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## Electrical conductivity studies of a pure C<sub>60</sub> single crystal

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**Abstract.** Single crystals free from solvent up to millimetre size were grown. The temperature dependence of the electrical conductivity of a C<sub>60</sub> single crystal was reported in this paper. A sharp decrease in conductivity related to the phase transition at 251 K was confirmed. A drop in the activation energy of around 274 K was observed for the first time. This activation energy drop suggests that the rotational dynamics of the C<sub>60</sub> molecule above 251 K are more complex than the uncorrelated diffusion reported by Neumann *et al.*

### 1. Introduction

Since Kratschmer *et al* [1] found a method for producing large quantities of fullerenes, much work on the chemical and physical properties of fullerenes has been performed [2–5]. Recently it has become possible to grow millimetre-size single crystals and this has allowed detailed study of the crystal structures and the phase transitions in these phases [6–8]. In this paper we report the temperature dependence of the conductivity measured from 230 to 290 K for an undoped C<sub>60</sub> single crystal. A sharp drop in conductivity related to the phase transition at 251 K was confirmed. Moreover, a drop in activation energy of around 274 K was observed for the first time. This necessitates more complex dynamics than envisaged as a result of the neutron scattering experiment with uncorrelated rotational diffusion of C<sub>60</sub> molecules above 251 K.

### 2. Experimental details

100 mg of purified (99.9%) C<sub>60</sub> powder were freed from the solvent by heating at 625 K for 8 h and then at 495 K for 10 h in a quartz tube in a vacuum of  $1.8 \times 10^{-7}$  Torr. The powder was sealed in a quartz tube (10 mm ID and 150 mm long) under this vacuum. The quartz tube was then placed in a horizontal furnace with one temperature controller to control the hot raw material end. The hot end was kept at 890 K, while the crystal-growth end was held at 660 K. Crystal growth was continued for 5 d. Single crystals up to a size of 1.5 mm were thus obtained. The structure was found by x-ray diffraction to be face-centred cubic (FCC), with a lattice parameter of 14.13 Å.

For conductivity measurements on the single crystal, Ag electrodes were deposited onto the surface of the crystal (dimensions, 1.5 mm × 0.3 mm × 0.5 mm, with a gap of 0.1 mm through the middle part of the crystal). The sample was then placed in a cell which was pumped to a vacuum of 0.1 Pa and sealed under this vacuum. The temperature was controlled with an electric heater in the sample cell which was immersed in liquid nitrogen. The temperatures were measured with a thermoelectric couple and corrected with a platinum resistance thermometer.

The conductivity was measured at temperatures around the sharp phase transition temperature (251 K) and between 270 and 280 K with a heating rate of  $0.1 \text{ K min}^{-1}$ , and in the other temperature ranges with a heating rate of  $2 \text{ K min}^{-1}$ .

We measured the  $I$ - $V$  curves and found that a linear relation for the  $I$ - $V$  curves exists only at voltages above 40 V. Thus the applied voltage was fixed at 60 V.

### 3. Results and discussion

Figure 1 shows the results for the temperature dependence of the  $\text{C}_{60}$  single crystal. The electrical conductivity increases as the temperature is increased. A discontinuous change was observed as a sharp decrease at 251 K. The temperature width of this sharp change is about 0.6 K. This sharp change can be related to the phase transition from the orientationally ordered simple cubic (SC) to the FCC structure [2, 7, 8]. This sharp transition shows that the present single crystal is of high purity and homogeneity [8].

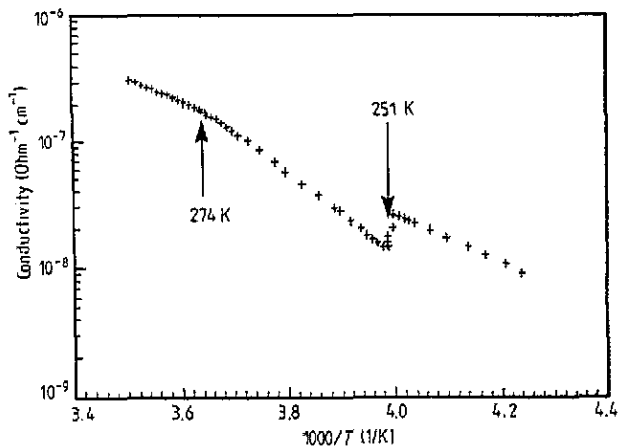


Figure 1. Logarithm of the electrical conductivity  $\sigma$  versus the reciprocal temperature for a  $\text{C}_{60}$  single crystal.

Figure 1 also shows another feature at around 274 K. Figure 2 shows this region in detail. The rate of conductivity increase with increasing temperature above this temperature is smaller than below this temperature. We calculated the activation energy versus temperature with seven-point linear fitting. The result is shown in figure 3. An apparent drop in activation energy of between 0.660 and 0.355 eV can be observed in this figure. The temperature range of this change is about 7 K.

Wen *et al* [8] first reported the temperature dependence of the conductivity from 250 to 295 K. A sharp drop in conductivity at 256 K (in our work at 251 K) was observed, but the activation energy drop at around 274 K was not observed. This may be attributed to their insufficient applied voltage (they did not report the applied voltage). At lower voltages, the Schottky barrier effect at the Ag- $\text{C}_{60}$  contact may partly mask the change in conductivity. The conductivity change of 10% which they reported at 256 K is also smaller than the change of 40% (251 K) that we measured. Also, the conductivity measurement at around 274 K was not so carefully made in their experiment (the heating rate was  $3 \text{ K min}^{-1}$ , and the temperature step was 5 K at around 274 K).

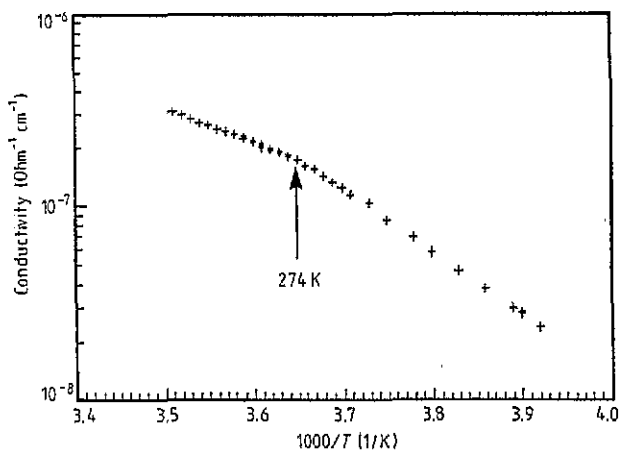


Figure 2. Logarithm of the electrical conductivity  $\sigma$  versus the reciprocal temperature at around 274 K.

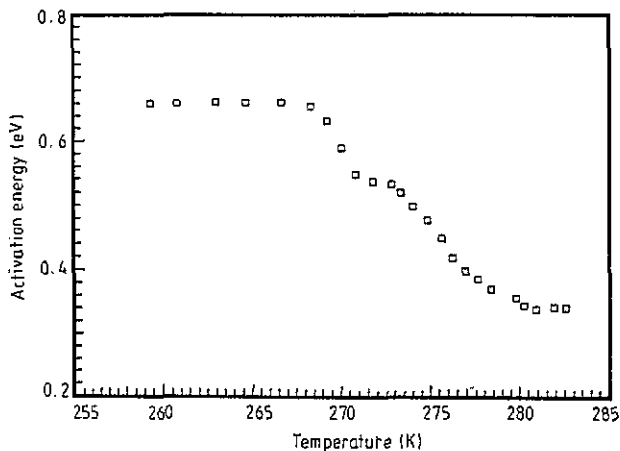


Figure 3. Activation energy versus temperature at around 274 K.

The activation energies below and above the transition temperature 251 K are 0.384 eV and 0.660 eV, respectively. These are slightly larger than reported by Wen *et al* [8]. The activation energy above 274 K is 0.355 eV.

The new feature at around 274 K does not appear in other measurements such as neutron scattering. We measured the conductivity carefully around this temperature, but no actual jumps in conductivity have been observed (figure 2). Recently the temperature dependence of the velocity of sound reported by Shi *et al* [9] shows a small maximum at around this temperature (at about 290 K), but they did not pay attention to this small feature. To our knowledge, no careful x-ray diffraction studies around this temperature have to date been reported. The most widely adopted microscopic picture above 251 K is that each molecule undergoes rotational diffusion which is uncorrelated with the motions of adjacent molecules, i.e. free rotations [4]. We think that this molecular diffusion model does not explain the activation drop at around 274 K.

The  $C_{60}$  crystal structure above 251 K is FCC, with an effective symmetry of  $Fm\bar{3}m$ .

Heiney [10] indicates that, besides the free rotation of  $C_{60}$  molecules, there are two other rotational disorder mechanisms which are of  $Fm\bar{3}m$  symmetry. One is merohedral twinning; different domains are separated by domain walls, each domain is of a standard orientation, and orientations of the adjacent domains are rotated by  $\frac{1}{2}\pi$  to another standard orientation. The other is merohedral disorder; the molecule on each site jumps between two standard orientations, and each orientation has a probability of 50%. Since no abrupt change in conductivity has been observed at around 274 K, we suggest that the activation energy drop at around 274 K is connected with the transition from merohedral twinning of the FCC structure to an orientationally disordered (free rotation) FCC structure, while the sharp drop in conductivity at 251 K is related to a phase transition from the orientationally ordered SC to the merohedral twinning FCC structure.

In summary, we have confirmed the sharp conductivity decrease at 251 K, which is associated with the first-order phase transition from the orientationally ordered SC to the FCC structure. This sharp conductivity decrease also shows that the  $C_{60}$  single crystal is of high purity and homogeneity. Moreover, we have for the first time observed an activation energy drop at around 274 K. This suggests that there are different rotational diffusion mechanisms above 251 K. Considering the  $C_{60}$  crystalline symmetry, a possible explanation is that the activation energy drop at around 274 K is related to a transition from a merohedral twinning FCC to a rotationally disordered FCC structure, while the sharp conductivity decrease at 251 K is related to the phase transition from the orientationally ordered SC to the merohedral twinning FCC structure.

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