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Thermal properties of C_{70}

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Low-temperature specific heat and differential-scanning-calorimetry (DSC) measurements have been performed on polycrystalline C_{70}. At high temperature, the DSC measurements reveal two phase transitions at 280 and 337 K, respectively. At low temperatures, the measurements reveal an excess of specific heat with respect to that of graphite, with a classical behavior and a Debye temperature of 145 K. At 50 K a second-order transition is observed.

Intensive work has recently been performed pertaining to the experimental investigation and interpretation of the structural and thermal properties of C_{60} and other fullerenes.[1-9] In the fullerenes family, C_{70} is the next stable molecule following C_{60}. Its elongated shape corresponds to that of a C_{60} molecule with an additional ring of hexagons on the equatorial plane. A pentagon is situated at the top and the bottom of the molecule.[10]

At low temperatures, the lattice structure is hexagonal close packed (hcp), while above 440 K it becomes face centered cubic (fcc). The low-temperature crystal structure results from the Van der Waals bonds between the electron-poor regions—the centers of the equatorial hexagons—and the electron-rich regions—the equatorial interhexagonal edges of the neighbors.[11,12]

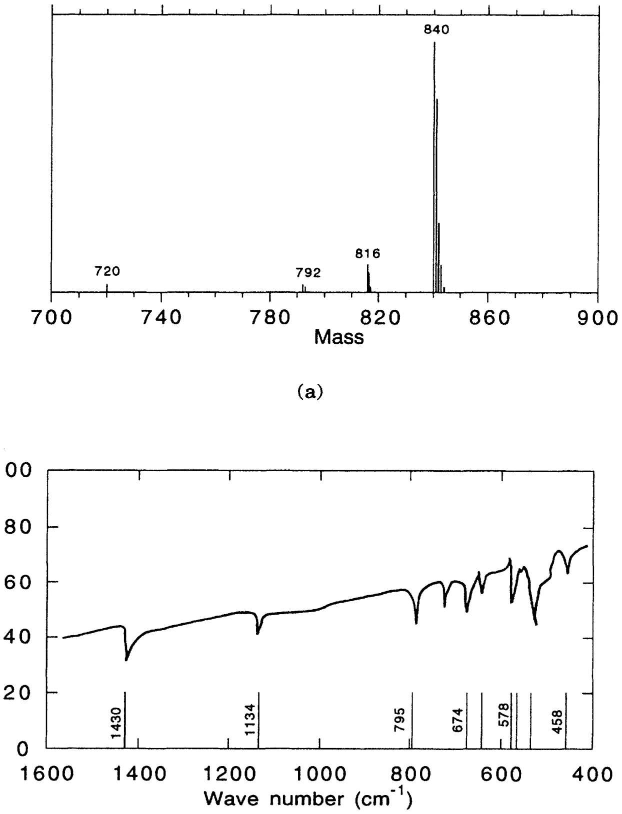
While some data were recently reported on the specific heat of C_{60} (Refs. 5 and 6) and its mixtures,[8] we report here specific-heat measurements of a C_{70} sample.

The C_{60}-C_{70} fullerene extract has been purchased from Texas Fullerenes Corp. Its components, C_{60} and C_{70}, were chromatographically separated on a neutral alumina (activated grade 1) column with hexane-toluene (95:5 volume ratio) as eluant for C_{60} and hexane-toluene (80:20 volume ratio) for C_{70}. Mass and infrared spectrometry indicated that the isolated C_{70} contained less than 5% of C_{60} (Fig. 1).

A differential-scanning-calorimetry (DSC) measurement was first realized on the first sample before any thermal treatment of the C_{70} powder. The measurement has been performed by means of a DuPont 2000 system on a 6-mg sample with a heating rate of 10 °C per minute. The results are presented in Fig. 2.

During the first heating cycle [Fig. 2(a)] an endothermal peak was observed at 430 K. This peak may be attributed to the decomposition of the toluene-C_{70} complex.[5]

During the second heating cycle [Fig. 2(b)], two endothermal peaks were observed at 280 and 337 K, respectively. The heats of transition of these peaks are, respectively, equal to 3.2 and 2.2 J g^{-1}. These two transitions, which correspond to those previously reported,[11] are related to phase transitions from the low-temperature hcp structure to the high-temperature fcc structure.[11,12] The fact that two transition peaks are observed is consistent with the existence of a complicated mechanism. This involves the gradual transition from the low-temperature



(a)

(b)

FIG. 1. Mass spectrum (a) and IR spectrum (b) of the chromatographically purified C_{70} powder. In (b) one can observe all C_{70} infrared line positions already reported (Ref. 17).

phase, i.e., the enlogated molecule of C_{70} rotating along its *c* axis, to the high-temperature phase, i.e., the molecule rotating freely and isotropically. This is confirmed by electronic-microscopy observations (TEM) which have brought to the fore the existence of different structure between the low-temperature and the high-temperature phases.[12]

The absence of these two transition peaks during the first heating cycle shows that the structure of the solvated C_{70} power is different from that of the pure crystalline C_{70}. It is only after the first heating cycle that the solvent is removed and that solid C_{70} may crystallize. The absence of the solvent in the heat-treated powder is confirmed by the disappearance of the peak at 430 K in the second run. Further heating cycles were performed and the results were the same as that of the second cycle.

The second sample was used for the low-temperature specific-heat measurements. A pellet of 12 mg was pressed under 12 kbar during 5 min. The sample was then heat treated at 440 K under vacuum ($p \approx 10^{-1}$ Torr) for two days in order to remove the solvent.

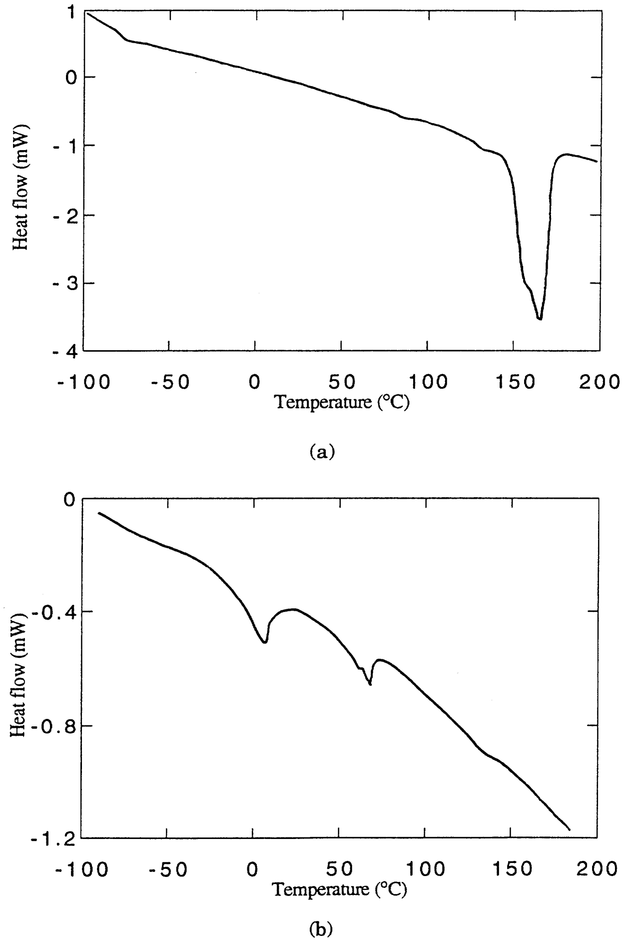


FIG. 2. (a) First heating cycle of the DSC measurement showing a large endothermal peak at 430 K corresponding to the desolvation of C_{70}. (b) Second heating cycle of the DSC measurements with the two endothermal peaks at 280 and 337 K attributed to the phase transitions.

The specific-heat measurements were performed by means of a system based on the relaxation-time method.[13] The data were recorded in the temperature range of $3 < T < 300$ K. The sample was fixed by a small amount of apiezon grease to a tiny copper plate on which was also attached the thermometer (Rivac Technology thin-film carbon resistor) and the heater. The heat capacity of addenda was previously determined and subtracted from the measured value. The effects of the internal relaxation time of the sample on the measurement were negligible at all temperatures. At low temperatures, the heat capacity of the sample represented 80% of the heat capacity of the addenda while at high temperature, around 300 K, it is smaller than 10%.

In Fig. 3, the temperature variation of the specific heat is presented. It is compared to that of a C_{60}-C_{70} extract[8] and to that of graphite.[14] At low temperature, the C_{70} presents the same excess in specific heat with respect to graphite as does the fullerene extract powder[8] or the pure C_{60}.[5–7] Note that the C_{70} specific heat is almost ten times larger than the specific heat of graphite.

At very low temperatures ($T < 8$ K) the temperature variation of the specific heat tends to a T^3 law (Fig. 4). The Debye temperature estimated from the fit of the data is equal to 145 K. The high value of the specific heat at these temperatures is due to the low-lying vibrational modes and by the librational modes such as those already observed in C_{60}.[15,16]

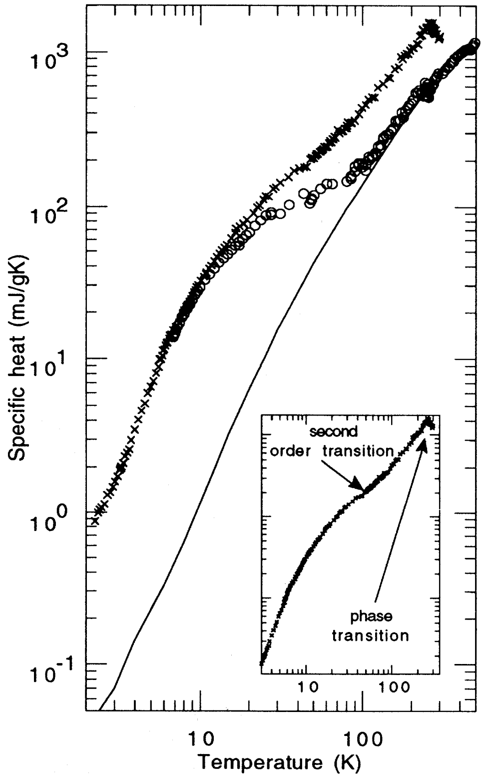


FIG. 3. Temperature dependence of the specific heat of C_{70} (+) compared to that of C_{60}/C_{70} extract (Ref. 8) (○) and to that of graphite (Ref. 14) (——). For the C_{70} sample two anomalies can be observed at 50 and 270 K, respectively.

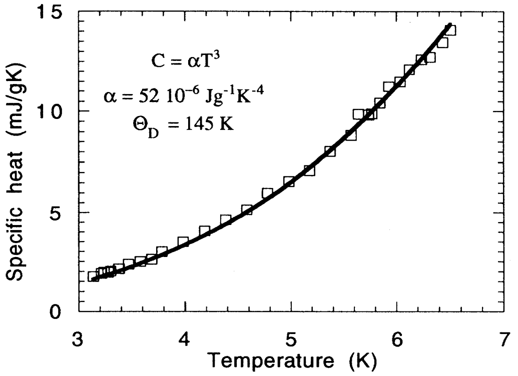


FIG. 4. Specific-heat temperature variation below 8 K showing the T^3 fit used in the Debye approximation.

An anomaly having the form of a second-order transition is observed around 50 K. The same type of change in slope is observed in the specific heat of C_{60} (Refs. 5 and 7) and of the fullerene extract[8] around 90 K and in the temperature variation of the thermal conductivity of C_{60}.[9] This second-order transition is attributed to the freezing of orientational disorder in the structure.[2] The appearance of such transitions in C_{70} suggests that there also exists nearly degenerate orientations of the molecules in the lattice, and that some orientational disorder may be frozen at low temperatures ($T < 50$ K).

A second anomaly is observed at 270 K with an onset at 260 K. This anomaly was already apparent in the form of the first phase transition observed in the DSC measurements. The measured specific heat of C_{70} at high temperatures is much higher than that of C_{60} or C_{60}-C_{70} powder.

All these observations may be understood if we consider that the C_{70} molecule is very similar to that of the C_{60}. They have similar shapes and the nature of the crystals and the vibrational modes is also similar. These similarities are reflected in the temperature variation of the specific heat. The same excess is observed at low temperatures. A kind of glassy transition due to the freezing of rotational disorder and orientational ordering transitions appear. However, the observation of two transition temperatures in solid C_{70} reflects the fact that the mechanism leading to the orientational transition is more complicated than in solid C_{60}.

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