A New Ambient-pressure Superconductor, $\kappa$-(BEDT-TTF)$_2$I$_3$

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Electrochemical oxidation of a solution containing BEDT-TTF,
(n-C$_4$H$_9$)$_4$NI$_3$, and small amount of (n-C$_4$H$_9$)$_4$NAuI$_2$ gave a new
ambient-pressure superconductor ($T_c=3.6$ K), which coexisted with
the superconducting $\sigma$-type salt but was clearly distinguished by
the X-ray examination. The crystal data are: (C$_10$H$_8$S$_8$)$_2$I$_3$,
monoclinic, P2$_1$/c, a=16.387(4), b=8.446(2), c=12.832(8) Å, $\beta=$
108.56(3)$^\circ$, V=1687.6 Å$^3$, Z=2.

The organic donor BEDT-TTF (bis(ethylendithio)tetrathiafulvalene) has
offered multiphasic crystal and electronic structures, some of which show
superconductivity (Table 1). Recently we have found a new superconducting salt
$\sigma$-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ ($x<0.02$) which has exhibited strong two-dimensional
character.¹) This $\sigma$-salt was obtained by the electrochemical crystallization using
the mixed supporting electrolyte, (n-C$_4$H$_9$)$_4$NI$_3$ and (n-C$_4$H$_9$)$_4$NAuI$_2$. 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 $\kappa$ phase) which is definitely distinguished
from the $\sigma$ 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)-I₃-(AuI₂) system. BEDT-TTF is abbreviated to ET.

<table>
<thead>
<tr>
<th>Phase</th>
<th>α-(ET)₂I₃</th>
<th>γ-(ET)₃I₃₂,₅</th>
<th>θ-(ET)₂I₃</th>
<th>κ-(ET)₂I₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>T</td>
<td>O</td>
<td>O</td>
<td>M</td>
</tr>
<tr>
<td>Space group</td>
<td>Pitamin</td>
<td>Pbnm</td>
<td>Pnma (P2₁/c)</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>6.609</td>
<td>15.243</td>
<td>13.76</td>
<td>10.076</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.083</td>
<td>9.070</td>
<td>14.73</td>
<td>33.853 (10.076)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.267</td>
<td>6.597</td>
<td>33.61</td>
<td>4.964 (34.220)</td>
</tr>
<tr>
<td>α (°)</td>
<td>85.63</td>
<td>109.73</td>
<td>95.62</td>
<td>95.56</td>
</tr>
<tr>
<td>β (°)</td>
<td>95.62</td>
<td>95.56</td>
<td>94.33</td>
<td></td>
</tr>
<tr>
<td>γ (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V (Å³)</td>
<td>852</td>
<td>849</td>
<td>6812</td>
<td>1693</td>
</tr>
<tr>
<td>ρ₉R, T (S cm⁻¹)</td>
<td>20-30</td>
<td>ca. 20</td>
<td>30-100</td>
<td>40-150</td>
</tr>
<tr>
<td>Tc (K)</td>
<td>1.5</td>
<td>2.5</td>
<td>3.6-4</td>
<td>3.6</td>
</tr>
<tr>
<td>Ref.</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

T: triclinic, O: orthorhombic, M: monoclinic

Fig. 1. Weissenberg photographs. (a) The α-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 \( \kappa \)-type salt were also prepared by the electro-
chemical crystallization using the mixed supporting electrolyte, \((n-\text{C}_4\text{H}_9)_4\text{NI}_3\) and
\((n-\text{C}_4\text{H}_9)_4\text{NAuI}_2\). For example, electrochemical oxidation of a THF solution (20 ml)
containing BEDT-TTF (11 mg), \((n-\text{C}_4\text{H}_9)_4\text{NI}_3\) (101 mg), and \((n-\text{C}_4\text{H}_9)_4\text{NAuI}_2\) (6 mg) with
a constant current of 1.0 \( \mu \text{A} \) at 20-19\(^\circ\text{C}\) under \( \text{N}_2 \) gave \( \alpha \)-type salt as main product
and small amount of \( \theta \) and \( \kappa \)-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 \( \theta \)-phase. The X-ray diffraction patterns
of the \( \theta \)-phase which contain two quite different types of reflections (normal
type-I and monotonous type-II reflections) indicate the twinning arising from the
\( \text{I}_3 \) sublattice.\(^2\) The average structure of the \( \theta \)-phase solved using the type-I
reflections has orthorhombic symmetry. In the case of \( \kappa \)-phase, however, there is
not the type-II reflection, and simple monoclinic symmetry is observed (Fig. 1).
The crystal data are: monoclinic, \( P2_1/c \), \( a=16.387(4) \), \( b=8.466(2) \), \( c=12.832(8) \) \( \text{Å} \),
\( \beta=108.56(3)^\circ \), \( V=1687.6 \) \( \text{Å}^3 \). The cell volume is equal to that of \( \alpha \) and
\( \theta-(\text{BEDT-TTF})_2\text{I}_3 \) (average structure) and twice of \( \beta-(\text{BEDT-TTF})_2\text{I}_3 \). In all these
crystals, BEDT-TTF molecules construct two-dimensional network. In the \( \kappa \)-phase,
there also exists two-dimensional molecular arrangement of BEDT-TTF parallel to the
bc plane.\(^3\) The composition of the \( \kappa \)-type salt determined by the X-ray
microanalysis (XMA) was \( \text{S:I}=16.0:3.0 \). The Au content was under the lower
determination limit of XMA (\( x<0.006 \) in \( (\text{BEDT-TTF})_2(\text{I}_3)_{1-x}(\text{AuI}_2)_x ) \)).\(^4\)

D.C. resistivity measurements were carried out using the four-probe method
with gold wire (15 \( \mu \text{m} \) diameter) and gold paint contact. Three samples with
typical dimensions of 1×0.8×0.1 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 \( \beta \) and \( \theta \)-type salts. With lowering
temperature, the resistivity decreases rather moderately (Fig. 2a). The resistivity ratio \( \rho(\text{R.T.})/\rho(4.2 \text{ K}) \) is 30-55. The superconducting transition
occurs at 3.6 K (Fig. 2b). This value is very close to that of the \( \theta \)-phase
The anisotropy of the resistivity \( \rho \) (normal to the bc plane)/\( \rho \) (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 \( \beta \) and \( \theta \)-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-(AuF_2) system. The crystal and electronic structures and detailed physical measurements will be reported soon.

References


4) We are much grateful to Prof. A. Masuda, Dr. H. Shimizu, and Mr. T. Saito of The University of Tokyo, for the X-ray microanalyses.
