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LETTER TO THE EDITOR

An interpretation of the strain-sensitive resistance in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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Abstract. Recently Kang and co-workers reported that the electrical resistance of an organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ noticeably decreases as a function of hydrostatic pressure; especially up to 1 kbar at 77.4 K where the resistance rapidly decreases by a factor of almost 10. These strain-sensitive resistance behaviours are consistently explained by the extended Hubbard model for a quarter-filling: an inter-site Coulomb repulsion is assumed to open an energy gap (300–500 K at room temperature) at the Fermi level and delicately interplay with the strain-sensitive transfer integrals of quasi-two-dimensional itinerant π-electrons.

During the last decade there have been considerable developments in synthesizing a variety of (BEDT–TTF)$_2$X charge-transferred salts. These materials, which are quasi-two-dimensional conductors with low density of carriers of about 1×10^{21} cm^{-3}, show a wide spectrum of electrical properties from insulating (or semiconducting) to metallic ground states at low temperatures. Among these salts, superconducting κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is an outstanding system, because the T_c reaches 10–11 K, the highest found so far in organic materials. Experimental observations of Shubnikov–de Haas quantum oscillations and careful analyses of the data have established that this material is a Fermi liquid, that itinerant π-electrons correlate with each other, and their effective mass m_c and relaxation time τ are enhanced by a factor of the so-called renormalisation constant Z of 3–4 [1].

One of the puzzling problems in this high-T_c compound is a resistance maximum observed around 100 K [2]. Recently we proposed a quasi-particle band model on the basis of an extended Hubbard model [3]: for the present quarter-filling case (0.5 hole per BEDT-TTF for (BEDT-TTF)$_2$X salts), a lower Hubbard band, which is induced by the splitting of the bare band due to the on-site Coulomb U, is assumed to be again split due to the inter-site Coulomb repulsion V. (See figure 1 of [3].) For this quarter-filling of the bare band, the system will be either an insulator if $W_{SB} < V$ with an energy gap $E_G = \frac{1}{2}(V - W_{SB})$, or a metal if $W_{SB} > V$ with the gap closed, where W_{SB} is a renormalised band width W_B (=0.6 eV)/Z (=3–4) = 0.2 eV. The magnitudes of U and V, which can in principle be estimated from the optical conductivity spectrum, are still controversial; U = 1.3 eV and V = 0.2–0.5 eV obtained by Pratt *et al* [4] and U^* = 0.7 eV (effective U) by Tajima *et al* [5]. These estimations suggest that the intermediate strong coupling regime of the model, $U > V \fallingdotseq W_{SB}$ might be applicable to the present system. Therefore we assume that, around room temperature and at ambient pressure, the system might be an insulator (semiconductor). For this hypothetical band with the constant density

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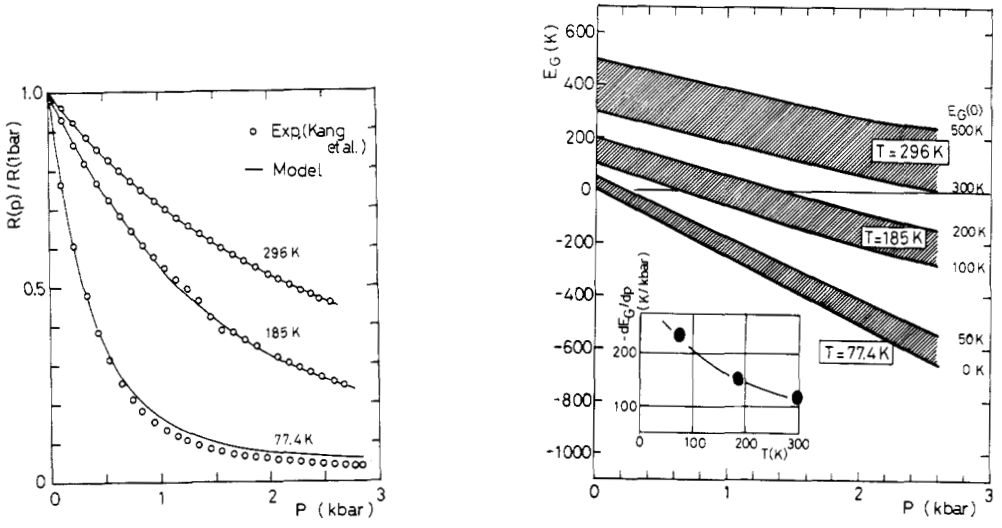

Figure 1. (*a*) Pressure dependence of the isothermal resistance normalised at 1 bar, for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Data are shown by open circles [7]. (*b*) Pressure dependence of the energy gap. The inset shows the pressure derivative of the energy gap as a function of temperature.

of states g_0, the temperature- and pressure-dependent conductivity $\sigma(T, p)$ is determined by the change in the carrier density $n_c(T, p)$ and is expressed as

$$\sigma = 2n_c e\mu = 2e\mu g_0 k_B T \ln[1 + \exp(-E_G/k_B T)] \tag{1}$$

where e is an electron charge and μ is a mobility [3]. The resistance maximum, which is suppressed so sensitively by applying the contraction strains ([2, 6]), is well explained as an insulator-to-metal transition as follows [3]. As the temperature is lowered or the pressure is applied, the transfer integrals of π-electrons are expected to increase as a consequence of lattice contraction. This leads to an increase in W_{SB} and hence reduces E_G. Here the resistance maximum at ambient pressure is simply understood from the competing effects: with decreasing temperature, the resistance becomes enhanced due to the reduction in the number of carriers thermally activated across the gap, while the gap becomes narrower due to the strain-induced spreading bandwidth. In our previous analyses [3], we obtained the room temperature gap $E_G(T = 300\ \text{K}, p = 0) = 300$–$500$ K which explains the data on $\sigma(300\ \text{K}, p)$, the pressure dependence of the conductivity at room temperature [2].

Recently the results of the ideal experiments by use of gas pressure by Kang *et al* [7] have been published. In contrast to liquid-pressure experiments ([2, 6]), these measurements not only give quantitatively reliable data, but also enable the measurement, at low temperatures, of the pressure dependence of the isothermal conductivity. These data are quite important for the examination of our model. In this letter, we show how the pressure-sensitive resistance is explained by our model and how the measured compressibility and the calculated strain dependence of the band structures are consistent with our model.

Figure 1(*a*) shows the isothermal resistance normalized at 1 bar, $R(p)/R(0)$, as a function of pressure at 296 K, 185 K and 77.4 K. It can be seen that the resistance decreases sensitively with pressure. In particular, at 77.4 K, around which the resistance

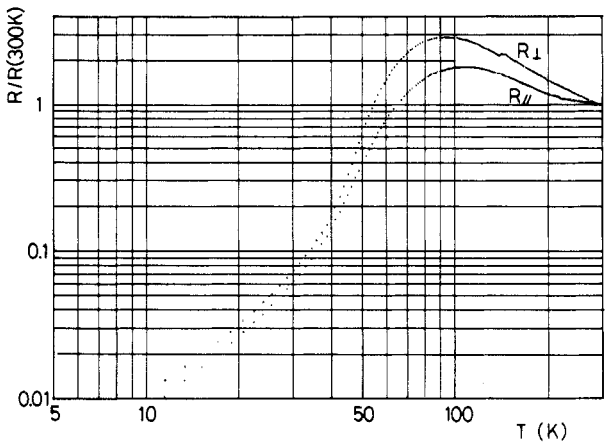

Figure 2. Logarithmic plots of the in-plane ($R_{\parallel}$) and inter-plane ($R_{\perp}$) resistance normalised at room temperature versus temperature, for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

at ambient pressure rapidly falls (see figure 2), the resistance rapidly decreases by a factor of almost 10, even at the very small pressure of about 1 kbar, and then tends to saturate. To compare this characteristic dependence of the resistance with our model, we assume that μ and g_0 remain unchanged under pressure and obtain

$$R(T,p)/R(T,0) = \ln\{1+\exp[-E_G(T,0)/k_BT]\}/\ln\{1+\exp[-E_G(T,p)/k_BT]\}. \quad (2)$$

The data are well fitted to this formula by assuming the pressure dependence of E_G as shown in figure 1(b). In our previous paper, [3], we determined $E_G(3000\text{ K}, 0) = 300$–$400$ K by taking into account that, at $p > 4$ kbar, the system might already be metallic over the whole temperature range without any resistance maximum [6, 7] and the dominant contribution to the temperature-dependent resistance might be from the regular electron–phonon interactions. With this $E_G(300\text{ K}, 0)$, we can reproduce the resistance maximum at ambient pressure $E_G(T, 0)$ as shown in figure 4 of [3]. Estimating $E_G(296\text{ K}, 0) = 300$–$500$ K, $E_G(185\text{ K}, 0) = 100$–$200$ K and $E_G(77.4\text{ K}, 0) = 0$–$50$ K from this figure, we can again reproduce the data of figure 1(a) by assuming the pressure dependence of the gap as shown in figure 1(b). It is noted that E_G decreases almost linearly with these low pressures.

Next we proceed to examine the temperature- and pressure-sensitive energy gap $E_G(T,p) = \frac{1}{2}(V - W_{SB})$. For the intersite Coulomb repulsion V, we can approximate $V = e^2/r = e^2/r_0(1+u)$, where r_0 is an equilibrium distance between adjacent BEDT-TTFs in a dimer at $T = 300$ K and $p = 0$, and u is a strain. On the other hand, the strain dependence of W_{SB} is determined by the band structure calculations [8]. From $W_{SB} = 0.2$ eV and $E_G(300\text{ K}, 0) = 300$–$500$ K, $V(300\text{ K}, 0) = 0.26$ eV is obtained. The temperature dependence of lattice constants at $p = 0$ [9] (see figure 4 of [3]) shows that $u = -0.03$ is induced along the c direction at 100 K. Then, $V(100\text{ K}, 0)$ increases by 3%, while $W_{SB}(100\text{ K}, 0)$ is expected to be much enhanced by 30% from the band structure calculations and reaches 0.26 eV. Therefore we come to the conclusion that, at around 100 K, W_{SB} becomes almost comparable in magnitude with V, leading to the vanishing of the gap. This is due to the fact that W_{SB} proportional to the transfer integral is sensitive to u much more than V. Therefore the strain dependence of V can be neglected and hence the strain-sensitive $W_{SB}(u(T,p))$ is mainly responsible for $E_G(T,p)$.

The pressure dependence of W_{SB} is expressed as

$$\partial W_{SB}/\partial p = Z^{-1}(\partial W_B/\partial u)(\partial u/\partial p) \tag{3}$$

where the second and third factors are the strain dependence of the bare band width and the compressibility, respectively. Recently Chasseau *et al* [10] have calculated the former to get $\partial W_B/\partial u = -1 \times 10^5$ K, which is in agreement with the result of Mori *et al* [8], and also measured the latter at room temperature; $\partial u/\partial p = -0.36 \times 10^{-4}$ and -0.25×10^{-4} MPa^{-1} for the c and b direction, respectively. Substituting these parameters into (3), we get $\partial W_{SB}/\partial p = 100$ and 80 K $kbar^{-1}$ for the c and b direction, respectively. These values agree with 100 K $kbar^{-1}$ obtained from the analysis in figure 1(b) (at $T = 296$ K).

It is interesting to note that our analyses, resulting in the enhancement of $\partial W_{SB}/\partial p$ at low temperatures as shown in the inset of figure 1(b), indicate the enhancement of $\partial u/\partial p$ at low temperatures, because $\partial W_B/\partial u$ should be temperature-independent. This implies that, when the temperature is lowered, there might appear some lattice softening manifested in the enhancement of the compressibility.

Next we make a comment on our data for the inter-plane resistivity. Figure 2 shows the temperature dependence of the in-plane ($R_\parallel$) and inter-plane ($R_\perp$) resistance normalized at each room-temperature value. From that $R_\perp(T)$ also takes a maximum around 100 K, which is quite similar to $R_\parallel(T)$ over the whole temperature range, we might conclude that the gross features of the temperature-dependent inter-plane resistance could be caused by the hopping of the in-plane carriers, the density of which is determined by the present model.

Finally, as stressed our our previous papers [1, 3], the tight-binding band calculations for the non-interacting π-electrons give a good prediction of the Fermi surface topology which has been experimentally determined by the Shubnikov–de Haas effect at low temperatures around 1 K. At these low temperatures, the present material must be a 'good metal' with high-T_c superconductivity. In the present model, nevertheless, an assumption is made of the presence of the small energy gap of 300–500 K at room temperature which is assumed to be caused by the comparable magnitudes of the inter-site Coulomb repulsion and the transfer integral. Thus the resistance maximum is phenomenologically interpreted as the insulator-to-metal transition connecting these high temperature semiconducting and low temperature metallic states, by use of the characteristic anharmonicity and softness of the (BEDT-TTF)-stacked lattice, e.g., high sensitivity of the transfer integrals to the strain.

Some fundamental problems remain unsettled. Concerning the question as to whether such a small energy gap can really be observed, we point out that the low frequency optical conductivity spectrum [11] at room temperature, quite in contrast to the low temperature one, might be suggestive of semiconducting behaviour. The difficult, but interesting question is why the band calculations gave a good prediction of the Fermi surface topology for the highly correlated electron system. The Luttinger theorem [12] seems to still hold here. Further studies experimental as well as theoretical are encouraged, because $(BEDT\text{-}TTF)_2X$ might be a model system for the two-dimensional extended Hubbard model at quarter-filling.†

† After submitting this paper, we noticed an interesting article by L I Buravov *et al* (1989 *Zh. Eksp. Teor. Fiz.* **95** 322; 1989 *Sov. Phys.—JETP* **68** 182). From their measurements of the DC and microwave conductivity, thermoelectric power and magnetic susceptibility, they suggest that a paramagnetic insulator-to-metal transition might occur at 45 K. Although this temperature is lower than 60–80 K, the gap-vanishing temperature predicted from the present model, their arguments are qualitatively consistent with the present model.

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