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LETTER TO THE EDITOR

Some properties of the organic superconductor κ-(BEDT TTF)$_2$Cu(SCN)$_2$ under pressure

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Abstract. We report on some pressure-related properties of the organic superconductor κ-(BEDT TTF)$_2$Cu(SCN)$_2$ in the range 1 bar–3 kbar. The pronounced resistance maximum at around 100 K is very sensitive to the pressure and so is T_c, which decreases rapidly at a rate $dT_c/dP = -3.6$ K kbar^{-1}. The resistivity anisotropy parallel to the transverse ratio does not show any anomalous behaviour across the resistance maximum. Instead, it shows a zig-zag shape when the resistance decrease is steepest.

Organic superconductors based on the BEDT TTF (ET) molecule have been synthesised with numerous monovalent anions in the 2:1 stoichiometry and now form an important family. One of the most recently synthesised is κ-(ET)$_2$Cu(SCN)$_2$ whose T_c is the highest in this series [1]. One of the special features of κ-(ET)$_2$Cu(SCN)$_2$ is the temperature dependence of its resistance. On cooling down to $\simeq$90–120 K, the resistance increases by a factor from less than two and up to six. In a recent study performed on thermally elongated samples a ratio as high as 100 was reported [2]. From a comparison between several data that have appeared in the literature we may infer that the higher the resistance ratio, the lower the temperature where the resistance shows its maximum. To explain this peculiar behaviour, a small-polaron model was suggested [3], where the resistance increase is explained by the formation of small polarons through the strong electron–phonon interaction, and the metallic downturn can be explained by the coherent motion of the polarons at low temperature. But this model is applicable only when the polarons are dilute, in contrast to the actual case.

There have already been some pressure related studies of this material, where a very fast decrease in T_c with pressure has been found [4]. One of the recent studies shows somewhat peculiar results, different from the others [5]. They suggest a first-order phase transition under moderate pressure (2.5 kbar) at around 100 K and the authors have correlated this transition with the finding of a pressure independent T_c in the same pressure region. As is well known, low-pressure experiments using a liquid transmitting medium sometimes encounter serious difficulties because of the pressure loss accompanying the cooling process and more particularly at the freezing point of the pressure medium. The helium pressure generating technique is better suited to this purpose and we have performed experiments on several single crystals.

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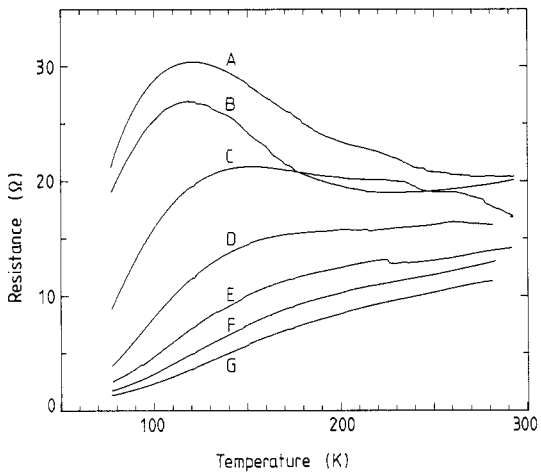

Figure 1. Pressure dependence of the electrical resistance under various pressures between liquid nitrogen and ambient temperature. A: 1 bar, heating; B: 1 bar, cooling; C: 0.5 kbar, heating; D: 1 kbar, heating; E: 1.5 kbar, cooling; F: 2 kbar, cooling; G: 2.5 kbar, heating. The difference in resistance between A and B at 77.4 K is due to the adjustment of the resistance in B to remove three jumps below 163 K.

Figure 1 shows the pressure dependence of the electrical resistance under various pressures between liquid nitrogen and ambient temperature. Because of the delicacy of the solidification of the pressurised helium gas, the high- and the low-temperature experiments are performed independently. In our sample, the ratio of the maximum resistance and RT resistance is less than two, and T_c is $\simeq$8.7 K at the midpoint. The maximum resistance was found at 120 K, a temperature that is a little higher than what was reported in [1]. Under pressure, the amplitude of the maximum decreases and its temperature shifts towards high temperature ($\simeq$150 K under 500 bar). Under 1 kbar, the temperature dependence of the resistance has already become very flat down to 175 K. Above 1 kbar the resistance decreases monotonically without any anomaly as the temperature falls. Under low pressure, say $P < 1$ kbar, the resistance shows some hysteretic behaviour which we attribute to the sample cracking rather than to the intrinsic behaviour of the sample. As a result, the resistance between 170 and 240 K on heating under 500 bar is higher than that on cooling under 1 bar but not than that on heating. As clearly shown in the figure, there is no abrupt change of the temperature dependence but only a continuous change with pressure.

The rapid disappearance of the resistance maximum appears as an unusual pressure dependence of the resistance at fixed temperature as illustrated in figure 2. Figure 2(*a*) shows the case of β-$(ET)_2I_3$ which represents the general case: the sensitivity to the pressure decreases as the temperature falls. We found only a minor difference between β-H and β-L phases. However, the case of κ-$(ET)_2Cu(SCN)_2$ in figure 2(*b*) shows the opposite behaviour, namely that the sensitivity increases as temperature falls. Unlike β-$(ET)_2I_3$, which shows a gradual decrease with pressure, κ-$(ET)_2Cu(SCN)_2$ shows a rapid decrease up to 1 kbar at liquid nitrogen temperature where it is still dominated by the resistance maximum.

The pressure dependence is also peculiar for the superconducting transition temperature, T_c. We have solidified helium gas via a carefully controlled cooling and the pressure in the solid state was determined from the melting point of solid helium derived from the accompanying anomalies in sample resistance. We focused our attention mainly on the low-pressure region, and we present the results in figure 3. The initial decrease is linear in pressure with a coefficient $dT_c/dP = -3.6\,\mathrm{K\,kbar^{-1}}$ which corresponds approximately to that measured by the induction method [4]. This coefficient is more

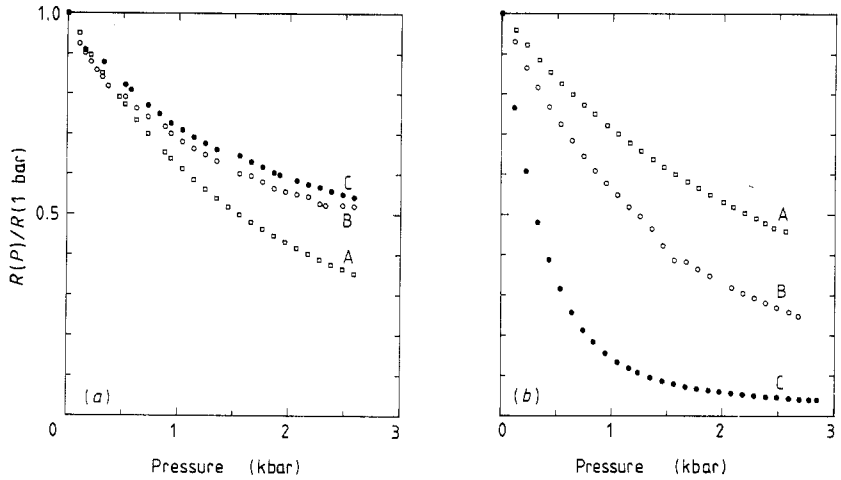

Figure 2. Pressure dependence of the resistance at fixed temperatures. (*a*) β-$(ET)_2I_3$; A: 296 K; B: β_H-phase at 77.4 K; C: β_L-phase at 77.4 K. (*b*) κ-$(ET)_2Cu(SCN)_2$; A: 296 K; B: 185 K; C: 77.4 K.

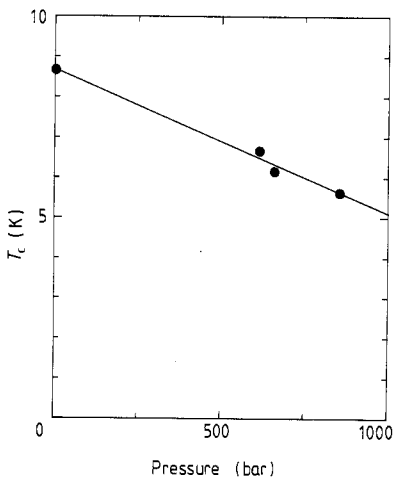

Figure 3. Pressure dependence of T_c for κ-$(ET)_2Cu(SCN)_2$.

than three times larger than that of β-$(ET)_2I_3$ in the β-H phase [6]. Figures 2(*b*) and 3 show that this compound is very sensitive to pressure across the range of temperature. In comparison with the unit cell parameters measured at 298 K and 104 K, the perpendicular *a* axis has shown a thermal dilation instead of a contraction. This could mean that the anisotropic compressibility plays an important role via the modification of the band structure. The pressure dependent structure study can give some hints on this unusual response to pressure.

To go further, we have measured the resistivity anisotropy between the most conducting *b* direction and the perpendicular a^* direction under 1 bar and 2.3 kbar as shown in figure 4. At variance with the normal resistance behaviour, the anisotropy increases monotonically through the temperature range where the resistance shows a maximum. Instead, it has a pronounced zig-zag anomaly between 35 K and 60 K which is suppressed

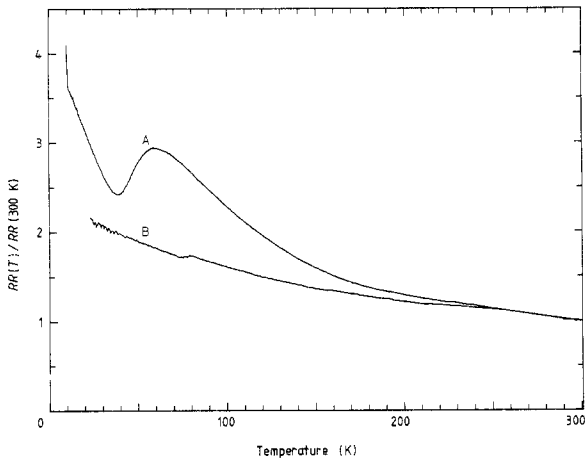

Figure 4. Temperature dependence of normalised electrical resistivity anisotropy of κ-$(ET)_2Cu(SCN)_2$ under 1 bar (A) and 2.3 kbar (B). RR means R_b/R_{a^*}.

completely under 2.3 kbar. At this temperature, there also exists an anomaly in the first derivative of the resistance on temperature. There is no concrete evidence of the phase transition around this temperature, but the broadening of the Bragg peaks in single-crystal x-ray scattering is observed when the sample is cooled below $\simeq$60 K [7].

From our experiment, we arrived at the conclusion that the anomalous pressure dependence in [5] is very likely an experimental artifact with the following explanation. When the pressure cell is cooled, the capillary tube cools faster because of its small heat capacity. Thus, the pressure transmitting liquid in the tube solidifies and isolates the pressure cell from the external pressure reservoir. Consequently, the sample space in the cell loses its pressure through freezing as in a simple clamp cell, and the sample will display an 'unattended' behaviour.

In conclusion, we have reported some pressure related properties of κ-$(ET)_2Cu(SCN)_2$. The position and the magnitude of the resistance maximum are very sensitive to the applied pressure. Its rapid disappearance is accompanied by a fast decrease of T_c, with $dT_c/dP = -3.6\,K\,kbar^{-1}$ at the beginning. The overall pressure dependence is continuous and the possibility of a phase transition in the vicinity of the temperature of the resistance maximum can be ruled out.

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