

## Pressure Dependence of the Orientational Ordering in Solid C<sub>60</sub>

G. A. Samara, J. E. Schirber, B. Morosin, L. V. Hansen, D. Loy, and A. P. Sylwester

*Sandia National Laboratories, Albuquerque, New Mexico 87185*

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Pressure studies of the molecular orientational ordering in solid C<sub>60</sub> have exhibited three principal effects: (1) The simple-cubic (sc) to face-centered-cubic (fcc) ordering transition temperature ( $T_c = 249$  K) increases with pressure at a rate of  $10.4 \pm 0.2$  K/kbar corresponding to  $d \ln T_c / d \ln a_0 = -22.8$ , where  $a_0$  is the lattice parameter; (2) pressure greatly reduces orientational fluctuations of the C<sub>60</sub> molecules in the ordered low-temperature sc phase; and (3) the results suggest the presence of two ordering transitions instead of one near 249 K. The implications of these results are discussed.

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The identification [1] of the truncated icosahedral molecular structure of C<sub>60</sub> and its subsequent synthesis and separation in solid form [2] have generated tremendous interest in this exciting form of carbon. Currently a broad research effort is being aimed at determining and understanding the physical and chemical properties of C<sub>60</sub> and at identifying potential applications. Pure solid C<sub>60</sub> molecules form a face-centered-cubic (fcc) Bravais lattice at room temperature with lattice parameter  $a_0 = 14.2$  Å. A key issue to understanding the crystal structure is the orientational order of the C<sub>60</sub> molecules. <sup>13</sup>C nuclear magnetic resonance (NMR) studies [3,4] revealed a very narrow spectral line at room temperature (300 K) which proves the existence of dynamical disorder and leads to the conclusion that the C<sub>60</sub> molecules are rotating rapidly ( $> 10^9$ /s) and isotropically. We note that in the absence of molecular rotation, the <sup>13</sup>C NMR spectrum of solid C<sub>60</sub> is expected to be a broad resonance [3]. On lowering the temperature, this rotational motion is slowed down, and the rotational correlation time of the molecules becomes  $> 5 \times 10^{-5}$  s at  $\sim 100$  K [3,4]. These studies suggested the possible growth of a new phase of solid C<sub>60</sub> below 300 K, and this suggestion has now been confirmed [5] by high-resolution synchrotron x-ray powder diffraction and differential-scanning-calorimetry (DSC) measurements. This latter work [5] has established the existence of a reversible phase transition from the high-temperature fcc phase to a low-temperature simple-cubic (sc) phase at a transition temperature  $T_c = 249 \pm 1$  K. The transition is of the order-disorder type resulting from the development of orientational order of the C<sub>60</sub> molecules in the sc phase.

The exact model for this transition is not established at this time. A detailed knowledge of the orientational and rotational properties of the molecules and of the nature of the transition are necessary for understanding the properties of solid C<sub>60</sub>. Toward this end, high-pressure studies provide crucial insights and information necessary for testing proposed models. Specifically, by the application of pressure it is possible to delicately and continuously tune the strength of intermolecular potentials and rotational barriers which control the molecular motions. These considerations motivated the present work in which

we examined the influence of hydrostatic pressure on the sc-fcc transition temperature. As the transition is believed to be an order-disorder transition involving the rotational and orientational motions of the C<sub>60</sub> molecules, one can intuitively anticipate that decreasing the intermolecular separations in the solid would hinder these motions, resulting in a higher  $T_c$ . This is indeed found to be the case, and the present results quantify this expectation and demonstrate that the pressure effects are large, in addition to revealing new features.

The sample used was pure ( $> 99.4\%$ ) C<sub>60</sub> powder prepared by column chromatography using hexane as the solvent. The material was annealed at 400 K for 4 h in vacuum. The starting material was a toluene-soluble soot obtained from Texas Fullerenes. The high purity of the chromatographed C<sub>60</sub> product was confirmed by ir, UV, and mass spectroscopies. No evidence for any trace amounts of hydrogen-containing solvent impurities was found, as also evidenced by a preliminary neutron-diffraction study on material from the same sample. Care was taken to minimize the exposure of the C<sub>60</sub> powder to light before use. The phase transition was detected by differential thermal analysis (DTA). The sample and an adjoining inert reference material (NaCl powder) were encapsulated and enclosed in a 10-kbar pressure cell using helium gas as the pressure transmitting fluid. The pressure was measured to an accuracy of better than 1% by a calibrated Manganin gauge. Temperature was measured by a copper-Constantan thermocouple placed near the sample, and the DTA scans were run at a heating rate of 10 K/min.

Figure 1 shows a number of DTA scans taken at different pressures on heating. Examining the zero-pressure (1-bar) scan first, we note that the negative-going peak indicates that the sc  $\rightarrow$  fcc transition is endothermic as has been demonstrated by DSC measurements [5]. Also as seen in the DSC measurements, there is a broad precursor in the sc phase (shaded area in Fig. 1) terminating in the sharp peak. We take the sharp peak temperature to represent  $T_c$ . Since our DTA scans are taken with increasing temperature at a relatively rapid heating rate, the temperature inferred from the peak is higher than the equilibrium  $T_c$ ; however, this difference

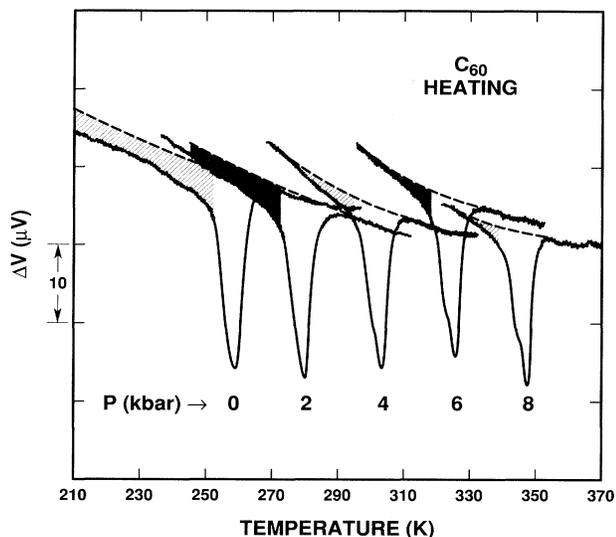


FIG. 1. Differential-thermal-analysis (*heating*) scans of solid  $C_{60}$  at different pressures showing the behavior in the vicinity of the sc-fcc transition.

does not materially affect the shift of  $T_c$  with pressure, which is the effect we seek.

The results in Fig. 1 reveal several pressure effects. First, note that the transition shifts to higher temperatures with increasing pressure. Figure 2 shows that the shift is linear over the 8-kbar pressure range of the measurements with  $dT_c/dP = 10.4 \pm 0.2$  K/kbar—a large effect. Second, there is a hint (asymmetry) in the 1-bar ( $\approx 0$ -kbar) scan that there could be a second feature on the low-temperature side of the peak. With increasing pressure this feature evolves into a well-defined shoulder suggesting the presence of two nearly degenerate configurational states even at 1 bar. Because of its relatively large size (see below) and pressure dependence, we believe this feature to be intrinsic and not due to trace impurities or residual solvent (hexane-toluene) in the sample; however, we cannot completely rule out the possible involvement of impurities. Measurements on other samples would be desirable and are planned. Third, the broad precursor on the low-temperature side of the transition (shaded regions in Fig. 1) decreases markedly with pressure. We now discuss each of these pressure effects.

The  $+10.4$  K/kbar shift of  $T_c$  is a large effect corresponding to an initial increase of  $4.2\%/kbar$  in  $T_c$ . This effect undoubtedly reflects the weak van der Waals intermolecular bonding and the concomitant high compressibility of the  $C_{60}$  lattice as well as the high sensitivity of the orientational energy barriers to the intermolecular separations. It is not likely that the modest pressures employed in the present work will significantly change the single  $C_{60}$  molecule's rotational states, and thus the main effect of pressure is to reduce the intermolecular separations. The magnitude of this reduction is proportional to the axial compressibility,  $\kappa_a = -d \ln a_0 / dP$ . The com-

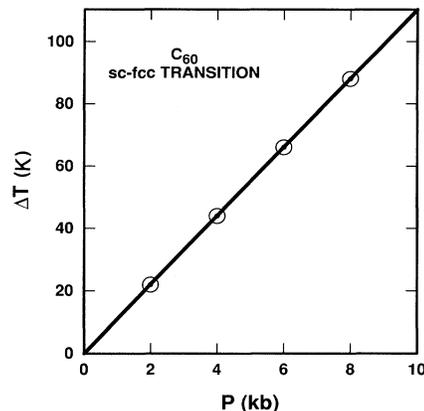


FIG. 2. Shift of the sc-fcc transition temperature of solid  $C_{60}$  with pressure.

pressibility of solid  $C_{60}$  at room temperature was recently determined by Fischer *et al.* [6] and confirmed by Duclos *et al.* [7] from x-ray-diffraction data at high pressure. The latter more extensive results (to 200 kbar) yield  $\kappa_a = 1.83 \times 10^{-3}/kbar$  for the low-pressure ( $< 25$  kbar)  $\kappa_a$ , which corresponds to a volume compressibility  $\kappa_v = -d \ln V / dP = 5.5 \times 10^{-3}/kbar$ . These authors believed that this compressibility is that of the fcc phase because of the limited accessibility of diffraction lines; however, it is clear from the present results that the  $C_{60}$  phase which is stable at the high-pressure condition of their experiments is the sc phase. Apparently, the somewhat subtle changes in the diffraction pattern on going from the fcc to the sc phase [5] could not be detected in the high-pressure experiments. Although it is necessary to make this clarification, we nevertheless believe that the compressibilities of the fcc and sc phases are not too different, and we take them to be the same for our present purposes. This conclusion is supported by the fact that there is no measurable change in unit-cell volume [5] at  $T_c$ .

A measure of the strength of the  $T_c(P)$  dependence is the Grüneisen-parameter-like quantity  $d \ln T_c / d \ln a_0$ , i.e., the fractional change in  $T_c$  over the fractional change in  $a_0$ , or, alternatively,  $d \ln T_c / d \ln V$ . Based on the above  $\kappa$ 's for  $C_{60}$ , these quantities are  $-22.8$  and  $-7.6$ , respectively.

The fcc  $\rightarrow$  sc transition in  $C_{60}$  is accompanied by the development below  $T_c$  of inequivalent molecular orientations on the four fcc Bravais sites [5]. The analogy of this behavior to that observed in other orientational ordering transitions, specifically those in solid methane ( $CH_4$  or  $CD_4$ ) and solid hydrogen ( $H_2$ ), has been noted [5]. In this regard it is of interest to mention that the order-disorder transition temperatures of these latter materials also increase with pressure. Specifically, at 1 bar,  $T_c$  and  $dT_c/dP$  are 22 K and  $+3.5$  K/kbar for  $CH_4$  [8] and 2.8 K and 1.7 K/kbar for the  $Pa3$  transition in ortho- $H_2$  [9]. It is not appropriate to directly compare these  $T_c$ 's and their pressure derivatives with those for

$C_{60}$  because, at the low temperatures involved, orientational ordering in  $CH_4$  and  $H_2$  is strongly influenced, or controlled, by quantum-mechanical fluctuations, whereas in  $C_{60}$  the motion should be essentially classical ( $T_c = 249$  K). The main point, however, is that orientational ordering  $T_c$ 's in molecular solids increases with pressure, and this behavior is observed for many solids, including, e.g., some ferroelectric transitions [10] with high  $T_c$ 's. In all cases, decreasing the intermolecular separation hinders orientational motion and raises  $T_c$ .

On the basis of its sharpness, Heiney *et al.* [5] suggested that the transition in  $C_{60}$  is "weakly first order," although they note that there is no measurable hysteresis or change in unit-cell volume at  $T_c$ . These latter features actually indicate that the transition is thermodynamically of second order with no change in enthalpy. It is worth noting that the transitions in  $CH_4$  and  $H_2$  exhibit slight hysteresis and appear to be weakly first order [8,9], but many orientational order-disorder transitions with high  $T_c$ 's are known to be of second order [10].

The indication that there are actually two transitions involving very nearly degenerate orientational configurations in  $C_{60}$ , as noted above and shown in Fig. 1, is an intriguing one. Clearly pressure breaks this near degeneracy. As noted by Heiney *et al.* [5], the low-temperature sc lattice imposes severe constraints on possible models for the transition, since the equivalence of the  $x$ ,  $y$ , and  $z$  axes and the corresponding threefold rotation axes must be maintained. In order to explain their x-ray peak and intensity data, these authors proposed a specific model which captures some but not all of the features of the x-ray spectra. The model essentially consists of rotations of the four molecules through the same angle but about different threefold axes. Subsequently, Sachidanandam and Harris [11] identified the space group of the sc phase to be  $Pa3$  (instead of the  $Pn3$  used by Heiney *et al.*) which yields a better fit both to the x-ray data [12] as well as to a powder neutron-diffraction study by Copley *et al.* [13]. Such a model requires a minimum of several additional parameters from the fit for the fcc model and yields a rotation parameter of  $26^\circ$  for the molecules situated on the four different threefold axes [11].

The two transitions indicated in the data suggest the possibility of two orientational configurations of the molecules in the sc phase. To explain such a possibility one can speculate that in the sc lattice the relative orientation for the molecule at (000) needs to be different from that at the faces of the cube (e.g., the orientations of the five- and six-membered rings relative to the unit-cell axes would be different). This distinction would suggest that the onsets of the rotational motion of the two orientations would be different, and that there should be a 1:3 ratio in the areas of the two DTA peaks, assuming that the energies of the two transitions are not too different. Decomposition of the 8-kbar DTA scan in Fig. 1 into two peaks, by taking due account of the influence of the low-

temperature precursor on the base line, does indeed show that the area of the high-temperature peak is about 3 times that of the low-temperature peak in agreement with such a proposed model. While tempting, this model is not, however, consistent with the space group  $Pa3$  for the sc phase. Thus, the interpretation of the observed two transitions remains an open question.

Finally, the remarkable pressure-induced decrease in the magnitude of the low-temperature precursor to the transition(s) deserves some emphasis. The precursor is most likely due to the existence of orientational fluctuations in the ordered sc phase. Indeed, the  $^{13}C$  NMR results [3,4] suggested the existence of static and mobile C nuclei down to  $\sim 140$  K, and the diffraction results [5-13] do not rule out such a possibility. In fact, the integrated intensity of the 451 x-ray peak in the spectrum, which is proportional to the square of the order parameter in the sc phase, loses about half of its value between 4 and  $\sim 240$  K with the remaining intensity disappearing fairly abruptly near  $T_c$  [5]. Thus, both the NMR and x-ray results give strong evidence for orientational fluctuations in the sc phase. Other evidence has come from a very recent  $^{13}C$  NMR study [14] of the molecular reorientational dynamics which suggest some rapid motion of the  $C_{60}$  molecules below  $T_c$ . We interpret the rapid decrease with pressure in the DTA precursor to be due to a sharp pressure-induced reduction in these fluctuations. This result is consistent with intuitive expectations—bringing the  $C_{60}$  molecules closer together can be expected to increase motional correlations and reduce fluctuations. Perhaps the most remarkable aspect of this result is the near complete suppression of the fluctuations by the very modest pressure of 8 kbar suggested by the data in Fig. 1. It will be highly desirable to further explore this finding by performing microscopic experiments, including NMR and neutron and synchrotron x-ray diffraction, at high pressure and possibly between our two peaks in order to better understand the nature of molecular motions in the sc phase. A high-pressure neutron-diffraction study is planned.

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