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Existence of high-order superlattices in orientationally ordered C_{60}

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We correlate the presence or absence of high-order modulated structures in solid C_{60} with the differential scanning calorimetry signature of the orientational ordering transition and other diagnostic data. We have searched for, but not observed, the **2a** face-centered cubic structure recently observed in low-temperature electron and single-crystal x-ray diffraction. We conclude that the *intrinsic* ground state is the previously reported simple cubic structure [space group $Pa\bar{3}$, **a**(14 K) = 14.06 Å), and that other structures may be stabilized by defects or impurities.

Orientational ordering of the fullerene molecules in solid C_{60} continues to attract considerable attention.[1,2] At high temperature, rapid and quasirandom rotations about fixed centers[3,4] lead to a "plastic crystal" phase with close packing of quasispheres in a face-centered cubic (fcc) lattice. The four molecules per conventional cubic cell are equivalent on the x-ray time scale, and the lattice constant **a** = 14.16–14 Å is consistent with an ~ 10 Å van der Waals molecular diameter.[5,6] Upon cooling below $T_m = 249$–260 K, a phase transition to a simple cubic (sc) structure is observed in powder[5] or single-crystal[7,8] x-ray diffraction, neutron diffraction,[2,9] and electron diffraction.[10,11] Differential scanning calorimetry (DSC) confirms that the transition is first order.[5,12–14] The orientationally ordered phase is derived from the disordered one by first orienting the molecules with their threefold axes along crystallographic $\langle 111 \rangle$ directions and twofold axes along $\langle 100 \rangle$ cube edges. The equivalence of the four molecules per cube is then broken by rotating each by the *same* angle Γ_0 about a *different* one of the four previously equivalent $\langle 111 \rangle$ crystal axes. Several independent refinements lead to an optimum $\Gamma_0 \approx 24°$–26°. This *approximately* locates an electron-rich short C=C bond adjacent to an electron-deficient pentagon center on the neighboring molecule,[9] strongly suggesting that weak Coulomb interactions are the driving force for the low-T ordering transition. The strength of this interaction should vary rapidly with intermolecular separation, an effect which has been probed using hydrostatic pressure.[13,14]

In a very recent report, it is claimed that the ground state of solid C_{60} is fcc with a doubling of the lattice constant to 2a$\sim$28 Å.[11] This is based on the observation of half-order electron diffraction spots in a [110] zone axis pattern at ~ 113 K, even weaker than the already weak sc spots. The proposed structure consists of four sets of two molecules each, coherently rotated by $+\phi$ and $-\phi$ about the four different $\langle 111 \rangle$ directions with respect to a reference orientation, producing two different interpenetrating sc sublattices with overall fcc symmetry. The sc-a $\rightarrow$ fcc-2a transition occurs "slightly below"[15] the T_m of the fcc-**a**$\rightarrow$sc-**a** transition. A similar structure has been deduced from a single-crystal monochromatic Laue

experiment, the new transition occurring 4 K below T_m in this paper.[8]

We considered the possibility that the fcc-2a structure might be the reason we needed to include an *ad hoc* correction for a fraction of randomly oriented molecules in our original powder profile analysis, although this has been justified *a posteriori* by the observation of diffuse scattering in low-T neutron powder diffraction.[2] A new fit to our powder x-ray data based on the ground-state structure proposed above has been performed, with notably worse results.[16] Furthermore, it has been shown that the specific orientations proposed for the fcc-2a model are incompatible with the observed cubic symmetry, although other choices do result in cubic ground states.[16] In this paper we describe our unsuccessful attempts to reproduce the fcc-2a TEM superlattice reflections, although we do observe a different low-T modulated structure in crystals from one batch of C_{60}.

Several batches of chromatographically pure C_{60} powder were prepared by rapidly eluting soot extract in pure toluene using an argon overpressure, on a column composed of two parts silica and one part alkaline decolorizing carbon (Norit A ©).[17] The resulting powder was washed three times in pure hexane, then vacuum-dried for several hours at 150–200 °C and $\sim 10^{-7}$ Torr using a turbopump system. Combined thermogravimetric analysis and mass spectrometry (TG-MS) confirmed that free solvents are effectively removed by this process. The absence of higher fullerenes at the level of 0.1% was verified by high-performance liquid chromatography. Sample quality was also studied using the DSC signature of the orientational ordering transition endotherm on heating,[5] infrared reflectivity (calibrated against a reference C_{60} sample) of residual C-H bond concentrations,[18] combined thermogravimetric and differential thermal analysis (TG-DTA), crystal coherence length, and stacking faults from x-ray powder profiles.[19] Transmission electron diffraction was performed using a Phillips 400T operating at 120 kV. TEM samples were prepared by crushing dry powder between Cu grids. High-resolution x-ray powder diffraction was performed on the National Synchrotron Light Source (NSLS) beamline X7A at Brookhaven National Laboratory.

Sample A, eluted once at a fairly rapid 12 mL/min rate, gave an unusual two-peak DSC trace shown as the upper curve in Fig. 1. The major peak has an onset temperature of 257 K, with a weaker peak ~ 3 K lower and a broad onset at still lower temperature. This sample gave a strong Fourier transform infrared (FTIR) hydrogen signature corresponding to 6.0 at.%, an order of magnitude greater than the reference sample. High-resolution x-ray powder diffraction at 300 K revealed nothing unusual. The lattice constant was 14.162(2) Å, the x-ray coherence length was ~ 1400 Å, and the density of stacking faults, as indicated by the intensity of the sawtooth line shape under the $\langle 111 \rangle$ reflection,[19] was low. We were immediately led to consider whether or not the second, weaker DSC peak at lower temperature could be associated with the fcc-2a phase. Figure 2(a) shows a [110] zone axis TEM diffractogram taken at 104 K under normal conditions, 5 min exposure at 0.9 nA current on high
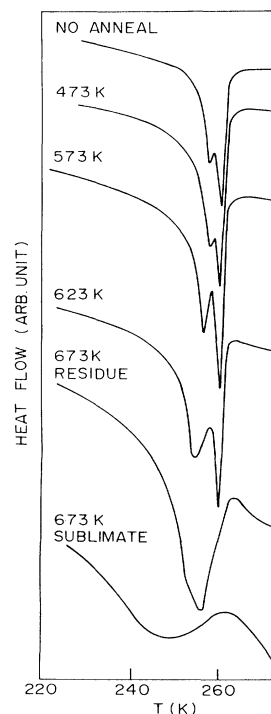

FIG. 1. DSC traces of sample A (6.0 at.% hydrogen) as prepared and after vacuum annealing at the indicated temperatures. Note especially that the traces from the residue and sublimate after the 673 K anneal bear little resemblance to those from near-ideal samples (Refs. 5 and 12–14); in particular the transition width in the sublimate exceeds 10 K.

sensitivity Mitsubishi MEM film. This reveals only the usual intense fcc-allowed and weaker sc-a spots, the latter denoted by the large arrows. Figure 2(b) is the same zone axis pattern using a 45 min exposure; it shows an additional set of even weaker spots (small arrows) cor-
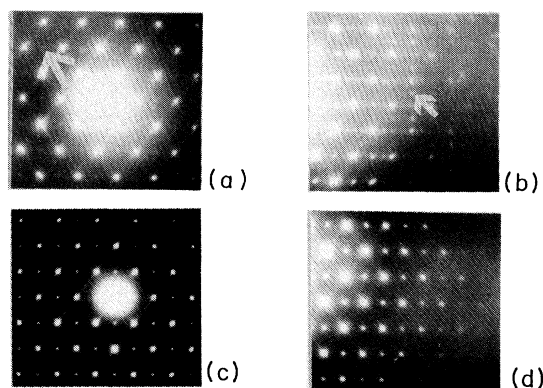

FIG. 2. [110] zone axis electron diffractograms taken at 104 K. (a) Sample A, normal exposure (see text). The bright spots are fcc-allowed reflections and the sc reflections are denoted by large arrows. (b) A portion of the same pattern approximately ten times overexposed, showing the extra superlattice reflections; small arrows indicate a rectangular modulation pattern, twofold along [001] and fourfold along [$\bar{1}$10]. (c) and (d) Sample B, normal and a portion overexposed, respectively, both showing only the fcc-allowed and sc spots.

responding to a superlattice with twofold modulations along [001] and fourfold modulations along [$\bar{1}$10]. None of the latter coincide with fcc-2a reflections. Similar patterns were observed in all 17 crystals of sample A which were examined, and are thus typical of the bulk material. In particular, no evidence was found in any crystal for spots corresponding to the fcc-2a structure. Neither the sc-a nor the superlattice reflections were present at 300 K.

Sample B was chromatographed twice using a slower elution rate, 8 mL/min. This sample exhibited a single very sharp DSC peak with a 258 K onset (Fig. 3), and no detectable hydrogen in FTIR (the upper limit is significantly smaller than the 0.57 at.% present in the reference sample). The lattice constant of this sample is slightly greater, 14.167(1) Å, than that of sample A, while the > 3000 Å coherence length is significantly greater. The stacking fault density is slightly higher. TEM at 104 K gave no evidence for the fcc-2a structure nor for any other superlattices. Figure 2(c) shows a [110] zone axis pattern taken under normal exposure conditions. Extended exposure for 1 h, Fig. 2(d), failed to reveal any new spots, in contrast to sample A. Four crystals of sample B were examined; all gave results identical to Figs. 2(c) and 2(d). Similar negative TEM results were obtained from two additional batches of C_{60} exhibiting sharp DSC peaks and containing as much as 1.2 at.% hydrogen.

Since we did not observe the fcc-2a structure in any of our samples, we cannot address its possible origin.[20] It is, however, significant that we do observe a *different* high-order TEM superlattice, other than the sc structure, but only in one sample containing substantial hydrogen. All the samples described here are free of residual solvent but could in principle contain nonvolatile hydrocarbons not removed by chromatography. After vacuum drying there were no detectable peaks corresponding to toluene or hexane in TG-MS. The reference sample contains roughly one H atom per three fullerenes, sample A contains four H atoms per fullerene, and H is below detectability in sample B. If the hydrogen were present as a nonbonded random impurity (e.g., intercalated or clathrated H_2), one might expect a slight dilation of the lattice, i.e., a negative "chemical pressure" effect, with a concomitant *decrease* in T_m. The hydrostatic pressure data[13,14] combined with the compressibility[6] imply that a dilation of only 0.003 Å in a will depress T_m by 1 K. On the other hand, hydrogen bonded to fullerenes[21] would almost certainly *increase* T_m relative to pure C_{60}, as observed for $C_{60}O$ (Ref. 22) and $C_{61}H_2$.[23] The situation could well be further complicated by reactions between hydrogen and intercalated oxygen.[24] None of our observations are consistent with either hypothesis. Both DSC peaks in the hydrogen-rich sample are lower in T than the peak in the purer sample, consistent with a chemical pressure effect, but the lattice constants differ slightly in the wrong sense if at all. Furthermore, if we take 258 K as the intrinsic value of T_m, the lower values in the impure sample argue against an effect of nucleophilic substitution by solvent fragments.

The evolution of sample A's DSC traces with annealing (Fig. 1) suggests that samples of otherwise (i.e., chro-
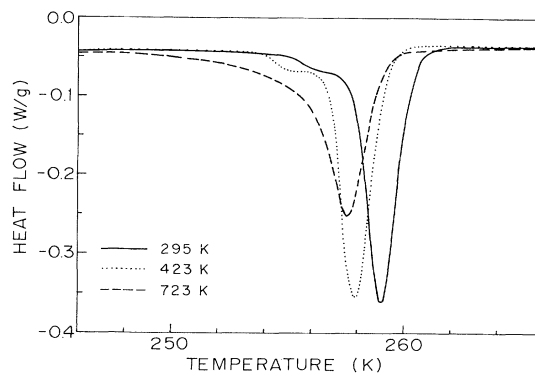

FIG. 3. DSC traces of sample B (no detectable hydrogen) after vacuum annealing at the indicated temperatures (note smaller T scale compared to Fig. 1). Unlike sample A, annealing has only a minor effect on DSC; after the 723 K anneal the onset temperature is still within the range of values reported for near-ideal samples (Refs. 5 and 12–14), and the transition width is ~ 1 K.

matographically) pure C_{60} may undergo solid-state reactions in vacuum which affect the orientational ordering transition. The low-T component shifts to even lower T and broadens with increasing annealing temperature, and finally the main peak merges with it to give a single, extremely broad transition. The purer sample B shows much less dramatic evolution of DSC with annealing, Fig. 3. Annealing for 10 h at 423 K reduces T_m by ~ 1 K with no change in the 9.4 J/g heat of transition. After 10 h at 723 K, T_m is further reduced by a similar amount, and the peak is noticeably broader but still sharp compared to sample A annealed to a comparable temperature. Note also from Fig. 1 that the material *sublimed* from sample A also shows a very broad transition, implying that sublimation *per se* (as was employed by van Tendeloo *et al.*) is no guarantee of obtaining near-ideal material.[25]

We summarize as follows. Solid C_{60} exhibits a first-order orientational melting at 250–260 K, possibly depending on small variations in a and almost certainly on the presence of hydrogenic impurities. The intrinsic ground-state structure is simple cubic, a = 14.06 Å at 14 K. Higher-order symmetries can occur, but these are most likely related to impurities and/or defects. The extrinsic phenomenon responsible for the low-T superlattice has no apparent effect on the x-ray structure of the high-T plastic crystal phase (lattice constant, coherence length, and stacking fault density).

Shortly after we began this study, we learned that the single-crystal x-ray evidence for the fcc-2a structure has been retracted.[26]

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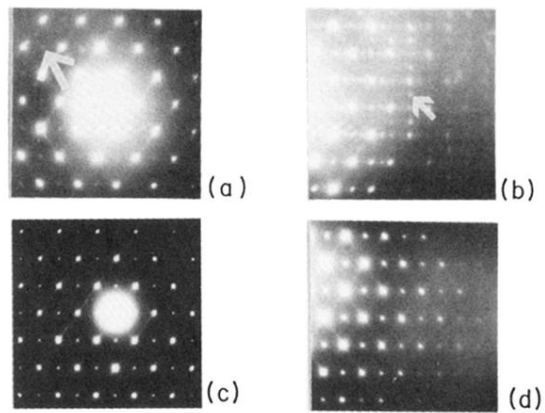
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