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1989 J. Phys.: Condens. Matter 1 5671

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The magnetic susceptibility and EPR of the organic conductors α' -(BEDT-TTF)₂X, X = AuBr₂, CuCl₂ and Ag(CN)₂

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Received 5 December 1988

Abstract. We have investigated the magnetic properties of some linear chain anion salts of BEDT-TTF which adopt the α' -structure. These are (BEDT-TTF)₂X, where X = AuBr₂⁻, CuCl₂⁻ and Ag(CN)₂⁻. In the α' -morphology the donor stacks are formed from twisted BEDT-TTF dimers, with the BEDT-TTF molecules within the dimeric unit rotated with respect to each other about the stacking axis by about 32°. Contact between the dimer pairs along the stacking axis is poor, and this has a strong influence on the electronic properties. We find that this series of compounds are highly localised, low-dimensional spin systems with $S = \frac{1}{2}$ per BEDT-TTF dimer. We describe this behaviour as that of a Mott–Hubbard insulator, and consider that it is due here to the narrow band width along the stacking direction. The behaviour of the susceptibility at low temperatures indicates weak antiferromagnetic coupling, with an exchange energy of about 50 K. The Ag(CN)₂⁻ salts show a sharp fall in susceptibility at 7 K, and we consider that this is probably associated with a spin-Peierls transition.

1. Introduction

The donor molecule BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene, has provided a series of charge-transfer salts with a wide range of electronic properties. Several of these salts are superconductors, and since the first report of superconductivity near 1 K for the perrhenate salt at high pressure [1], higher critical temperatures at ambient pressure have been steadily reported. There has been a great deal of interest in the salts formed with linear chain anions, and there is a family of superconducting salts of stoichiometry (BEDT-TTF)₂X with X = I₃⁻, AuI₂⁻ etc [2, 3, 4] that show values for the superconducting transition temperatures, T_c , of up to 7 K [4]. More recently, a value for T_c of 10.4 K has been found for (BEDT-TTF)₂Cu(SCN)₂ [5, 6]. A feature of the charge-transfer salts formed with BEDT-TTF is the very large range of polytypes that are found in samples grown by electrochemical oxidation of the BEDT-TTF. These polytypes show some structural features in common, such as the segregation of BEDT-TTF molecules into sheets separated by sheets of the anion, but within the BEDT-TTF sheets rather small variations in the stacking arrangements can produce very different electronic properties. The family of superconducting salts based on the I₃⁻ salt [2–4] all adopt the β -structure, with well defined one-dimensional stacks of BEDT-TTF although there is considerable inter-stack

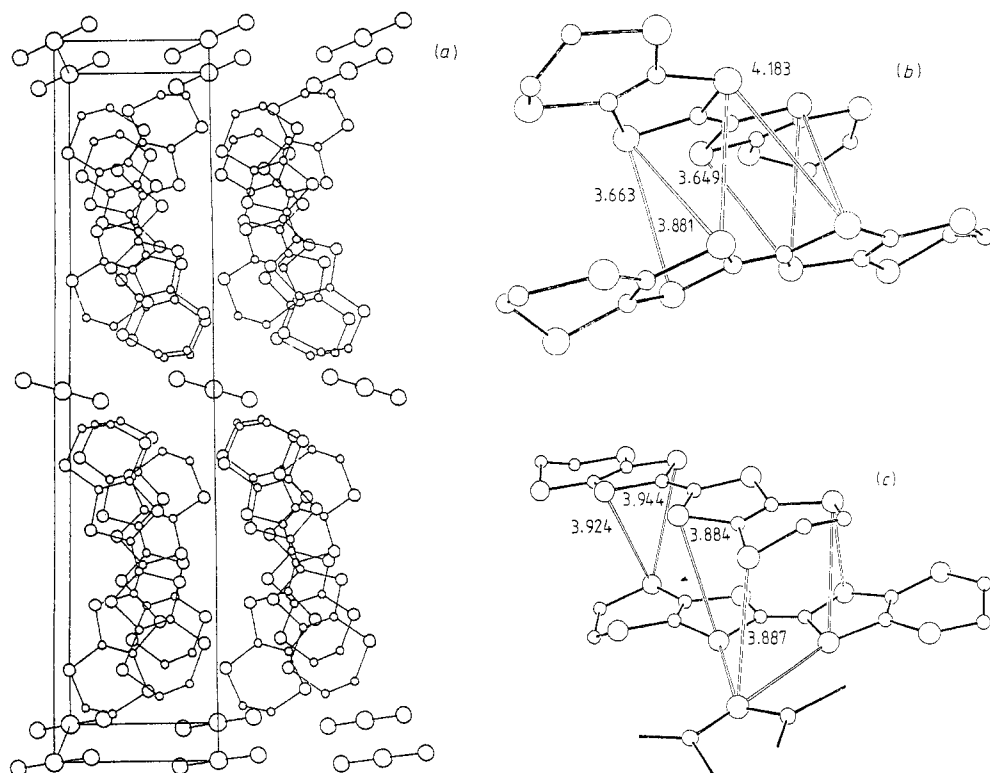


Figure 1. The structure of α' -(BEDT-TTF) $_2$ CuCl $_2$ (a) showing the organisation of BEDT-TTF stacks and CuCl $_2^-$ anions, (b) intra-dimer contacts, with inter-molecular distances shown in Å, (c) inter-dimer contacts, with inter-molecular distances shown in Å.

contact. The newly reported Cu(SCN) $_2$ salt has a different arrangement of the BEDT-TTF molecules, with BEDT-TTF dimers arranged to form a sheet with no obvious one-dimensional character.

We wish to report here the temperature-dependent magnetic properties (measured using static susceptibility and electron paramagnetic resonance) of an isostructural series of BEDT-TTF charge-transfer salts α' -(BEDT-TTF) $_2$ X, where X = AuBr $_2$ [7, 8], CuCl $_2$ [9], and Ag(CN) $_2$ [7], reported on previously. The structure of this polytype bears some similarity to the β -phase, with 'one-dimensional' stacks of BEDT-TTF, but the BEDT-TTF molecules are rotated with respect to each other about the stacking axis, and we can see firstly a more strongly dimerised chain, and secondly rather poor contact between dimers along the chains. This is illustrated in figure 1. We find that the electronic properties of these salts are quite different from those of the β' -phase. Instead of metallic behaviour we find that this series of compounds are highly localised, low-dimensional spin systems with $S = \frac{1}{2}$ per BEDT-TTF dimer. We describe this behaviour as that of a Mott-Hubbard insulator, and consider that it is due here to the narrow band width along the stacking direction. The behaviour of the susceptibility at low temperatures indicates weak antiferromagnetic coupling, but the low-dimensional magnetic exchange does not establish long-range antiferromagnetic order above 4 K. We do find a sudden reduction in the magnetic susceptibility of the Ag(CN) $_2^-$ salt at 7 K, and we consider that this is probably associated with a spin-Peierls transition.

In the following paper [10] we report measurements of the transport and optical properties which we explain within the Mott–Hubbard insulator model.

2. Experimental procedure

Crystals were grown by electrochemical oxidation of BEDT-TTF in dichloromethane or tetrahydrofuran using platinum electrodes and (n-Bu₄N)X, where X = AuBr₂⁻ [11], CuCl₂⁻ [12], or Ag(CN)₂⁻, as supporting electrolyte. The constant-current mode (3–5 μ A) of oxidation was used. Crystals of the α' -phase were first checked taking x-ray Weissenberg photographs and later by shape (long four- or six-sided needles of typical dimension 3 \times 0.5 \times 0.2 mm³).

Susceptibility was measured against temperature using the Faraday balance technique over the temperature range 4–300 K. Each sample was measured in at least two fields between 0.3 and 0.8 T. Honda–Owen corrections were made to correct for ferromagnetic impurities which were found to be below 10 ppm in all cases. Samples were in the form of large numbers of small crystals (8–12 mg) randomly oriented in a silica bucket. Different batches were run to test reproducibility.

Electron paramagnetic resonance spectra were recorded by use of a Varian E-series reflection spectrometer. Samples were mounted on a cut edge of a Spectrosil quartz rod and rotation was achieved using a home-built goniometer. Samples were cooled using an Oxford Instruments (CF) cryostat. The temperature was measured with a AuFe thermocouple (5 mm from the sample).

3. Results

The temperature dependence of the excess molar susceptibility χ_{EMS} , for the three compounds is plotted in figure 2. The data have been corrected in all three cases for a diamagnetic core contribution calculated using Pascal's constants [13, 14]. The respective corrections for (BEDT-TTF)₂X are: for X = AuBr₂⁻, 489×10^{-6} emu mol⁻¹; for CuCl₂⁻, 458×10^{-6} emu mol⁻¹; and for Ag(CN)₂⁻, 453×10^{-6} emu mol⁻¹. The (BEDT-TTF)₂AuBr₂ data have been corrected for a small Curie tail corresponding to 1700 ppm $S = \frac{1}{2}$ spins. The room-temperature values of the corrected susceptibility are 9.0×10^{-4} , 9.0×10^{-4} , and 9.3×10^{-4} emu mol⁻¹ for the AuBr₂⁻, CuCl₂⁻, and Ag(CN)₂⁻ salts respectively. With decreasing temperature χ_{EMS} goes through a broad maximum in all three cases, which is characteristic of short-range antiferromagnetic coupling in low-dimensional systems [15]. Long-range order is suppressed for all ideal 1D chains and also for 2D square lattice systems with nearest-neighbour Heisenberg interactions. The experimental data have been fitted with model for both 1D and 2D Heisenberg antiferromagnets. Fits for the linear chain (Bonner–Fisher) ([16]; see also [17] and references therein) and the quadratic layer antiferromagnet (QLAF) [18, 19] are also shown in figure 2. In obtaining the fits shown, we have fixed the number of spin sites equal to the number of BEDT-TTF dimers, we have used the experimental values for g , and have adjusted only the strength of the antiferromagnetic exchange between them. The values for the exchange energy range from 35 to 56 K depending on the model chosen, and vary very little from one material to another. In the case of the Ag(CN)₂ salt (figure 2(c)), at 7 K there is a sharp decrease in susceptibility toward a non-magnetic state. The susceptibility measurement is limited to temperatures above 4.2 K, so the temperature range over

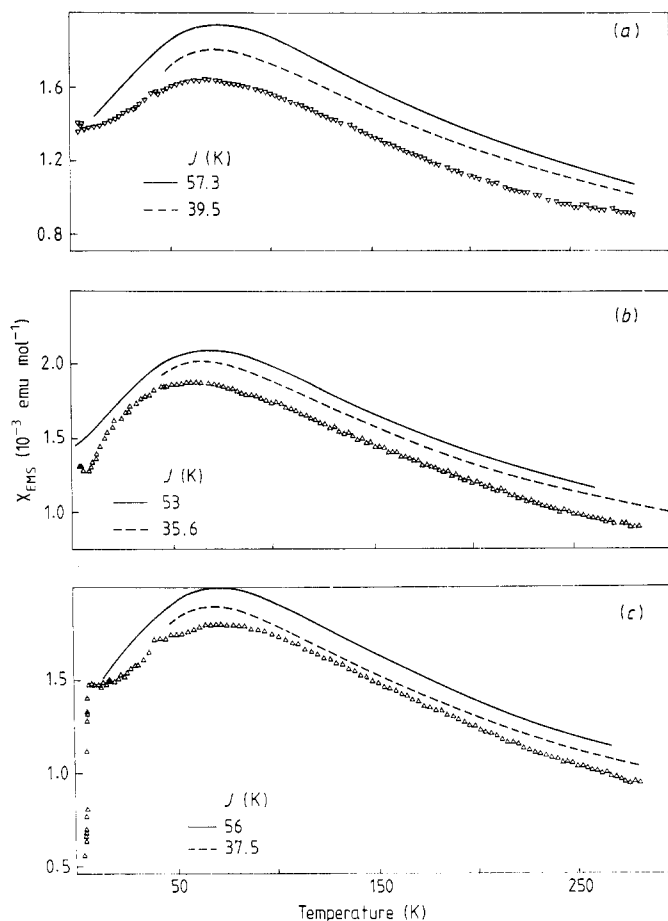


Figure 2. Static susceptibility data for randomly oriented crystals of α' -(BEDT-TTF) $_2$ X, X = AuBr $_2^-$ (a), CuCl $_2^-$ (b) and Ag(CN) $_2^-$ (c) as a function of temperature. The full and broken curves are the calculated susceptibilities for the Bonner–Fisher (BF) and quadratic linear antiferromagnet (QLAF) models respectively (see the text).

which this ordered magnetic phase could be measured was too restricted to carry out a detailed analysis. However, we can fit the variation of the susceptibility between 6.25 and 4.5 K to the relation $\chi = (\chi_0/T) \exp(-T_A/T)$, where χ_0 is the susceptibility above the spin-Peierls transition, and T_A , the activation energy, is equal to about 24 K. This transition is similar to that seen in the TTF metal dithiolenes [20–22] and in MEM(TCNQ) $_2$ [23] where the transition is to a spin-Peierls ground state.

EPR properties of the three compounds were studied as a function of orientation and temperature. Room-temperature g -values were similar for all three salts; for the Ag(CN) $_2^-$ salt, $g = 2.003$ with the static magnetic field, H_0 , parallel to the needle axis, a , and with H_0 perpendicular to a , maximum and minimum values of 2.006 and 2.009 were found on rotation about the needle axis. g -values for all three salts showed little variation with temperature. With H_0 perpendicular to the needle axis, the room-temperature EPR linewidths (ΔH_{P-P}) vary with rotation of the crystal about the needle axis in the ranges 37–50, 41–52 and 24–34 Oe for α' -(BEDT-TTF) $_2$ AuBr $_2$, α' -(BEDT-TTF) $_2$ CuCl $_2$, and α' -(BEDT-TTF) $_2$ Ag(CN) $_2$ respectively. The temperature dependence of

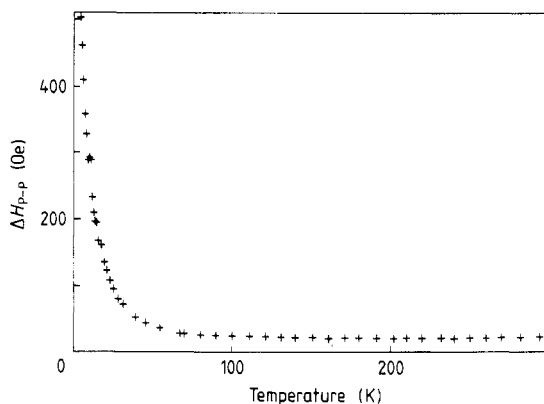


Figure 3. The EPR linewidth (ΔH_{p-p} —peak to peak in the first derivative of the absorption line) versus temperature for a single crystal of α' -(BEDT-TTF)₂Ag(CN)₂ with the static field H_0 perpendicular to the crystallographic a axis.

ΔH_{p-p} at the orientation chosen to set ΔH_{p-p} to its minimum value is shown in figure 3 for the Ag(CN)₂ salt. As the temperature is decreased, the linewidth is nearly of independent temperature down to 100 K, although there is a slight minimum near 150 K. Below 100 K, the linewidth gradually increases and diverges at low temperature until at 4.2 K, ΔH_{p-p} of α' -(BEDT-TTF)₂Ag(CN)₂ is in excess of 500 Oe. The temperature dependence of ΔH_{p-p} for the other salts is qualitatively the same, and the minimum values at 4.2 K for the AuBr₂⁻ and CuCl₂⁻ salts are 100 and 300 Oe respectively. The temperature dependence of χ_{spin} as determined by EPR generally follows that determined by the static measurement, although at low temperatures the broad linewidths lead to a high degree of uncertainty.

In their paper on the structure of the AuBr₂⁻ and Ag(CN)₂⁻ salts, Beno and co-workers [7] reported superlattice reflections at 125 K corresponding to a doubling of the unit-cell axis transverse to the stacking axis (a, b, c) \rightarrow ($a, 2b, c$). We have followed the transition with fixed-crystal x-ray photographs and find that the distortion occurs (accompanied by small changes in the activation energy of the conductivity) at 248 and 295 K for the AuBr₂⁻ and Ag(CN)₂⁻ salts respectively [27]. We were unable to obtain photographs below the magnetic phase transition at 7 K in the Ag(CN)₂ salt. However, fixed-crystal x-ray photographs at 30 K for the Ag(CN)₂⁻ salts show the persistence of diffuse scattering along the axis where the high-temperature (a, b, c) \rightarrow ($a, 2b, c$) transition is seen at 295 K. In contrast, photographs at 30 K of the AuBr₂⁻ salt show no evidence for the existence of this soft mode [27].

4. Discussion

4.1. The Mott–Hubbard transition

As with other BEDT-TTF phases [24], the α' -salts are composed of 2D organic layers which are isolated from one another by a layer of counter-ions [7–9]. It is the arrangement of the BEDT-TTF donors within the organic layers that largely determines the transport and magnetic properties in these materials. The characteristic feature of the α' -morphology is that the donor stacks are formed from twisted BEDT-TTF dimers. That is, the BEDT-TTF

molecules within the dimeric unit are rotated with respect to each other about the stacking axis by about 32° (32.3° , 32.6° , and 31.0° for the $\text{Ag}(\text{CN})_2$ [7], AuBr_2 [7] and CuCl_2 [9] salts respectively). Between stacks, but still within the organic layer, the BEDT-TTF molecules are arranged side-by-side. This side-by-side arrangement (parallel and coplanar) between stacks has been seen in other BEDT-TTF salts such as β'' -(BEDT-TTF) $_2$ AuBr_2 [25] and β -(BEDT-TTF) $_2$ PF_6 [26], but contrasts with the ‘step-like’ or ‘diagonal’ inter-stack arrangement seen in the superconducting β -phases [24] of I_3^- , IBr_2^- and AuI_2^- . There is a strong degree of dimerisation within the stacks (the inter-planar distance within a (BEDT-TTF) $_2$ dimer is 3.401 Å in α' -(BEDT-TTF) $_2$ $\text{Ag}(\text{CN})_2$ while between dimers it is 3.913 Å) [7].

Both the magnetic properties and the transport properties (these salts are semi-conductors [9, 10, 27]), demonstrate that these materials are not band conductors, but are instead ‘magnetic’ insulators of the Mott–Hubbard type. It is well recognised that the behaviour of the π conduction electrons in these materials is not likely to be well described by the simple one-electron model, because the widths of the π -bands, formed by inter-molecular delocalisation, are not large (no more than 1 eV), and a question of topical interest is whether or not the pairing mechanism for superconductivity in these salts is due just to the electron–phonon interaction or whether it also involves electron–electron interactions. In the α' -salts, the π -band width along the stacks is expected to be well reduced from that in the β -salts, and we consider that band formation is no longer energetically favoured over localisation of the charge on the BEDT-TTF molecules, as one ‘hole’ per BEDT-TTF dimer.

Traditionally, organic charge-transfer salts exhibit pseudo-1D properties corresponding to the 1D stacks formed by the planar organic molecules. However, salts based on BEDT-TTF are known to show 2D behaviour with strong electronic interactions in the transverse direction as well as along the stacks [24–26]. With this in mind, along with the structural considerations discussed above, it is not immediately clear whether these α' -salts behave magnetically as 1D or 2D systems, and we have therefore fitted the experimental data with models for both 1D ($S = \frac{1}{2}$) Heisenberg chain [16, 17] and a quadratic layer Heisenberg antiferromagnet [18, 19] (figure 2). For both models, J corresponds to nearest-neighbour Heisenberg exchange defined as

$$H = 2J \sum S_i S_{i+1}.$$

Experimental g -values were used; the small g -value anisotropy justifies the use of a Heisenberg model. The linear chain plot, after [16], is a series expansion to seven terms in T/J [17]. The 2D plot [18] is a series expansion to six terms in J/T using the constants calculated by Rushbrook and Wood [19]. To fit the data, J was varied in order to reproduce the temperature dependence of χ including the temperature of χ_{max} . This procedure allowed the magnitude of χ to be fitted to about 10% over the whole temperature range. Because of the limited number of terms used, the QLAF expansion fails at temperatures below $kT = 1.8JS(S + 1)$ and is therefore only plotted above 45 K. It is clear from inspection of figure 2 that it is not possible to distinguish between the 1D and 2D models with the available evidence.

In assessing the fit of the experimental susceptibility data to the models used, it must be borne in mind that the absolute magnitude of the susceptibility is fixed by the number of spins present. That we can obtain reasonable agreement with experiment with the assumption that all charge on the BEDT-TTF is present as localised, spin- $\frac{1}{2}$ wavefunctions is proof that these materials are Mott–Hubbard insulators [28]. The magnitude of the

magnetic susceptibility for any ‘metallic’ model, such as the Peierls distortion model proposed in [7], must always be much lower than we measure here. The exchange energy between the spins on adjacent dimers should be given by the expression $J = \alpha t_2^2/U_0$, where t_2 is the transfer integral for the inter-molecular interaction, U_0 is the Hubbard Coulomb energy for two charges present on one molecule in the dimer, and α is a function of U_0/t_1 which goes from 2 ($U_0 < t_1$) to 2.5 ($U_0 > t_1$) [29]. Using a value for U_0 of 1.3 eV (estimated from optical data [10]) and $J = 50$ K we find t_2 is of the order of 50 meV. This value is a factor of four or so lower than estimated for metallic polytypes such as the β -structure, and is fully consistent with our proposal that t_2 is lower than usual in the α' -salts.

The conduction mechanism is necessarily different from that for a band semiconductor, and is discussed in the following paper [10]. The excitations of the chain have been calculated by Pincus [29], and the activation energy for the conductivity, E_A , of about 0.3 eV [9, 10] is consistent with this model.

4.2. The spin-Peierls transition

Although first discovered in 1975 [20, 21] the number of known examples of a spin-Peierls ground state in low-dimensional systems is still quite small. The best characterised cases remain the metal bisdithiolene complexes of tetrathiafulvalene (TTF) [20, 21], (TTF)Cu(S₂C₂(CF₃)₂)₂ and (TTF)Au(S₂C₂(CF₃)₂)₂, and MEM(TCNQ)₂ [23] (N-methyl-N-ethyl-morpholinium ditetracyanoquinodimethanide). A spin-‘Peierls ground state has also recently been assigned to (TMTTF)₂PF₆ at ambient pressure [30–32] (TMTTF is tetramethyltetrathiafulvalene). Qualitatively, a spin-Peierls transition can be described as a magnetoelastic transition whereby a 1D antiferromagnetically coupled chain of localised spins couples with a 3D phonon, resulting in a lattice distortion to an alternating linear Heisenberg chain. The theoretical treatment of the spin-Peierls transition has been reviewed by Schulz [33]. Below the transition temperature, the degree of dimerisation progressively increases to a maximum value at $T = 0$. The spin-Peierls ground state is non-magnetic.

The spin-Peierls transition is rare for several reasons. Whereas the normal Peierls transition (the electronic analogue to the magnetic spin-Peierls transition) will occur at a temperature of the order of $kT_P \approx E_F \exp(-1/\lambda)$, where λ is the electron–phonon coupling constant and E_F is the energy of the Fermi level, the spin-Peierls transition will occur at $kT_{SP} \approx J \exp(-1/\lambda)$ where J is the exchange interaction between adjacent spins. Since J is in general much smaller than E_F (e.g. 50 K as against 5000 K), T_{SP} is always small. The transition temperatures of the TTF copper and gold bisdithiolene complexes are 12 K and 2 K respectively [20, 21] while the values of T_{SP} for MEM(TCNQ)₂ and (TMTTF)₂PF₆ are 18 K [23] and 16 K [30–32] respectively. Since the spin-Peierls transition temperature is low, it is likely that there will be competing mechanisms for 3D ordering. Thus, if there is a weak 3D exchange, J_\perp , this may drive a 3D antiferromagnetic ordering a $kT_{AF} \approx J_\perp \xi_{1D}/a$ where ξ is the coherence length of the 1D fluctuations on the chain of spacing a .

The spin-Peierls transition is to a non-magnetic ground state, with a vanishing spin susceptibility as $T \rightarrow 0$. This behaviour is distinct from that associated with an antiferromagnetic or spin-density-wave ordering. Comparison of the variation of the susceptibility with temperature below T_{SP} with that modelled within mean-field theory (assuming a BCS-like variation of the excitation gap with temperature) has been made for the spin-Peierls systems mentioned [21, 23]. We have used a similar procedure; we

assume a BCS-like variation of the gap, Δ , with temperature, and the BCS relation between the gap at $T = 0$ and T_{SP} , $\Delta(0) = 1.76 kT_{\text{SP}}$. From this we calculate the amplitude of the dimerisation amplitude, γ (the ratio between the two inter-dimer J 's after tetramerisation) [21], and use the model of Bulaevskii [34] to calculate the susceptibility from this. In the temperature range 6.25 to 4.5 K we find that the calculated variation of susceptibility with temperature is acceptably close to the measured susceptibility within the limits of the experiment, and is characterised by an activation energy for χT of about 24 K. This activation energy translates to a dimerisation with $\gamma = 0.89$. We have used this value to estimate the value of the magnetic gap at $T = 0$, $\Delta(0)$, to be 11 K; we thus find $\Delta(0)/T_{\text{SP}} = 1.57$. We thus have good evidence for a spin-Peierls transition in α' -(BEDT-TTF)₂Ag(CN)₂, although we are not able at present to confirm this with structural measurements of the superlattice. A spin-Peierls transition here, where $S = \frac{1}{2}$ per dimer, would correspond to a 'dimerisation of dimers', similar to that seen in MEM(TCNQ)₂ [22]. Without structural evidence for the spin-Peierls superlattice we cannot identify the direction in which the spin dimerisation takes place. We presume that it lies in the ab plane, and $(2a, b, c)$, $(2a, 2b, c)$ or $(a, 2b, c)$ are possible choices for the superlattice. We can briefly try to address the question of why the spin-Peierls state exists in the Ag(CN)₂ salt, but is not seen in the AuBr₂⁻ or CuCl₂⁻ analogues. In the cases of the TTF metal bisdithiolenes [35, 36] and MEM(TCNQ)₂ [37], well characterised spin-Peierls systems, there is, in addition to the structural change observed at T_c in these systems, evidence at higher temperatures (up to 240 K) for a soft mode corresponding to the eventual spin-Peierls dimerisation. Although there are no structural data available below 6 K, fixed-crystal x-ray photographs at 30 K for the Ag(CN)₂ salt show the persistence of diffuse scattering along the axis where the high-temperature $(a, b, c) \rightarrow (a, 2b, c)$ transition is seen at 295 K. Photographs at 30 K of the AuBr₂⁻ salt show no evidence for the existence of this soft mode. Given that the 295 K transition is uncoupled to the π -electrons (the transition does not influence the magnetic properties, and only a small change in the activation energy of the conductivity is seen), this mode cannot drive the spin-Peierls transition. However, the persistence of diffuse scattering down to 30 K (the lowest temperature thus far investigated) may be due to another phonon branch softening at the same value of q , but one that modulates the interstack S-S contacts and thus is able to drive the spin-Peierls transition.

5. Conclusion

The α' -polytypes of the BEDT-TTF salts we have investigated here show very different properties from the metallic and superconducting behaviour found in other polytypes. We have here a series of salts that are Mott-Hubbard insulators, with poor π -electron delocalisation between the BEDT-TTF dimers. That a relatively small adjustment in the size of the π -electron band widths is sufficient to switch the BEDT-TTF salt from metal and superconductor (e.g. the β -polytype) to a Mott-Hubbard insulator is clear indication that Coulomb interactions are significant in this class of materials. We have carried out an extensive study of the transport properties, and of the stability of the Mott-Hubbard insulating phase under pressure, and this will be reported in the following paper [10].

The magnetic properties of the CuCl₂⁻ and AuBr₂⁻ salts are characteristic of low-dimensional antiferromagnets. The Ag(CN)₂⁻ salt is more interesting; we have some evidence that the magnetic phase transition near 7 K is due to a spin-Peierls transition,

but further experiments are required to confirm this. Measurements of the magnetic properties in high magnetic fields and of the low-temperature structure are planned.

Acknowledgments

We thank the SERC and Oxford University Research and Equipment Committee for financial support, and Judith Howard, Andrew Stringer, Anne Renault, Francis L Pratt and Ian D Parker for communicating and discussing their results prior to publication.

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