

## Orientational Ordering Transition in Solid C<sub>60</sub>

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Synchrotron-x-ray powder-diffraction and differential-scanning-calorimetry measurements on solid C<sub>60</sub> reveal a first-order phase transition from a low-temperature simple-cubic structure with a four-molecule basis to a face-centered-cubic structure at 249 K. The free-energy change at the transition is approximately 6.7 J/g. Model fits to the diffraction intensities are consistent with complete orientational disorder at room temperature, and with the development of orientational order rather than molecular displacements or distortions at low temperature.

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The recent discovery<sup>1</sup> of an efficient synthesis of C<sub>60</sub> has spurred intense interest in the chemical, electronic, and physical properties of these highly symmetric molecules, which take the form of truncated icosahedra.<sup>2,3</sup> At room temperature, single-crystal x-ray diffraction shows<sup>4</sup> that the molecules are centered on sites of a face-centered-cubic (fcc) Bravais lattice,  $a_0 = 14.2$  Å, with a high degree of rotational disorder. The center-to-center distance between neighboring molecules is 10.0 Å; the calculated<sup>2</sup> C<sub>60</sub> diameter is 7.1 Å. The crystal is quite soft, with the compressibility at low pressure along *any* axis being comparable to that of graphite along its *c* axis.<sup>5,6</sup> Nuclear magnetic resonance (NMR) clearly indicates the existence of dynamical disorder (presumably free rotation) which decreases with decreasing temperature.<sup>7,8</sup> This implies several possible low-temperature structures: icosahedral glass, quasicrystal, or an orientationally ordered crystalline phase. In this Letter we present x-ray data and analyses which are consistent with only the last option. We also show that the ordered phase is stable to 249 K which is a surprisingly high temperature.

We used high-resolution synchrotron-x-ray powder diffraction to study solid C<sub>60</sub> between 300 and 11 K. A powder sample was prepared and purified using standard techniques as previously detailed,<sup>5</sup> resulting in better than 99.5%-pure C<sub>60</sub> and no detectable solvent. About 1 mg was loaded into a 0.7-mm-diam glass capillary tube. Measurements were performed at beam line X7/A of the National Synchrotron Light Source. A wavelength of  $\lambda = 1.1992$  Å was selected by a channel-cut Si(111) monochromator. Measurements of the strongest peak with a Ge(220) crystal analyzer gave  $\Delta(2\theta) = 0.07^\circ$  full width at half maximum (FWHM), implying a positional correlation length  $\xi \geq 1000$  Å at 300 K. In order to obtain adequate counting rates, subsequent measurements were made with a narrow receiving slit (0.5 mm), in-

stead of a crystal analyzer, in front of a Kevex detector, resulting in an instrumental resolution of  $\Delta(2\theta) \sim 0.10^\circ$  FWHM.

Figure 1 shows full diffraction profiles measured at 300 and 11 K. All of the peaks at 300 K can be indexed<sup>9</sup> as fcc, with  $a_0 = 14.17 \pm 0.01$  Å, as previously reported.<sup>4,5</sup> Note that *no*  $h00$  peaks are present in this profile, despite the fact that  $h00$  is allowed for  $h$  even. At 11 K,  $a_0$  has decreased to  $14.04 \pm 0.01$  Å and many new peaks have appeared. The new peaks can all be indexed as simple-cubic (sc) reflections with mixed odd and even indices (i.e., forbidden fcc reflections). The crystal has therefore undergone a transition to a simple-cubic structure, but since the cube edge has not changed appreciably the basis must still consist of four molecules per unit cell, which were equivalent in the fcc structure but which somehow become inequivalent at low temperature.

Figure 2, top, shows the  $T$ -dependent integrated intensity of the 451 peak. This peak is fcc forbidden, and its intensity is therefore proportional to the square of the sc order parameter. About half the 0-K intensity is lost in a continuous precursor extending from 0 to  $T_c$ ; the remainder disappears much more abruptly at  $T_c = 249 \pm 1$  K. There is no measurable hysteresis, and no measurable cell volume change at  $T_c$ . These observations are all consistent with weakly first-order behavior. Scans of the range  $2.7 \text{ \AA}^{-1} < q < 4.5 \text{ \AA}^{-1}$  at 230 and 255 K show that all of the sc peaks have the same qualitative  $T$  dependence.

Figure 2, bottom, shows differential-scanning-calorimetry (DSC) measurements on a 12-mg sample (N<sub>2</sub> flow, 20°C/min heating). The DSC endotherm also shows a broad precursor terminating in an abrupt transition whose onset appears a few degrees above  $T_c$  due to the more rapid heating rate. The area under the precursor and the sharp endotherm is about 6.7 J/g. Attribut-

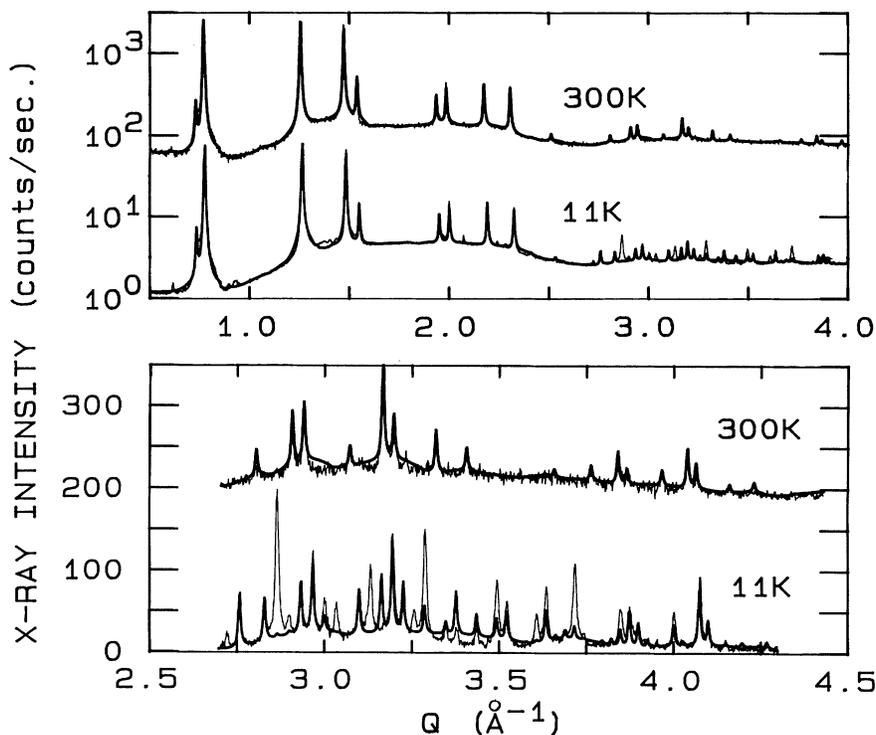


FIG. 1. Total x-ray scattering intensity (powder sample plus capillary) of pure  $C_{60}$  at 300 and 11 K. Light and heavy curves are data and model fits, respectively. Intensities are normalized to counts/sec at a synchrotron ring current of 100 mA; the data were typically collected for 5 sec/point at a current of 150 mA. Top panel shows the entire profile on a semilogarithmic scale, and bottom panel shows a blowup of the same data in the region  $2.5 \leq q < 4.5 \text{ \AA}^{-1}$  on a linear scale. All profiles have been offset for clarity.

ing this entirely to a change in configurational entropy gives  $\Delta S = R \ln(8)$  per  $C_{60}$ , but this attribution underestimates the correct value since the DSC scan misses some of the precursor, and overestimates it to the extent that there could be a small energy contribution as well.

We now discuss the analysis of the x-ray intensities. The atoms of the  $C_{60}$  molecule are placed at the vertices of a truncated icosahedron.<sup>2,10</sup> The x-ray structure factor is given by the Fourier transform of the electronic charge density; this can be factored into an atomic carbon form factor times the Fourier transform of a thin shell of radius  $R$  modulated by the angular distribution of the atoms. For a molecule with icosahedral symmetry, the leading terms in a spherical-harmonic expansion of the charge density are  $Y_{00}(\Omega)$  (the spherically symmetric contribution) and  $Y_{6m}(\Omega)$ , where  $\Omega$  denotes polar and azimuthal coordinates. The corresponding terms in the molecular form factor are proportional to  $S_0^{\text{mol}}(q) \propto j_0(qR) \equiv \sin(qR)/qR$  and

$$S_6^{\text{mol}}(Q) \propto j_6(qR) \sum_m A_{6m} Y_{6m}(\Omega_q),$$

where  $j_0$  and  $j_6$  are spherical Bessel functions, the constants  $A_{6m}$  are derived from the details of the charge distribution, and  $\Omega_q$  is the orientation of the momentum transfer  $\mathbf{q}$  in the reference frame of the icosahedron.

For the high-temperature fcc structure of  $C_{60}$ , both NMR<sup>7,8</sup> and previous structural studies<sup>4,5</sup> indicate a high degree of orientational disorder. Accordingly, it is reasonable to truncate the spherical-harmonic expansion at the first term, thus approximating the molecule by a spherical shell of charge as appropriate for a freely rotating molecule. The solid curve shown with the 300-K data in Fig. 1 is the best fit to the measured integrated intensities with this model. The integrated intensity at Bragg vector  $\mathbf{q} = \mathbf{G}_{hkl}$  is calculated as

$$I(\mathbf{G}_{hkl}) = I_0 |j_0(G_{hkl}R) f_C(G_{hkl})|^2 \times L_P \times M_{hkl},$$

where  $f_C$  is the carbon atomic form factor,  $L_P$  is the Lorentz-polarization factor, and  $M_{hkl}$  is the multiplicity. The only adjustable parameters are  $I_0$ ,  $R$ , and the cube edge length  $a_0$ . The best fit gave  $R = 3.52 \pm 0.01 \text{ \AA}$  and  $a_0 = 14.17 \text{ \AA}$ . Incorporating a Debye-Waller term  $\exp(-G^2 u^2)$  did not improve the fits, indicating that the thermal disorder is primarily rotational rather than translational. The fit clearly captures most of the important features of the data, including the absence of  $h00$  peaks which fortuitously coincide with zeros of  $j_0$  for even  $h$ . This gives strong additional evidence for a high degree of molecular orientational disorder at 300 K. The data are equally well described on the basis of a static

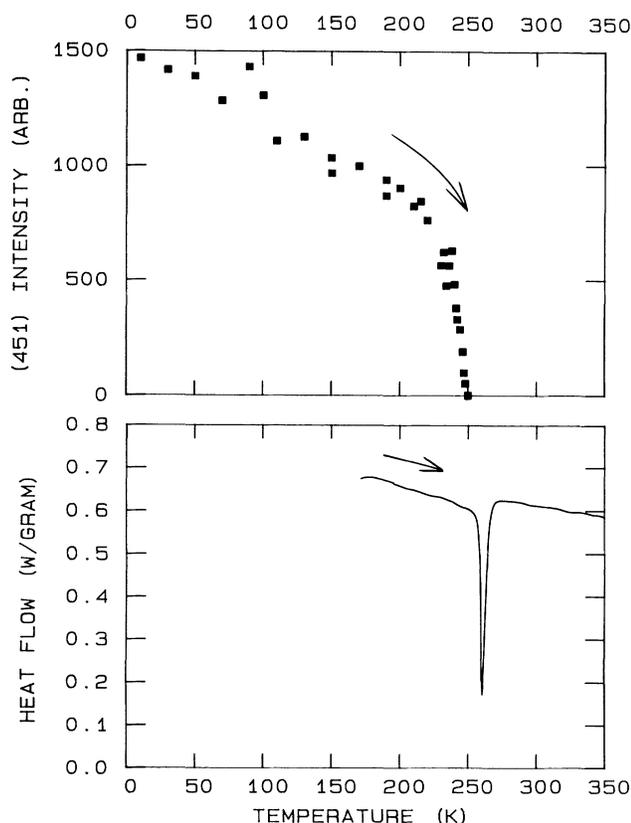


FIG. 2. Top: Integrated intensity of the  $C_{60}$  451 peak as a function of temperature. This peak is forbidden for a fcc lattice. Bottom: Results of a differential-scanning-calorimetry measurement on a powder sample of  $C_{60}$ .

model similar to that proposed by Fleming *et al.*,<sup>4</sup> i.e., with inequivalent carbon atoms C(1) in  $48(h)$  sites at 0,  $y$ ,  $z$ , and C(2) and C(3) in  $96(i)$  positions at  $x$ ,  $y$ ,  $z$  in space group  $Fm\bar{3}$ . This model requires an additional seven adjustable parameters and also gives a much larger value of  $u \sim 0.3 \text{ \AA}$ , indicative of pronounced translational thermal fluctuations. We accordingly believe that the free-rotation model is more appealing physically.

We can imagine several models for the onset of simple-cubic order below  $T_c$ . The molecules at the corner and three face-centered sites must be made inequivalent. This could be accomplished, for example, by displacements away from fcc Bravais lattice sites, quadrupolar distortions into a "football" shape, or development of orientational order. The first two mechanisms correspond, respectively, to finite  $Y_{1m}$  or  $Y_{2m}$  spherical-harmonic components, resulting in terms in the structure factor proportional to  $j_1(qR)$  or  $j_2(qR)$ . However, maxima in  $j_1$  and  $j_2$  occur at small arguments (corresponding to  $q = 0.59$  and  $0.93 \text{ \AA}^{-1}$  in the units of Fig. 1 if  $R = 3.52 \text{ \AA}$ ), so these two mechanisms would predict detectable 100 and 200 intensities which are not ob-

served. Indeed, fits to the entire spectrum allowing these symmetries yielded zero amplitudes for  $Y_{1m}$  and  $Y_{2m}$ . A displacive transition can also be ruled out on physical grounds, given the proximity of neighboring molecules. Molecular-dynamics simulations<sup>11</sup> do show football-shaped instantaneous distortions at very high  $T$ , but a static (or average) distortion of this kind at low  $T$  is certainly unfavorable energetically.

By contrast, the development of orientational order is to be expected at low temperature. Such order could be represented in  $S(q)$  by  $j_6(qR)$  and higher-order terms; the first maximum of  $j_6$  in the units of Fig. 1 is at  $q = 2.3 \text{ \AA}^{-1}$ , consistent with the observation that the strongest sc-allowed peaks are observed between  $2.5$  and  $4.5 \text{ \AA}^{-1}$ . This gives us confidence that the fcc  $\rightarrow$  sc transition is due to the existence of inequivalent molecular orientations on the four fcc Bravais sites at low  $T$ . The transition is analogous to the orientational ordering transitions observed in  $CD_4$  and related systems,<sup>12</sup> and in particular to solid  $H_2$ , in which the long axes of the molecule are oriented along different  $\langle 111 \rangle$  cubic axes.<sup>13</sup>

The low- $T$  sc lattice imposes severe constraints on possible models, since the equivalence of the  $x$ ,  $y$ , and  $z$  axes and the corresponding threefold rotation axes must be maintained. One model which satisfies these criteria and gives reasonable agreement with the data is as follows. Four molecules, centered on the fcc Bravais lattice sites, are oriented such that one of the ten threefold icosahedral axes (normal to the pseudo-hexagonal faces) is aligned with one of the four  $\langle 111 \rangle$  directions, and three mutually orthogonal twofold molecular axes are aligned with  $\langle 100 \rangle$  directions.<sup>3</sup> It follows<sup>14</sup> that three *other* molecular threefold axes are *also* aligned with the three remaining  $\langle 111 \rangle$  crystal axes. At this point there are no remaining rotational degrees of freedom; all molecules are equivalent and the structure is still fcc. The equivalence is now broken by rotating the four molecules through the same angle  $\Gamma$  but about *different*  $\langle 111 \rangle$  axes: the molecule at  $(000)$  about  $[111]$ , that at  $(\frac{1}{2} 0 \frac{1}{2})$  about  $[\bar{1} 1 \bar{1}]$ , that at  $(\frac{1}{2} \frac{1}{2} 0)$  about  $[\bar{1} \bar{1} 1]$ , and that at  $(0 \frac{1}{2} \frac{1}{2})$  about  $[1 \bar{1} \bar{1}]$ . This choice preserves the cubic symmetry, although the twofold axes are no longer aligned along  $\langle 100 \rangle$  directions.

The above-described structure could be modeled by a sufficient number of terms in the  $Y_{1m}$  expansion. We chose instead to embed sixty *discrete* atoms in a smooth spherical shell of charge, with atomic angular coordinates taken from an equilibrium structure derived from *ab initio* Hartree-Fock calculations of Scuseria,<sup>10</sup> and with molecular rotations as described above. This model requires the addition of only two parameters to the 300-K model (the rotation angle  $\Gamma$  and a fraction  $\alpha$  of spherically symmetric  $j_0$  amplitude). The best fit to the measured intensities with the above model is shown in Fig. 1; this fit gave  $R = 3.54 \pm 0.01 \text{ \AA}$ ,  $\Gamma = 22^\circ \pm 5^\circ$ , and  $\alpha = 0.5 \pm 0.3$ . The model captures some but not all features of

the data. It incorporates the cubic symmetry, and correctly predicts that the new peaks should only have appreciable intensity above  $2.5 \text{ \AA}^{-1}$ . Out of sixty allowed peaks in the  $2.5\text{--}4.5\text{-\AA}^{-1}$  range, the model seriously underestimates eight intensities, overestimates one, and reproduces the rest to within a factor of 2. Work is in progress on more sophisticated models involving correlated or anisotropic rotational disorder.

Note that the low-temperature structure is neither a quasicrystal nor an icosahedral glass. Given the molecular symmetry, one might have predicted the latter, whereas icosahedral quasicrystals require two distinct structural units to satisfy space filling. While the precise energetic requirements for crystal versus icosahedral glass formation are not understood, it seems likely that the structural order at low  $T$  is driven both by a preference for close packing and by local orientational order.

The x-ray results presented here show both consistencies and discrepancies with NMR observations. The most serious discrepancy is the implied coexistence of static and mobile C nuclei well below our  $T_c$ , deduced from the NMR observation of superposed motionally narrowed and powder pattern signals at temperatures as low as 140 K.<sup>7,8</sup> On the other hand, a minimum in  $T_1$  at 233 K is observed in one NMR experiment.<sup>7</sup> In fact, the two techniques probe different aspects of the structure. NMR experiments to date cannot distinguish between free rotation and jump rotational diffusion between symmetry-equivalent orientations. X-ray diffraction is sensitive to orientational order (as a canonical average of snapshots) even in the presence of substantial thermal disorder, as long as one set of orientations is statistically preferred and the orientational order is long range. Indeed, our measurements indicate that much of the sc order is reduced by orientational fluctuations at  $T_c$ .

An orientational ordering transition temperature of 249 K is unusually high compared with, for example, the value of 20.4 K measured<sup>12</sup> for  $\text{CD}_4$ . However,  $\text{C}_{60}$  is a large molecule, with a rotational inertia several orders of magnitude larger than that of  $\text{CD}_4$ . This means that its motion will be much closer to the classical limit, and quantum tunneling will be substantially suppressed. A quantitative calculation of  $T_c$  would incorporate the angular dependence of the two-molecule  $\text{C}_{60}$  pair potential, and also the high symmetry of the  $\text{C}_{60}$  molecule. The large number of equivalent orientations of a single molecule implies that the decrease in entropy per molecule from free rotation to fixed orientation is relatively small, resulting in an increased value of  $T_c$ . Our estimate  $\Delta S \sim R \ln(8)$  should provide some guidance in this regard.

We have shown that orientational ordering below 249 K is the only reasonable explanation for the low- $T$  sc structure, and that this occurs by breaking the equivalence of the four sites per fcc cell in the high- $T$

phase. Similar phenomena are expected to occur in solid  $\text{C}_{70}$ , the smallest nonspherical fullerene.<sup>2</sup>

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<sup>3</sup>An icosahedron possesses twelve fivefold vertices, twenty triangular faces, and thirty edges with twofold rotation symmetry. In the truncated icosahedron, the fivefold vertices are replaced by pentagons with atoms at the vertices, and the triangular faces are replaced by pseudo-hexagonal faces.

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<sup>7</sup>C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, *J. Phys. Chem.* **95**, 9 (1991).

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<sup>9</sup>There are two exceptions to the cubic indexing. A low-angle shoulder on the 111 peak has been identified from electron-microscopy studies as a truncation rod arising from planar defects [D. E. Luzzi (private communication)]. The very weak unindexed peak at  $0.61 \text{ \AA}^{-1}$  is attributed to an unknown impurity.

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<sup>11</sup>Q. M. Zhang, Jae-Yel Yi, and J. Bernholc, *Phys. Rev. Lett.* **66**, 2633 (1991).

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<sup>13</sup>I. F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).

<sup>14</sup>See, e.g., J. W. Cahn, D. Shechtman, and D. Gratias, *J. Mater. Res.* **1**, 13 (1986), for a discussion of Cartesian representations of the icosahedron.