THERMAL PROPERTIES OF FULLERENES

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ABSTRACT

We present the results of specific heat measurements on single crystals of C_{60} in (pure) fcc and (toluene containing) orthorhombic phases. The orientational ordering phase transitions are at surprisingly close temperatures (26OK and 239K) for the two polytypes. The single crystal results are compared with DSC measurements on powders.

The thermal properties of solid C_{60} are interesting because of their implications regarding interactions between fullerene molecules [1-8]. Especially noteworthy is the orientational ordering phase transition observed slightly below room temperature [2-8]. Most measurements have been on powders and pellets [1-5] for which the transition is >10K wide and has sample dependent transition temperatures and precursor effects. The sample dependence has been associated with defects such as stacking faults caused by impurities and/or growth conditions [4].

We have recently reported on specific heat measurements using ac calorimetry on small (~10μg), well characterized single crystals [8]. In this paper, we will elaborate on these results and compare them with differential scanning calorimetry (DSC) results on powders.

Measurements were made on an orthorhombic single crystal containing toluene and a (pure) fcc crystal. The latter was prepared by vapor transport in argon from a purified powder [8], and its structure verified by x-ray diffraction. Orthorhombic crystals were prepared by the slow evaporation of a solution of C_{60} in a toluene-hexane mixture [8]. X-ray diffraction measurements [9] show that the unit cell (a x b x c = 10.34 x 31.53 x 10.18 $Å^3$) contains four C_{60} molecules and four toluene sites, with ~50% random occupancy. Each fullerene has 10 near neighbors, at separations varying from 10.1Å to 10.3Å [9], compared to 12 neighbors at 10.0Å for the fcc polytype [2].

The specific heat was measured by heating the sample with light chopped at frequency f ~ 5Hz. A chromel-constantan thermocouple was attached to the sample with GE 7031 varnish to measure the temperature oscillations at f, which are inversely proportional to the total heat capacity of the sample and its addenda, C [8]. Determining the specific heat, c_p, of these small samples from C is difficult because accurate measurements of the addenda masses (typically 3μg of varnish and 14μg of wire) were not possible and the contribution of the addenda to C is large (~50%). Because the absorbed powers were unknown, the molar specific heats of the crystals were normalized to that determined by DSC by Jin et al at 200K (40.7R) for a (nominally fcc) powder [3]; this normalization is of course only approximate for the orthorhombic crystal. Here R= 8.31 $JK^{-1}mol(C_{60})^{-1}$ is the gas constant.

The specific heats of the two samples are shown in Figures 1 and 2 using our best estimates for the addenda masses. (The uncorrected values for C are shown in Reference 8). For the fcc crystal, the error bars show the specific heat values if we change the varnish mass by ±50% and the wire masses by ±10%. Similar error bars will hold for the orthorhombic sample.

Also shown in Figure 1 are the low temperature values measured for a pellet [1]. Extrapolation to our results would suggest that there is a small peak (Δc_p ~ R) near 30K, e.g. due to an "orientational Schottky" anomaly [7,8], but from the size of the error bars, it is premature to state whether this is so or whether the peak is an artifact of our overestimating the addendum mass. The latter is also consistent with the expected "plateau" value of c_p=6R [3,5]. In any case, the "plateau" in specific heat between 30 and 80K is wider than that calculated by Jin et al [3] from molecular dynamic simulations (also shown in
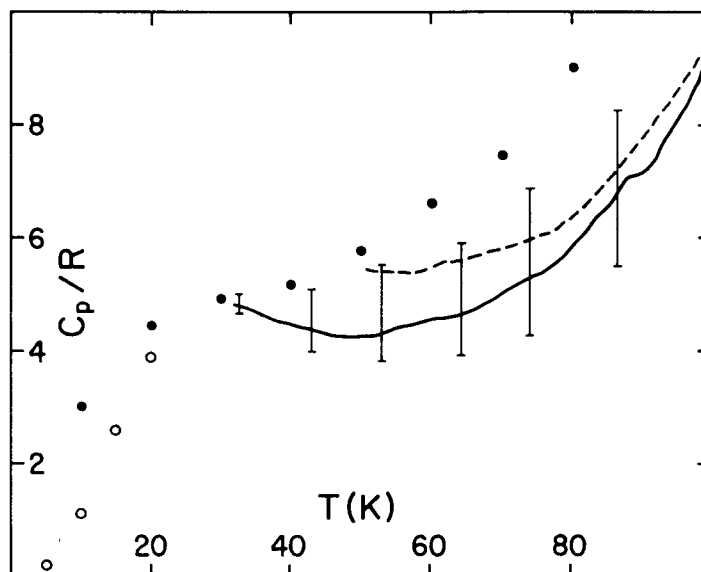
Fig. 1. Low temperature specific heats of the fcc (solid curve) and orthorhombic (dashed curve) crystals. The upper (lower) error bars for the fcc crystal show the effects of decreasing (increasing) the masses of the addendum varnish and thermocouple wires by 50% and 10%, respectively, from their estimated values. The open circles are the measured fcc values of Reference 1; the closed circles are the calculated values of Reference 3.

Figure 1), implying a large separation between acoustic and optical phonon energies.

The specific heat over a wider temperature range for the two crystals, as well as the measured DSC results of Jin et al [3], are shown in Figure 2. The three data sets are all very similar below 200K; the higher temperature data suggest that the DSC powder was a mixture of polytypes. For the fcc crystal, the anomaly (at 260K) is slightly hysteretic ($T_{warming}$-$T_{cooling}$~0.6K) [6,8], so that the measured lambda-shaped anomaly presumably includes a distributed latent heat. Comparison with the DSC results, however, shows that most of the latent heat is missed in our measurement. Our anomaly for the fcc crystal is only 3K wide, and there are discontinuities in both c_p (11.6R) and dc_p/dT (0.28R/K) at the transition [8].

On the other hand, the anomaly for the orthorhombic crystal (at 239K) is 20K wide, non-hysteretic ($\Delta T<0.1K$), and presumably second order [8]; the area under the peak implies an entropy change of R1n12 at the transition, similar
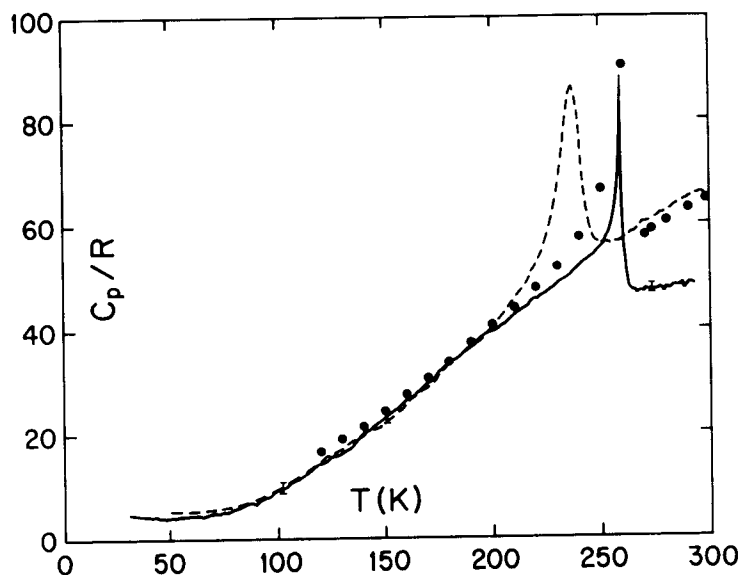
Fig. 2. Specific heats of the fcc (solid curve) and orthorhombic (dashed curve) crystals. The error bars show the effects of changing the masses of the fcc addendum as in Figure 1. The closed circles are the values <u>measured</u> by DSC in Reference 3.

to fcc powders. The closeness of the two transition temperatures is surprising. If T_c were to simply scale with the number of near neighbors, one would indeed expect $T_{orth}=5/6T_{fcc}=217K$. However, T_c is also expected to be a strong function of intermolecular separation [7], which would suppress T_{orth} much further. Since interactions with the toluene molecules should increase T_c, the fact that $T_{orth} \sim T_{fcc}$ may be caused by a fortuitous cancellation of competing effects.

To study this possibility further, we have begun DSC measurements on powders prepared from toluene [10]. Fullerenes were extracted from soot by stirring and sonicating with toluene at room temperature. Nearly saturated solutions were chromatographed on a Waters 600E HPLC/GPC system (500Å and 100Å Ultrastyrgel Gel Permeation Chromatography columns, UV/visible detection at 600 nm); the purity of C_{60} purified by GPC is generally higher than that purified by conventional column chromatography on alumina [10]. Elution with toluene produced a C_{60} fraction which was dried at 82°C for >8h in vacuum. HPLC analysis showed that the powder had <1.1% C_{70} and <7% nonsolvent species, based on peak integrals at 590 nm.

DSC data for a coarse-grained (~150µm diameter), as-grown powder are shown in Figure 3 (Curve A). As compared to previous DSC measurements [2-4,8], the transition endotherm is quite sharp ($\Delta T \sim 5K$), in part due to our slow sweep rate. However, the low transition temperature (245K) and low temperature shoulder suggest that either the sample is not fcc or that there are considerable faults and/or impurities [4]. Also, the transition entropy is small ($\Delta H = 2RT_c$), suggesting that there is still considerable disorder below Tc. Results for a finer grained (<5µm diameter) as-grown powder are shown in Curve C. Although the transition temperature is 4K higher, the transition is considerably broader, with two well-separated peaks, and ΔH only = $1.2RT_c$.

Samples of both powders were also slowly heated (in 4h), to avoid agglomeration, to 250C-300C under a dynamic vacuum of ~20 µtorr, and held in these conditions for >20h. Such an annealing treatment probably completely removes toluene [11]. For the coarse-grained sample (Curve B), there is no change in T_c or ΔH, although there is a reduction in the low-temperature shoulder. For the fine-grained sample (Curve D), the peak shifted down by 3K and sharpened considerably, although ΔH again did not change.

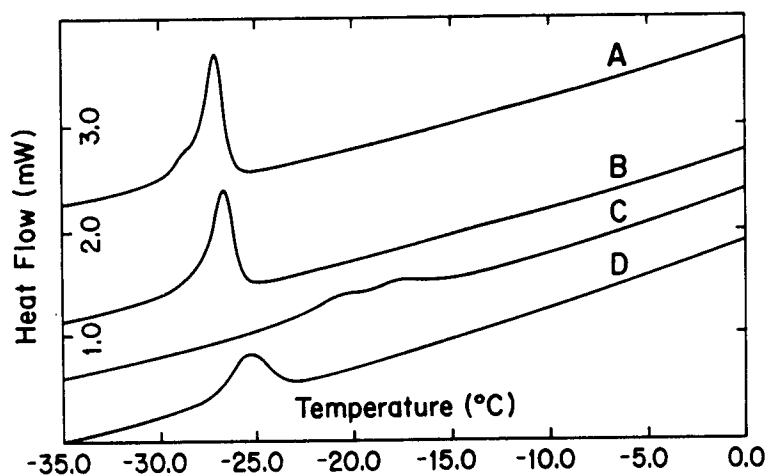
Fig. 3. Differential scanning calorimetry heating curves for four powders (shifted vertically for clarity). A: as-grown coarse powder (10.5 mg, 2°C/min); B: annealed coarse powder (9.2 mg, 2°C/min); C: as-grown fine powder, (4.6 mg, 3°C/min); D: annealed fine powder (5.8 mg, 3°C/min).

Interpreting these results will require further structural and chemical analyses on the powders, which are in progress. Assuming that broad transitions are associated with defects, comparison of curves C and D shows that a lower transition temperature does not necessarily imply a poorer quality sample. (This, of course, is consistent with our results on the orthorhombic single crystal.) If the vacuum annealing is effective in removing the solvent molecules, their presence apparently does not greatly affect the transition. In this case, it is especially surprising that structures as different as the fcc and orthorhombic have such similar transition temperatures.

ACKNOWLEDGEMENTS

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