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CRYSTAL AND ELECTRONIC STRUCTURES OF LAYERED MOLECULAR SUPERCONDUCTOR, θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$

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The crystal and electronic structures of molecular superconductor θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$ ($x<0.02$) were examined. BEDT-TTF molecules form a two-dimensional network. The dihedral angle between the planes of the neighbouring molecules interrelated by the screw axis is about 80°. Examination of the band structure suggests that this complex is the first example of the molecular conductor with a completely round two-dimensional Fermi surface.

To date, several ambient-pressure superconductors based on BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) have been reported.$^{1-5)}$ Unlike the first organic superconductor (Bechgaard salt), these systems have two-dimensional(2D) electronic structures$^{6)}$ and considerably high transition temperatures (T_c).$^{1-5,7)}$

In this paper, we will report the crystal and electronic structures of $(BEDT\text{-}TTF)(I_3)_{1-x}(AuI_2)_x$ ($x<0.02$), whose superconducting transition has been reported recently.$^{5)}$

The crystals with fairly large size (2x1x0.5 mm^3) were obtained electrochemically using the mixed electrolyte of $(n\text{-}C_4H_9)_4NI_3$(95%) and $(n\text{-}C_4H_9)_4NAuI_2$(5%). This complex exhibits a superconducting tansition at 3.6 K.$^{5)}$ The X-ray diffraction patterns were examined by oscillation and Weissenberg photographs. Two quite different diffraction patterns appear alternately in the reciprocal space. The one shows a normal intensity distribution (named hereafter type-I reflections) but the other (type-II reflections) shows a monotonous intensity dependence on the Bragg angle, indicating that these reflections arise from the I_3 sublattice. Same diffraction patterns were observed for all the crystals examined. Moreover, similar characteristic diffraction patterns were found also in the crystals prepared from the mixed electrolyte of $(n\text{-}C_4H_9)_4NI_3$(50%) and $(n\text{-}C_4H_9)_4NAuI_2$(50%) and that of $(n\text{-}C_4H_9)_4NI_3$(95%) and $(n\text{-}C_4H_9)_4NI_2Br$(5%). By examining these characteristic features of the diffraction patterns, the "average structure" could be easily deduced from the structure analysis based on the type-I reflections. The crystal data and the results of the structutre analysis show that

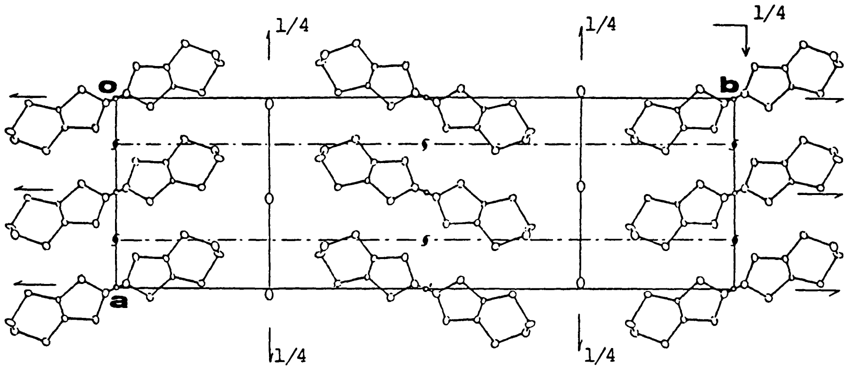


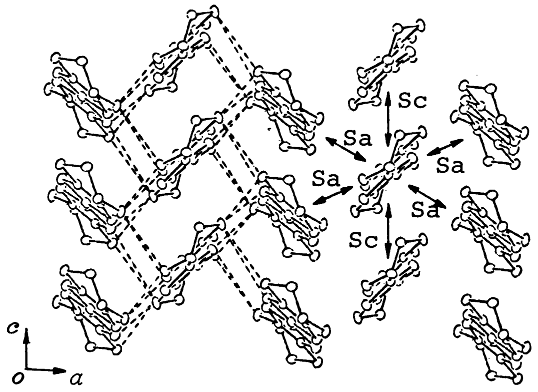
Fig. 1. Crystal structure of θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$($x<0.02$).

the structure is not identical to any structures of BEDT-TTF-polyhalides ever known (α, β, γ, δ, ε).[1,2,6,8] Very recently, Shibaeva et al. have shown the new modifications, η-$(BEDT\text{-}TTF)I_3$ and ζ-$(BEDT\text{-}TTF)_2I_{10}$.[9] So it may be appropriate to call this new structural type θ-type. The crystal data are: θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$ ($x<0.02$), orthorhombic, Pnma, a=10.076(2), b=33.853(5), c=4.994(1) Å, V=1693.2 $Å^3$, Z=2. The structure was solved by the direct method and refined by the block-diagonal least-squares method. Since the content of AuI_2 is very small ($x < 0.02$),[5] all the anions were assumed to be I_3. In the orthorhombic "average structure", each I_3 anion occupies one of the two independent positions in the tunnel formed by BEDT-TTF molecules with the occupancy probability of 50%.[8] Considering this complicated feature of the I_3 arrangement, the final R factor of 0.109 is fairly satisfactory.

The structure is shown in Fig. 1. BEDT-TTF molecules are on the centrosymmetric sites. It should be noted that the temperature factors of the carbon atoms of ethylene group are not so large, indicating the ordering of the ethylene group. BEDT-TTFs form a 2D-sulfur network parallel to (010) (Fig. 2). The dihedral angle between the planes of the neighbouring molecules interrelated by the screw axis symmetry is 79.6°, which makes the molecular arrangement to be completely 2D. As frequently stressed by us, the molecular stacking is no longer an inevitable requirement for the design of the molecular metals. In the well-known organic superconductor β-$(BEDT\text{-}TTF)_2I_3$, the molecular planes of all BEDT-TTF molecules are parallel to each other. On the other hand, molecular arrangements in α- and α'-type structures resemble that of θ-type structure.[2,10,11] Similar 2D molecular array can be also found in $(BMDT\text{-}TTF)_3ClO_4(DCE)$(DCE=1,2-dichloroethane), which crystallizes in the same space group Pnma.[12] In the 2D molecular conductor, the charge distribution tends to be inhomogeneous.[6,12] However, the charge separation (or isolation), which plays an essential role in determining the electronic structure, cannot occur in the θ-type structure, because there exists only one crystallographically independent molecular site of BEDT-TTF.

The tight-binding band calculation was performed. The intermolecular overlap integrals(S) of the highest occupied molecular orbital (HOMO) of BEDT-TTF, which form the conduction band, are given in Fig. 2. Using the simple approximation, $t \simeq E$ ES (t is transfer integral and E is the constant of the order of the orbital energy of HOMO ($\simeq -10$ eV)), the band energy was calculated as, $\varepsilon = 2t_c\cos(k_z) \pm 4|t_a|\cos(k_z/2)$

Fig. 2. The 2D molecular arrangement of BEDT-TTF. The broken lines indicate the short S···S contacts (<3.70 Å). The intermolecular overlap integrals of HOMO, S_c and S_a are -6.4×10^{-3} and -4.2×10^{-3}, respectively. The A.O. parameters reported by Clementi and Roetti were adopted.[13)]



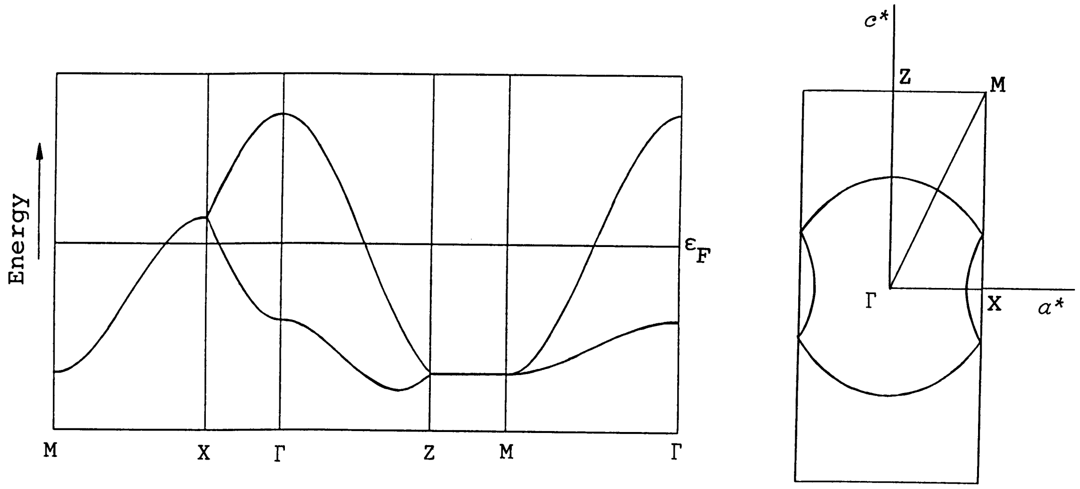
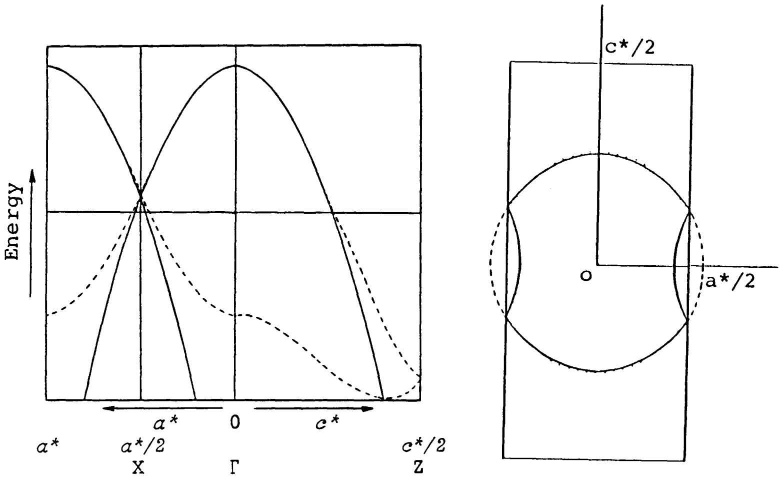


Fig. 3. Tight-binding band and Fermi surface.

$\times\cos(k_x/2)$. Two energy branchs are degenerated when $k_z=\pi$ or $k_x=\pi$. The energy dispersion is isotropic and the Fermi surface is an approximately ideal circle (Fig. 3). Such an ideally 2D energy band has been never reported so far. The β-(BEDT-TTF)$_2$I$_3$ system has a similar 2D electronic structure but the Fermi surface is not so isotropic and is easily transformed into 1D one by a slight modification of the molecular arrangement.[6,14)] On the other hand, as shown in Fig. 2, the 2D nature is much stronger in θ-type structure. Every BEDT-TTF molecule is surrounded by six neighbouring molecules as if the system has a 2D hexagonal packing structure. This is the origin of the isotropic 2D metallic band. In this connection, it might be worthwhile to recall that the holes in the similar 2D network of (BMDT-TTF)$_3$ClO$_4$(DCE) forms a "Wigner lattice", where every BMDT-TTF cation is surrounded by six neutral BMDT-TTF molecules.[6,12)]

The calculated energy band can be fairly reproducible by the nearly free electron model. Since the c^* is about twice of a^*, the Fermi surface crosses the zone boundary XM (see Figs. 3 and 4). Thus, a small hole region is produced around X($=a^*/2$). In Fig. 4, the tight-binding energy band is compared with that derived from the 2D free electron model. The agreement is fairly satisfactory.

In summary, we have reported the 2D structure of the molecular superconductor, θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$, which has a 2D metallic band with a round Fermi sufface. The 2D metal layers and the anion sheets are stacked alternately. From the molecular designing point of view, this structural feature seems to suggest a route to design of so-called Ginzburg superconductor models, where a metal layer is sandwiched by two polarizable nonmetallic layers.[15] The existence of an ideally 2D molecular metal will promise a further developement of the design of the molecular conductors.



(a) (b)

Fig. 4. (a) Energy bands based on nearly free electron model (solid lines) and on tight-binding approximation (broken lines). The effective mass of holes are assumed to be $|m^*| \approx 8m_e$. (b) Fermi surface of the nearly free electron model.

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