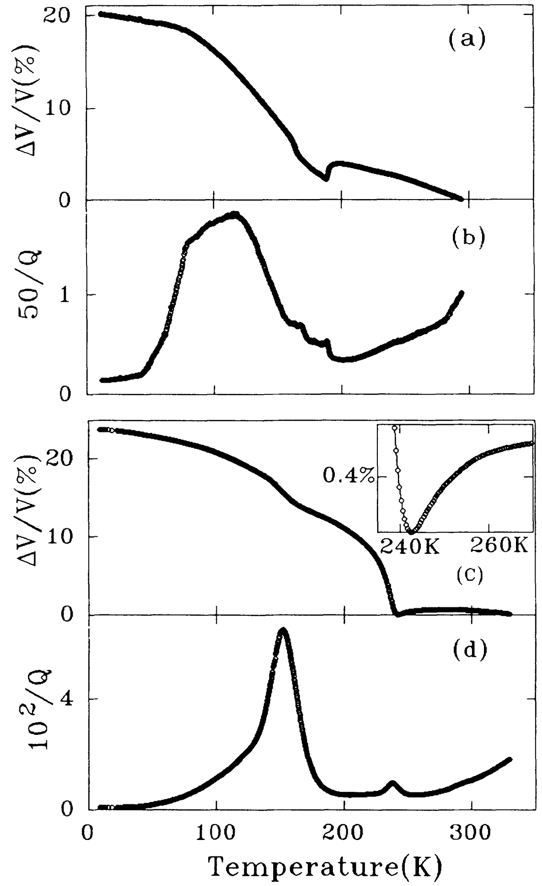

FIG. 4. The temperature dependences of sound velocity and attenuation in a monoclinic C_{60} crystal grown from CS_2 solvent. (a),(b) *Prior* to heating; (c),(d) *After* the crystal has been heated to above 200 °C. The inset in (c) shows the sound velocity near the 242-K transition.

From the measured resonant frequencies (~10 kHz) and the dimensions of the samples, the Young's modulus of the solvated crystals is determined to be $E = 1.59 \times 10^{10}$ N/m^2 at room temperature, very close to the compressibility result [16] and comparable to the modulus of graphite. The very dramatic increase of the modulus in the heated samples which starts at 242 K is shown in detail in the inset in Fig. 4(c). Even though the velocity enhancement is dramatic, it is nevertheless not a discontinuous jump as was seen in the sublimation-grown C_{60} crystals; furthermore, hysteresis in the temperature dependences is absent, suggesting the second-order nature of the transition. The gradual softening of the modulus preceding 242 K is another signature of a second-order transition from the Buckingham-Fairbank relationship $\Delta E \sim -\Delta C_p(dT_c/dP)^2$, where ΔC_p is the specific-heat change at the transition [17]. For $T < 220$ K, the behaviors of both the sound velocity and attenuation, especially the anomaly at ~ 160 K, are very similar to that in sublimed fcc crystals. Since the monoclinic structure can be treated as a distorted fcc lattice, we might expect some similarities in the orientational ordering and freezing process between the two systems. From the proximity of the $\sim$250-K transitions and the coincidence of the 160-K anomalies, it can be speculated that the 242-K transition is also from orientational ordering and that the 160-K feature is a relaxational crossover.

In summary, we have observed that C_{60} crystals with fcc symmetry show a 8% discontinuous increase in their elastic constant at 260 K, which is related to the first-order transition to an orientationally ordered sc lattice. The jump in the elastic modulus sets a scale for the change in the interaction energies between the C_{60} molecules upon the transition from effectively spherical to anisotropic configurations. The elastic anomaly at $T \sim 160$ K is associated with the "freezing" of a stress relaxation mechanism with an activated characteristic rate. It may correspond to C_{60} jumping between *inequivalent* orientations. The typical relaxation frequency is about 20 kHz at 160 K. Heating the solvated crystals does not yield crystals with the same elastic response as the sublimed fcc crystals. In the monoclinic C_{60} samples, the orientational ordering transition is of second-order nature and the frequency-dependent 160-K anomaly resembles that in the fcc crystals.

We are appreciative to J. E. Fischer, R. M. Fleming, A. B. Harris, P. A. Heiney, E. J. Mele, R. Tycko, C. C. Wan, and H. X. Wang for many helpful discussions. This work is supported by the NSF under Grant No. DMR 88-22532 at Princeton and by DOE Office of Basic Energy Sciences, Department of Material Sciences under Contract No. W-31-109-ENG-38 at Argonne. B.M.S. acknowledges support from the Argonne Educational Programs.

[a] Correspondence should be sent to the Princeton address.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[3] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. J. Denenstein, J. P. McCauley, Jr., and A. B. Smith, III, Phys. Rev. Lett. **66**, 2911 (1991).

[4] R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhiji, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).

[5] C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, J. Phys. Chem. **95**, 9 (1991).

[6] W. I. F. David, R. M. Ibberson, J. C. Mathewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton, Nature (London) **353**, 147 (1991).

[7] R. M. Fleming, B. Hessen, T. Siegrist, A. R. Kortan, P. Marsh, R. Tycko, G. Dabbagh, and R. C. Haddon, in *Large Carbon Clusters*, edited by G. S. Hammond and V. J. Kuck (American Chemical Society, Washington, DC, 1991).

[8] R. M. Fleming, T. Siegrist, P. M. Marsh, B. Hessen, A. R. Kortan, D. W. Murphy, R. C. Haddon, R. Tycko, G. Dabbagh, A. M. Mujsce, M. L. Kaplan, and S. M. Zahurak, Mater. Res. Soc. Symp. Proc. **206** (1991).

[9] X. D. Shi, R. C. Yu, Z. Z. Wang, N. P. Ong, and P. M. Chaikin, Phys. Rev. B **39**, 827 (1989), and references therein.

[10] X. D. Shi, Ph.D. thesis, University of Pennsylvania (unpublished).

[11] P. A. Heiney, G. B. M. Vaughan, J. E. Fischer, N. Coustel, D. E. Cox, J. R. D. Copley, D. A. Neumann, W. A. Kamitakahara, K. M. Creegan, D. M. Cox, J. P. McCauley, Jr., and A. B. Smith, III, Phys. Rev. B (to be published).

[12] W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides (to be published).

[13] K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959).

[14] R. M. Fleming, A. R. Kortan, B. Hessen, T. Siegrist, F. A. Thiel, P. Marsh, R. C. Haddon, R. Tycko, G. Dabbagh, M. L. Kaplan, and A. M. Mujsce, Phys. Rev. B **44**, 888 (1991).

[15] Y. Murayama, University of Pennsylvania workshop on C_{60} (unpublished).

[16] J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. J. Denenstein, J. P. McCauley, Jr., and A. B. Smith, III, Science **252**, 1288 (1991).

[17] M. J. Buckingham and W. M. Fairbank, Prog. Low Temp. Phys. **3**, 80 (1961).