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A New Ambient-pressure Superconductor, κ-$(BEDT\text{-}TTF)_2I_3$

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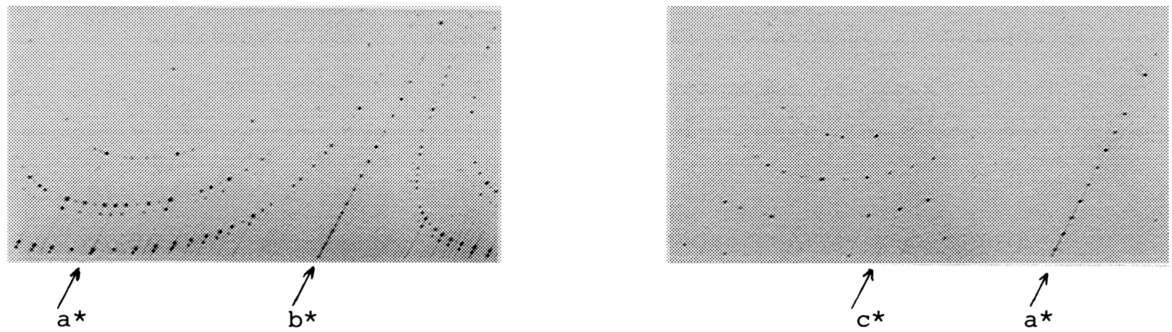
Electrochemical oxidation of a solution containing BEDT-TTF, $(n\text{-}C_4H_9)_4NI_3$, and small amount of $(n\text{-}C_4H_9)_4NAuI_2$ gave a new ambient-pressure superconductor (T_c=3.6 K), which coexisted with the superconducting θ-type salt but was clearly distinguished by the X-ray examination. The crystal data are: $(C_{10}H_8S_8)_2I_3$, monoclinic, $P2_1/c$, a=16.387(4), b=8.446(2), c=12.832(8) Å, β= 108.56(3)°, V=1687.6 Å^3, Z=2.

The organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) has offered multiphasic crystal and electronic structures, some of which show superconductivity (Table 1). Recently we have found a new superconducting salt θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$ ($x<0.02$) which has exhibited strong two-dimensional character.[1] This θ-salt was obtained by the electrochemical crystallization using the mixed supporting electrolyte, $(n\text{-}C_4H_9)_4NI_3$ and $(n\text{-}C_4H_9)_4NAuI_2$. We have continued the same kind of electrochemical crystallization and chemical and physical characterization of the products. We report here that there exists another new phase (hereafter we call it κ phase) which is definitely distinguished from the θ phase by the X-ray diffraction patterns and exhibits superconductivity at ambient pressure.

Table 1. Crystal data and physical properties of the ambient-pressure superconductors in the (BEDT-TTF)-I_3-(AuI_2) system. BEDT-TTF is abbreviated to ET.

Phase	β-$(ET)_2I_3$		γ-$(ET)_3(I_3)_{2.5}$	θ-$(ET)_2I_3$		κ-$(ET)_2I_3$
System	T		O	O	(M)	M
Space group[a]	P$\bar{1}$		Pbnm	Pnma	($P2_1/c$)	$P2_1/c$
a (Å)	6.609	15.243	13.76	10.076	(9.928)	16.387
b	9.083	9.070	14.73	33.853	(10.076)	8.466
c	15.267	6.597	33.61	4.964	(34.220)	12.832
α (°)	85.63	109.73				
β	95.62	95.56			(98.39)	108.56
γ	70.22	94.33				
V ($Å^3$)	852	849	6812	1693	(3387)	1688
$\sigma_{R.T.}$ ($S\ cm^{-1}$)	20-30		ca. 20	30-100		40-150
T_c (K)	1.5		2.5	3.6-4		3.6
Ref.	5	6	5	1	2	This work

[a] T; triclinic, O; orthorhombic, M; monoclinic



(a) (b)

Fig. 1. Weissenberg photographs. (a) The θ-type salt. The 0-th layer reflections (type-I) around the orthorhombic c axis. (b) The κ-type salt. The 0-th layer reflections around the monoclinic b axis.

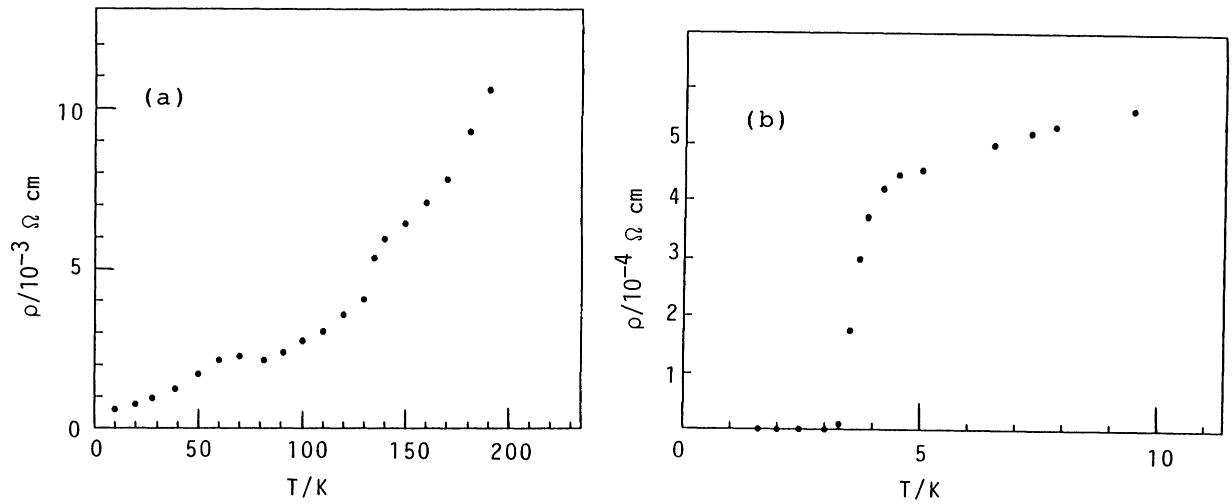


Fig. 2. Temperature dependence of electrical resistivity of the κ-type salt.

Black thick plates of the κ-type salt were also prepared by the electrochemical crystallization using the mixed supporting electrolyte, $(n\text{-}C_4H_9)_4NI_3$ and $(n\text{-}C_4H_9)_4NAuI_2$. For example, electrochemical oxidation of a THF solution (20 ml) containing BEDT-TTF (11 mg), $(n\text{-}C_4H_9)_4NI_3$ (101 mg), and $(n\text{-}C_4H_9)_4NAuI_2$ (6 mg) with a constant current of 1.0 μA at 20-19°C under N_2 gave α-type salt as main product and small amount of θ and κ-type salts. It is very difficult to identify each modification by its crystal shape and we carefully carried out characterization of the products with combination of X-ray diffraction study and physical measurements.

The X-ray diffraction patterns were studied by oscillation and Weissenberg photographs on the samples whose superconducting behavior was established by the resistivity measurements. There exists a new phase which is different from any one of the known structures including the θ-phase. The X-ray diffraction patterns of the θ-phase which contain two quite different types of reflections (normal type-I and monotonous type-II reflections) indicate the twinning arising from the I_3 sublattice.[2)] The average structure of the θ-phase solved using the type-I reflections has orthorhombic symmetry. In the case of κ-phase, however, there is not the type-II reflection, and simple monoclinic symmetry is observed (Fig. 1). The crystal data are: monoclinic, $P2_1/c$, a=16.387(4), b=8.466(2), c=12.832(8) Å, β=108.56(3)°, V=1687.6 $Å^3$. The cell volume is equal to that of α and θ-$(BEDT\text{-}TTF)_2I_3$ (average structure) and twice of β-$(BEDT\text{-}TTF)_2I_3$. In all these crystals, BEDT-TTF molecules construct two-dimensional network. In the κ-phase, there also exists two-dimensional molecular arrangement of BEDT-TTF parallel to the bc plane.[3)] The composition of the κ-type salt determined by the X-ray microanalysis (XMA) was S:I=16.0:3.0. The Au content was under the lower determination limit of XMA ($x<0.006$ in $(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$).[4)]

D.C. resistivity measurements were carried out using the four-probe method with gold wire (15 μm diameter) and gold paint contact. Three samples with typical dimensions of $1\times0.8\times0.1$ mm^3 from three batches were examined. The room-temperature conductivity along the direction in (100) is 40-150 Scm^{-1} which is comparable to the conductivities of the β and θ-type salts. With lowering temperature, the resistivity decreases rather moderately (Fig. 2a). The resistivity ratio ρ(R.T.)/ρ(4.2 K) is 30-55. The superconducting transition occurs at 3.6 K (Fig. 2b). This value is very close to that of the θ-phase

(Table 1). The anisotropy of the resistivity (ρ (normal to the bc plane)/ρ (parallel to the bc plane)) is very large (ca. 10^3). The resistivity measurement along the direction normal to the bc plane has also shown the superconducting transition at 3.6 K. The effect of the magnetic field on the resistivity was examined (Fig. 3). The anisotropic nature of the superconductivity in the plane containing the a axis, as is shown in Fig. 3, is also observed in the β and θ-type salts.

In conclusion, X-ray diffraction study and physical measurements have revealed existence of a new superconducting phase in the (BEDT-TTF)-I_3-(AuI_2) system. The crystal and electronic structures and detailed physical measurements will be reported soon.

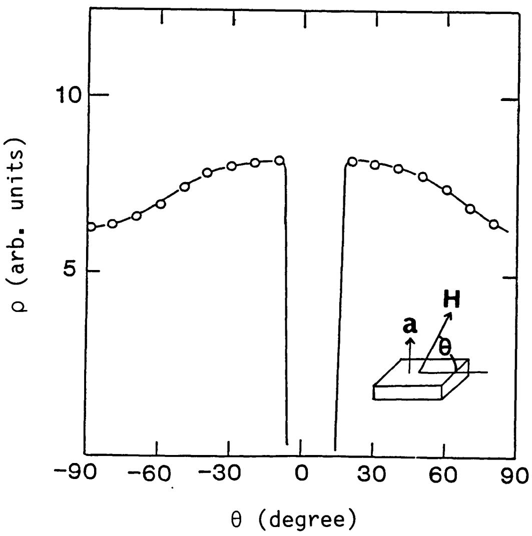


Fig. 3. Electrical resistivity ρ at 1.5 K against the direction of the magnetic field H (1.4 T).

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