

A NEW MOLECULAR SUPERCONDUCTOR,  $(\text{BEDT-TTF})_2(\text{I}_3)_{1-x}(\text{AuI}_2)_x$  ( $x < 0.02$ )

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A new molecular superconductor based on BEDT-TTF molecule was prepared electrochemically by using the mixed supporting electrolyte,  $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$  and  $(n\text{-C}_4\text{H}_9)_4\text{NAuI}_2$ . The superconducting transition takes place at ambient pressure at 3.6 K. X-Ray diffraction patterns show that the system can be approximately assigned to a pseudo orthorhombic one with the lattice constants of  $a=10.076(2)$ ,  $b=33.853(5)$ ,  $c=4.964(1)$  Å.

Since the discovery of the superconductor  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ ,<sup>1)</sup> several ambient-pressure superconductors have been reported (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene).<sup>2-5)</sup> Shibaeva et al. have reported three superconducting polyhalide systems of BEDT-TTF ( $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ ,  $\epsilon\text{-(BEDT-TTF)}_2\text{I}_3(\text{I}_8)_{0.5}$ , and  $\gamma\text{-(BEDT-TTF)}_3(\text{I}_3)_{2.5}$ ).<sup>2)</sup> Unlike the first organic superconductor,  $(\text{TMTSF})_2\text{X}$  (Bechgaard salt),<sup>6,7)</sup> the superconducting transitions of BEDT-TTF compounds are frequently found at atmospheric pressure and the transition temperatures ( $T_c$ ) are fairly high.

In this paper, we will report a new molecular superconductor,  $(\text{BEDT-TTF})_2(\text{I}_3)_{1-x}(\text{AuI}_2)_x$  ( $x < 0.02$ ).

It is well-known that  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  exhibits low- and high- $T_c$  states.<sup>8,9)</sup> The high  $T_c$  state has the transition temperature as high as 8 K. In order to examine the effect of the incommensurate lattice distortion wave which develops below 200 K,<sup>10)</sup> we tried to control the modulation wave by the introduction of the disorder in the anion sites.

The crystals were prepared electrochemically by using the supporting electrolyte of the mixture of  $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$  (95%) and  $(n\text{-C}_4\text{H}_9)_4\text{NAuI}_2$  (5%) dissolved in tetrahydrofuran. The constant current of 1.0  $\mu\text{A}$  was applied. Large black plates with maximum dimension of about 3 mm were obtained. As mentioned later, the obtained crystals were not  $\beta$ -type ones and the resistivity measurements showed the crystal to be a new molecular superconductor. The X-ray diffraction patterns were examined by oscillation and Weissenberg photographs on the sample used for the resistivity measurements. Strong Bragg reflections showed that the crystal had "pseudo orthorhombic" symmetry with the lattice constants of  $a=10.076(2)$ ,  $b=33.853(5)$ ,  $c=4.964(1)$   $\text{\AA}$ . The cell volume ( $1693.2$   $\text{\AA}^3$ ) is almost equal to that of  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  and twice of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ .<sup>2)</sup> But the intensity distribution of weak Bragg reflections indicates that the crystal belongs to a monoclinic system with the lattice vectors of  $\mathbf{a}^*=(\mathbf{c}_0^*+\mathbf{b}_0^*)/2$ ,  $\mathbf{b}^*=\mathbf{a}_0^*$ , and  $\mathbf{c}^*=\mathbf{b}_0^*$ , where  $\mathbf{a}_0^*$ ,  $\mathbf{b}_0^*$ , and  $\mathbf{c}_0^*$  are those of the orthorhombic cell.<sup>11)</sup> BEDT-TTF molecules form a two-dimensional network parallel to (010). The X-ray microanalysis indicated an existence of Au but the content was too small to be determined accurately. The composition of the complex was determined as, S:I(:Au) $\approx$ 8.00:1.51(:0.009). The corresponding x value is less than 0.02.<sup>12)</sup>

The resistivities along the direction in (010) (approximately parallel to [100]) were measured by the d.c. four-probe method. The room-temperature conductivity of  $30$   $\text{Scm}^{-1}$  is approximately equal to that of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  ( $30$   $\text{Scm}^{-1}$ ). The resistivity  $\rho$  decreases with lowering temperature, the slope of the  $\rho$ -T curve becomes sharp below 100 K and  $\rho$  reaches  $1 \times 10^{-4}$   $\text{Scm}^{-1}$  at 5 K (Fig. 1). The resistivity ratio  $\rho(300 \text{ K})/\rho(4 \text{ K})$  is about 300, which is smaller than that of the superconducting  $\beta$ -type  $\text{I}_3$  or  $\text{IBr}_2$  salts of BEDT-TTF and almost equal to that of  $\beta\text{-(BEDT-TTF)}_2\text{I}_2\text{Br}$ , which remains metallic down to 500 mK.<sup>13)</sup> The superconducting transition takes place at 3.6 K (Fig. 1). Thus  $(\text{BEDT-TTF})_2(\text{I}_3)_{1-x}(\text{AuI}_2)_x$  ( $x < 0.02$ ) is a new molecular superconductor with the fairly high  $T_c$  (Table 1). The magnetic field effects on the superconducting transition were measured with rotating the crystal. As shown in Fig. 2, the resistivity under magnetic field shows a very simple angular dependence, which clearly shows the two-dimensional nature of the system analogous to  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ .<sup>14,15)</sup>

Details of the structural and electrical studies will be reported in the near future.

Table 1. List of superconducting BEDT-TTF complexes with linear anions

BEDT-TTF is abbreviated as ET

	System	Space group	$V/\text{\AA}^3$	$z$	$\sigma/S \text{ cm}^{-1}$	$T_c/K$	Ref.
$\beta$ -(ET) $_2$ I $_3$	triclinic	$P\bar{1}$	852	1	30	1.5, 8	1,2,8,9
$\gamma$ -(ET) $_3$ (I $_3$ ) $_{2.5}$	orthorhombic	Pbnm	6812	4	20	2.5	2
$\epsilon$ -(ET) $_2$ I $_3$ (I $_8$ ) $_{0.5}$	monoclinic	$P2_1/c$	4211	4	20	2.5	2
$\beta$ -(ET) $_2$ IBr $_2$	triclinic	$P\bar{1}$	829	1		2.7	3
$\beta$ -(ET) $_2$ AuI $_2$	triclinic	$P\bar{1}$	845	1		3.9-5	4,5
(ET) $_2$ (I $_3$ ) $_{1-x}$ (AuI $_2$ ) $_x$	pseudo orthorhombic	Pnma	1693	2	30	3.6	this work

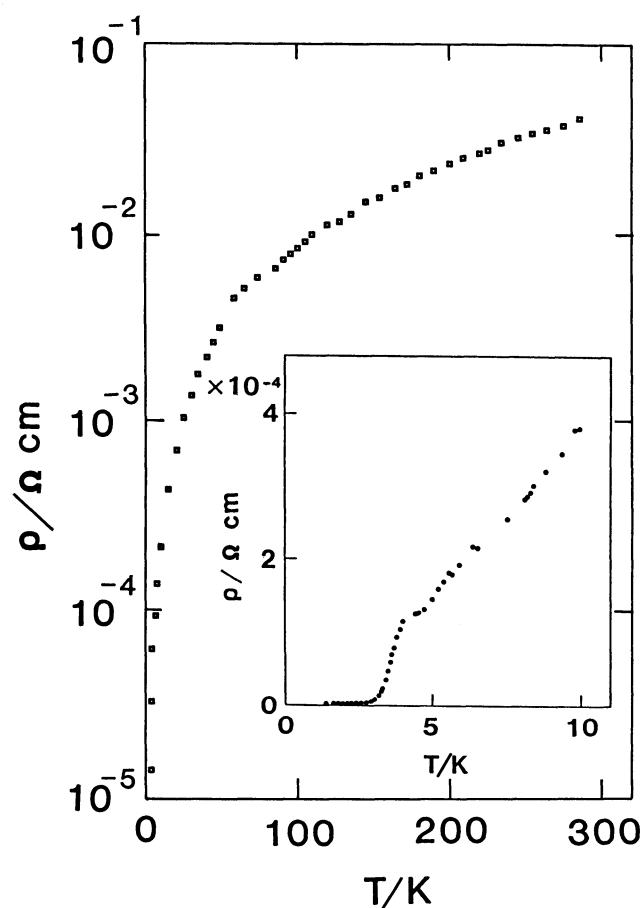


Fig. 1. Electrical resistivity of  
 $(\text{BEDT-TTF})_2(\text{I}_3)_{1-x}(\text{AuI}_2)_x$ .

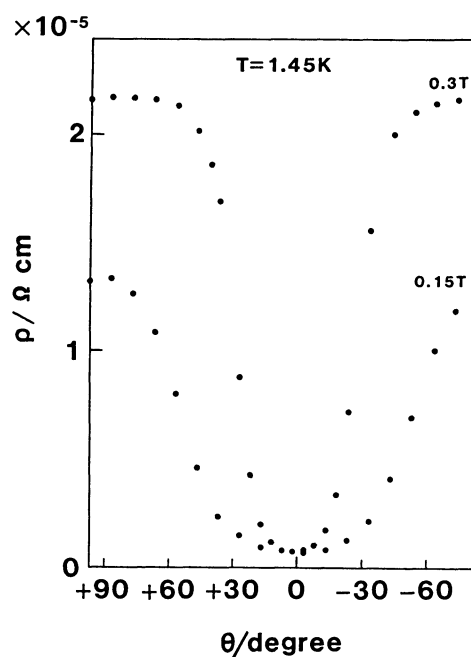


Fig. 2. Angular dependence of the  
 resistivity under the magnetic  
 field. The value  $\theta$  is the angle  
 between the (010) plane and the  
 magnetic field.

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- 11) Examination of the intensity distribution in the reciprocal space revealed the possibility of twinning of the crystal. The same diffraction patterns have been observed also in the crystals prepared from the solution of the 1:1 mixture of  $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$  and  $(n\text{-C}_4\text{H}_9)_4\text{NAuI}_2$  and those prepared from the mixture of  $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$  (95%) and  $(n\text{-C}_4\text{H}_9)_4\text{I}_2\text{Br}$  (5%). The details will be reported in a separate paper.
- 12) We are much obliged to Prof. A. Masuda, Dr. H. Shimizu and Mr. K. Takahashi, the University of Tokyo, for the X-ray microanalyses.
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