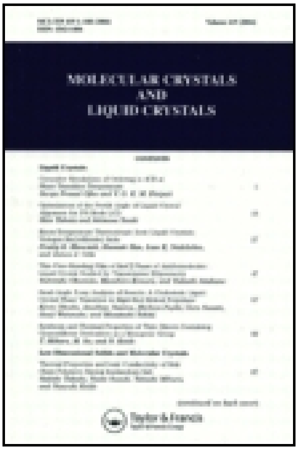

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A MODEL FOR THE MAGNETIC PROPERTIES OF (BEDT-TTF)$_3$CuX$_2$Br$_2$, XCl OR Br

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(BEDT-TTF)$_3$CuX$_2$Br$_2$, XCl or Br displays two magnetic transitions; one (T_P) associated with a loss of moments accounted for by two $S=1/2$ ions and the second to a long range (LRO) antiferromagnetic ordering (T_N). The experimental data in the paramagnetic regions have been modeled by the sum of two contributing components, the BEDT-TTF and the Cu(II), the first to a hexagonal layer of BEDT-TTF ($S=1/2$) where the ions dimerize at T_P and the second to a triangular layer of Cu ions. A possible mechanism for the LRO-AF transition involving RKKY is proposed.

Keywords: BEDT-TTF; copper; layered; magnetism

INTRODUCTION

Bis(ethylenedithio)-tetrathiafulvalene, BEDT-TTF, displays one of the richest chemistry and physics amongst the radical cations of the TTF derivatives [1]. Such richness in chemistry is derived from its geometry, its electrochemical properties, its ability to form charge transfer compounds of the general formula (cation$^+$)$_c$(BEDT-TTF$^+$)$_m$(BEDT-TTF)$_n$(anion$^-$)$_{m+c}$·y solvent, its structural polymorphism, and the ease of synthesis of the charge transfer salts with a whole gamut of organic, inorganic and organic-inorganic hybrid anions. The rich physics manifests itself in a range of electrical properties including superconductivity, magnetic properties

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including ferrimagnetism [2] and weak ferromagnetism [3], and in particular, its simple Fermi surface compared to metals such as copper. [4]

Incorporation of anions carrying magnetic moments adds to the diversity of the physical properties. [5] One aim in this area is to establish the presence of π-d interaction between the π-electrons of the BEDT-TTF and the d-electrons of the inorganic anions. In most cases studied so far the compounds display the sum of the individual properties [6,7]. Only a few cases have been found where clear evidence of π-d interactions has been identified. These are the ferrimagnets of TTF derivatives with paramagnetic Reineke's derivatives of chromium and iron with isoquinoline and phenanthroline where the TTF and the Reineke salt form the two sublattices [2]. Another two possible examples are (BEDT-TTF)$_3$CuX$_2$Br$_2$, XCl or Br [7a]. However, the evidence for π-d interaction in the latter compounds is not clear. Here, we present a model to account for their observed magnetic properties and proposed a mechanism for the long range magnetic ordering at low temperature.

EXPERIMENTAL

The crystals were prepared and characterized as described earlier and the magnetization measurements have been performed as described previously [7a]. The calculations were performed on a CRAY machine at the IDRISS facility of the CNRS, France.

RESULTS AND DISCUSSION

Before discussing the magnetic properties it is worth looking at the crystal structures of the compounds and noting some important distances. The principal feature of the structure is the segregation of the organic and inorganic components into alternate layers (Figure 1) [8]. The bond distances of the BEDT-TTF indicate two independent molecules; a neutral one and two singly charged ones per formula unit (Figure 2). The latter are arranged in a hexagonal fashion with the neutral molecules sitting in the middle of hexagons of charged molecules. The overall arrangement is that described as α-phase. Each positively charged species carries an $S = 1/2$ spin. The minimum distance between the BEDT-TTF molecules is 3.65 Å if one takes the shortest S-S distance or 5.95 Å from center to center. The copper halide layer is arranged in a triangular fashion with nearest Cu-Cu distances of 8.6 and 10.1 Å and Br-Br of 4.05 and 6.66 Å. The distance between copper atoms on adjacent layers is 16.9 Å.

The model uses a Heisenberg Hamiltonian with only nearest neighbor interactions. Due to the size of the matrix the model is limited to 12 sites

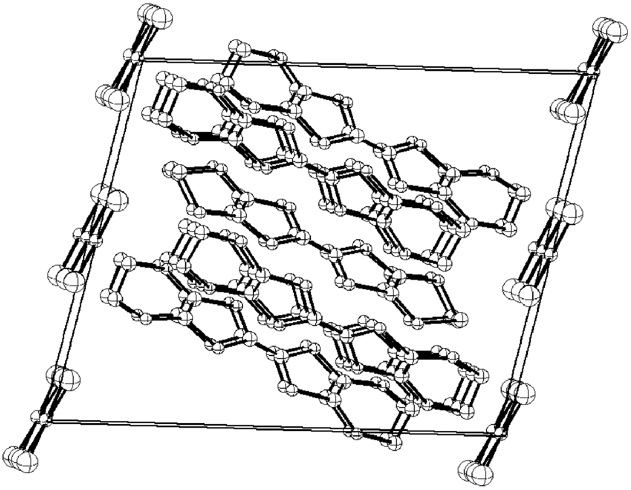

FIGURE 1 View of the structure of (BEDT-TTF)$_3$CuX$_2$Br$_2$ showing the organic sheets separated by the layers of copper halides.

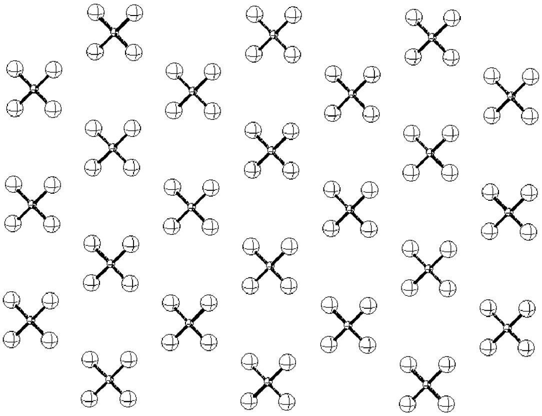

FIGURE 2 View of a triangular copper halide layer in (BEDT-TTF)$_3$CuX$_2$Br$_2$.

for the copper layer and 13 sites (three hexagons) for the BEDT-TTF layer. In each case full diagonalization was performed and the partition functions generated from which the susceptibility is calculated. The other parameter introduced is the g-value of the ions. We used the average value obtained from EPR measured on single crystals (Figure 4) at low temperatures [7a] for the copper ion. Since there is only one EPR line at high temperatures which is thought to be due to π-d interaction we took the average g-value

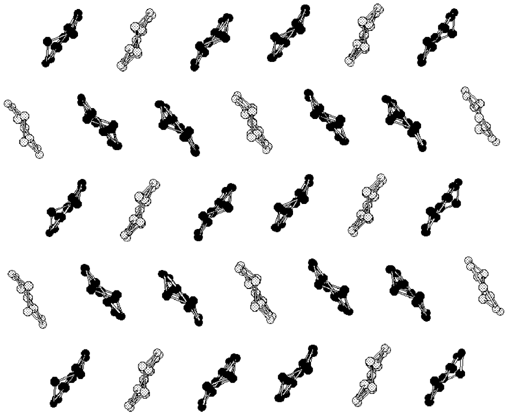

FIGURE 3 View of a hexagonal BEDT-TTF layer in $(BEDT\text{-}TTF)_3CuX_2Br_2$; the molecules in black are positively charged and the molecules in grey are neutral.

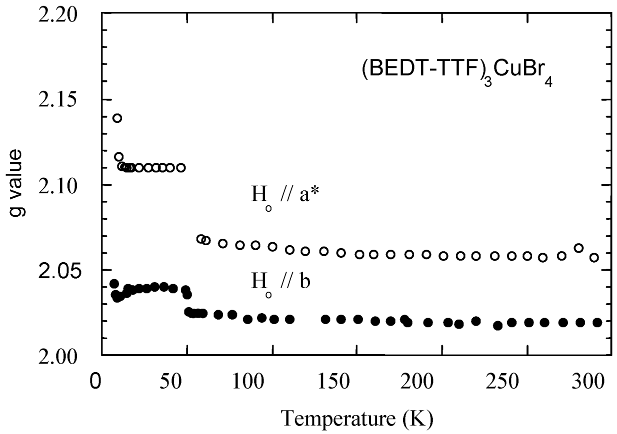

FIGURE 4 Temperature dependence of the g-values for two orientations of the magnetic field [7a].

obtained for the α-phase with a non magnetic anion, α-$(BEDT\text{-}TTF)_2Ag(CN)_2$ [9].

The susceptibility as a function of temperature is common to that expected for low dimensional magnetic compounds. The drop in susceptibility in both compounds at ca. 60 K is equivalent to the moment of two spins with $S = 1/2$. The 60 K transition is thought to be a dimerization of the BEDT-TTF which, however, could not be shown by the crystallographic study at low temperature [8c]. The resulting moments below the transition

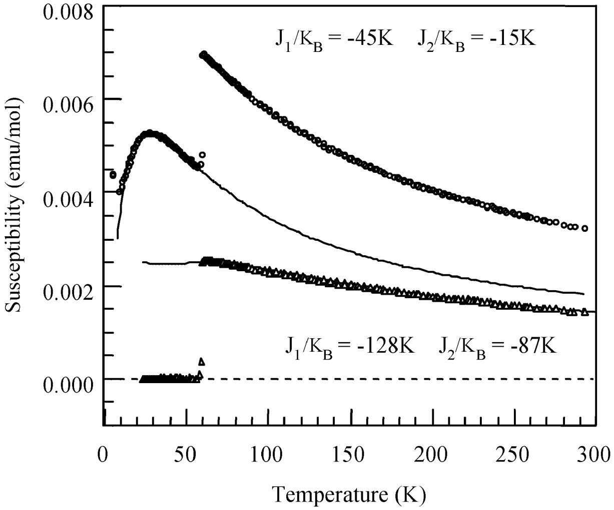

FIGURE 5 Temperature dependence of the magnetic susceptibility of (BEDT-TTF)$_3$CuBr$_4$ (upper trace) and that obtained for the BEDT-TTF after subtracting the contribution of the Cu (lower trace). Lines are theoretical fits.

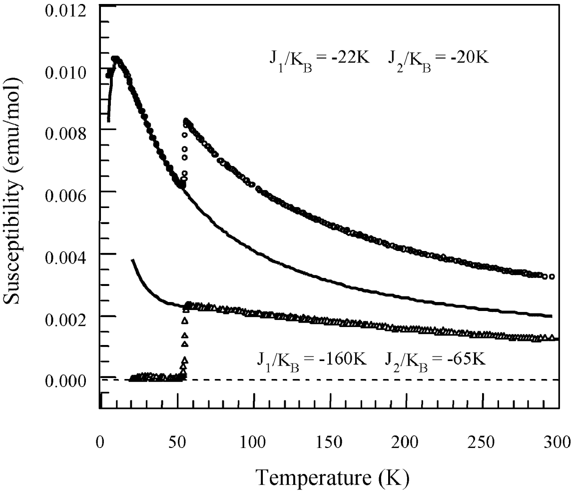

FIGURE 6 Temperature dependence of the magnetic susceptibility of (BEDT-TTF)$_3$CuCl$_2$Br$_2$ (upper trace) and that obtained for the organic after subtracting the contribution of the Cu (lower trace). Lines are theoretical fits.

temperature (T_P) are thus solely from the copper layer. The low temperature data were therefore fitted to a triangular lattice model with J_1 corresponding to Cu-Cu at 8.6 Å and J_2 for those at 10.1 Å. The values of the J_1 (−45 K for $CuBr_4$ and −22 K for $CuCl_2Br_2$) are consistent with those expected if the halogen atoms are involved in the exchange. On the other hand J_2 (−15 K and −20 K) is barely dependent of the halogen. Once the contribution from the copper layer has been calculated, that of the BEDT-TTF is obtained from the difference from the observed total susceptibility. Finally, the resultant was fitted to a spin 1/2 hexagonal lattice between 60 and 300 K. The parameters of the model consist of two exchange interactions between nearest neighbor BEDT-TTF; one along the stack (J_1) and the other between stacks (J_2). The values are given in the Figures.

All the values of J within the BEDT-TTF layers are normal for BEDT-TTF salts [10]. However, those found for the copper layer are enhanced considering the distance between moment carriers that are not connected by covalent bonds. Furthermore, $(BEDT\text{-}TTF)_3CuBr_4$ shows a long range antiferromagnetic transition at 8 K [7b]. To explain this observation two possible scenarios can be invoked; one where the interactions are dipolar in nature and the second where exchange is dominant and takes place via the conduction electrons. The first mechanism is unlikely since the interaction is AF and therefore the moments of any correlated cluster will be small, and therefore not effective at such long distance. The second is therefore more plausible. Given that the compound is still conducting at low temperatures, there are some mobile electrons at 8 K which may involve in RKKY interaction with the moment localized on the Cu(II) to drive the long range ordering.

CONCLUSION

The magnetic susceptibility of the two charge transfer salts $(BEDT\text{-}TTF)_3CuX_2Br_2$ (X = Cl or Br) has been successfully modeled. Evidence is presented for long range magnetic ordering via RKKY interactions between conduction electrons of the organic donor, BEDT-TTF and localized moments on Cu(II). Amongst the BEDT-TTF family these are the only two to exhibit such behavior.

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