The influence of point defects on the dielectric response of C_{60} fullerite

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Abstract. C_{60} samples as well as C_{60} containing O_2, C_{70} or both were studied. The dielectric loss and constant of the pressed pellets have been measured at 1 and 10 kHz as the temperature was cycled between 85 and 273 K. The low-temperature parts of the dielectric-loss spectra of doped C_{60} contain Debye relaxational features that have been analysed by other authors. Our data suggest that the electric dipoles responsible relate not only to intrinsic orientational defects but also to dissolved O_2. At the higher temperature of 256 K, sharp peaks appeared in the spectra of both dielectric loss and constant, but only during the heating cycle and only if the sample had previously stayed at 85 K for 2 h. Our explanation for their total absence from the cooling curves invokes the masking effect of the random dipolar fields arising from orientational disorder, suppressed by annealing at below 90 K.

1. Introduction

Phase transitions and relaxation processes relating to the rotation of C_{60} molecules in the solid state have been studied with various experimental methods. This fullerite undergoes a glass transition [1] that is associated with the freezing of molecular rotations, at the approximate temperature of 90 K. In a sound attenuation experiment at ~ 10 kHz, a frequency-dependent elastic anomaly resulting from time-dependent stress relaxation occurs near 160 K [2]. This structural relaxation is shown to be approximately exponential and linear (i.e., simple in form) and the relaxation time nearly follows an Arrhenius temperature dependence over some 15 decades [2]. At $T_c = 260$ K, an order–disorder phase transition, as revealed by powder x-ray [3] and neutron diffraction [1], NMR [4], sound attenuation technique [2] etc, is known to be a first-order transformation. The crystal structure changes from simple cubic, to FCC with a lattice parameter a_0 above T_c.

O_2 molecules diffuse readily into the solid under ambient conditions [5, 6] and their dissolution leaves the crystal structure unchanged, but it does affect the 260 K order–disorder transition [4]. The molecules may enter the octahedral interstices [7, 8] and couple to the lattice vibrational modes [10]. Also they impede the orientational motion of C_{60}, as revealed by NMR [9]. Differential scanning calorimetry (DSC) shows that C_{60} samples previously submitted to a high O_2 pressure exhibit the phase transition at 258 K, as well as an additional small and broad endothermic peak at a lower temperature. The enthalpy of the latter and its shift from 258 K both decrease as the sample is then kept under vacuum for lengthening periods of time, presumably corresponding to decrease in O_2 concentration [11].

Complex impedance spectroscopy is a useful experimental technique for investigations into orientational order–disorder phenomena in polar materials. Alers *et al* [13] have determined the dielectric responses of two single crystals of C_{60}. They found discontinuities at T_c in their real and imaginary components, and a Debye-like relaxational contribution near 160 K at 10 kHz, which suggest that the high degree of frozen-in orientational disorder of the C_{60} clusters is responsible for the existence of electric dipolar activity. More recent impedance measurements by the group of Loidl have shown that the dielectric loss peak decreases in height after high-temperature annealing of the samples in vacuum, i.e., removal of O_2 [12]. It is thus likely that the dielectric measurements probe only those C_{60} with O_2 molecules nearby. It is also likely that in C_{60} co-evaporated with C_{70} from solution, C_{70} as a solute causes the same effect as a dopant in this respect, producing point defects that induce permanent dipoles on C_{60} and contribute to the dielectric response. To study further the said order–disorder transition and the structural relaxation, we have measured the impedance spectra of polycrystalline C_{60}, and of C_{60}/C_{70} mixtures for comparison, that have undergone various treatment and as they go through temperature cyclings.

2. Materials and procedures

The materials were prepared with the Krätschmer and Huffman techniques [14, 15], from a graphite rod in 100 Torr He atmosphere. C_{60}/C_{70}, extracted from the soot with toluene, was dried in vacuum at about 510 K for 6 h to outgas solvent. As characterized by NMR, IR, mass spectrometry and x-ray diffraction, it consisted approximately of 85% C_{60} and 15% C_{70}. C_{60} powder of high purity (>99.6%) was subsequently obtained by HPLC followed by vacuum drying. Then, about 500 mg of the C_{60}/C_{70} mixture was exposed to dry air inside a dessicator for 24 h, and similarly about the same amount of the pure C_{60} for 1 h.

Some of the pure C_{60} powder was set aside for experiments in a DSC (from Rigaku, Model 8150). Samples in 10–15 mg in mass were examined at the same heating rate of 10 K min^{-1}, either in vacuum or in N_2 flowing at 5 ml min^{-1}.

Finally, batches of both C_{60} and C_{60}/C_{70} were compacted uniaxially under 40 kbar, staying under pressure for 10 min, in air. The rigid pellets thus produced measured 6 mm in diameter and 1 mm in thickness, with mirror-like surfaces exhibiting a metallic-like splendour. Their x-ray diffraction patterns matched those reported in the literature. Ag films were evaporated onto the two flat surfaces for dielectric spectral measurement by the three-terminal method, using a GR 1615A transformer ratio-arm capacitance bridge. An NiCr–AuFe thermocouple located within 1 mm of the sample monitored its temperature.

For C_{60}, the dielectric constant and loss at 10 kHz were recorded for the pellet *immediately after its removal from the mould, whilst it was cooled from room temperature to 85 K in 2 h then held at 85±0.5 K for two more hours, and finally returned to room temperature over another 2 h. For the C_{60}/C_{70} mixture, the dielectric constant and loss at 1 and 10 kHz of the pellet were recorded immediately after its removal from the mould, as first it was cooled to 85 K in 2 h, then kept at this temperature for two more hours, and finally returned to room temperature over another 2 h. Subsequently it was annealed at 510 K in 10^{-5} Torr for 24 h, after which measurements at 10 kHz were repeated five times, each time with the sample subjected to the same temperature cycling as before. In addition measurements were made, twice, with the sample heated immediately after cooling, i.e., without staying at 85±0.5 K for 2 h. Lastly, experiments were performed, again twice, whilst the sample proceeded from room temperature to 150 K in about half an hour, was held at 150±1 K for 2 h, and then brought back to room temperature in 1 h.

3. Results

Figure 1 shows a typical DSC thermogram from pure C$_{60}$. Essentially the same behaviour has been observed with the sample in vacuum or in flowing N$_2$; the figure depicts the former case. Two endothermic features may be discerned: a broad peak centred near 240 K, and a sharp peak with onset temperature of 252 K and peak temperature of 257 K. They may be ascribed to the order–disorder phase transition at 260 K [1–4].
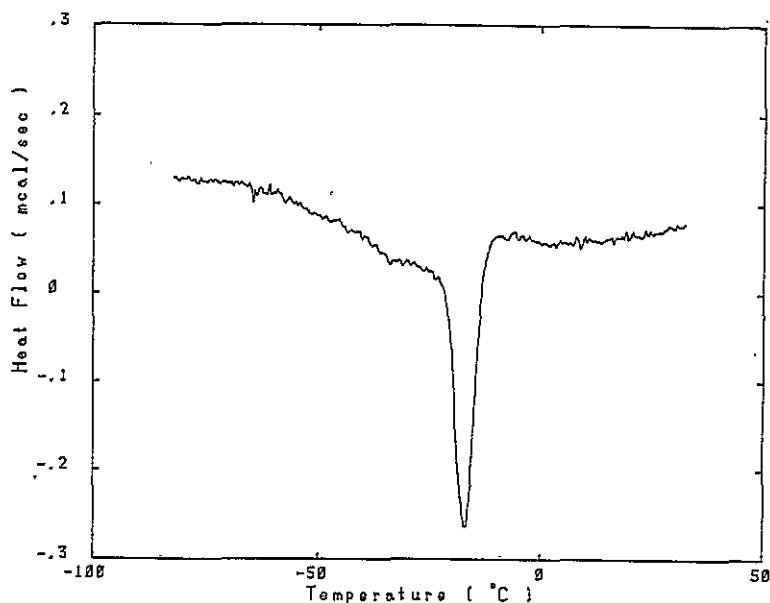

Figure 1. A DSC endotherm of pure C$_{60}$ heated at 10 K min^{-1} in vacuum.
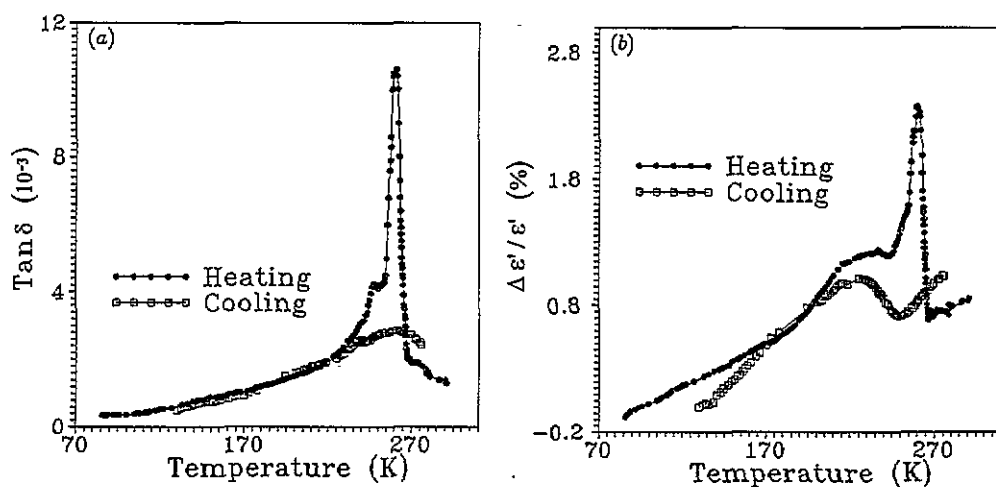

Figure 2. The temperature dependence of (a) dielectric loss and (b) dielectric constant at 10 kHz during cooling (open squares), and during subsequent heating after the sample has remained at 85 K for 2 h (solid circles).

Figure 2 presents the impedance data from pure C_{60}. Sharp peaks in dielectric constant ($\Delta\varepsilon'/\varepsilon'$) and loss (tan δ) appeared at 260 K on heating, and may again be ascribed to the order–disorder transition. However the 160 K relaxation peak at 10 kHz reported by Alers *et al* [13], who attributed it to intrinsic permanent dipole moments arising from orientational disorder of C_{60}, is too small to be detected in our case. Even more remarkably the sharp peaks at 260 K were entirely absent from the cooling curves.
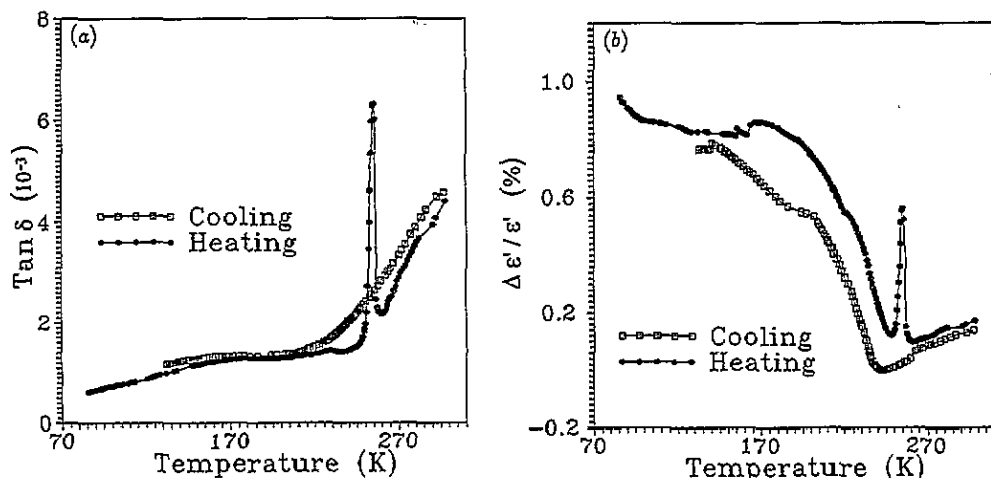

Figure 3. The same as in figure 2 with the C_{60}/C_{70} mixture as sample.

Figure 3 shows spectra measured from our 'fresh' C_{60}/C_{70} samples. Corresponding to an upward cusp of dielectric constant, and superimposed on a similar discontinuity, a sharp dielectric-loss peak emerged at 256 K and correlates therefore with the order–disorder transition. By contrast on cooling no distinct peak occurred at T_c in either dielectric loss or constant. This observation fits with our results for the pure C_{60} described in the last paragraph, but contrasts with the case of internal friction for fullerite-film [16] and single-crystal samples [2], where DSC curves again have peaks associated with this transition on both heating and cooling. On the other hand, hysteretic behaviour, present in internal-friction and sound-velocity data upon cycling through T_c, does likewise exist in both figures 3(a) and (b). From this thermal hysteresis a smeared first-order phase transition on cooling can be deduced. Additionally figure 3(a) contains a broad maximum near 160 K. The dielectric-loss curve obtained at 1 kHz resembles that at 10 kHz (figure 3(a)), with a sharp peak at the same temperature of 256 K, except that its broad maximum shifts to 142 K. From this shift with the measurement frequency an activation energy $E \approx 250$ meV can be deduced, in agreement with the single-crystal results of Alers *et al* [13].

Figure 4 depicts the temperature dependence of tan δ and $\Delta\varepsilon'/\varepsilon'$ after sample annealing at 10^{-5} Torr at 510 K for 24 h. In figure 4(a), the broad maximum reported above 160 K disappears and the curve below 250 K becomes featureless, apart from some subtle changes near 90 K due to the glass transition. We found no peak in the dielectric spectra if the sample, before heating, had not stayed down at 85 K for 2 h, or had spent the 2 h at the higher temperature of 150 K. Otherwise, the spectra resemble those in figure 3.

4. Discussion

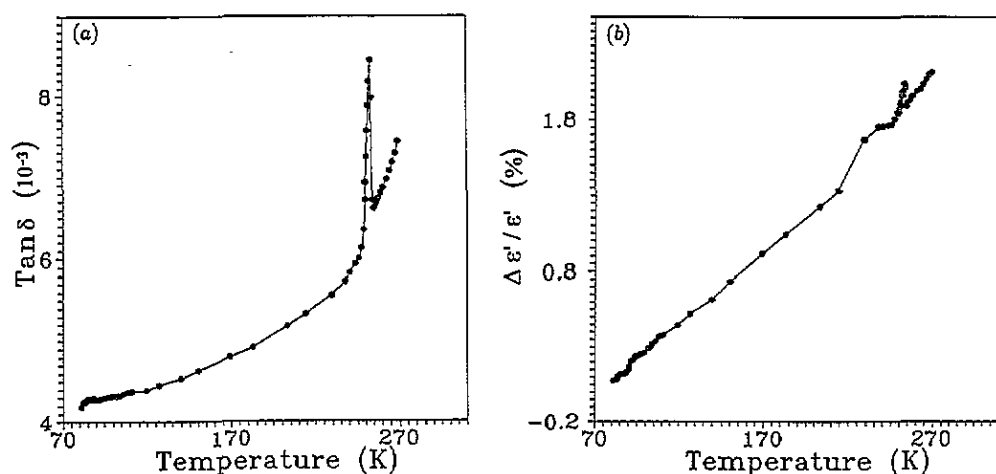No doubt O_2 molecules have diffused into our C_{60} and C_{60}/C_{70} powders after exposure to

Figure 4. Dielectric (a) loss and (b) constant at 10 kHz, for the C$_{60}$/C$_{70}$ mixture after being vacuum annealed at 510 K for 24 h.

air for several hours. In our DSC results (figure 1), the broad endothermic peak centred near 240 K relates, following Dworkin *et al* [11], to a phase transition in those parts of the C$_{60}$ sample containing oxygen. Correspondingly, the increase in $\Delta\varepsilon'/\varepsilon'$ (figure 2(b)) from 250 to 230 K on the cooling cycle may be associated with this transition. The plateau in $\Delta\varepsilon'/\varepsilon'$ (figure 3(b)) below T_c may originate from ferroelectric and ferroelastic domain walls [18] that have been doped with O$_2$, but which can be erased after annealing: hence its disappearance in figure 4(b). Annealing in vacuum at high temperature removes O$_2$ from the sample. The spectra in figure 4 are thus attributable to C$_{60}$/C$_{70}$ with little or no O$_2$, whereas figure 2 corresponds to C$_{60}$ with a little O$_2$, and figure 3 to C$_{60}$/C$_{70}$ with an appreciable O$_2$ content. We may then deduce that the 160 K relaxation peak at 10 kHz arises from C$_{60}$ molecules that have O$_2$ nearby, but the effect of C$_{70}$ solute in C$_{60}$/C$_{70}$ is too weak to be detected. On the other hand, in figure 4, distinct peaks do show up at about 256 K on heating, indicating that the electric dipoles responsible for this peak must be intrinsic, independent of O$_2$. Taken together, these data suggest two kinds of permanent dipole: one is a C$_{60}$ cluster polarized by adjacent O$_2$ molecules, which is involved in the thermally activated relaxational process near 160 K at 10 kHz or 142 K at 1 kHz, while the other is polarized by nearest-neighbour orientational defects, and gives rise to the order–disorder transitional peak.

Next we address the question as to why no marked peak appears at 260 K for C$_{60}$ and at 256 K for C$_{60}$/C$_{70}$ on cooling. The explanation may be the random dipolar fields resulting from disorientation of the permanent dipole moments. David *et al* [1] fitted neutron-diffraction data to a model that allows two possible orientations of C$_{60}$ differentiated by 60° rotation about the threefold axes. As just below T_c the fractions of C$_{60}$ in the two distinguishable orientations are approximately equal. This random distribution of C$_{60}$, i.e. an orientational glassy state erases the net dipole moment. However, by the stage when the temperature goes below 9 K, the fraction locked into the $\phi = 90°$ anti-clockwise position has increased to 0.83, whereupon the uniaxial jump reorientation becomes frozen, although a small amount of static disorder of C$_{60}$ can be suppressed and the majority of C$_{60}$ lie in the $\phi = 98°$ sites for the period in question. According to the two-defect model of Alers *et al* [13], this fraction of orientationally disordered C$_{60}$, which is greater than $\frac{1}{12}$, suffices to induce a dipole on essentially all molecules. This situation bears analogy with that for high-

x $K_{1-x}Li_xTaO_3$ [17]. There, the random dipolar field due to frozen-in off-centre Li^+ ions masks a smeared first-order phase transition, but such behaviour is suppressed and the sharp peak in dielectric response restored under zero-field-heating conditions if the ferroelectric has previously been field cooled. For C_{60} fullerite, lowering the temperature to below 90 K and holding for rather a long time has the same effect on the orientational disorder as that of applying an electric field in $K_{1-x}Li_xTaO_3$. This provides the reason for the absence of a dielectric spectral peak if the sample, before heating, has not stayed below 85 K for 2 h, or has spent the 2 h at the higher temperature of 150 K.

For single crystals [2] and O_2-doped C_{60} films [16], on both heating and cooling, internal-friction experiments have clearly revealed λ-shaped peaks. This is understandable, since they originate from stress-induced motion of interphase boundaries caused by the discontinuous change in lattice constant at T_c, in which electric dipoles play no role.

5. Conclusions

In the dielectric response of C_{60} fullerite, the dissolution of O_2 induces the electric dipoles that are responsible for the 160 K relaxation peak at 10 kHz. O_2 doping serves therefore as a probe into the orientational order of C_{60} fullerite. The orientational defects lead to dipolar moments that are responsible for sharp T_c peaks on the heating curves if the samples have previously been cooled below 90 K, when the dipoles become substantially aligned.

Acknowledgments

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