Pressure dependence of the transport properties of the molecular superconductor, κ-(BEDT TTF)$_2$Cu(NCS)$_2$

LETTER TO THE EDITOR

Pressure dependence of the transport properties of the molecular superconductor, κ-(BEDT TTF)$_2$Cu(NCS)$_2$

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Abstract. The molecular superconductor κ-(BEDT TTF)$_2$Cu(NCS)$_2$, which has a super-conducting transmission temperature, T_c, as high as 10.5 K, exhibits a very high resistivity at ambient pressure ($\simeq 10^{-1}$ Ω cm at room temperature) which rises on cooling to reach a maximum near 90 K. We find that with the application of pressures of up to 2.5 kbar this peak remains strong and is progressively sharpened, but that above 2.5 kbar the size of the resistive peak falls very quickly. In our crystals the resistively measured T_c is 7 K at ambient pressure and remains constant up to 3 kbar, before falling steeply at 1.8 K kbar^{-1} above this pressure. We attribute the unusual temperature dependence of the normal state conductivity to a structural phase transition which at pressures below about 3 kbar couples to the con-duction electrons. We discuss whether or not the superconducting properties are affected by the proximity of the material to the phase transition.

In recent years several organic superconductors based on the BEDT TTF donor molecule have been synthesised. In 1987, the salt κ-(BEDT TTF)$_2$Cu(NCS)$_2$ was shown to super-conduct at ambient pressure at 10.5 K [1], the highest transition temperature of any organic superconductor yet discovered. In common with the other organic super-conductors, (BEDT TTF)$_2$Cu(NCS)$_2$ is a type-II, bulk superconductor, but its normal state conductivity shows a curious temperature dependence. On cooling, the resistivity decreases to a shallow minimum near 250 K, before increasing to reach a maximum near 110 K. The ratio $\rho_{max}/\rho_{300 K}$ appears to be sample dependent, and has been reported to be as high as 6 [1], but more generally, and as in this work, is found to be nearer 3 [2–5]. Below 110 K the resistivity decreases steeply to the superconducting transition which has been reported between about 7 and 10.5 K [1–5]. The room-temperature conductivity is isotropic in the bc plane at $\simeq 10$–20 S cm^{-1}, with a value about 600 times lower in the a direction [2]. This conductivity is low in comparison with other organic metals for which values $\simeq 100$–1000 S cm^{-1} are more common.

   The crystal structure at ambient pressure and various temperatures has been studied [6] and is found to differ from the majority of the organic charge transfer salts in that there is no well defined one-dimensional character to the structure. The BEDT TTF molecules arranged as orthogonal dimers to form an isotropic sheet in the bc plane. The BEDT TTF molecules are linked by short *intra*- and *inter*-dimers $S \ldots S$ contacts less than the sum of the Van der Waals radii, to form layers separated by sheets of the

$Cu(SCN)_2-$ anions. On cooling, the gross features of the packing change little from room temperature down to 100 K, with no structural changes corresponding to the upturn in the resistance near 250 K. However, there is an anomalous expansion of the unit cell dimensions on cooling. Within the conducting plane, the b and c axes both contract on cooling from 300 K, but the a axis lattice parameter remains constant down to 260 K and increases below this temperature at an average rate of $\Delta a / aT = 4.3 \times 10^{-5}$ K^{-1}. Such an increase in cell dimension is very unusual and has only been noted once before in the BEDT TTF system, for β-$(BEDT\ TTF)_2I_2Br$, where its magnitude is about 40 times smaller [7]. Despite this remarkable expansion of the a axis, the separation of the layers ($a \sin \beta$) remains almost unchanged, indicating a shearing of the structure along the 2D plane direction.

The magnetic susceptibility of κ-$(BEDT\ TTF)_2Cu(NCS)_2$ is paramagnetic and approximately constant down to 90 K as indicated by static [8, 9] and ESR [10] data. This temperature-independent paramagnetism strongly suggests that the upturn in resistance below 250 K is not due to gap formation, a point that will also be returned to later. However, the susceptibility does show a small temperature dependence, with a weak maximum near 100 K best seen in the static susceptibility measurements, falling by about 10% at low temperatures and by rather less than this at room temperature.

Various groups have measured the variation of the superconducting transition temperature with pressure, and have reported that T_c falls very steeply [11–13], with an initial slope as high as -3 K kbar^{-1} [11]. This is the largest pressure derivative found for the superconducting transition reported; the previous highest value, of -1 K kbar^{-1}, was observed in the related β-$(BEDT\ TTF)_2X$ compounds [14].

Shubnikov–de Haas (SDH) measurements show a cylindrical pocket of holes with an area of 18% of the Brillouin zone, which agrees well with the calculated Fermi surface [15]. Under pressure, this SDH frequency is slightly reduced [12], and this can be interpreted in terms of a compression of the lattice by about 5% GPa^{-1}, comparable to many other organic metals. This small change in frequency suggests that there is little change in the band structure under pressure.

To gain a better understanding of the nature of the unusual normal state and superconducting properties, we have measured their pressure dependence under well controlled conditions with particular emphasis on the pressure regime below 4 kbar.

The samples were grown by the method given in [1]. Crystals show an EPR linewidth of about 60 Oe with the applied DC field parallel to the a axis at room temperature, and lattice parameters $a = 13.12(2)$ Å, $b = 8.441(2)$ Å, $c = 16.231(2)$ Å, $\beta = 110.32(1)°$, $V = 1685.7$ Å^3. Conductivity was measured by a low-frequency AC technique, with four terminal measurements. Sample dimensions were typically 1 mm $\times \frac{1}{2}$ mm $\times 50$ μm. Electrical contacts were made with 10 μm gold wire attached to evaporated gold pads with silver paste, and with a contact geometry that gives measurements of the in-plane resistivity. Measurements of the Hall coefficient were attempted using the five-contact geometry and current-balancing circuit described previously [16]. The high-pressure system used here has also been described previously [17]. Pentane was used as the pressure-transmitting medium in a beryllium–copper pressure cell in communication with a large intensifier/pressure reservoir, which remains at room temperature, via a stainless steel capillary tube. This system allows accurate control of pressure down to the freezing point of the pentane (120 K at ambient pressure), and shows little pressure variation below the freezing. It does not, therefore, suffer from the considerable pressure losses with cooling usually encountered with 'clamp' cells, and provides a particularly convenient system for the present set of measuremens. The results reported here were reproduced consistently within the batch of crystals measured.
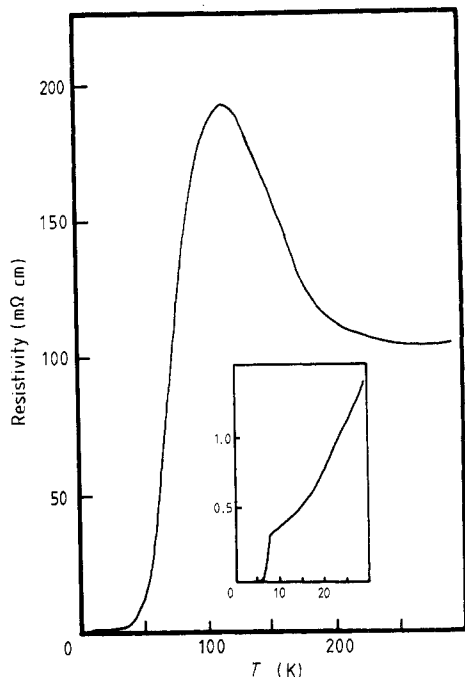
Figure 1. The temperature dependence of the ambient pressure resistivity. The inset shows detail around the superconducting transition.
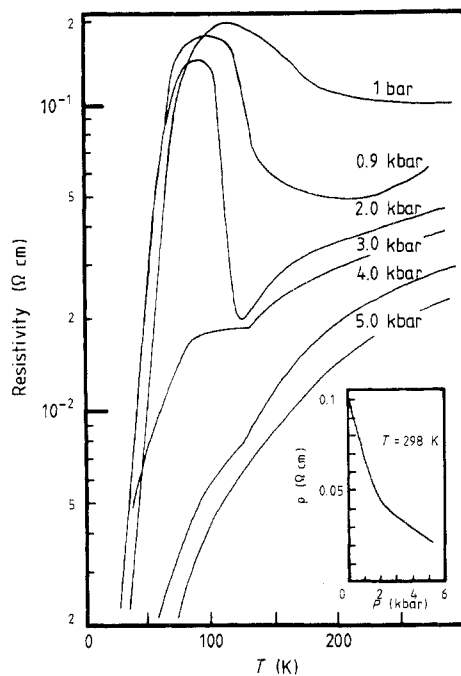
Figure 2. The temperature dependence of the resistivity at various pressures. Data are shown for cooling. The inset shows the pressure dependence of the resistivity at room temperature.

The ambient pressure resistivity is shown in figure 1. We measure the room-temperature conductivity at $\simeq 10 \, \mathrm{S \, cm^{-1}}$, in agreement with the findings of other groups. On cooling, the resistivity initially decreases to a shallow minimum near 250 K (this minimum was not found in all samples) and then increase to a broad maximum near 110 K. The ratio of $R_{\mathrm{peak}}/R_{300\mathrm{K}}$ was found to be about 2 for our crystals. This is close to the ratio reported by other groups. Below 100 K, the resistance drops sharply and the onset of superconductivity is observed near 8 K. The ratio $R_{300\mathrm{K}}/R_{10\mathrm{K}} \simeq 270$. Temperature cycling shows no evidence for hysteresis in the resistivity at ambient pressure.

Under pressure, the room-temperature conductivity increases sharply, initially at 30% kbar^{-1}, as shown in the inset to figure 2. The temperature dependence of the resistivity for several pressures is also shown in figure 2. At 0.9 and 2.0 kbar, the resistivity shows the same general form as at ambient pressure, with an initial fall with decreasing temperature, followed by an increase to a maximum and a further fall at lower temperatures. However, in comparison with the ambient-pressure behaviour, the resistivity anomaly is much more strongly pronounced, having a sharp transition from the 'metallic' behaviour at higher temperatures to the anomalous regime. Thus, for example, at 2.0 kbar the sample is metallic down to 122 K, but the resistance rises by a factor of 7 to a sharp peak at 95 K. Furthermore, the resistance of the sample around the resistive peak shows substantial hysteresis between cooling and warming data, as indicated in figure 3. Within this pressure regime T_{c} remains constant. However, with further increase of the pressure the resistive anomaly is rapidly suppressed. At 3.0 kbar the peak in resistivity is completely suppressed, and only a slight anomaly remains to
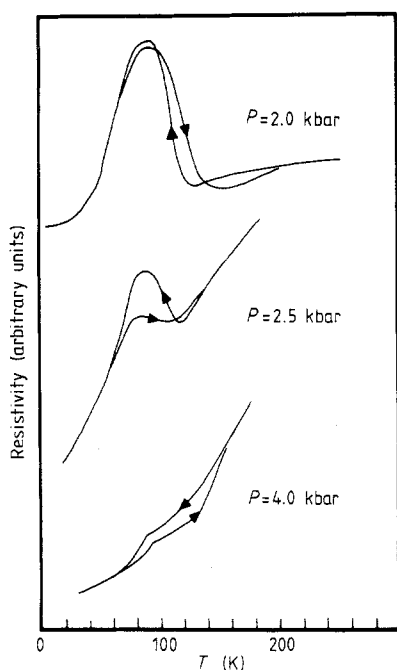
Figure 3. Hysteresis in the resistivity around the resistance anomaly at various pressures. Typical cooling and warming rates were in the range 0.3 to 1 K min^{-1}.
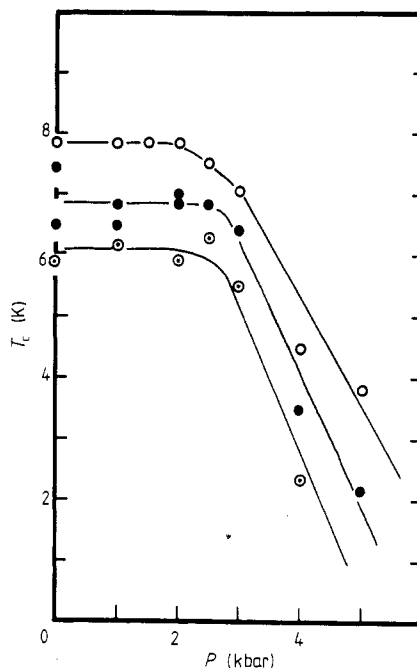
Figure 4. The pressure dependence of T_c at various pressures. $\bigcirc$ indicates the onset of superconductivity, $\bullet$ indicates the resistance $\frac{1}{2}$ height and $\odot$ indicates zero resistance.

indicate its position. It appears that the temperature at which it is observed is little affected by pressure, though it is increasingly difficult to detect it as pressure is further raised, and at 5.0 kbar all traces of the anomaly are removed.

The pressure dependence of the superconducting transition temperature, T_c, is shown in figure 4. For pressure below 2.5 kbar, T_c remains constant, with an onset at 8.0 K, half-height resistance at 7.0 K and zero resistance at 6.0 K. Above 2.5 kbar, T_c drops rapidly, at a rate of 1.8 K kbar^{-1}. At all pressures, the transition width is fairly broad ($\simeq 2$ K) but this is typical of organic superconductors and probably not indicative of pressure variations across the sample. It should be noted that the pressure is non-hydrostatic since the sample is encased in frozen pentane, and as such, it is exposed to shear stresses due to the differential contraction of the sample and frozen pressure medium.

Measurement of the Hall coefficient with the magnetic field perpendicular to the bc plane was attempted under ambient pressure at several temperatures down to 50 K. In all cases the Hall coefficient was below the detection limit set by the noise level, of $\pm 4 \times 10^{-9}$ m^3 C^{-1}. The Fermi surface calculated from the Hückel band model of [15] is made up of an open electron surface that gives maximum contribution to electronic transport in the b^* direction, and closed hole cylinders that give maximum contribution in the c^* direction. The SDH oscillations are attributed to the hole cylinders [15], and in further support of this Fermi surface, the thermopower is found to be positive in the c direction and negative in the b direction [10, 18]. However, the component of the Hall tensor measured here is only determined by the direction of the applied magnetic field,

and the very low value for the Hall coefficient is due to the cancellation between the electron and hole contributions.

The temperature and pressure dependence of the resistivity observed in this material is reminiscent of that measured in TiSe$_2$ [19] and (BEDT TTF)$_2$ReO$_4$ [20] (under pressure). These two materials have anomalous peaks in the resistivity, which are suppressed under pressure, leading to a metallic state, or, in the case of (BEDT TTF)$_2$ReO$_4$, a superconducting ground state as found for the (BEDT TTF)$_2$Cu(NCS)$_2$ samples studied here. However, both of these transformations involve a reorganisation of the Fermi surface with the formation of a superlattice and corresponding change in the carrier concentration, and, as such, cannot be carried over to explain the apparently similar behaviour in (BEDT TTF)$_2$Cu(NCS)$_2$. There is considerable evidence that for (BEDT TTF)$_2$Cu(NCS)$_2$, the carrier concentration changes little on cooling. This evidence is notably (i) the weakly temperature-dependent paramagnetic susceptibility for temperatures above 90 K (χ_p is proportional to the density of states at the Fermi level), though there is a fall below 90 K, (ii) the absence of an anomaly in the thermopower corresponding to the resistance anomaly [10], (iii) the fact that R_H remains small, and (iv) the observation that the Fermi surface calculated at room temperature corresponds well with the low-temperature SDH data [15]. Thus it appears that there is no reorganisation of the Fermi surface that leads to a large reduction in the density of states at the Fermi energy.

The increase in resistance without a commensurate decrease in the number of carriers is thus somewhat puzzling. Urayama and co-workers (1) suggested that the resistivity upturn was due to disorder, with the scattering rate increasing as the sample is cooled. This gains some support from structural studies which shows disorder of one of the ethylene groups on the BEDT TTF molecule for temperatures above 100 K [5]. However, temperature-dependent impurity scattering will only be important if the system exhibits incipient localisation, and the electronic properties suggest that this is not the case. Furthermore, disorder effects cannot explain the fact that pressure sharpens the resistance peak very considerably, along with the substantial degree of hysteresis in the resistance around this peak.

A model that can explain our data is one in which a metal–metal phase transition occurs. At ambient pressure, this transition is either very sluggish or second order, and appears to take place just below room temperature. The structural reorganisation couples to the conduction electrons, changing from a lower-resistivity to a higher-resistivity state. That the transition sharpens under pressure, with a rapid onset and hysteresis, is clear evidence that it becomes first order, a change which, although unusual, is not without precedent, e.g. the α'(BEDT TTF)$_2$X salts [21]. The metal–metal phase transition, and associated change from a lower-resistivity to a higher-resistivity state (below 2.5 kbar), gives rise to a step in the resistance. The disappearance of the high-resistivity state above 2.5 kbar without evidence for the disappearance of the phase transition suggests that coupling of the structure of the low-temperature phase to the conduction electrons is accidental, and can be either strong (below 2.5 kbar) or weak (above 2.5 kbar).

There is considerable variation in the behaviour of T_c with pressure reported here and in the literature [11–13]. Schirber and coworkers [11] report a very rapid fall in T_c of 3.1 K kbar^{-1} from an initial onset of 9.1 K. Murata and co-workers [13] report a similarly rapid rate of fall of T_c with pressure. Oshima and co-workers [12] also report a monotonic fall in T_c from an initial value of 20.5 K, but at a slower rate of -1.3 K kbar^{-1}. We find that T_c remains constant up to about 3 kbar, before falling at 1.8 K kbar^{-1}. It is

very likely that differences in the non-hydrostatic stresses in the different pressure systems play an important role (the solid helium pressure generation technique used in [11] produces the most closely hydrostatic conditions, the clamp-cell used in [12] probably introduces the largest non-hydrostatic stresses).

There are several unusual characteristics of the normal and superconducting properties of this material. These include the sensitivity of the pressure dependence of T_c to sample condition and the pressure environment, the appearance of an apparently first-order phase transition under moderate pressure (<2.5 kbar) at around 100 K, and, for our crystals, the correlation between the disappearance of the strong resistance anomaly associated with this phase transition and the change in pressure variation of T_c. We consider that there is indeed a structural phase transition, at a temperature between 300 K and the superconducting transition, that is sluggish and possibly incomplete at ambient pressure, but sharp and first order under pressure. It may be associated with the large thermal motion of one of the ethylene groups noted in [6], and it couples strongly to the conduction electrons, affecting both the normal and the superconducting properties. Further structural measurements, preferably under pressure, are now required.

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