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"PARTIALLY" SUPERCONDUCTING BEHAVIOR OF θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(A)$_x$ (A=AuI$_2$, I$_2$Br) SYSTEM

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Electrochemical crystallization with the use of a mixed supporting electrolyte gave θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(A)$_x$ (A=AuI$_2$ and I$_2$Br), where x is very small but non-zero. When A=AuI$_2$ (x=0.03) or A=I$_2$Br ($x\simeq0$), the crystals exhibited "partially" superconducting behavior.

Recent discovery of the ambient-pressure superconductor θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ ($x<0.02$) (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene) will arouse renewed interest in the design of the organic superconductor.$^{1)}$ The highly significant feature of this compound is its strong two-dimensionality observed in the crystal and electronic structures, which reminds us of a route to the "Ginzburg superconductor model". Compared to the θ-type salt, the β-type salt, which is the first organic superconductor with a closed two-dimensional Fermi surface, has rather anisotropic intermolecular interactions and small structural modifications reduce the system to one-dimensional one.$^{2)}$

In this paper, we present the effect of the contaminating anion (A) on the superconducting transition of the θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(A)$_x$ (A=AuI$_2$, I$_2$Br).$^{3)}$

We have carried out electrochemical oxidation of THF solutions containing BEDT-TTF and a mixed supporting electrolyte ((n-C$_4$H$_9$)$_4$NI$_3$ and (n-C$_4$H$_9$)$_4$NAuI$_2$) with various I$_3$/AuI$_2$ molar ratios, keeping the total number of moles constant. The θ-type salts were obtained in the wide range of the I$_3$/AuI$_2$ ratio (95/5>I$_3$/AuI$_2$ >ca.1). Crystallization of the θ-type salt was frequently accompanied by that of the α-type salt. Surprisingly, the I$_3$/AuI$_2$ ratios in the crystals were quite

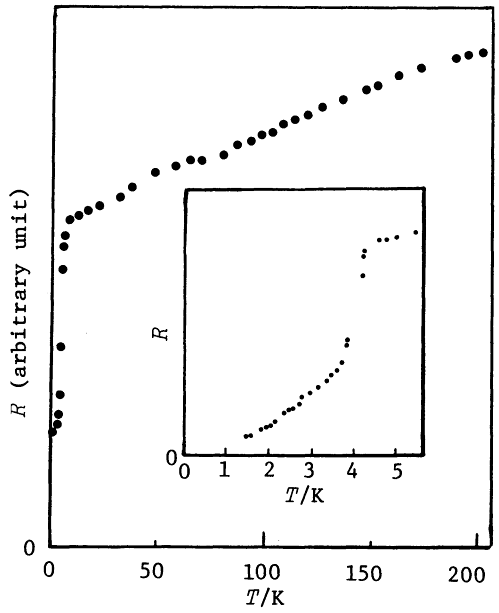

Fig. 1. Resistance (*R*) of θ-(BEDT-TTF)$_2$ (I$_3$)$_{0.97}$(AuI$_2$)$_{0.03}$ parallel to (010).

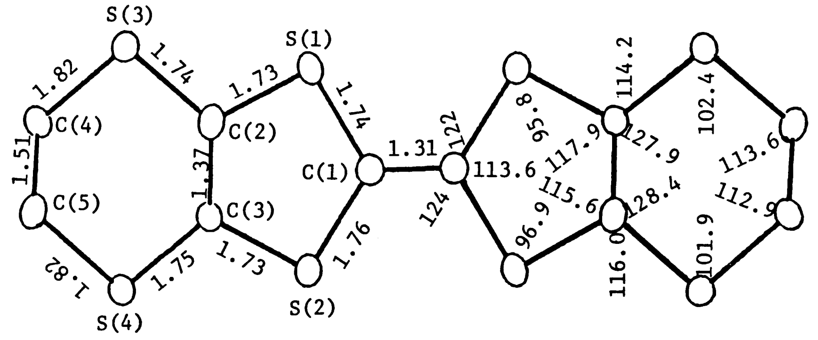

Fig. 2. Molecular structure of BEDT-TTF in θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(I$_2$Br)$_x$ (x≈0). The standard deviations of the bond lengths and angles are 0.01-0.02 Å and 0.6-2°, respectively.

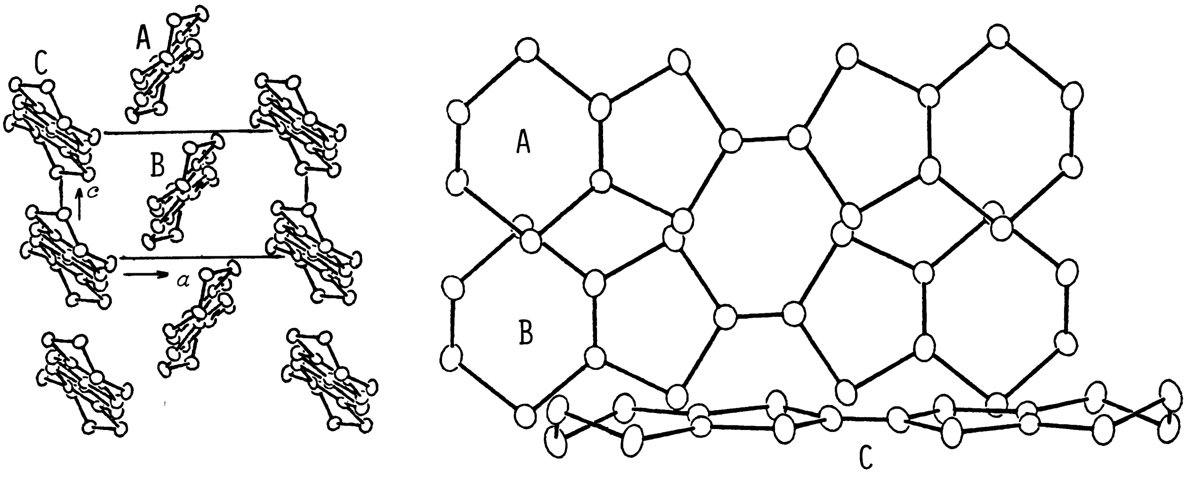

Fig. 3. Molecular arrangement of BEDT-TTFs in θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(I$_2$Br)$_x$ (x≈0).

different from the starting I_3/AuI_2 ratios. The I_3 anion is incorporated into these crystals selectively. For example, from the solution with $I_3/AuI_2=1$, crystals of θ-(BEDT-TTF)$_2$(I_3)$_{0.97}$(AuI_2)$_{0.03}$ were obtained (the x value was determined by the X-ray microanalysis).[4)]

The AuI_2-rich solutions (I_3/AuI_2<ca.1/9) gave crystals isostructural with δ-(BEDT-TTF)$_2$$AuI_2$[5)] mainly.

The solutions containing pure electrolyte gave α-(BEDT-TTF)$_2$$I_3$ and δ-(BEDT-TTF)$_2$$AuI_2$ as main products, respectively. To date, the θ-type salts without contaminating anion have not been obtained.

The crystal of θ-(BEDT-TTF)$_2$(I_3)$_{0.97}$(AuI_2)$_{0.03}$ is isostructural with that of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$).[1,6)] Although there is no significant difference between the "average" crystal structures of these two salts, we observed apparent difference in the temperature dependence of the electrical resistance. Figure 1 shows the "partially" superconducting behavior observed by the resistance measurement of θ-(BEDT-TTF)$_2$(I_3)$_{0.97}$(AuI_2)$_{0.03}$. The room temperature conductivity is comparable to that of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$; $\sigma_{R.T.}\simeq 30$ Scm^{-1}).[1)] The resistance gradually decreases with lowering the temperature down to 4 K. At 4.0 K, corresponding to the onset of the superconductivity of θ-(BEDT-TTF)$_2$ (I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$), a sharp drop in resistance is observed. The resistance, however, does not vanish and then decreases down to 1.5 K. Such behavior is similar to that of β-(BEDT-TTF)$_2$$I_3$ after release of pressure where the high-T_c state partially remains.[7)] The nature of this "partially" superconducting state below 4 K would be of special interest and we are much interested in the presence or absence of the "completely" superconducting state below 1.5 K.

The I_2Br anion has asymmetric charge distribution and only β-(BEDT-TTF)$_2$$I_2Br$ does not show the superconducting transition in the β-type salts.[7)] The crystal of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(I_2Br)$_x$ obtained from the solution with $I_3/I_2Br\simeq 95/5$ contained very small amount of Br which was detectable but could not be determined by the X-ray microanalysis. The crystal data; orthorhombic, space group Pnma, a=10.068 (3), b=33.851(11), c=4.970(4) Å, V=1693.8 Å^3, Z=2. As is the case of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$, $x=0.03$), this crystal had the I_3 sublattice.[1,6)] The "average" structure was solved by the direct method and refined by the block-diagonal least-squares method. Independent 1289 reflections ($2\theta\leq 60°$, $|Fo|\geq 3\sigma(|Fo|)$) were used for calculations. The final R value was 0.079. The molecular and crystal structures are shown in Figs. 2 and 3. This crystal is isostructural with that of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$, $x=0.03$).[1,6)] The two-dimensional S•••S network parallel to (010) is highly isotropic. Figure 3 shows that this compound does not have a vestige of the conventional one-dimensional column structure. This means that the molecular design for the organic metal (superconductor) is liberated from the restriction of the column formation. Although the intermolecular overlap integrals of HOMO (highest occupied molecular orbital) of BEDT-TTF are slightly different from those of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(AuI_2)$_x$ ($x<0.02$), there is no fundamental change in the band structure derived from the simple tight-binding approximation.[1)] The superconducting transition of θ-(BEDT-TTF)$_2$(I_3)$_{1-x}$(I_2Br)$_x$ ($x\simeq 0$), however, is incomplete and temperature dependence of resistance is similar to that of θ-(BEDT-TTF)$_2$(I$_3$)$_{0.97}$(AuI$_2$)$_{0.03}$; in the resistance measurement, we observed a sharp drop at 4 K follewed by gradual decrease down to 1.5 K.

In conclusion, in the θ-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(A)$_x$ (A=AuI$_2$, I$_2$Br) system, the content of the contaminating anion A is quite small but non-zero. The superconducting transition turns incomplete by slight increase of AuI$_2$ content or existence of I$_2$Br with asymmetric charge distribution, without no significant change of the molecular arrangement of BEDT-TTF. This means that a small change in the anion site has serious influence on the electronic properties. The nature of the "partially" superconducting state and the precise X-ray analysis of the anion arrangement will be reported elsewhere.

References

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2) H. Kobayashi, R. Kato, A. Kobayashi, G. Saito, M. Tokumoto, H. Anzai, and T. Ishiguro, Chem. Lett., 1986, 89; R. Kato, H. Kobayashi, and A. Kobayashi, ibid., 1986, 785.
3) Very recently, we have obtained θ-(BEDT-TTF)$_2$(IBr$_2$)$_{1-x}$(AuI$_2$)$_x$ by the use of a mixed electrolyte of (n-C$_4$H$_9$)$_4$NIBr$_2$ and (n-C$_4$H$_9$)$_4$NAuI$_2$. Details of the structural and physical studies will be reported in the near future.
4) We are much grateful to Prof. A. Masuda, Dr. H. Shimizu and Mr. K. Takahashi, the University of Tokyo, for the X-ray microanalyses.
5) H. Kobayashi, R. Kato, A. Kobayashi, M. Tokumoto, H. Anzai, and T. Ishiguro, submitted to Chem. Lett.
6) Crystal data; orthorhombic, space group Pnma, a=10.079(1), b=33.822(6), c=4.972(2) Å, V=1694.9 Å^3, Z=2. The crystal had the I$_3$ sublattice. The orthorhombic "average" structure was solved by the direct method and refined to the conventional R value of 0.066, using 1405 independent reflections ($2\theta \leq 60°$, $|Fo| \geq 3\sigma(|Fo|)$). All the anions were assumed to be I$_3$.
7) For example, M. Tokumoto, H. Bando, K. Murata, H. Anzai, N. Kinoshita, K. Kajimura, T. Ishiguro, and G. Saito, Synthetic Metals, 13, 9 (1986).

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