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Anion Arrangement in a New Molecular Superconductor, θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$,($x<0.02$)

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Three-dimensional arrangement of the anions in the recently found molecular superconductor θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ ($x<0.02$) was determined by the use of weak reflections which were omitted in the previous analysis of the "average structure".

We have recently found a molecular conductor of θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ ($x<0.02$), which exhibits a superconducting transition around 3.6 K.[1,2] In this report, we present the analysis of the I$_3$ arrangements of this system.

Crystals of the θ-salt were obtained electrochemically.[1] Since the content of AuI$_2$ is very small, the θ-salt is considered to be essentially I$_3$ salt of BEDT-TTF. The X-ray diffraction patterns were examined by oscillation and Weissenberg photographs and a Rigaku four-circle diffractometer. Two quite different X-ray diffraction patterns (type-I and type-II reflections) appear alternately in the reciprocal space (Fig. 1). Examination of the relatively weak type-II reflections revealed that all the crystals examined are composed of twinning domains. X-Ray intensity distribution of the type-I reflections arising from each domain is identical. Relatively strong type-I reflections show that the "average" crystal structure has orthorhombic symmetry with the lattice constants of a_o=10.076(2), b_o=33.853(5), c_o=4.964(1) Å, space group Pnma, and Z=2, and were used to analyse the average structure.[1] On the other hand, type-II reflections show that each domain has a monoclinic lattice with the space group $P2_1/c$ and lattice vectors of $\mathbf{a}_m=2\mathbf{c}_o$, $\mathbf{b}_m=\mathbf{a}_o$, and $\mathbf{c}_m=\mathbf{b}_o-\mathbf{c}_o$, where $\mathbf{a}_o$, $\mathbf{b}_o$, and $\mathbf{c}_o$ are those of the orthorhombic cell: a_m=9.928, b_m=10.076, c_m=34.220 Å, β=98.39°. The orthorhombic symmetry of the average structure is originated from the twinning of the domains (Fig. 2b). A monotonous intensity dependence on the Bragg angle indicates that the type-II reflections arise from the I$_3$ sublattice. The orthorhombic average structure deduced from the structure analysis based on the type-I reflections has been already reported (Fig. 3).[1] The crystal contains the

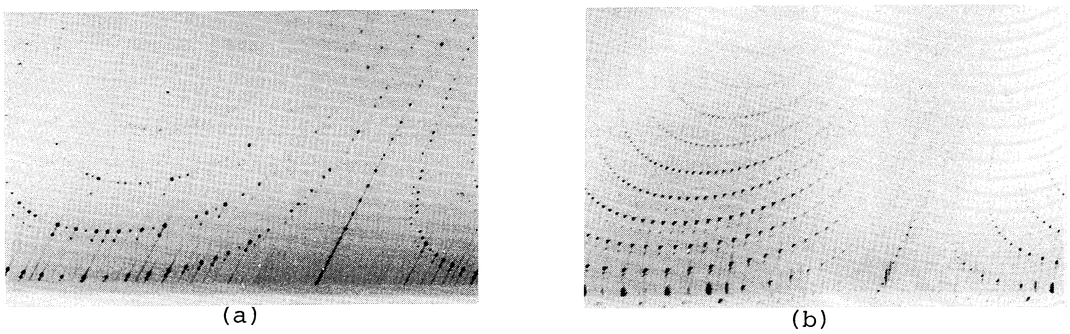
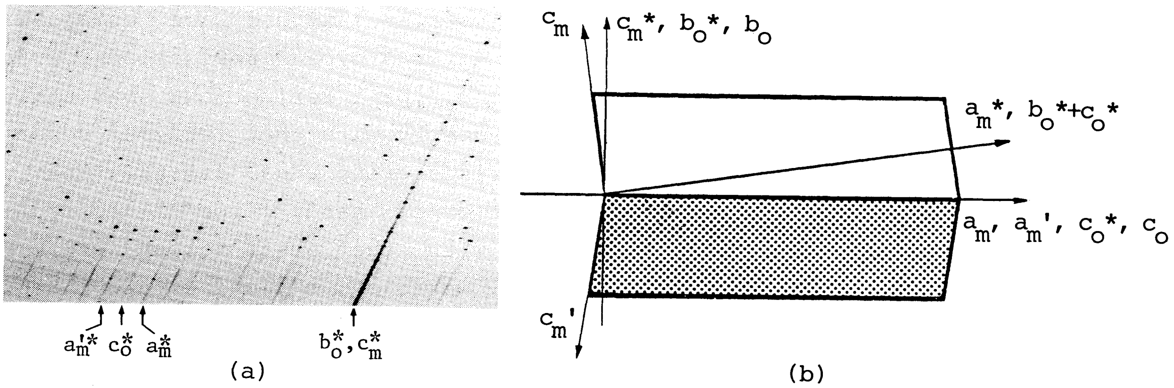

(a) (b)

Fig. 1. (a) X-Ray diffraction patterns of type I reflections. The 0-th layer reflections around the orthorhombic c(c_o) axis. (b) X-Ray diffraction pattern of the type-II reflections. The 1-st layer reflections around the monoclinic a(a_m) axis.

metal layers composed of BEDT-TTF molecules and anion sheets stacked alternately along **b**(b_o).

Type-II reflections were collected by the four-circle automated diffractometer ($2\theta < 50°$(Mo Kα)). The intensities were estimated by the use of the parameter representing the ratio of the volumes of the twin components. In the average structure, each I_3 anion occupies one of the two independent positions in the tunnel formed by BEDT-TTF molecules along the c_o axis with the occupancy probability of 50%. In the "true" monoclinic structure, the period of anion arrangement becomes a_m(=$2c_o$ (=2x4.972 Å)), twice of that of the average structure. Sharpness of the type-II reflections indicate that the anion arrangement is three-dimensionally ordered. Two models of the periodical arrangements of I_3 were derived (Fig. 4). Both I_3 arrangements are equivalent. Of type-II reflections, reflections with k=odd, especially k=1,3,5 are stronger. At the first stage, we used only these reflections assuming the type II reflections arising from the I_3 sublattice. Then, including the weak reflections of k=even, the I_3 arrangement was further refined by recycling the block-diagonal least-squares procedure on the



(a) (b)

Fig. 2. (a) The diffraction patterns show the relation of the orthorhombic axes (b_o^*,c_o^*) and the monoclinic axes of twinning domains(a_m^*,c_m^*,$a_m'^*$).
(b) The relation between the crystal axes of the orthorhombic average structure and those of the monoclinic structure of twinning domains.

basis of the 1434 independent reflections. Considering the relatively weak intensities of the type-II reflections and the twinned structure, the final R value of 0.17 is satisfactory. The atomic coordinates of the I_3 anions in the monoclinic lattice are :I(1) (-0.09055,-0.06326, 0.25008), I(2)(0.19520,-0.08210 ,0.25035), I(3)(-0.40882, -0.03763,0.24962). In the average structure, the I_3 anions are on the mirror planes perpendicular to the b axis. While, in the real structure they are on the general positions. But the refined positions of I_3 well correspond to those of the average structure. The mean bond length of I-I is 3.00 Å, almost equal to the I-I lengths in analogous systems (2.90 Å (β-(BEDT-TTF)$_2I_3$), 2.94 Å (α-(BEDT-TTF)$_2$ I_3)). The shortest inter-anion I...I contact along the a_m axis is 4.20 Å, which is comparable to those in the α- and β-salts (4.20 Å(β), 3.90 Å(α)). The I...I distances between the anions interrelated by the screw axis symmetry are larger than 4.8 Å.

In these analyses, the positions of the BEDT-TTF molecules are assumed to be identical to those of the average structure. Small dimeric displacement of BEDT-TTF molecules along the orthorhombic c axis might be possible because the lattice spacing along this direction is doubled by the three-dimensional ordering of the I_3 anions. However, the monotonous intensity distribution of type II reflections and the relatively loose contact between ethylene groups of BEDT-TTF and I_3 anion suggest that the magnitude of the displacement of BEDT-TTF molecules will be small, even if the displacement can actually occur. There is no short H...I contact less than 3.1 Å. In contrast, in β-(BEDT-TTF)$_2I_3$ two disordered ethylene groups have very short H...I contacts (2.73 Å, 2.64 Å).$^{3)}$ Moreover, the BEDT-TTF arrangement of the average structure minimizes the intermolecular H...I interaction energy when the position of I_3 accords with that obtained by the above analysis. In order to analyze I_3 arrangement in the θ-salt, the interaction

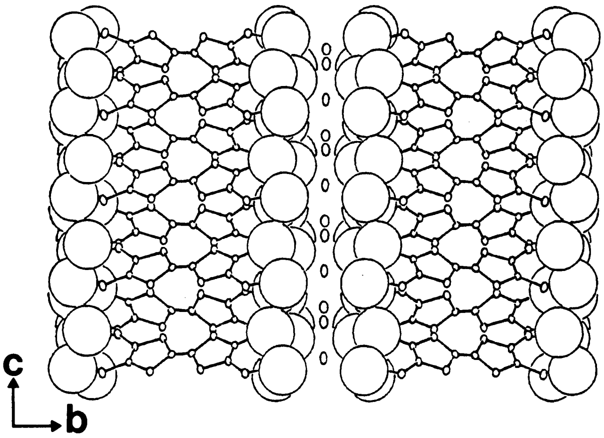


Fig. 3. Structure of θ-(BEDT-TTF)$_2$ $(I_3)_{1-x}(AuI_2)_x(x< 0.02)$ viewed along the orthorhombic a axis. Large circles indicate the van der Waals spheres of hydrogen atoms of ethylene groups.

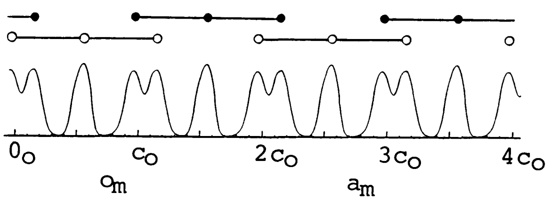


Fig. 4. Fourier peaks show the arrangement of I_3. Open and closed circles indicate two possible ordered arrangement of I_3.

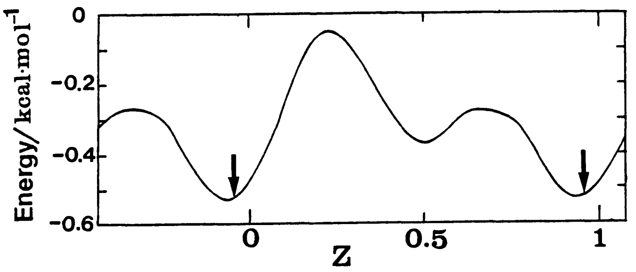


Fig. 5. The energy of H...I interactions U(z) as a function of z (the z-coordinate of I(1) of the orthorhombic cell). The arrow indicates the position of I(1) determined by X-ray analysis.

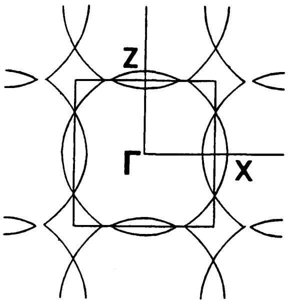


Fig. 6. Schematic drawing of the revised Fermi surface of θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$.

between the hydrogen atoms of ethylene groups and I_3 has been calculated with varying the position of I_3 along the c_o direction. The following empirical equation of the energy (ϕ) of the H...I interaction was used,

$$\phi(r) = 3.813\ 10^4\exp(-3.61r) - 589r^{-6}\ \text{kcal/mol},^{3)}$$

in which r is the H...I distance. The energy of H...I interaction U(z) is $U(z) = \sum_i\sum_j \phi(r_{ij})$, where the double summations are over all I(j)(j=1,2,3) and H(i) in ethylene groups less than 3.9 Å from I(j) (arbitrary cutoff value), and z is the z-coordinate of the central iodine atom of I_3(I(1)). The result of the calculations is shown in Fig. 5. There is a favorable I_3 site in the crystal where U(z) is minimum. This site (z=-0.091) is in accord with the site obtained by the X-ray structure analysis within 0.1 Å.

The calculated electronic structure of the θ-salt has been reported to be almost ideally two-dimensional($|m^*| \simeq 2.5m_e$).1) It should be recalled that the reported band calculation was based on the orthorhombic average structure. Considering the doubling of the lattice spacing along the c_o(or a_m) axis, the form of the Fermi surface must be changed. Although the effect of the periodical potential of I_3 is unknown, it is concluded that the revised Fermi surface crosses all the Brillouin zone boundaries (Fig. 6). The change of the periodicity will be important for the consideration of the physical properties of this system.

References

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