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High-pressure transport measurements of α' -BEDT-TTF salts

I D Parker[†], R H Friend[†], M Kurmoo[‡] and P Day[‡]

[†] Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

[‡] Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

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Abstract. We report on transport and optical measurements of some α' -phase (BEDT-TTF)₂X salts with X = AuBr₂⁻, Ag(CN)₂⁻ and CuCl₂⁻. These salts are shown to be Mott–Hubbard semiconductors. Transport measurements were made under hydrostatic pressures up to 20 kbar and temperatures down to 4 K. At room temperature all three systems have low conductivities, $\approx 0.05 \text{ S cm}^{-1}$ and small activation energies, $\approx 300 \text{ meV}$. On cooling, the AuBr₂⁻ and Ag(CN)₂⁻ salts show a transition between two semiconducting phases with slightly different activation energies, and for both salts the transition temperature increases under pressure. For all three salts the activation energy for conductivity decreases under pressure. In the AuBr₂⁻ system the transition changes abruptly from second to first order at 8.5 kbar. This is not seen for Ag(CN)₂⁻. The thermopower has been measured for all three salts at ambient pressure. There are differences, with the AuBr₂⁻ system showing hole conduction and the others showing electron conduction. We have measured the optical absorption spectrum of the Ag(CN)₂⁻ salt, and this shows a peak at 1.3 eV in the solid state which is missing in a dilute solution of BEDT-TTF. We attribute this to a Hubbard correlation. Finally we suggest an explanation for the similarities of and differences in behaviour between these three systems and discuss the general properties in terms of a large- U model.

1. Introduction

The organic charge-transfer salts in the (BEDT-TTF)₂X family show many diverse properties. Metallic, antiferromagnetic insulator, charge-density wave, spin-Peierls and superconducting ground states are all known. The particular ground state adopted depends sensitively upon the inter-molecular contacts determined by the crystalline structure of the material, and this is influenced, amongst other things, by the size of the anion X. It is found for example that the β -superconducting phase only forms with symmetrical anions of length greater than 9.3 Å [1][†]. The family has recently been extended to include Mott–Hubbard insulators by introducing smaller anions (the α' -phase). Of particular interest here are the isostructural members of the α' -series with the anions AuBr₂⁻ (8.7 Å), Ag(CN)₂⁻ (9.0 Å) and CuCl₂⁻ (7.8 Å).

Synthesis of these materials is as described in the previous paper in this journal [2]. The structure consists of dimeric BEDT-TTF units that repeat along the stacking axis (the a axis). Within the dimer, the BEDT-TTF molecules are nearly parallel but are rotated with respect to each other about the stacking axis by about 32°. Adjacent stacks are

[†] In addition, the anion length for β -(BEDT-TTF)₂AuI₂ ($T_c = 5 \text{ K}$) is 9.4 Å and that for (BEDT-TTF)₂Cu(NCS)₂ ($T_c = 10.4 \text{ K}$) is $> 10.2 \text{ Å}$.

parallel and coplanar. The *inter*-dimer distances (3.836, 3.913 and 3.877 Å for the AuBr_2^- , $\text{Ag}(\text{CN})_2^-$ and CuCl_2^- salts respectively) are significantly larger than the *intra*-dimer distances (3.436, 3.401 and 3.432 Å), leading to poor contact between the dimers. This has a strong influence on the electronic properties. Many side-by-side S...S contacts are less than the Van der Waals sum for sulphur (3.6 Å) giving rise to a 2D network of S...S interactions in the *ab* plane. These sheets are separated in the *c* direction by the anions. Despite the 2D nature of the structure, a tight-binding calculation of the band electronic structure carried out by Beno and co-workers [3], suggests that it is electronically 1D, with the conductivity along the *a* axis much greater than that along the *b* axis. As with other charge-transfer systems, the bands are formed from overlapping π -orbitals formed from the HOMO on the BEDT-TTF molecules. We believe that this one-electron calculation is an inappropriate model for these materials, in which Coulomb interactions are important. However, it gives a measure of the various inter-molecular interactions, including the intra-dimer transfer integral, t_1 , which we estimate, by setting $2t_1$ equal to the splitting between the two π -bands of bonding and anti-bonding intra-dimer character, to be about 0.25 eV. Beno and co-workers [3] also reported the formation of a superlattice, involving a doubling of the *b* axis at a temperature between 125 K and room temperature. In light of the assumed one-dimensionality of the system, this was attributed to a Peierls distortion. The magnetic susceptibility work by Obertelli and co-workers reported in the previous article [2] shows very clearly that these materials are not 1D metals but are Mott–Hubbard insulators with highly localised spins. The room-temperature value for the magnetic susceptibility, $\approx 9 \times 10^{-4}$ emu mol $^{-1}$, is far too high for a metallic system as suggested by Beno and co-workers. The magnetic properties show one spin per dimer ($S = \frac{1}{2}$) and a temperature dependence of the magnetic susceptibility, typical of a low-dimensional 1D or 2D localised system. At low temperatures the magnetic susceptibility indicates weak antiferromagnetic coupling; modelled by the Bonner–Fisher theory for a 1D chain, the inter-dimer exchange energy is about 50 K and the transfer integral, t_2 , about 50 meV.

To compliment the magnetic and structural work reported in the preceding paper [2], we report here a study of the transport properties under hydrostatic pressure, and some of the optical properties of these materials.

2. Experimental results

2.1. The AuBr_2^- salt

The temperature and pressure dependences of the conductivity in $(\text{BEDT-TTF})_2\text{AuBr}_2$ are shown in figures 1 and 2. At room temperature and ambient pressure, the conductivity is ≈ 0.1 S cm $^{-1}$. From 370 K, the limit of the experiment, down to 248 K, the conductivity shows an activated behaviour, with $E_A = 240$ meV. At 248 K there is a phase transition to a second activated phase, with E_A increasing slightly to 305 meV. Under pressure, the activation energy both above and below the transition temperature decreases linearly at a rate of 5 meV kbar $^{-1}$.

Pressure increases the conductivity rapidly, with a factor of seven increase in 17 kbar at room temperature. The kinks in these conductivity pressure curves indicate the phase transition. The transition temperature, T_c , also increases rapidly with pressure, moving upwards from 248 K to almost 340 K under 17 kbar, albeit with a slight initial decrease and a ‘knee’ at 8.5 kbar (figure 2). Below 8.5 kbar this transition is a second-order one, with the conductivity increasing continuously, but with a jump in the activation energy.

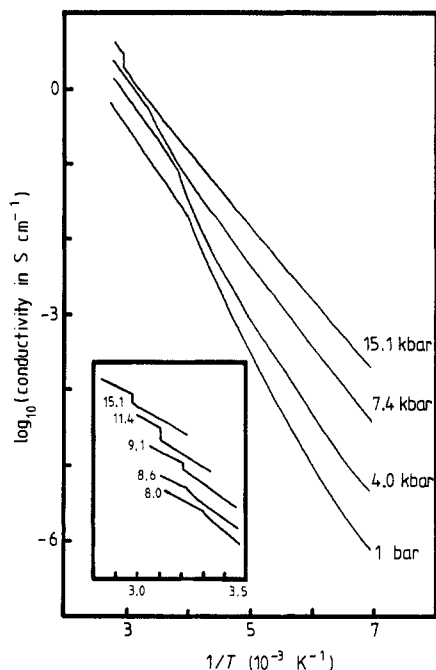


Figure 1. The temperature dependence of the conductivity for the AuBr_2^- salt. The inset shows the details of the transition near 8.5 kbar.

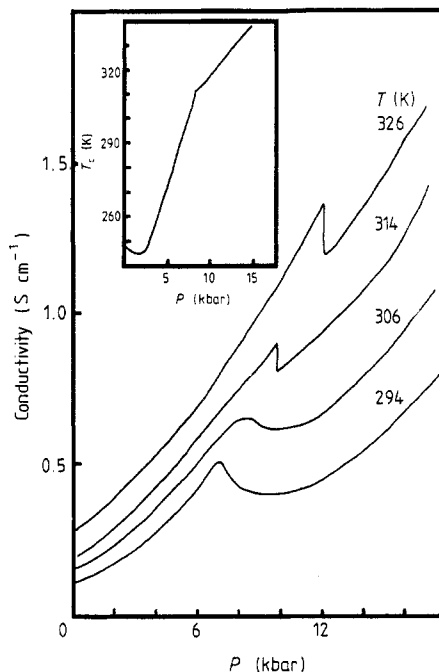


Figure 2. The dependence on pressure sPs , of the conductivity in the AuBr_2^- salt at room temperature. Note the change from a second to a first-order transition above 8.5 kbar. The inset shows the pressure dependence of the transition temperature with a knee at 8.5 kbar.

However, above 8.5 kbar it becomes a first-order transition, with a discontinuity in the conductivity about 1.5 K wide. The changing nature of the transition is also apparent from the conductivity–pressure curves at different temperatures. Below 8.5 kbar, the curves show a smooth and continuous peak in resistance at the transition, and this becomes discontinuous above 8.5 kbar. The changing nature of the transition is also indicated by the knee in the T_c –pressure curve.

The thermopower results shown in figure 3 indicate typical semiconducting behaviour, with the thermopower, S , proportional to the reciprocal temperature. At room temperature, the thermopower is $\approx 50 \mu\text{V K}^{-1}$, increasing to $350 \mu\text{V K}^{-1}$ on cooling to 200 K. The phase transition at 248 K appears as a change in slope.

2.2. The $\text{Ag}(\text{CN})_2^-$ salt

The temperature and pressure dependence of the conductivity in $(\text{BEDT-TTF})_2\text{Ag}(\text{CN})_2$ is shown in figure 4. The room-temperature, ambient-pressure conductivity is slightly lower than in the AuBr_2^- salt with a value of $\approx 0.03 \text{ S cm}^{-1}$. In common with the AuBr_2^- salt, it shows activated behaviour at room temperature. From 370 K, down to 297 K, $E_A = 300 \text{ meV}$. At 297 K there is a phase transition to a second activated phase, with E_A decreasing slightly to 200 meV. This fall in activation energy is in contrast with the behaviour of the AuBr_2^- salt, and we discuss this below. Under pressure, the activation energy both above and below the transition temperature decreases linearly at a rate of 5 meV kbar^{-1} , in common with the AuBr_2^- salt.

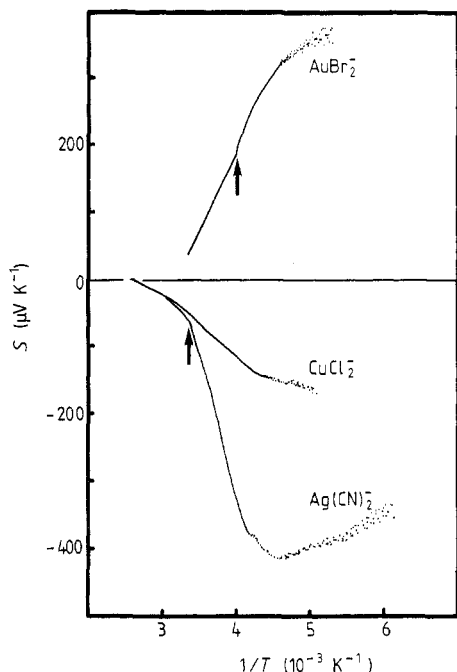


Figure 3. The temperature dependence of the thermopower at ambient pressure.

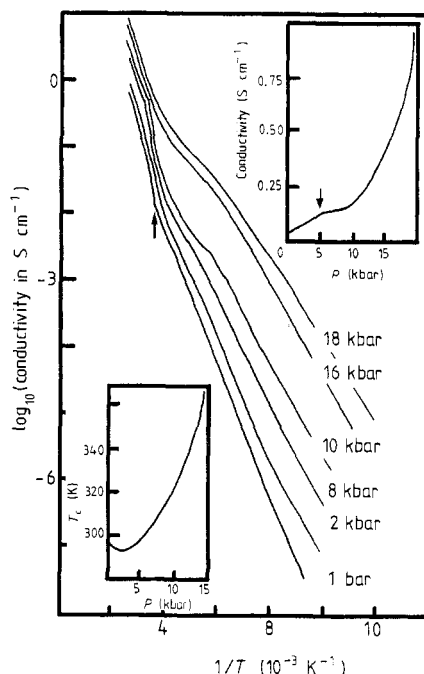


Figure 4. The temperature dependence of the conductivity for the $\text{Ag}(\text{CN})_2^-$ salt. The transition at 297 K is indicated. The inset shows the pressure dependence of the conductivity at room temperature (the kink near 5 kbar indicates the transition from the higher-activation-energy phase to the lower one), and the pressure dependence of the transition temperature.

Under 20 kbar pressure, the conductivity increases by a factor of ten, comparable to the pressure dependence of the AuBr_2^- salt. The transition temperature is also strongly pressure dependent, rising from 297 K to almost 370 K with 15 kbar pressure. In common with the AuBr_2^- salt, this transition temperature shows a slight decrease for pressures below 3 kbar. The transition is a second-order one to at least 13 kbar, with simply a change in the activation energy. The phase transition can also be seen as a kink in the conductivity–pressure curve near 5 kbar.

Thermopower (figure 3) again shows typical semiconducting behaviour but, in contrast to the AuBr_2^- salt, is negative. It is virtually zero near 370 K, and becomes $\approx -400 \mu\text{V K}^{-1}$ at 220 K. Below 220 K the thermopower curve turns over. We attribute this to the effect of extrinsic defects. The transition at 297 K separating the two phases is again visible.

2.3 The CuCl_2^- salt

The pressure and temperature dependence of the conductivity in $(\text{BEDT-TTF})_2\text{CuCl}_2$ is shown in figure 5. At room temperature and ambient pressure, the conductivity is very similar to the values for the AuBr_2^- and $\text{Ag}(\text{CN})_2^-$ salts, at $\approx 0.03 \text{ S cm}^{-1}$. Below 370 K, the conductivity is activated with $E_A \approx 200 \text{ meV}$. The transition between the two activated phases seen for the AuBr_2^- and $\text{Ag}(\text{CN})_2^-$ salts is not observed in this salt up to

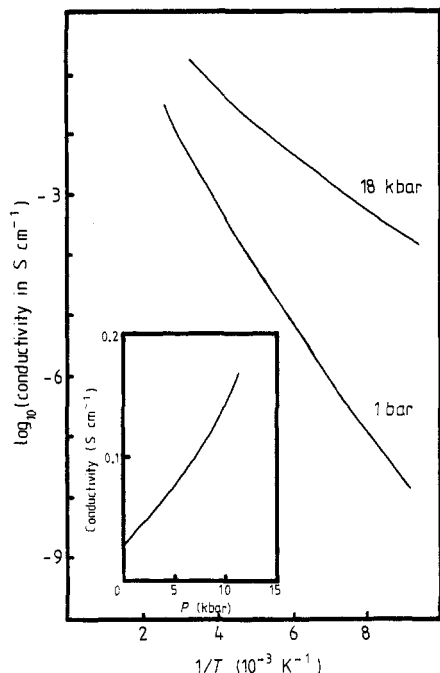


Figure 5. The temperature dependence of the conductivity for the CuCl_2^- salt. The inset shows the pressure dependence of the conductivity at room temperature.

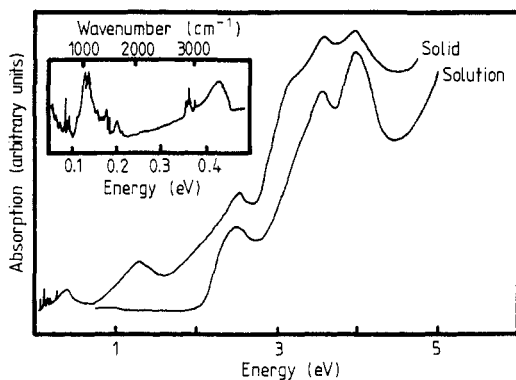


Figure 6. Optical absorption for $(\text{BEDT-TTF})_2\text{Ag}(\text{CN})_2$ and for neutral BEDT-TTF in solution. The inset shows detail below 0.5 eV.

370 K. Pressure increases the conductivity by a factor of six at 11 kbar, which is very similar to what happens for the other salts. E_A decreases linearly at a rate of -5 meV kbar^{-1} as for the other salts.

The thermopower is negative (figure 3), as for the $\text{Ag}(\text{CN})_2^-$ salt, and shows typical semiconducting behaviour. The magnitude of the thermopower is smaller than that for the $\text{Ag}(\text{CN})_2^-$ salt, rising from zero near 370 K to $-150 \mu\text{V K}^{-1}$ at 200 K.

2.4. The optical spectra

The optical absorption for one of the salts ($\text{Ag}(\text{CN})_2^-$) and that of BEDT-TTF in dilute solution are shown in figure 6. The spectra of the three salts are all very similar. In the solid state, optical absorption measurements were made by finely grinding the crystals with dry KBr and pressing into thin transparent discs. For the solution measurements, neutral BEDT-TTF molecules were dissolved in dichloromethane to a concentration of

$\approx 10^{-3}$ M. At this low concentration the molecules are dissociated, and are not present as dimer pairs as in the solid. In the solid state, the absorption could be measured from 0.05 to 5 eV (400 to 40 000 cm^{-1}). For the solutions, it was only possible to measure from 0.8 to 5 eV.

In the solid state, below 0.5 eV, the infrared-active bending and stretching modes of the BEDT-TTF molecule are clearly observed, with absorption bands at 487, 698, 1030, 1074, 1600, 2851, 2921 and 3025 cm^{-1} , the absorptions at 1030 and 1074 being particularly strong (these data are for the $\text{Ag}(\text{CN})_2^-$ salt). Similar results are observed from Kramers–Kronig analysis of single-crystal reflectivity spectra and from absorption spectra for thin crystals [5]. A large, broad peak is also present near 3400 cm^{-1} (0.42 eV), which shifts slightly between the three salts. For the AuBr_2^- , $\text{Ag}(\text{CN})_2^-$ and CuCl_2^- salts respectively, the peak of the absorption is at 3263, 3443 and 3592 cm^{-1} (0.405, 0.427 and 0.445 eV). We discuss the significance of this peak below.

At higher energies (up to 6 eV), structure due to intra-molecular excitations is visible, identified by the fact that the absorption peaks are also present in the spectrum of neutral BEDT-TTF molecules in dilute solution. There is one notable difference, however: the peak at 1.3 eV is absent for the solution spectrum. The significance of this peak is also discussed below.

3. Discussion

The transport measurements are quite clearly in agreement with the Mott–Hubbard insulating model of Obertelli and co-workers [2]. In particular, it is found that:

(i) at room temperature the conductivity, of around 0.1 S cm^{-1} , is several orders of magnitude too low for a metal, and shows an activated temperature dependence typical of a semiconductor;

(ii) the magnitude of the thermopower (several 100 $\mu\text{V K}^{-1}$) is about 100 times too large for a metal and shows a temperature dependence proportional to $1/T$, also typical of a semiconductor;

(iii) the phase transition seen for the AuBr_2^- and $\text{Ag}(\text{CN})_2^-$ salts cannot be a Peierls transition (as proposed in [3]) since the transition temperature should scale with the activation energy [4], whereas we find that the transition temperature increases under pressure whilst E_A decreases. Obertelli and co-workers [2] also find that the transition cannot be a Peierls transition since they see no evidence for it in magnetic susceptibility data.

For electrical conduction to take place, the carriers must move between the lattice sites creating an intrinsic electron–hole pair. This involves placing two carriers on one dimer, costing energy U_{eff} due to the Coulomb repulsion between the carriers. Allowing for the configurational entropy of both electron and hole, E_A is equal to $U_{\text{eff}}/2$. The states of a dimer with intra-dimer transfer integral t_1 and Hubbard energy for a single molecule U_0 are known [6, 7]. With two charges present U_{eff} is given [6] by

$$U_{\text{eff}} = 2t_1 + \frac{1}{2}(U_0 - \sqrt{U_0^2 + 16t_1^2}).$$

In the limit where U_0 is much greater than t_1 , $U_{\text{eff}} = 2t_1$, while for U_0 much less than t_1 , $U_{\text{eff}} = U_0/2$. The optical evidence indicates that U_0 is 1.3 eV (see below), and with $t_1 = 0.25$ eV the expression above gives $U_{\text{eff}} = 0.33$ eV, in reasonable agreement with the experimental values obtained from the conductivity activation energy.

Under pressure, the activation energy for the conductivity is observed to fall for all three salts measured. U_0 is not sensitive to pressure, and t_1 will always increase as the intra-dimer separation is decreased. The analysis above, for isolated dimers, must always require that U_{eff} increases with increasing t_1 , and thus fails to account for the pressure dependence. We consider that the effects of inter-dimer contact, characterised by a transfer integral t_2 , must be taken into account. Pincus [7] shows that the minimum energy for creation of electron-hole pairs, U_{eff} , is reduced by inter-dimer coupling by αt_2 , where for the values of t_1 and U_0 used here, $\alpha = 1.8$. We consider that under pressure, t_2 will increase much more rapidly than t_1 and that this is responsible for the fall in activation energy under pressure.

The phase transition in the AuBr_2^- and $\text{Ag}(\text{CN})_2^-$ salts seems to be uncoupled from the conduction π -electrons of the system since only a small change in E_A is seen. Structural work [2, 3] has shown a doubling of the b axis (inter-stack direction) which is consistent with a structural reorganisation that does not involve the conduction electrons directly. This is clear evidence that E_A is governed by t_1 and t_2 , rather than U_0 , since U_0 is an intra-molecular property and is insensitive to lattice parameters, whereas the transfer integrals will depend sensitively upon inter-molecular spacing. The fact that the change in E_A increases below the transition temperature for the AuBr_2^- salt whilst decreasing for the $\text{Ag}(\text{CN})_2^-$ salt indicates that the change in the transfer integrals is merely an accidental by-product of the inter-stack reorganisation.

The change in nature of the transition in the AuBr_2^- salt from first to second order at 8.5 kbar is of some interest. Preliminary high-pressure x-ray structural measurements indicate that there may be a considerable reorganisation of the anion positions at the transition, with rotation of the anions towards the a axis at 7 kbar at room temperature [8].

Further evidence for the large- U_0 model, with correlated electron behaviour, comes from the optical spectra of these salts in the solid state. The absence of an absorption band edge, corresponding to the conduction band gap, is direct evidence that these materials are not simple uncorrelated semiconductors with single-particle excitation across the band gap. The low-energy feature near 0.45 eV is probably due to a bonding-anti-bonding transition on a single dimer. The predicted energy of this transition is $2t_1$, giving $t_1 = 0.22$ eV in close agreement with the value derived from the band-structure calculations of 0.25 eV. Support for the identity of this optical feature is given by the significant shift in peak energy, from 0.405 to 0.427 to 0.445 eV in the AuBr_2^- , $\text{Ag}(\text{CN})_2^-$ and CuCl_2^- salts respectively. In these salts, the intra-dimer distances are different (3.436 to 3.401 and 3.432 Å), and hence a change in $2t_1$ would be expected. These intra-dimer distances indicate the distance between the geometrical centre of the molecules, and as such do not give a true measure of t_1 since the molecules are rotated with respect to each other, and this rotation is slightly different for the three salts. Consequently, the shift in peak energy is not expected to correlate exactly with the intra-dimer distance. However, the shift is a good indication that the peak is related to an inter-molecular interaction.

The peak in the optical spectra of the solids at 1.3 eV, which is missing in solution, must involve inter-molecular interactions. Since there are no missing peaks at any higher energy it is probable that it corresponds to the Hubbard U_0 with two electrons on one molecule. This value of 1.3 eV would be typical for organic charge-transfer systems where U_0 almost invariably lies in the range 1.2–1.8 eV [9], and is consistent with the model we have developed above.

At temperatures above about 220 K we consider that the thermopower results shown in figure 3 are typical of those for an intrinsic semiconductor, with both electrons and

holes present. The thermopower varies linearly with reciprocal temperature, with its sign and magnitude dependent on the ratio of the mobilities of the thermally generated electrons and holes. There is no obvious reason for which this should be reversed for the AuBr_2^- salt in comparison with the other salts. Below 220 K, there is deviation from the $1/T$ dependence, and it appears that extrinsic carriers begin to dominate the thermopower.

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