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1995 J. Phys.: Condens. Matter 7 7475

(http://iopscience.iop.org/0953-8984/7/38/006)

J. Phys.: Condens. Matter 7 (1995) 7475–7479. Printed in the UK

Thermoanalytical studies on the order–disorder transition in C_{60} doped with C_{70}

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Received 4 April 1995, in final form 7 June 1995

Abstract. C_{60} crystals containing C_{70} at various dopant levels, from 0 to 10%, have been grown via the novel method of 'solvent dilution'. Their crystallographic structures were examined with x-ray diffractometry, and their order-disorder phase transitions with differential scanning calorimetry. An extra HCP lattice structure was clearly seen in more highly doped C_{60}. On the other hand, both the phase transition temperature and the heat of transition decreased with rising C_{70} concentration. This suppression of the order–disorder transition may be explained by a weakening of the correlation among C_{60} molecules due to their dilution by the dopant.

1. Introduction

The order–disorder phase transition in solid C_{60} at 240–260 K has been investigated by various experimental methods including differential scanning calorimetry (DSC) [1, 2], x-ray diffraction (XRD) [1], nuclear magnetic resonance [3], neutron diffraction [4], sound attenuation [2, 5] and dielectric spectroscopy [6, 7]. This fullerite has a face-centred cubic (FCC) lattice which accommodates a rotational disorder of C_{60} clusters but which transforms, below T_c, into a simple-cubic (SC) structure. This transition is of first order and in DSC measurements gives rise to a sharp endothermic peak upon heating, with an enthalpy of about 9.1 J g^{-1} for high-purity samples [8]. However, the behaviour during phase transition is strongly influenced by solvents, dissolved gases and trace impurities. There is a substantial precursor [8] at lower temperatures in the presence of solvents. Also, molecular species diffuse readily into the octahedral interstitial sites of the FCC lattice [9]. In the case of interstitial oxygen [10], DSC thermograms exhibit the transition at 258 K and also a broad peak on the low-temperature side, whose exact position and area (heat of transition) depend on oxygen concentration. In the case of dissolved hydrogen [11], the major peak has an onset temperature of 257 K, accompanied by a minor peak about 3 K lower which was explained as a negative chemical pressure effect, as well as a broad onset at still lower temperature. Then, a sample of C_{60} and C_{70} in 3:1 ratio displayed two sharp peaks at 250 and 255 K, the former attributable to C_{70} or impurities [12].

The work to be reported here focuses on C_{70} as a solid dopant. It is incorporated as a substitutional impurity, due to its almost identical size; yet, within the temperature range of interest, its rotations about all axes are frozen in and so, unlike its host, it lacks rotational symmetry even above T_c. There is also practical relevance. To account for the observed coexistence of the FCC and the SC phases over a nonzero temperature interval, Heiney [8]

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0953-8984/95/387475+05$19.50

has argued that even the most purified samples of C_{60} contain other fullerenes. In particular, C_{60} and C_{70} are often encountered together in the condensed phase [13]. To assess the effects of C_{70} on the order–disorder transition, we prepared a series of two-component materials with a range of C_{60}:C_{70} ratios, which we then examined with DSC and XRD.

2. Experimental details

The basic ingredients were produced by the contact-arc method [14], using graphite rods in a 100 Torr helium atomosphere. C_{60} and C_{70} were extracted from soot with toluene and then separated with high-pressure liquid chromatography that used neutral alumina as the stationary phase (for which activated charcoal in silica gel had also been tried, but with less satisfactory results). NMR and IR spectroscopies and mass spectrometry showed that the C_{60} attained a purity of 99.9%, and the C_{70} a purity of 98% (the main contaminant in C_{70} is C_{60}).

In total, six batches of samples have been studied, namely samples 0, 1, 2, 3, 5, and 10, where the numeral denotes the percentage of C_{70}, the balance being made up by C_{60} (whose nominal concentration is 90% in sample 10, for example). Their growth proceeded by a new method. The two constituents in the appropriate mass ratio were mixed and homogenized by dissolution in *o*-xylene and placed in an ultrasonic bath. After complete dissolution the flask, its stopper removed, was put inside a beaker containing ether, which was then tightly sealed. Gradual dilution of the *o*-xylene due to the recondensation of ether in the flask caused a slow recrystallization of C_{60}–C_{70}; the process was completed usually in 3 d during which the C_{60} and C_{70} dissolved in the *o*-xylene has been completely crystallized. The residual solutions, in which no C_{60} and C_{70} can be detected by NMR, become colourless and transparent. After being washed in ether, the grown crystals were crushed into fine powder, annealed at 220 °C in a high vacuum for 60 h and then kept under vacuum in a desiccator.

The order–disorder transition was characterized by DSC measurements, carried out in a Setaram subambient differential scanning calorimeter model 92, at a heating rate of 10 K min^{-1} in either vacuum or in helium flowing at 10 ml min^{-1}. Alumina powder served as the reference. To provide information on crystallographic modifications due to doping with C_{70}, room-temperature powder XRD data were recorded in a D/Max-VA rotating-anode diffractometer that provided 4 kW Cu Kα radiation.

3. Results

The crystals that we obtained using the novel method of solvent dilution were needles and hexahedron like in form (figure 1). It should be noted that, when the *o*-xylene solution contained over 10% C_{70}, no crystals could be produced in this way, although the two fullerenes have been reported as being mutually soluble in the solid state to the extent of about 30% [17].

DSC thermograms measured on a sample in flowing helium (figure 2) and in vacuum were essentially identical, except that the latter condition generally led to a noisier trace. Sample 0, i.e. nominally pure C_{60}, gave the sharpest endothermic peak, the highest peak temperature T_m and the largest heat ΔH of transition. Also its trace contained a slow-rising precursor, which had previously been attributed to residue solvent [8], an explanation corroborated by our observation of larger precursors in samples annealed in vacuum for shorter times. As the concentration of C_{70} increased, both T_m and ΔH decreased. (T_m

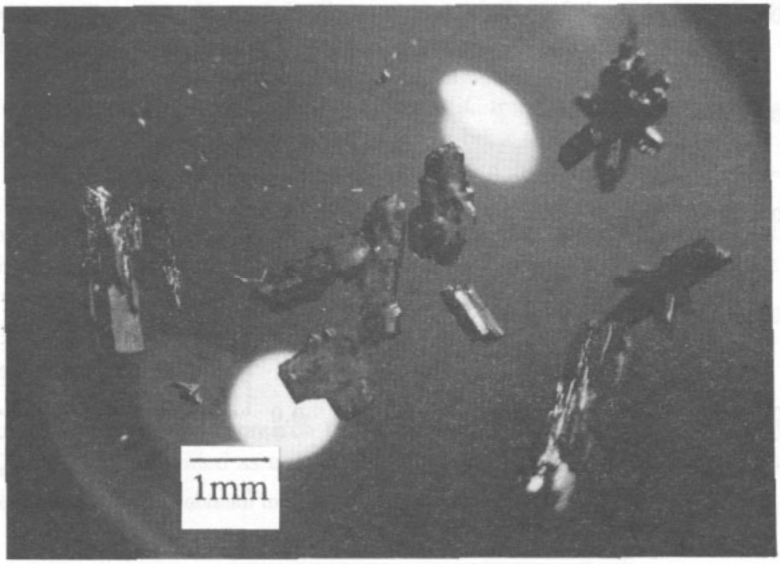

Figure 1. Photomicrographs of a C_{60}–C_{70} alloy crystal grown with the diluted solution method.

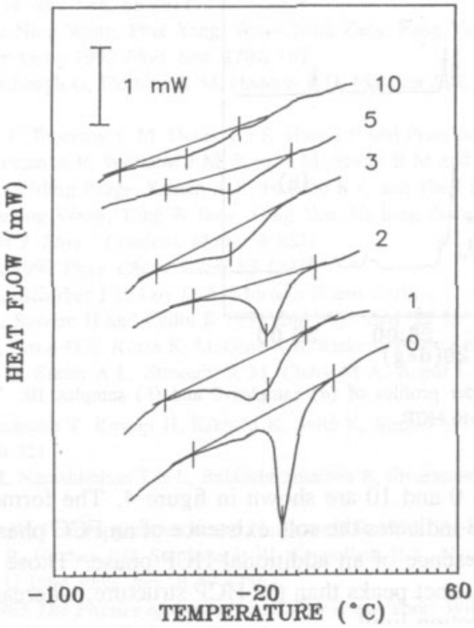

Figure 2. DSC traces scanned at +10 K min^{-1}, of various samples in flowing helium; the numbers besides the traces specify the percentages of doped C_{70} in the respective samples.

was considered instead of the onset temperature, which could not be determined from the thermogram as accurately, but which nevertheless scaled with T_m, since the same heating rate applied to all thermograms.) Plots of T_m and ΔH against $x \equiv [C_{70}]/[C_{60}]$, in figures 3(*a*) and 3(*b*) respectively, show that the decreases are approximately linear and exponential respectively.

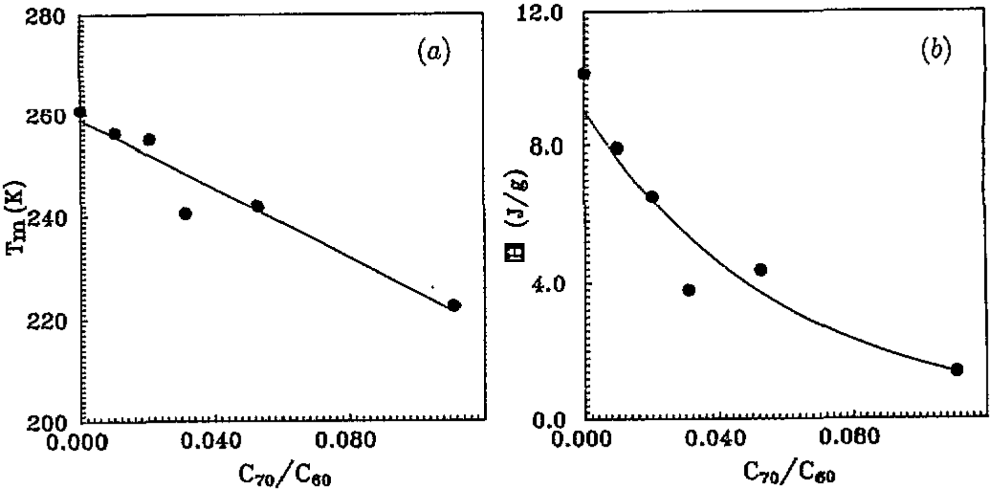

Figure 3. (*a*) Peak temperature and (*b*) heat of transition versus concentration ratio.

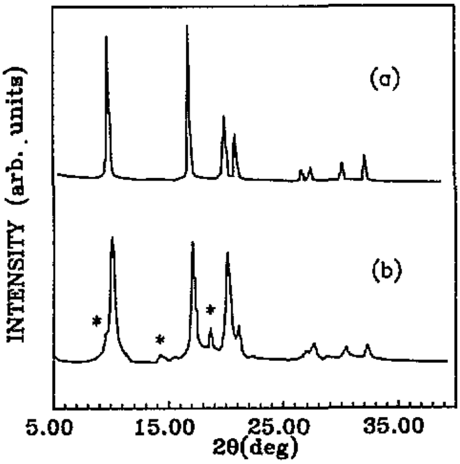

Figure 4. X-ray powder profiles of (*a*) samples 0 and (*b*) samples 10: *, peaks uniquely indexable as pertaining to HCP.

The XRD profiles of samples 0 and 10 are shown in figure 4. The former agrees with published data in the literature and indicates the sole existence of an FCC phase. In contrast, that for sample 10 reveals the presence of an additional HCP phase. Those for samples 3 and 5 (not shown) exhibits less distinct peaks than the HCP structure, whereas in samples 1 and 2 it was below the XRD detection limit.

4. Discussion

The reductions in T_m and ΔH due to the C_{70} impurity cannot be simply attributed to a negative pressure effect. However, the detection of an extra crystallographic phase may point to a natural explanation. The HCP and the FCC lattices differ, of course, only in the stacking sequences of their close-packed planes. Their intergrowth in nano-sized crystals results therefore in stacking faults, and second-neighbour effects [15] should lead to the suppression of both T_m and ΔH, and finally to the extinction of the transition itself. The weakening of the correlation among C_{60} molecules because of their dilution by C_{70} is analogous to, for example, the situation of a diluted ferromagnetic crystal [16].

Another feature is the two-peak structure of the DSC trace for C_{60}–1% C_{70}. The same structure with a matching peak separation of 5 K has been seen by Atake *et al* [12] and Samara *et al* [17], who explained the phenomenon by a model of hindered as well as unhindered rotations of C_{60}. In our case, the lower-temperature peak may relate to C_{60} adjacent to interstitial oxygen and substitutional C_{70} [7], because oxygen readily diffuses into C_{60} under ambient conditions [7, 9]. The exact mechanism of rotation hindrance is not known, however.

Acknowledgments

MG was supported by a Faculty Research Grant from Hong Kong Baptist University. The Subambient DSC-92 was obtained as a result of the generosity of the Croucher Foundation in Hong Kong.

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