Discontinuous volume change at the orientational-ordering transition in solid C_{60}

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X-ray and neutron-diffraction measurements have been used to study the evolution of the lattice parameter of solid C_{60} through the orientational-ordering transition. The lattice parameter jumps by $+0.044 \pm 0.004$ Å on heating, indicating a strongly first-order transition. The average isobaric volume thermal-expansion coefficient both above and below the transition is $6.2 \pm 0.2 \times 10^{-5}$ K^{-1}. We observe phase coexistence over a 5-K range, but little if any hysteresis.

The recent discovery of an orientational-ordering phase transition in solid C_{60} (Refs. 1 and 2) has led to several theoretical and experimental investigations of this intriguing molecular crystal. Both high- and low-temperature structures are characteristic of cubic close-packed quasispheres, consistent with the icosahedral molecular geometry.[3] At high T, a face-centered-cubic (fcc) structure is formed, in which all four molecules in the conventional cubic cell are crystallographically equivalent due to dynamic orientational disorder.[4] The orientational correlation time deduced from NMR measurements is only three times larger than that expected for completely unhindered rotation,[5] and coherent quasielastic neutron scattering measurements can be described by a model in which each molecule undergoes rotational diffusion which is uncorrelated with the motions of adjacent molecules.[6] Below the phase transition the orientational equivalence of the four molecules in the cubic cell is broken,[1] and a simple cubic (sc) structure is formed with $Pa\bar{3}$ symmetry.[7-10] The orientational correlation time is significantly slower in the sc phase, and is described as "ratcheting" between symmetrically equivalent orientations.[4,5] Furthermore, recent inelastic-neutron-scattering measurements clearly demonstrate that molecules rapidly librate about their equilibrium

orientations in the sc phase. The transition temperature T_c increases linearly with pressure at a rate of 10.5–11.5 K/kbar.[11-13] A Landau-theory analysis indicates that the transition should be first order.[14] Structural calculations using a variety of empirical atomic interactions[15-17] have predicted large symmetry-breaking tetragonal or rhombohedral distortions, perhaps indicating that the ground-state structure is highly sensitive to the potential chosen. Indeed, the most recent calculation,[18] using a modified interaction potential, has succeeded in reproducing the experimentally observed low-temperature structure.

In this paper we report x-ray and neutron-diffraction measurements in the vicinity of the phase transition. The measured lattice-parameter jump at the transition is consistent with calorimetric measurements as a function of pressure. In addition, our measurement of the 450 and 451 simple-cubic peak-intensity evolution with temperature indicates that the transition is more strongly first order than previously supposed.[1]

Our samples were prepared using standard methods.[19,20] The sample used for the neutron measurements was the same as that used in previous measurements.[6,10] 1.5 g of this sample were prepared at the University of Pennsylvania and 1.0 g at Exxon. The

sample used for the x-ray measurements came from the same batch as the Penn source for the neutron measurements. It differs from the sample used in the earlier structural measurement of the transition[1] in that greater care was taken to remove residual solvent. Specifically, the sample employed in Ref. 1 was dried by momentary heating to 200 °C in flowing nitrogen, during which toluene evolution was observed, while the sample in the present study was heated to 250 °C under a 10^{-2}-Torr dynamic vacuum for 12 h. Prompt γ-ray activation analyses of the Penn and Exxon powder samples showed hydrogen contents of (0.0057 ± 0.0011) and (0.008 ± 0.002) H atoms per C atom, respectively.[6]

The x-ray sample was sealed into a 0.7-mm-diameter glass capillary, which was mounted in a closed-cycle helium refrigerator. X-ray patterns were collected at beamline X7A at the Brookhaven National Synchrotron Light Source. A Si(111) channel-cut monochromator selected a wavelength of 1.170 27 Å. The incident beam intensity was monitored by an ion chamber, and the scattered intensity was analyzed with a Ge(220) crystal and a Peltier-cooled semiconductor detector. For the neutron measurements the sample was contained in aluminum and again mounted in a closed-cycle helium refrigerator. The BT1 multidetector powder diffractometer at the National Institute of Standards and Technology's research reactor was used at an incident wavelength of 1.5454 Å, obtained with a Cu(220) monochromator. Collimations were 10′, 20′, and 10′, before and after the monochromator and after the sample, respectively. Data were collected between 20 and 320 K.

Figure 1 shows characteristic x-ray diffraction patterns as a function of temperature. We measured the profiles of the 111, 220, 311, 222, and 620 peaks (which are found in both fcc and sc phases) and also the sc 450-621-344 and 451 peaks. We then performed least squares fits to determine the lattice constant, correlation length, and integrated intensities. The background was described by an empirical function which was linear in the vicinity of each Bragg peak; additional scattering just below the 111 peak was parametrized by a sawtooth line shape representing stacking disorder as previously described.[21,22]

In the pure-phase regions, all x-ray peaks could be adequately described by a Lorentzian line shape, $I(q) = [I(G)/2\pi\kappa]/[(\frac{q-G}{\kappa})^2 + \frac{1}{4}]$, with a fixed full width at half maximum (FWHM) $\kappa = 0.0038$ Å^{-1}.[23] This corresponds to a correlation length of 1650 Å, somewhat larger than the previously measured[1] correlation length of $\sim$ 1000 Å. The relative magnitude of the sawtooth "foot" at 0.72 Å^{-1} due to stacking disorder was also reduced by more than a factor of 10 in the present sample. Similarly, neutron measurements of the 711-551 reflection (which appears in both phases) were fitted to a Gaussian line shape and constant background. The instrumental resolution of 0.01 Å^{-1} FWHM precluded a determination of the correlation length from these data.

Figures 2(a) and 2(b) show the fitted values of the cubic lattice constant as a function of temperature derived from the x-ray and neutron measurements, respectively. The isobaric volume thermal expansion coefficient α_V is determined by a linear-regression analysis of the neu-

tron data between 260 and 320 K to be $6.1 \pm 0.6 \times 10^{-5}$ K^{-1}, and from the x-ray data to be $6.2 \pm 0.2 \times 10^{-5}$ K^{-1}. A similar analysis between 100 K and 245 K yields $\alpha_V = 5.8 \pm 0.6 \times 10^{-5}$ K^{-1} from the neutron data and $6.2 \pm 0.2 \times 10^{-5}$ K^{-1} from the x-ray data. Thus, α_V is quite similar above and below the transition. However, the *average* expansion coefficient from 10 K to 245 K is $4.6 \pm 0.4 \times 10^{-5}$ K^{-1}, i.e., the curve is not quite linear and the average slope thus depends on the range chosen. Furthermore, between 235 K and 250 K the average slope is $\alpha_V = 21 \pm 3 \times 10^{-5}$ K^{-1}; this precursive rise in the unit cell volume below the transition is observed in both the x-ray and neutron data.

The lattice constants of the fcc and sc phases just above and below the transition were determined from our x-ray measurements to be 14.154 ± 0.003 and 14.111 ± 0.003 Å, respectively, implying that the jump in the lattice parameter at the transition is 0.044 ± 0.004 Å. In the vicinity
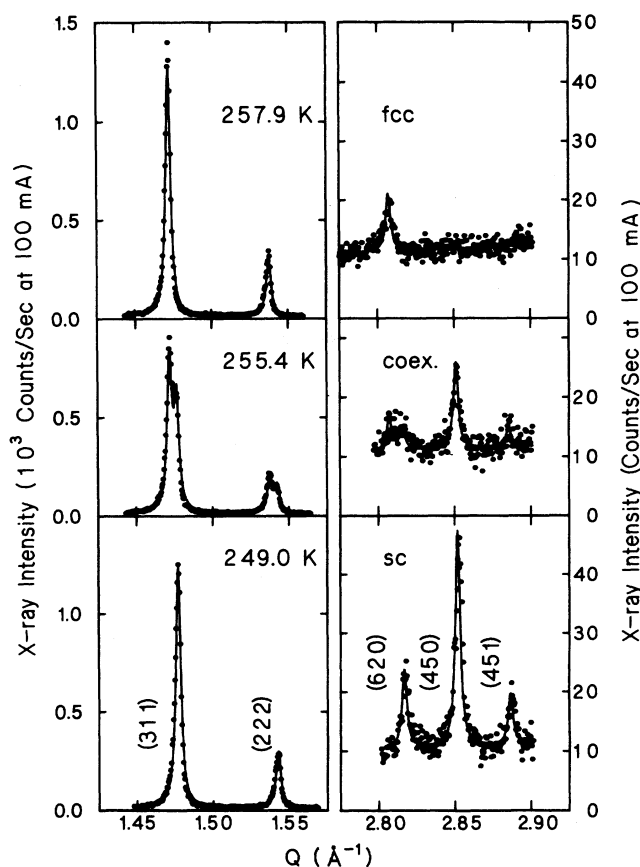

FIG. 1. C$_{60}$ synchrotron x-ray powder diffraction patterns in the face-centered cubic phase (top), coexistence region (middle), and simple-cubic phase (bottom). From left to right, peaks are indexed as the 311, 222, 620, 450-621-344, and 451. The 111 and 220 peaks (not shown) were also measured. X-ray intensities are normalized to counts per second at a synchrotron ring current of 100 mA; the 311 and 222 peaks were typically counted for 2 sec per point, and the 620, 450, and 451 for 10 sec per point, all at typical ring currents between 80 and 200 mA.

of 254 K, a set of double-peak x-ray profiles is observed, indicative of two-phase coexistence. The splitting between the peak positions is consistent with a 0.044-Å jump in lattice constant between the fcc and sc phases.[24] To model the profiles in the coexistence region, the lattice constant *difference* between the fcc and sc phases was held constant at 0.044 Å, and the lattice constant of the fcc phase was allowed to vary. (Similar results were obtained when the lattice constants of the fcc and sc phases were held fixed at their limiting values of 14.154 and 14.111 Å.) The profiles of the five mixed-phase peaks were described by a sum of two Lorentzians, each of fixed width $\kappa = 0.0038$ Å^{-1}. The total integrated intensity under each peak was an adjustable parameter, but the relative fraction of the fcc phase component, denoted by f, was required to be the same for all five peaks. The boundaries of the coexistence region were determined by several criteria: the width of the peaks is parametrized by single Lorentzians with variable κ, the goodness-of-fit of single-phase or coexistence fits with an equal number of fitting parameters, and visual observation of peak asymmetry. For each reflection the neutron measurements in the coexistence region were likewise fitted to a sum of

two Gaussians whose integrated intensities and centers were allowed to vary such that the separation of the centers was consistent with the lattice parameter difference determined in the x-ray measurements. Our results for the lattice constant in the coexistence temperature range appear in Figs. 2(a) and 2(b).

Figure 2(c) shows the fitted fractional amplitude f of the fcc phase as a function of temperature. It evolves rapidly from 0 to 1 between 252 and 257 K, implying that the coexistence region is roughly 5 K wide. The hysteresis of the transition was less than 0.5 K, consistent with the reproducibility of our cryostat.

Kriza *et al.*[11] have inserted their $T_c(P)$ data, and the measured latent heat of the transition, into the Clausius-Clapeyron equation to calculate a fractional jump of the unit cell volume of $\Delta v = (\Delta V)/V = 7.5 \times 10^{-3}$. This is in reasonable agreement with our measurement of $\Delta v = (9.3 \pm 0.8) \times 10^{-3}$. (The Clausius-Clapeyron calculation of course also assumes that the *same* transition is being measured at all pressures; the Raman data of Tolbert *et al.*[13] indicate that the high-pressure phase may consist of an orientational glass.) Structural calculations, while in general predicting a ground state with lower symmetry than the observed structure, do give the correct order of magnitude for the volume change: Guo *et al.*[15] and Lu *et al.*[16] calculate $\Delta v = 2.8 \times 10^{-2}$, while Cheng and Klein[17] calculate $\Delta v = 6.3 \times 10^{-3}$. The most recent calculation of Sprik *et al.*[18] yields $\Delta v = 8.4 \times 10^{-3}$, in good quantitative agreement with our measurement.

Figure 3 shows the fitted integrated intensities of the 450-621-344 and 451 peaks from x-ray measurements. The 451 intensity was also plotted in Ref. 1 for the original sample; in that experiment roughly half the 451 intensity was lost in a continuous precursor extending from $T = 0$ to T_c. In the present measurement, little or no pretransitional behavior is seen in the 451 peak, although the counting statistics are not as good as those in Ref. 1; its intensity in the coexistence region closely follows the fraction of simple-cubic phase calculated from other peaks. Somewhat more pretransitional behavior is seen in the 450 peak, but it also shows a relatively large jump at T_c.
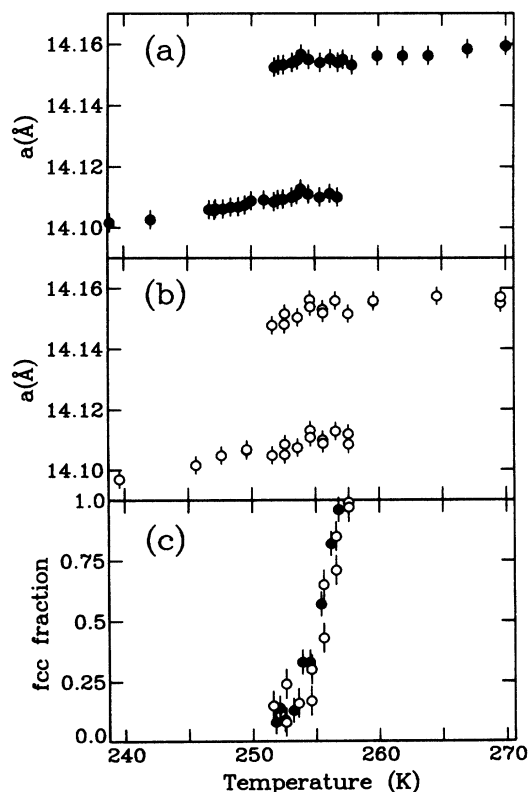

FIG. 2. (a) Fitted cubic lattice constants from x-ray data. In the coexistence region, the *difference* between the sc and fcc values was held fixed at the optimized value, but the fcc lattice constant was allowed to vary. (b) Fitted cubic lattice constants from neutron data, analyzed in the same manner as the x-ray data. (c) Fractional amplitude f of the fcc phase in the coexistence region. Open and closed circles represent neutron and x-ray data, respectively.
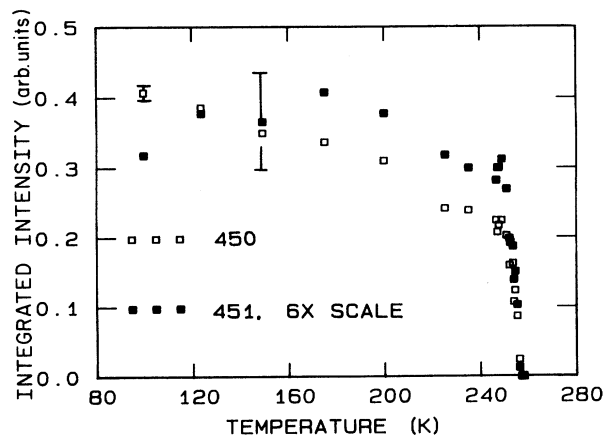

FIG. 3. Fitted integrated intensities of the 450 and 451 peaks from x-ray measurements.

The x-ray and neutron results are completely consistent, indicating a lattice parameter discontinuity at the transition of 0.044 ± 0.004 Å, roughly one-third of the change from 20 K to 300 K. This observation, together with the relatively sudden disappearance of the 450 and 451 peak intensities at the transition, indicates that the transition is more strongly first order than we had previously supposed. The increased period of thermal annealing under vacuum has resulted in a dramatic enhancement of the sample quality, by decreasing the amount of solvent, increasing the correlation length, and decreasing the density of stacking faults. Nevertheless, the presence of a coexistence region indicates that there are still residual impurities that affect the transition since there should be no such region for a single-component system. Our results emphasize the importance of determining the levels of not only the C_{70} and other fullerene impurities, but also the residual solvent concentration, in samples of C_{60} and its derivatives.

Note added. A recent structural calculation by Lu *et al.*[25] is consistent with the $Pa\bar{3}$ structure.

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[23] Here we use the convention $q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength and 2θ is the scattering angle. $G = 2\pi/d$ describes the position of a Bragg peak corresponding to planes with spacing d.

[24] In Ref. 1 it was incorrectly stated that no cell volume change was observed at T_c in x-ray diffraction. In fact, that experiment was not optimally designed to measure changes in lattice constant, since the strong fcc peaks were not measured at many points close to the phase transition. The results in the present work are completely consistent with the data on which Ref. 1 is based.

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