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ac calorimetry of C_{60} single crystals

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We have measured the (effective) specific heat of single crystals of C_{60} using ac calorimetry. For an fcc crystal prepared by sublimation, there is a sharp hysteretic lambda-shaped anomaly at 260 K, reflecting a latent heat spread over 3 K, similar to what is observed in powders using differential scanning calorimetry. There is also a discontinuity of $11.6R$ in the specific heat. For orthorhombic crystals prepared by slow evaporation from a toluene-hexane solution, a nonhysteretic, apparently second-order, transition is observed at 239 K. There is a peak in the specific heat consistent with a transition entropy of $R\ \ln 12$.

One of the most striking properties of crystalline C_{60} is the rotational ordering phase transition observed slightly below room temperature. Measurements by differential scanning calorimetry[1-3] (DSC) have shown that this transition, associated with a symmetry change from an fcc (high temperature) to a simple-cubic unit cell (low temperature) involves an entropy change ranging from $R\ \ln 8$ (Ref. 1) to $R \ln 27$.[3] ($R = 8.31$ J/K mole [C_{60}] is the gas constant.) Due to the rapid temperature changes used for DSC, the transitions also appear at least 10 K wide. In comparison, sharp (1 K wide) transitions have been observed in single-crystal acoustic[4] and Raman scattering[5] measurements.

In this paper, we report on measurements of the "effective" specific heat of single crystals of C_{60} using ac calorimetry.[6] This technique is in principle insensitive to latent heat at a first-order transition, unless the latent heat is distributed over a finite temperature interval, e.g., due to sample heterogeneity. Measurements are made on orthorhombic crystals[7] as well as on an fcc crystal, and normalized using DSC results on powder. For the fcc crystal, a 3-K-wide anomaly, with ~0.6-K hysteresis, is observed; however, we were not able to estimate an entropy change. For orthorhombic crystals, the transition is smoother and apparently second order; no hysteresis ($\Delta T < 0.1$ K) is observed. There is a large, 20 K wide, peak in c_p at 239 K, with an integrated area consistent with a transition entropy of $R\ \ln 12$.

Fullerenes were extracted from fullerene-rich soot (Texas Fullerenes, Inc.) using a Soxhlet extractor with benzene or hexane. The extracted C_{60} was separated from C_{70} and higher fullerenes using an alumina chromatographic column.[8] The C_{60} powder was then baked at 250 °C under dynamic vacuum for 24 h.

fcc crystals were obtained by vapor transport. The dry powder was sealed under a few hundred torr argon gas in a quartz tube which was placed in a 450–650 °C temperature gradient, with the powder at the hot end. In a few days, crystals of typical dimensions $1 \times 1 \times 0.2$ mm^3 were obtained at the cold end; x-ray diffraction confirmed that the structure of these crystals was the same as that previously reported for fcc material.[1]

Other crystals were observed by the slow evaporation and cooling from 80 to 20 °C of a solution of the pure powder in a ~1:1 toluene-hexane mixture. In a few days, small rectangular crystals ($1 \times 1 \times 0.1$ mm^3) were obtained. The residual solution was rinsed by ether. Mass spectra studies show that the crystals are $> 99.9\%$ pure C_{60} with respect to C_{70}, but an x-ray study[7] has shown that the crystals incorporate other small organic species; the unit cell is orthorhombic with $a \times b \times c = 10.34 \times 31.53 \times 10.18$ Å^3.[7]

Crystals of typical mass 10 μg ($\sim 0.7 \times 0.3 \times 0.03$ mm^3) were used for the specific-heat study. They were attached with a small amount of GE7031 varnish to a 25 μm Chromel-Constantan thermocouple. The thermocouple was formed by welding the two flattened wires together in a cross so that the sample was supported by four wires in a variable-temperature cryostat. It was heated with a chopped light source (a black PbS film was evaporated on the free face) and cooled primarily by the (~1 torr) helium atmosphere to the variable temperature of its "bath." One pair of thermocouple wires was used to measure the temperature oscillations ($\Delta T_{ac} < 0.1$ K) at the chopping frequency ω, and the other pair the dc temperature offset between the sample and its bath.[6] Details of the apparatus will be published elsewhere.[9]

Because the heating power absorbed by the sample is not known, only relative measurements of the total heat capacity of the sample and its addenda, C, can be made. $C \propto 1/(\omega \Delta T_{ac})$, in the limit $\tau_2 \ll 1/\omega \ll \tau_1$, where τ_1 and τ_2 are the external and internal thermal time constants of the sample respectively. [Errors are of order $(\omega\tau_2)^2$ and $1/(\omega\tau_1)^2$.[6,10]]

The time constants could be determined by measuring ΔT_{ac} as a function of ω. Typically, τ_2 varied from 2 to 5 ms between 30 K and room temperature and τ_1 from 250 to 400 ms. Chopping frequencies between 2 and 10 Hz were therefore used; data were taken at more than one frequency to check for consistency.

In Fig. 1 are shown the total heat capacities, in arbitrary units, of three crystals (two orthorhombic and one fcc) with their addenda. The most striking features are the large anomalies at 260 K for the fcc crystal and 239 K for the orthorhombic crystals. Otherwise, the heat capacities are featureless. This is significant because large anomalies have been observed at 155 K in the acoustic properties[4,11] and at 90 K in the thermal conductivity,[12] but these were attributed to relaxation effects rather than a phase transition; our results support this identification.

In Refs. 4 and 12, the low-temperature anomalies are associated with orientational hopping of the fullerene molecules, with an activated hopping time $\tau = \tau_0 \exp(T_0/T)$, with $T_0 \sim 3000$ K and $\tau_0 \sim 10^{-13}$ s. If the hopping is between equivalent orientations, as suggested by NMR measurements,[13] then there will be no associated specific-heat anomaly. If, however, the hopping is between inequivalent orientations, as suggested by the acoustic[4] and thermal conductivity[12] measurements, then one might expect a Schottky anomaly ($\sim R/2$) in the specific heat at $T \sim 0.4U/k_B \sim 55$ K,[12] where U is the energy difference between the orientations. However, for a chopping frequency $\omega/2\pi = 6$ Hz, the measured anomaly will be reduced by a factor of $1/\omega\tau \sim 10^{-12}$.

In Fig. 2, the total heat capacities near the transitions are shown for two samples in an enlarged plot. Data taken during both warming and cooling ramps, with $|dT/dt| < 0.1$ K/min so that the dc temperatures of the sample, bath, and thermometers were equilibrated, are shown. For the fcc crystal, the anomaly is 3 K wide and there is 0.6-K hysteresis, smaller than that reported (2.5 K) by Shi *et al.*[4] In view of the first-order nature of the transition, the measured anomaly should be viewed at least in part as a latent heat dispersed over 3 K due to sample heterogeneity. It is interesting, however, that the high-temperature side of the anomaly is much sharper than the low-temperature side, for both warming and cooling runs, suggesting that we may be "missing" much of the latent heat due to our finite temperature (0.1 K) steps; indeed, a larger anomaly is observed using DSC (see Fig. 3). Also, as discussed below, large discontinuities in the specific heat and its temperature derivative are observed.

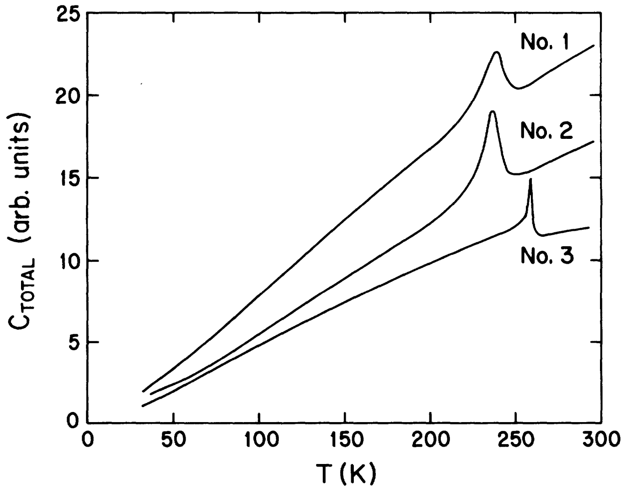

FIG. 1. Total heat capacities (samples plus addenda) for three C_{60} crystals; curves No. 1 and No. 2 are orthorhombic and curve No. 3 is fcc. The arbitrary units used for each are different.

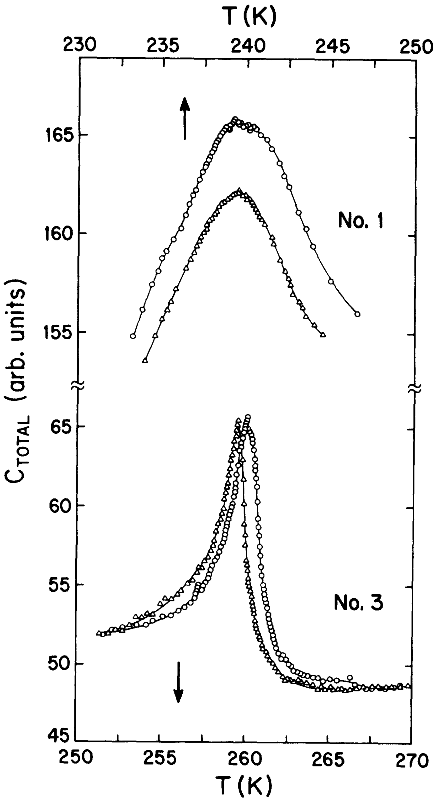

FIG. 2. Total (sample plus addendum) heat capacities of two crystals (identified in Fig. 1). The data shown by circles (triangles) were taken while warming (cooling); the lines are guides to the eye. The two runs for sample No. 1 are offset for clarity. Note the different scales used for the two samples.

In contrast, a much wider (20 K), nonhysteretic ($\Delta T < 0.1$ K) anomaly is observed in the orthorhombic samples, suggesting that the transition is second order. It is interesting that a second-order transition at 242 K was also observed in a monoclinic crystal grown from a carbon disulfide solution.[4] Despite the similarity in transition temperatures, the thermodynamics of the two transitions are apparently quite different, however, because the acoustic anomaly observed for the monoclinic sample[4] is very asymmetric, with significant pretransition softening observed above the transition, whereas the heat-capacity anomalies in the orthorhombic crystals are much more symmetric.[14]

An accurate determination of the samples' specific heats proved difficult due to their small sizes. The heat capacity of the sample addendum was comparable to that of the crystal, but the addendum mass, ~ 3 μg of varnish and 14 μg of wire ($\frac{1}{3}$ its length[10]), could only be determined to 10%. The sample's specific heat was then determined by normalizing the remainder to that which we determined by DSC (Ref. 15) of the power at 150 K. The

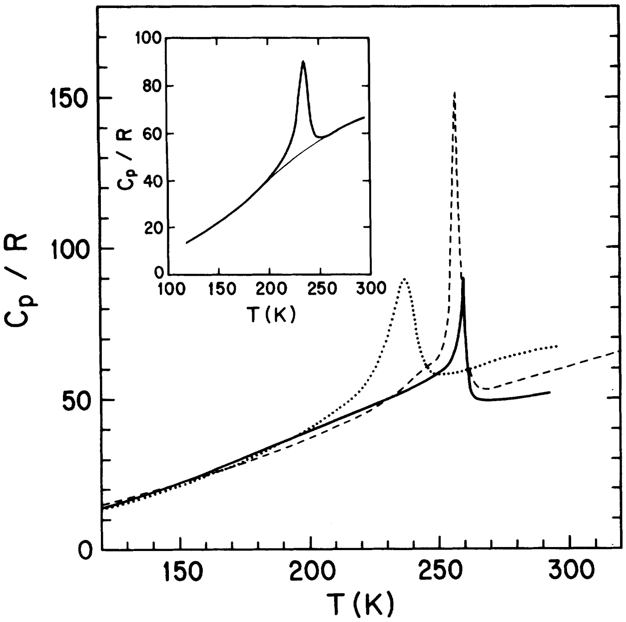

FIG. 3. Calculated molar specific heats for sample No. 2 (dotted curve) and sample No. 3 (solid curve). The dashed curve shows the DSC results on a powder. Inset: c_p of orthorhombic crystal No. 2 (thick curve), showing the polynomial background (thin curve) used to calculate the entropy change.

appropriateness of this may be questioned, as the power appears to be a mixture of phases (see below), but the calculated specific heats of crystals of both phases are similar to each other, and that of the powder, below the transitions. The uncertainty in the specific heats of the crystals at 300 K is ~8%.

The resulting specific heat of two of the crystals is shown in Fig. 3, along with our DSC data. Data are only shown above 120 K; at lower temperatures, the relative contribution of the addenda becomes more uncertain. In addition to the lambda-shaped anomaly associated with the latent heat of the fcc crystal, there are large discontinuities of $11.6R$ in c_p and $0.28R/\mathrm{K}$ in dc_p/dT. The weak temperature dependence of c_p immediately above the transition is similar to the behavior of the thermal conductivity.[12]

For the orthorhombic crystal, the specific heat varies more smoothly, so that it could be fit to a polynomial away from the transition, as shown in the inset. The peak in the specific-heat anomaly is $\Delta c_p = 38R$. The transition entropy, $\Delta S = \int (\Delta c_p/T)dT = R\ln 12$, is comparable to that previously observed from DSC for (fcc) powders.[1,3]

The powder specific heat, determined by DSC (Ref. 15) is also shown in Fig. 3. Away from the anomaly, it agrees well (within 10%) with the results of Jin *et al.*[3] From the lambdalike shape of the anomaly at 260 K, it is clear that the powder includes fcc material. However, there is also a shoulder at 243 K, which may indicate that the powder also includes other phases (that may incorporate other organic molecules). This is supported by the fact that, above the transition, the powder specific heat is between that calculated for the two single crystals. The maximum transition entropy consistent with the DSC data is $R\ln 12$, which is 30% less than that of Ref. 3, in which the material is thought to be pure fcc.

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