Heat capacity and the orientational transition in solid C_{60}

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We report near-adiabatic heat capacity data on high-purity powder and single crystal C_{60}, obtained by modulated differential scanning calorimetry which facilitates data collection on a very fine temperature mesh. The anomaly associated with the orientational melting transition at ~ 260 K is much sharper and more pronounced than previously reported, the full width at half maximum in the best sample being ≤ 0.2 K. Powder *and* crystal samples from three different sources all show a 0.1 – 0.3 K splitting of the anomaly, more pronounced on cooling than on heating. Among several possible interpretations, the most appealing (motivated by recent diffuse x-ray and neutron scattering results) is the occurrence of an intermediate ordered phase with symmetry different from that of the $Pa\overline{3}$ ground state. Hysteresis between melting and freezing onsets is ≤ 0.1 K in powder samples but ≥ 1 K in crystals, which we attribute to nucleation-limited freezing in the latter. We find no evidence for a number of effects reported recently, including hysteretic behavior between 165 K and 290 K and additional transitions near 240 K and 300 K.

I. INTRODUCTION

In common with many molecular solids, C_{60} exhibits an orientationally disordered plastic crystal phase at temperatures above a first-order transition, $T_m \sim 260$ K.[1,2] Signatures of the orientational order-disorder transition have been studied in detail by structural, dynamical, thermal, magnetic, elastic, dielectric, and other probes. Two unusual features are the persistence of detectable orientational order well above T_m (Ref. 3) and the existence of substantial disorder at all temperatures below T_m.[4,5]

The high-temperature crystal lattice is primitive face-centered cubic (fcc) with four orientationally equivalent molecules per conventional cube. Most but not all of the discrete charge from the 60 carbon atoms per molecule is spherically averaged out by the thermally driven rotational dynamics. Below T_m the equivalence is broken as the molecules lock into specific energetically favorable orientations, resulting in a nonprimitive simple cubic lattice with a four-molecule-basis space group $Pa\overline{3}$.[6] In this space group, the molecular point-group symmetry is compatible with orientational twinning which is indeed observed.[7] Just as the plastic crystal phase is complicated by the presence of 15% more charge density near $\langle 110 \rangle$ directions than would be the case for spherically averaged molecules (balanced by similar deficits along $\langle 111 \rangle$), the low-T ''ordered'' phase is complicated by the existence of two preferred orientations which are nearly degenerate in energy (in $Pa\overline{3}$ any rotation angle about spe-

cific $\langle 111 \rangle$ directions is allowed). These correspond to near-neighbor contacts along $\langle 110 \rangle$ directions in which electron-rich double bonds on one molecule are immediately adjacent to electron-poor pentagonal or hexagonal faces of the neighboring molecules. The former [pentagonal face (PF)] is the global minimum in the orientational potential while experimentally the latter [hexagonal face (HF)] lies only ~ 10 meV above it.[2]

These observations present particular challenges for theorists attempting to quantitatively model the orientational potential and the thermodynamics of the phase transition. Early attempts based on Lennard-Jones (6-12) atom-centered potentials required the inclusion of *ad hoc* Coulomb terms to reproduce the observed low-temperature structure.[8,9] These were motivated in part by an attempt to mimic what was thought to be the driving force for the ordering transition, namely, the *attractive* interaction between electron-rich double bonds and hexagon or pentagon centers on adjacent molecules.[5] More recent work based on the local density approximation (LDA) charge density of the molecule correctly reproduces the two nearly degenerate minima corresponding to the different near-neighbor configurations,[10,11] and identifies short-range *repulsive* interactions as the mechanism which stabilizes the observed orientations. In fact the Coulomb contribution from the LDA valence and core charges has a maximum at the observed global minimum.[10]

Calorimetry has been used extensively to study the orientational transition,[4,12–14] the signature of which has been

shown to be very sensitive to residual solvent,[15] particle size,[16] unidentified defects,[17] hydrostatic pressure,[18,19] intercalated gases,[20,21] and stacking faults.[22] Here we report modulated differential scanning calorimetry (MDSC) results obtained on high-purity powder and single-crystal samples from three different sources. Our findings are summarized as follows. (1) The C_P anomaly is much stronger and sharper than in previous measurements. This we attribute to sample perfection and our ability to make measurements at very slow scan rates. Hysteresis between the onset temperatures of orientational freezing and melting is less than 0.1 K in powder samples and of order 1 K in single crystals, which we attribute to supercooling in the latter [as observed previously in crystals of C_{70} (Ref. 23)]. (2) When scanned at very slow rates $\leqslant 0.05$ K/min, the anomaly splits into two distinct features separated by 0.1 – 0.3 K, more pronounced on cooling than on heating. (3) We find no evidence for three effects recently reported: a second transition near 300 K,[24] a second transition near 240 K,[25,26] and large hysteresis in C_P in the interval 165–290 K.[14]

II. EXPERIMENTAL DETAILS

Experiments were performed with a TA Instruments model 2100 thermal analyzer and model 2920 differential scanning calorimeter (DSC) equipped with a temperature modulation accessory.[23] This provides a sinusoidally varying component superposed on the usual linear temperature ramp, and the heat flow signal (representing the temperature difference between sample and reference) is Fourier transformed to yield in-phase (''reversing'') and out-of-phase (''nonreversing'') components.[27] This allows us to distinguish between true phase transitions and nonequilibrium effects, increases the sensitivity, and also provides a quantity related to the absolute specific heat, namely, the in-phase heat flow divided by the ramp rate, which can be calibrated relative to a standard (in our case single-crystal Al_2O_3 at six temperatures in the range 240–300 K). The primary advantages relative to adiabatic or relaxation methods are sensitivity (5 mg being adequate for quantitative measurements), convenience in ensuring near-adiabatic conditions, and the ability to record data on arbitrarily small temperature intervals. The disadvantages are the low-temperature limit of about 150 K with liquid nitrogen cooling and limited precision associated with the calibration procedure. Care must be taken in selecting operating parameters to avoid distorting the shape and/or amplitude of C_P anomalies associated with phase transitions. In particular, in MDSC the time derivative of the instantaneous temperature $T(t) = Rt + A\sin(2\pi t/\tau)$ must not change sign with t; i.e., the linear ramp R, the modulation amplitude A, and the modulation period τ must satisfy $R\tau/A \geqslant 2\pi$ in order to ensure purely heating and cooling responses for positive and negative R, respectively. We varied R by two orders of magnitude, 0.05–5 K/min, in order to identify the *intrinsic* behavior of the C_P anomaly. Variations in A and τ had only a minor effect on the anomaly as long as the above inequality was satisfied, and at most a 5% effect on the absolute value of the ''background'' C_P even when it was not. An additional criterion is that R and τ be consistent with the intrinsic transition width such that a sufficient number of modulation cycles is recorded as the anomaly is tra-
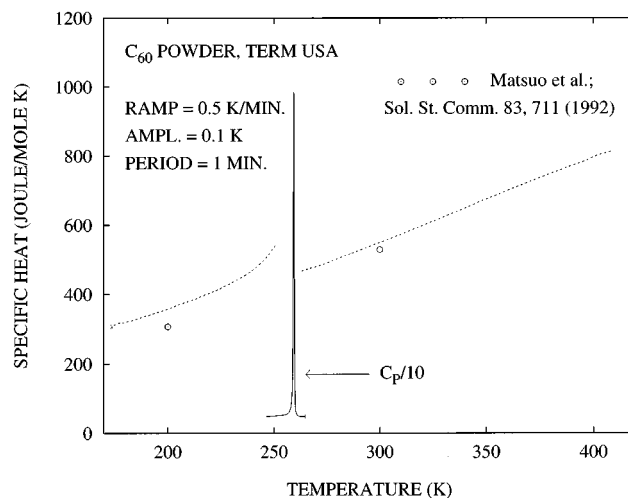

FIG. 1. Modulated differential scanning calorimetry measurement of heat capacity for C_{60} powder (dashed curve to scale, solid curve 1/10 scale), compared at two temperatures with adiabatic calorimetry results (Ref. 13) (open circles). Data measured on cooling. The peak value at the 260 K orientational transition is about 10 kJ/mol K.

versed; otherwise the Fourier transform will not be reliable.

Three samples were studied in detail: large-grain powder purchased from TERM,[28] crystals sublimed from Hoechst ''gold grade'' powder in Vienna using a double-gradient static vacuum,[29] and crystals sublimed in flowing He at 600 °C by Hoechst AG. All were checked for higher fullerene impurities, epoxides, etc., by high-performance liquid chromatography (HPLC); none were detected at the 0.2% level. All materials were briefly exposed to laboratory air while loading into aluminum pans and then quickly placed into the He flow of the calorimeter. No differences were found when hermetically sealed pans were used. We also examined many other samples from a number of commercial sources. These exhibited significant departures from the sought-after ideal behavior — detectable molecular impurities and/or stacking faults, weak or broad transitions, depressed T_m's, etc. — and were excluded from further study.

III. RESULTS

Figure 1 shows MDSC results from $\sim$ 15 mg of TERM powder using a ramp of 0.5 K/min. The background C_P well away from the phase transition (dashed curve) is essentially the same for all samples, depends very little on R,A, and τ, shows no difference between heating and cooling, and is in reasonable agreement with the data of Matsuo *et al.*[13] For the modulation conditions in Fig. 1 we have $R\tau/A = 5$ which does not quite satisfy the criterion described earlier. The peak C_P value on cooling is much larger than previously published values, with a full width at half maximum (FWHM) of 0.55 K and onset temperature 260.3(5) K. The background C_P below the transition is considerably greater than a linear extrapolation from above the transition, in agreement with Matsuo *et al.*

In principle the latent heat associated with a first-order transition is absorbed or released isothermally and the C_P anomaly is a reversible δ function. In practice the anomaly
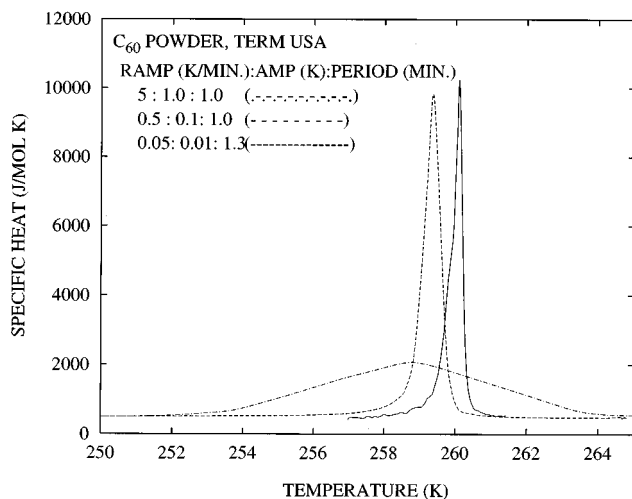
FIG. 2. Same as Fig. 1 for successively slower temperature ramp rates, the modulation amplitudes and periods being adjusted proportionately to satisfy the criterion described in the text. The slowest ramp reveals a dramatic sharpening and a shoulder on the low-*T* side of the anomaly.

FIG. 3. Heating ($\times$) and cooling ($+$) data for C_{60} powder, obtained with a ramp rate 0.05 K/min. Solid curves are fits to an *ad hoc* model consisting of a Gaussian and a Lorentzian with different widths and temperatures (dashed curves); the fit parameters are listed in Table I.

may be hysteretic and/or broadened by defects, impurities, poor thermal diffusivity, and other instrumental limitations. Figure 2 shows a dramatic sharpening of the orientational freezing anomaly in TERM powder by reducing R and A proportionately by one and two decades. The fastest ramp rate 5 K/min is typical of most published DSC and differential thermal analysis (DTA) results, and gives a peak value $\sim$ 2 kJ/mol K and a FWHM $\sim$ 5 K, while the peak in the slowest scan is $\sim$ 11 kJ/mol K, the FWHM is reduced to 0.2 K, and a shoulder on the low-*T* side appears. A similar effect is seen in the heating curves. Heating and cooling scans with R and A further reduced by half gave essentially the same result, indicating that the conditions of the solid curve in Fig. 2 reveal the intrinsic behavior of the anomaly. Conversely, by doubling R and A relative to the solid curve, the shoulder is only barely evident and the C_P peak is reduced in amplitude by 10%. The transition enthalpies, obtained by integrating the *total* heat flow from 250 to 265 K, are the same for all three ramp rates to within 10%. Conversely, areas under the C_P anomalies (derived from the *in-phase* heat flow) are not reliable at the slowest ramp rates because a substantial fraction of the total heat is out of phase, probably due to temperature gradients associated with the slow ramp, poor thermal conductivity, self-heating, and high sampling rate. Thus in what follows we focus on the shapes of the anomalies.

Figure 3 compares freezing and melting behavior for TERM powder using the slowest conditions of Fig. 2. The splitting of the cooling curve into two distinct processes is clearly evident. To facilitate comparison of heating and cooling responses, and results from different samples (see below), we tried several *completely arbitrary* algorithms to parametrize the MDSC peaks in terms of two components. We found that both the heating and cooling curves are well represented by an *ad hoc* model consisting of the sum of a Gaussian and a Lorentzian (solid curves). We emphasize that there is no physical basis for this choice; its sole significance
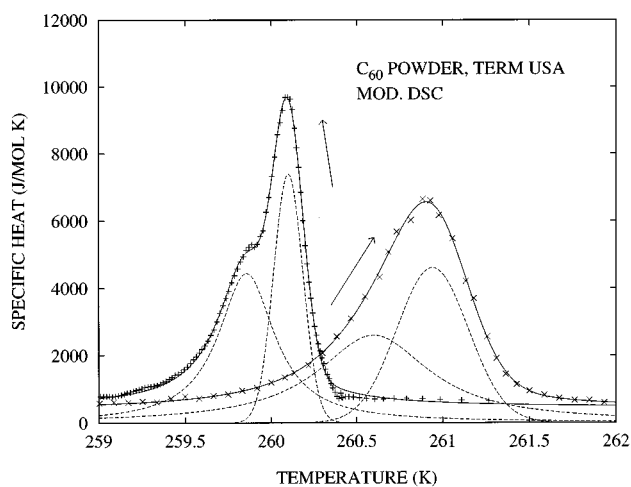
is that the fit quality convinces us that two components are present for heating and cooling, albeit unresolved in the former. The fact that the Lorentzian precedes the Gaussian on the temperature scale is consistent with the (typical) observation of precursor excess specific heat below the anomaly.[4,12–14] The fit parameters are collected in Table I. The splitting between Lorentzian and Gaussian peak positions is 0.3 K and 0.2 K on heating and cooling, respectively. The onset temperature (typically defined by the $C_P = 0$ intercept of the steepest tangent) is the same for both components on cooling, whereas the ''Lorentzian onset'' precedes the Gaussian one by $\sim$ 0.5 K on heating. This effect may be more apparent than real; in fact there is at most a 0.1 K difference in the onsets of the composite curves, suggesting little or no hysteresis or supercooling. On the other hand the shapes are dramatically different, the heating curve being considerably broader. The (total) heats of transition (257–262 K) are 5.3 and 5.5 kJ/mol from the heating and cooling curves, respectively; these are about 20% smaller than a recently reported ''near-to-standard'' single-crystal value obtained by integrating a regular DSC scan at 10 K/min over an interval more than twice as large.[16] Figure 4 shows that the splitting of the cooling curve is not an artifact of the modulation or signal processing since a similar splitting (and identical onset temperature) is observed in standard DSC at 0.05 K/min.

Figure 5 shows similar data for a 16 mg sample consisting of 12 small Vienna crystals, recorded under the same MDSC conditions as above, along with fits to the same algorithm (see Table I). Both the heating and cooling anomalies are dramatically sharper than in the powder sample; the fitted Gaussian widths are only 0.08 K and 0.06 K, respectively. Consequently, we were unable to find a combination of scan parameters and Fourier sampling rates in which spurious high-frequency oscillations could be avoided. (These are well known in many applications of Fourier spectroscopy, and occur whenever the integrand changes rapidly and the range of integration is limited by the experimental condi-

TABLE I. Parameters resulting from fitting the data in Figs. 3, 5, and 6 to the *ad hoc* model described in the text. Amplitudes in J/mol K; positions and widths in K. Splitting is between Gaussian and main Lorentzian components; a second Lorentzian component is required to obtain an acceptable fit to the Hoechst crystal data.

	TERM USA		Vienna		Hoechst	
	Heating	Cooling	Heating	Cooling	Heating	Cooling
Gaussian amplitude	4605	7382	2997	6404	4344	11600
Gaussian position	260.9	260.1	261.20	259.75	261.1	259.8
Gaussian FWHM	0.49	0.20	0.08	0.06	0.27	0.14
Lorentz (1) amplitude	2594	4436	3678	5173	2320	3846
Lorentz (1) position	260.6	259.9	261.12	259.71	260.9	259.6
Lorentz (1) FWHM	0.79	0.4	0.43	0.23	0.44	0.22
Splitting	0.3	0.2	0.08	0.04	0.2	0.2
Lorentz (2) amplitude	-	-	-	-	915	696
Lorentz (2) position	-	-	-	-	260.4	259.3
Lorentz (2) FWHM	-	-	-	-	1.41	0.90

tions.) Another consequence of the smaller widths (and the spurious oscillations) is that the splitting is no longer completely resolved in the raw data, which, however, are again well represented by a Gaussian plus a Lorentzian. For this sample the splitting between Gaussian and Lorentzian components is less than or comparable to the widths, 0.08 K and 0.04 K for heating and cooling, respectively. The major difference with respect to the powder sample is the greater hysteresis between heating and cooling, $\sim$ 1.5 K.

Figure 6 presents similar data for $\sim$ 12 mg of Hoechst crystals. The hysteresis is again much greater than in the powder sample (Fig. 3, comparable to what was observed with Vienna crystals (Fig. 5). Both cooling and heating curves are again asymmetric, the cooling curve exhibiting a distinct shoulder on the low-T side. The fitted Gaussian widths are intermediate between TERM powder and Vienna crystals; the cooling Gaussian is narrower than the heating one, as is the case for the other two samples. Both curves show substantial tails on the low-T side, necessitating a third,
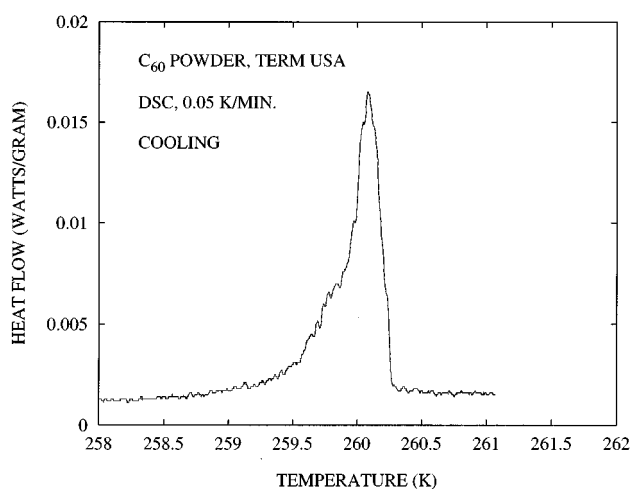

FIG. 4. Standard DSC (cooling curve) of the same sample, measured with the same ramp rate, as in Fig. 3.
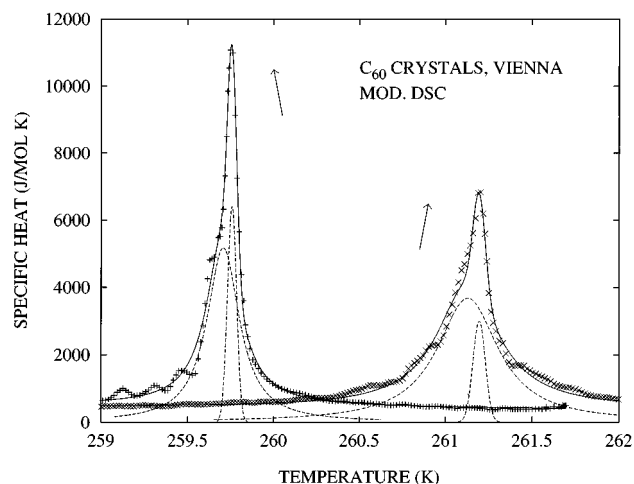

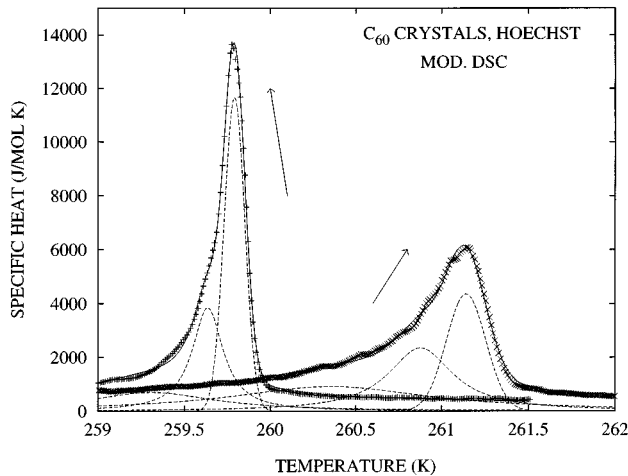FIG. 5. Same as Fig. 3 for sublimed single crystals prepared in Vienna.

FIG. 6. Same as Fig. 3 for sublimed crystals prepared by Hoechst AG.

very broad *ad hoc* Lorentzian to obtain an acceptable fit (see Table I).

IV. DISCUSSION

Our most surprising result is the splitting of the C_P anomaly into two closely spaced components, suggestive of two ordering transitions. This is not inconsistent with previous work since (a) its observation relies on measurements over much smaller temperature intervals than usually taken, and (b) DSC, $C_P(T)$, etc., are usually reported as heating rather than cooling curves (to avoid supercooling effects on T_m), and the splitting is less apparent on cooling compared to heating. A similarly small splitting was observed by mechanical spectroscopy, on the same Vienna crystals, also more readily on cooling than heating.[30] This is another technique in which the independent variable is recorded continuously vs temperature on an arbitrarily fine mesh, and is thus also well suited for observing small splittings. The fact that very similar behavior is observed in samples with no detectable impurities, from three different sources, gives us confidence that the effect is real. Based on the available information, we can only speculate about its origin.

We first considered the possibility of a small difference between surface and bulk *orientational* melting temperatures, the *positional* analog being well known. Bulk and surface processes would be assigned to, e.g., the Gaussian and Lorentzian components of the C_P anomaly. However, from Table I the relative intensities of these components are about the same in all three samples; the only difference between large surface area powder and small surface area crystal data is the larger hysteresis in the latter. So this hypothesis can be rejected.

Our next candidate derives from the nearly degenerate global (PF) and local (HF) minima in the orientational potential, and the observation that their relative fractions just below T_m (Refs. 5,31) are consistent with the relative intensities of the two anomaly components. Since the energy difference ΔU between a PF and HF is only about 0.4 kT at T_m,[2] one might imagine two distinct phases nucleating at slightly different temperatures upon cooling from above

T_m, one consisting of a PF with long-range orientational correlations plus uncorrelated HF ''defects,'' the other vice versa. The main problem with this argument is that it violates the requirements of thermal equilibrium. In a single-component system there can be at most one equilibrium phase present at any given temperature. While in practice it is found that defects can induce phase coexistence over a several-degree range,[32] the Gibbs phase rule prohibits the coexistence of two phases over an extended range. Furthermore, diffraction data below T_m are quite successfully modeled by a single ordered PF phase with a T-dependent fraction of isolated HF defects,[31] the latter being responsible for the characteristic Q dependence of diffuse neutron scattering.[33] Even if the system were not in equilibrium, coexisting ordered PF and HF phases at low T should be readily observable by the expected differences in lattice constants, the molar volume of the HF being substantially less than that of the PF.[34] Nonetheless, we decided to perform a qualitative test for generic nonequilibrium effects on the splitting by repeating the MDSC after quenching from 373 to 240 K. The results were identical to those obtained on slow cooling from above T_m. For all the reasons noted, this hypothesis is also considered unlikely.

We are thus led to consider scenarios in which the free energy is minimized for two distinct structures at very slightly different temperatures, giving rise to two closely spaced first-order transitions. There is ample precedent, e.g., the ''blue'' phase of some cholesteric liquid crystals.[35] For example, the onset of long-range order on cooling might involve successive freezing out of rotations about different molecular axes, leading to an intermediate phase with symmetry different from that of the ground state. In fact, two recent single-crystal diffuse x-ray scattering studies give evidence for orientational correlations 15–40 K above T_m which are distinctly different from those characteristic of the ordered ground state. Launois *et al.* observe L-point diffuse scattering at 300 K which cannot be ascribed to pretransitional fluctuations of $Pa\bar{3}$ ordering.[36] Similarly, Pintschovius *et al.* find short-range (40 Å) orientational correlations at $\sim$ 275 K with symmetry different from $Pa\bar{3}$.[37] These could be embryos of the postulated intermediate phase.

Another possibility for two transitions is a variation on the rejected HF-PF hypothesis. Suppose the PF and HF minima in the orientational potential have slightly different curvatures, such that HF and PF librons have different energies and T-dependent occupancies. If the competition between PF and HF orientations were governed entirely by differences in U, the PF would always win. But differences in libron energies could favor the HF via the TS term in the free energy, for some small range of T, similar to the manner in which the PV term overcomes ΔU at 2 kbar to make the HF the ground state.[34,38] Inelastic neutron scattering clearly shows the rapid buildup of libron intensity on cooling just below T_m,[33] while the large width could conceal a crossover between HF and PF libron frequencies through the small T range of the two-component C_P anomaly.

A completely different approach would be to argue that the splitting implies a morphology with two length scales, the populations of PF and HF orientations remaining in equilibrium throughout. The larger length scale would be PF-ordered regions with isolated HF defects, while the smaller

scale would be crystallites containing only one of the energetically equivalent *macroscopic* orientations allowed by rotational twinning in $Pa\overline{3}$.[7] Freezing and melting would then involve a temperature lag between two processes, e.g., supercooling on superheating of the crystallites and the overall freezing on melting of the larger PF regions.

We turn now to previously reported phenomena which we did not observe. Grivei *et al.* found that cooling C_{60} to at least 165 K induces dramatic hysteresis, whereby C_P on heating exceeds that on first or subsequent cooling by about a factor of 2 throughout the interval 165–290 K.[14] They ascribed this new anomaly at 165 K to a second ordering transition which had been observed in electron diffraction[39] but which we believe to be an impurity effect.[17] Since the practical lower limit of our equipment is 170 K, and since the effect was reported to be independent of cooling rate,[14] we looked for it by quenching a sample into liquid nitrogen, quickly loading it into the precooled calorimeter under a flow of dry gas, and measuring a heating curve up to 330 K followed by a cooling curve down to 180 K. Furthermore, since the reported hysteresis does not affect the 260 K anomaly, we chose MDSC conditions which maximized the signal to noise and minimized the total time, at the expense of possibly distorting the anomaly (namely, R, A, and $\tau = 2$ K/min, 0.2 K, and 1 min, respectively). The results are shown in Fig. 7. Clearly there is no evidence for any hysteresis beyond the small offset between freezing and melting onsets as described above.

Aside from the $\leqslant 1$ K splitting of the main transition, we find no evidence for a second transition at 300 K (Ref. 24), or for one at 240–248 K,[25,26] the latter having been directly correlated with stacking faults.[22] On the other hand, the overall agreement between our MDSC-derived C_P and a recent single-crystal measurement using the heat pulse relaxation method[40] is excellent. To date, calculations of C_V based on thermodynamic models fail to reproduce the overall behavior of $C_P(T)$ very well.[41,42]

The results reported here, along with several recent publications,[30,34,36,37] suggest that the ''standard model'' of orientational correlations in solid C_{60} is still missing an im-
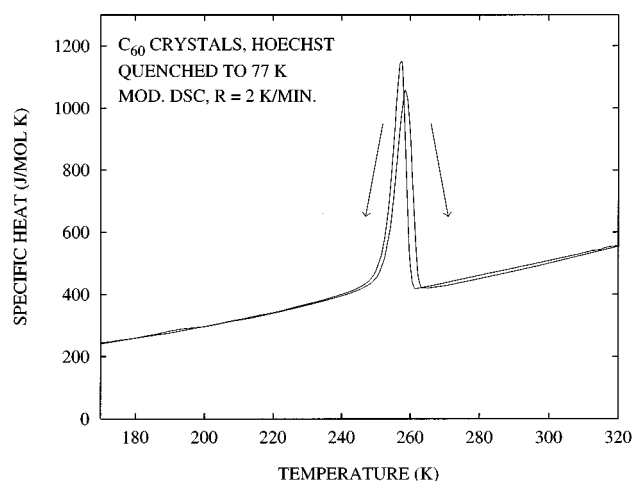

FIG. 7. Heating and cooling MDSC curves for Hoechst crystals after quenching in liquid nitrogen. There is no sign of transitions at 240 K or at 300 K or any evidence for hysteretic behavior other than the small displacement of the anomalies, all of which have been variously reported in the literature.

portant ingredient. We speculate that the splitting of the C_P anomaly is due to a second-order phase, stable only over a very small temperature interval and driven by L-point rather than X-point fluctuations. This phase would presumably have yet a third molar volume (i.e., different from both the PF and HF orientations in $Pa\overline{3}$) and would thus affect the elastic properties[30] as well as the heat capacity. This speculation can be tested in a straightforward but tedious manner by careful measurements of the L-point diffuse scattering at temperatures very close to T_m.

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