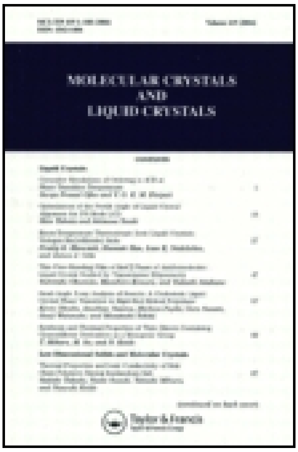

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Band Electronic Structure Study of the Metal-Insulator Transitions in (BEDT-TTF)$_3$Cl$_2$ · $_2$H$_2$O And (BEDT-TTF)$_4$Cl$_2$ · 4H$_2$O

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BAND ELECTRONIC STRUCTURE STUDY OF THE METAL-INSULATOR TRANSITIONS IN $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ AND $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$

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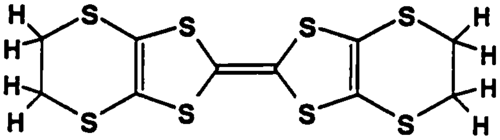
Abstract The nature of the metal-insulator transitions in $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ and $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ was examined by performing tight-binding band electronic structure calculations. Our work suggests that the metal-insulator transition of $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ originates from its essentially one-dimensional metallic character. $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ is predicted to be a two-dimensional metal, and its metal-insulator transition is likely to be caused by its nested Fermi surface.

INTRODUCTION

Charge transfer salts of the organic donor molecule BEDT-TTF (**1**) with monovalent anions have led to a number of metals and superconductors.[1] So far two salts of BEDT-TTF with chloride ion Cl^-, $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$[2-4] and $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$[4], have been synthesized and characterized. Both salts are metals at room temperature but undergo a metal insulator (MI) transition upon lowering the temperature.[2-4] $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ is a semimetal according to thermopower measurements,[3] and its MI transition at ~100K is suppressed by applied pressure.[5,6] At 16 kbar $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ becomes a superconductor with $T_c = 2K$.[5,6] The electrical resistivities of $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ along the intrastack, the interstack, and the interlayer directions (in our



BEDT-TTF, 1

notations, along the crystallographic **b**, **a**-, and **c**-axis directions, respectively) have the ratios 7:1:1000.[3] Namely, the electrical conductivity along the interstack direction is greater than that along the intrastack direction by nearly an order of magnitude. The available band electronic structure study[3] on (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O predicts that it is a semimetal in agreement with experiment, and that its Fermi surfaces consist of closed electron and hole pockets. The latter implies that (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O would have nearly isotropic electrical conductivities in the plane of the donor molecule layer, which is not consistent with experiment. In addition, the nature of its MI transition at ~100K is not well explained by these two-dimensional Fermi surfaces. Thus it is of interest to re-examine the electronic structure of (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O. As for (BEDT-TTF)$_4$Cl$_2$ · 4H$_2$O, electrical resistivity measurements show that it undergoes an MI transition at ~20K.[4] However, the origin of this MI transition has not been studied. Thus, with an objective of understanding the nature of the MI transitions in (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O and (BEDT-TTF)$_4$Cl$_2$ · 4H$_2$O, in this work we examine the band electronic structures of these two salts by performing tight-binding band calculations[7] based upon the extended Hückel method.[8]

RESULTS AND DISCUSSION

Figure 1 shows the dispersion relations of the six highest occupied bands calculated for a donor molecule layer of (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O. This salt has six donor molecules per unit cell, and the six bands shown in Figure 1 are largely derived from the HOMO of each donor molecule. With formal oxidation of (BEDT-TTF)$_6^{4+}$, there are 8 electrons to fill the bands so that the top three bands are partially filled: The bottom portions of bands a and b are partially filled, while the top portion of band c is partially empty. Thus (BEDT-TTF)$_3$Cl$_2$ · 2H$_2$O is predicted to be a semimetal in agreement with experiment.[3] It should be pointed out that the general features of our band electronic structure are similar to those calculated by Mori and Inokuchi.[3] However, in essential details, the dispersion relations of the partially filled bands shown in Figure 1 differ substantially from those reported by them: Band c lies above the Fermi level at Γ, and bands a, b are below the Fermi level at M in Figure 1. These are not the case in Mori and Inokuchi's calculations.[3]

Figure 2 shows the Fermi surfaces associated with bands a-c of Figure 1. Band a leads to a closed electron Fermi surface (Figure 2a), centered at M and elongated along the $\Gamma \rightarrow Y$ direction. Band b leads to an open electron Fermi surface (Figure 2b), and band c to an open hole Fermi surface (Figure 2c). The latter two surfaces are open along

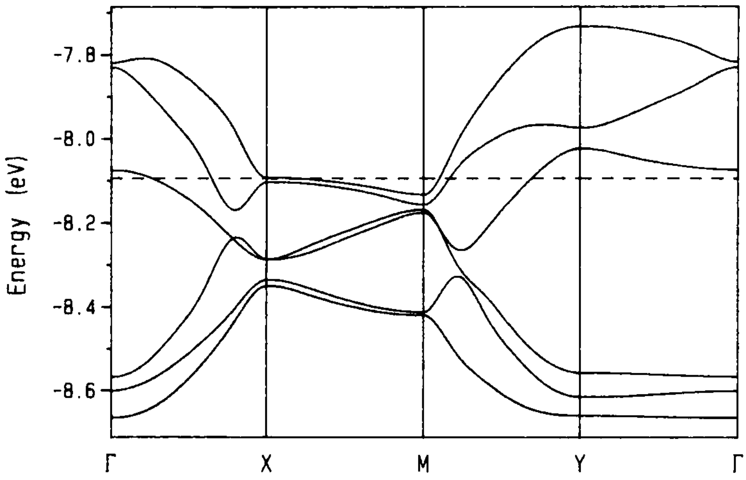


FIGURE 1 Dispersion relations of the six highest occupied bands calculated for $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$, where the dashed lines refer to the Fermi level. Γ = (0, 0), X = (a*/2, 0), Y = (0, b*/2), and M = (a*/2, b*/2).

the Γ → Y direction. Thus $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ has two- and one-dimensional metallic character. In general, the electrical conductivity of a metal is good in the direction orthogonal to its Fermi surface. Consequently, all three Fermi surfaces of Figure 2 predict that the electrical conductivity of $(BEDT\text{-}TTF)_3\ Cl_2 \cdot 2H_2O$ is better along the Γ → X (interstack) direction than along the Γ → Y (intrastack) direction, in agreement with experiment.[3] According to the Fermi surfaces of Figure 2, $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ is essentially a one-dimensional metal along the interstack direction. This is consistent with the structural property that short intermolecular S···S contacts between donor molecules are found predominantly along the interstack direction rather than along the intrastack direction. Therefore, the MI transition of $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ at ~100K is likely to be induced by a distortion which removes the semimetallic overlap of bands a, b with band c. This distortion should be one that does not increase the unit cell size, since a possible superlattice modulation is absent in this salt.[6]

$(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ has four donor molecules per unit cell. Figure 3 shows the dispersion relations of the four highest occupied bands calculated for a donor molecule layer of this salt, which are mainly represented by the HOMO of each donor molecule. Because of symmetry, the upper two bands merge into one, and so do the bottom two. The formal oxidation of $(BEDT\text{-}TTF)_4^{2+}$ gives six electrons to occupy these bands, so the upper band becomes half filled. Figure 4 shows the Fermi surface

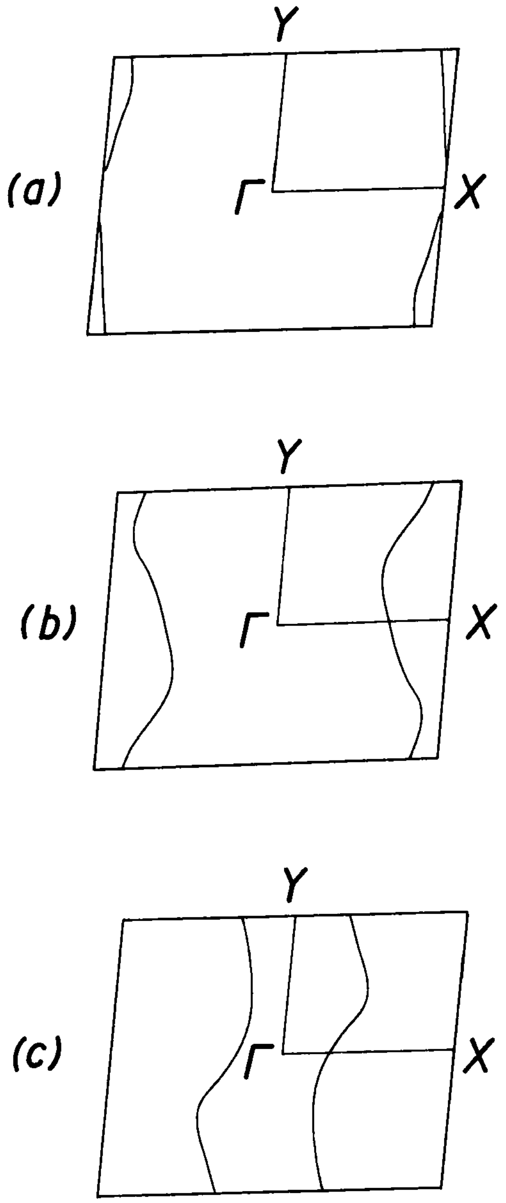


FIGURE 2 Fermi surfaces associated with the (a) top, (b) middle, and (c) bottom of the three partially bands in Figure 1.

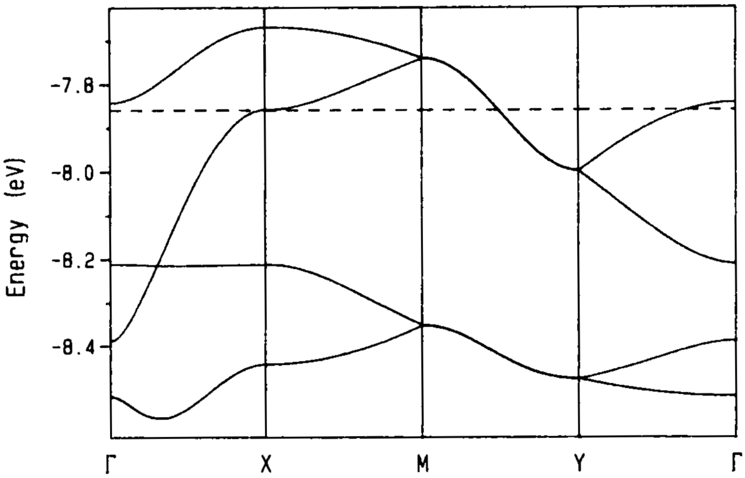


FIGURE 3 Dispersion relations of the four highest occupied bands calculated for $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$, where the dashed line refers to the Fermi level.

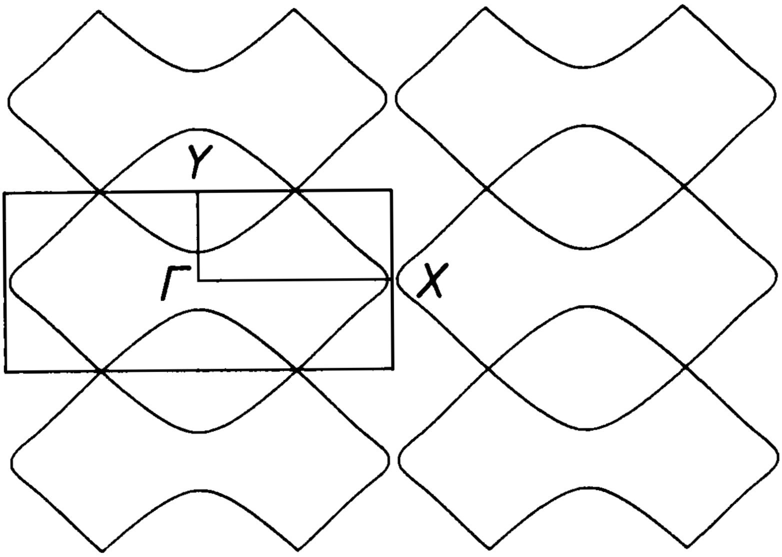


FIGURE 4 Fermi surface associated with the half-filled band of Figure 3 in an extended zone scheme.

associated with this band in an extended zone scheme, where the parallelogram represents a primitive unit cell in reciprocal space. The essential feature of Figure 4 may be described as overlapping rhombuses. Since each Fermi surface is closed, $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ is predicted to be a two-dimensional metal. However, the rhombus shape leads to Fermi surface nesting between its parallel sides. The electronic instability resulting from this nesting might be responsible for the MI transition of $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ at ~20K. A Fermi surface nesting can give rise to a charge density wave (CDW), a spin density wave (SDW), or even a superconductivity.[9] In general, the MI transition temperature associated with SDW formation is low. Therefore, it is possible that the MI transition of $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ is associated with SDW formation.

CONCLUDING REMARKS

The present work suggests that the MI transition of $(BEDT\text{-}TTF)_3Cl_2 \cdot 2H_2O$ at ~100 K originates from its essentially one-dimensional metallic character. This MI transition is likely to be caused by a distortion which does not increase the unit cell size but removes the semimetallic overlap of bands a, b with band c. An applied pressure could prevent such a distortion or even make greater the extent of the semimetallic band overlap. $(BEDT\text{-}TTF)_4Cl_2 \cdot 4H_2O$ is predicted to be a two-dimensional metal. However, its Fermi surface of a rhombus shape is well nested, and therefore is likely to cause the MI transition at ~20K. The calculations discussed herein are in good agreement with the physical properties measurements mentioned. The surprising finding is that hydrated BEDT-TTF salts are produced (by accident) during the electrocrystallization reaction. Thus, the purposeful addition of water during electrocrystallization[10] may offer a new method for producing organic conducting salts thereby presenting new challenges to both experimentalists and theorists.

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