ABSTRACT

The electrical conductivity and the static magnetic susceptibility of various semiconducting phases of (BEDT-TTF)$_2$X, where X = IBr$_2$(α'), IBrCl(α') and ICl$_2$(β'), are investigated. We show the presence of anomaly in the temperature dependence of conductivity, as well as phase transitions accompanying a distinct change in the magnetic susceptibility. The nature of these phase transitions is discussed.

INTRODUCTION

In our attempt to develop new organic superconductors by substitution of trilode anion (I$_3^-$) in β-(BEDT-TTF)$_2$I$_3$ with other linear trihalide anions (X'-'s), we obtained several new organic semiconductors (BEDT-TTF)$_2$X having various structural modifications, in addition to some organic metals. It is interesting to note that three of them (X=I$_2$Br, IBr$_2$ and AuI$_2$) which are isostructural to the β-(BEDT-TTF)$_2$I$_3$ are all metals which remain metallic down to low temperatures, and exhibit superconductivity except for the one having asymmetric anion (I-I-Br)$^-$ [1-6]. On the other hand, all other salts with the same stoichiometric ratio of 2:1 having modified (β'-type) or quite different (α-, α'-type) crystal
structures are found to be either (1) metallic at room temperature but encounter a metal-insulator transition as the temperature is lowered \((X=I_3; \alpha\text{-type})[7]\), or (2) semiconductive at room temperature and below \((X=IBr_2, IBrCl, ICl_2; \alpha', \beta'\text{-type})\).

In this paper we present the electrical and magnetic properties of the latter class of organic semiconductors \((BEDT-TTF)_2X\) with various structural modifications, namely, \(\alpha'\text{-IBr}_2\), \(\alpha'\text{-IBrCl}\), and \(\beta'\text{-ICl}_2\) salts.

**EXPERIMENTAL**

Samples were prepared by electrochemical oxidation of BEDT-TTF in the presence of \((nBu_iN)X (X=IBr_2, IBrCl or ICl_2)\) as a supporting electrolyte using various organic solvents including \(C_6H_5CN\) for \(\alpha'\text{-}(BEDT-TTF)_2IBr_2\), and \(C_6H_5Cl\) for \(\alpha'\text{-}(BEDT-TTF)_2IBrCl\) and \(\beta'\text{-}(BEDT-TTF)_2ICl_2[8]\). The electrical resistance was measured using Keithley model 619A electrometer with input impedance of \(2\times10^{13} \Omega\) as voltmeter. The static magnetic susceptibility was measured using a Variable Temperature Susceptometer (SHE 905). The induced magnetic moment of the sample was determined by moving it between a pair of counterwound coils, each of which is connected to a superconducting quantum interference device (SQUID)-based flux measuring system. The samples were measured in either plastic or Al-Si container which was suspended with a cotton thread. The measured magnetic moments were corrected for contributions from the container, which were measured separately.

**RESULTS AND DISCUSSION**

\(\alpha'\text{-}(BEDT-TTF)_2IBr_2\)

The crystals of \((BEDT-TTF)_2IBr_2\) is known to grow in two types of morphologies, that is \(\beta\text{- and } \alpha\text{-types. The } \beta\text{-}(BEDT-TTF)_2IBr_2\text{ is a metal and shows superconductivity with } T_c=2.3-2.7 \text{ K at ambient pressure}[1,2].\) Another modification named \(\alpha\) by Williams et al.\([1]\) was reported to show no superconductivity down to \(0.45 \text{ K}\) by use of \(n\text{-f. penetration depth measurements. Their statement was misleading since it implied that } \alpha\text{-IBr}_2\text{ was a metal. The crystal structure of our semiconductive } \alpha'\text{-}(BEDT-TTF)_2IBr_2\text{ crystals grown from } C_6H_5CN\text{ is identical to that of the } \alpha\text{-type salt reported by Williams et al.\([1]\)}\) and Yagubskii et al.\([9]\). The reason we call this salt as \(\alpha'\text{-type instead of } \alpha\text{-type is because it is not isostructural with the } \alpha\text{-}(BEDT-TTF)_2I_3[7].\) In \(\alpha'\text{-type salt, all the molecules are on the general position, in contrast to the } \alpha\text{-type salt where a half of the molecule is on the inversion centers.}

Figure 1 shows the temperature dependence of the conductivity of \(\alpha'\text{-}(BEDT-TTF)_2IBr_2\). The conductivity along the long direction of the crystal (the axis with 9.0 \text{ A length}) is about \(3 \text{ S/cm at room temperature, and shows a semiconductive temperature dependence with an activation energy of 0.16 eV at around room temperature. A large anomalous change in conductivity is observed at about 200 K,}
where a transition to a more resistive state with almost the same activation energy is seen to take place as the temperature is lowered. This anomaly around 200 K may be related to the molecular dimerization observed through the temperature dependence of the intensity of the Bragg reflection with odd indices in the "semiconducting" (BEDT-TTF)$_2$IBr$_2$[10], although the conductivity reported by Saito et al.[11] did not show such an anomaly at 200 K.

Figure 2 shows the temperature dependence of the static magnetic susceptibility of $\alpha'-(\text{BEDT-TTF})_2\text{IBr}_2$ single crystal of about 1 mg. The magnetic field of 10 kOe was applied parallel to the long side of the crystal. The susceptibility increases with decreasing temperature down to 80 K, shows a maximum around 60 K and decreases rapidly below 40 K until it reaches a minimum at about 20 K. A similar temperature dependence of the ESR intensity (spin susceptibility) was observed in the same material along with an increase in the g-value and a decrease in the ESR linewidth below 40 K[12]. The mechanism of this phase transition is not identified at present.

\[\text{Fig. 1. Temperature dependence of electrical conductivity along the long side (the axis with 9.0 Å length) of a single crystal of $\alpha'-(\text{BEDT-TTF})_2\text{IBr}_2$.} \]

\[\text{Fig. 2. Temperature dependence of static magnetic susceptibility of $\alpha'-(\text{BEDT-TTF})_2\text{IBr}_2$, with field of 10 kOe parallel to the long side of a single crystal.} \]

$\alpha'-(\text{BEDT-TTF})_2\text{IBrCl}$

The crystal structure of $\alpha'-(\text{BEDT-TTF})_2\text{IBrCl}$ is isomorphous to the $\alpha'-(\text{BEDT-TTF})_2\text{IBr}_2$ discussed above, i.e. triclinic, $\overline{P}$, with $a=16.307$ Å, $b=12.373$ Å, $c=8.871$ Å, $\alpha=113.44^\circ$, $\beta=91.50^\circ$, $\gamma=93.60^\circ$, $V=1636.3$ Å$^3$, $Z=2$[13]. The IBrCl anion takes a linear form as (Br-I-Cl)$^-$, and the thermal parameters of Br and Cl atoms indicate the existence of the orientational disorder. The ratio of the preferred
orientation to the inverted orientation is about 0.65:0.35. The cation-radical layer is constructed from two types of BEDT-TTF stacks, whose dihedral angle is 48°[13]. The structure is completely different from that of the \( \beta-(\text{BEDT-TTF})_2\text{IBrCl}[14] \).

Figure 3 shows a typical temperature dependence of electrical conductivity of \( \alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \) single crystal. The conductivity is about 3 S/cm at room temperature, and shows a semiconductive temperature dependence with an activation energy of 0.10 eV at around room temperature, which shows a slight increase with decreasing temperature. At about 200 K resistance jump takes place and sample breakage hinders measurement of resistivity at lower temperatures.

Figure 4 shows the temperature dependence of static magnetic susceptibility of \( \alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \) measured using many crystals whose total weight was about 5 mg. Note the prominent change in the susceptibility around 200 K, the temperature for which shows a marked difference between the two measurements with increasing and decreasing temperature. This thermal hysteresis strongly suggests the presence of a first order phase transition accompanied by a large structural change and fracture of crystals.

\[
\begin{align*}
\alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \\
1000/T [\text{K}] & \quad \text{CONDUCTIVITY (S/cm)} \\
3 & \quad 10^1 \\
4 & \quad 10^2 \\
5 & \quad 10^3 \\
6 & \quad 10^4
\end{align*}
\]

Fig. 3. Typical temperature dependence of electrical conductivity of a single crystal of \( \alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \).

\[
\begin{align*}
\alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \\
\text{TEMPERATURE (K)} & \quad \text{SUSCEPTIBILITY (emu/mole)} \\
100 & \quad 0 \\
200 & \quad 2 \quad \bullet \quad \text{UP} \\
300 & \quad 4 \quad \circ \quad \text{DOWN}
\end{align*}
\]

Fig. 4. Temperature dependence of static magnetic susceptibility of \( \alpha'-(\text{BEDT-TTF})_2\text{IBrCl} \) crystals with field of 10 kOe.

\[\beta'-(\text{BEDT-TTF})_2\text{ICl}_2\]

The crystal of \( \beta'-(\text{BEDT-TTF})_2\text{ICl}_2 \) has a modified structure of \( \beta-(\text{BEDT-TTF})_2\text{I}_3[16] \). The crystal is triclinic, \( \text{P}\bar{1} \), with \( a=12.937 \ \text{A}, b=9.778 \ \text{A}, c=6.636 \ \text{A}, \alpha=98.59^\circ, \beta=100.98^\circ, \gamma=87.19^\circ, V=814.6 \ \text{A}^3, Z=1[15] \). The centrosymmetric anion
(Cl-I-Cl)\(^-\) is on the origin of the unit cell. Although this structure is the same as the \(\beta-(BEDT-TTF)_2ICl_2\) reported by Emge et al.[14], we consider it more appropriate to distinguish it from the \(\beta\)-type. The structural change from \(\beta\) to \(\beta'\) indicates that the crystal cannot retain the \(\beta\)-type structure when the anion size becomes too small. Unlike \(\beta\)-type salt with 2D closed Fermi surface, \(\beta'-(BEDT-TTF)_2ICl_2\) has a 1D plane-like Fermi surface[15]. This difference comes from the large anisotropy of the intermolecular overlap integrals of the ICl\(_2\) salt, where the interaction is largest along [010]. Figure 5 shows the temperature dependence of the conductivity of \(\beta'-(BEDT-TTF)_2ICl_2\). Despite the band structure calculation and in contradiction with the previous report of ESR measurement[14], the temperature dependence of conductivity shows that it actually is a semiconductor with an activation energy of 0.12 eV. The room temperature conductivity is about 0.03 S/cm. The discrepancies are probably due to the effect of Coulomb interaction neglected in the calculation, and due to the poor predictability of metallic nature from the ESR measurements. We presently consider that this system is an example of Mott-Hubbard insulators.

Figure 6 shows the temperature dependence of the static magnetic susceptibility of many crystals of about 5 mg in total. Typical dimension of the crystals was 1x0.2x0.2 mm\(^3\). The magnetic susceptibility increases with decreasing temperature, shows a broad maximum around 120 K, and decreases again down to 20 K, where it shows an upturn characteristic to an antiferromagnetic phase transition. Absence of field dependence up to 50 kOe in the susceptibility at 6 K suggests that the

![Graph](image)

Fig. 5. Temperature dependence of electrical conductivity along the long side of a single crystal (the axis with 6.636 Å length) of \(\beta'-(BEDT-TTF)_2ICl_2\).

Fig. 6. Temperature dependence of static magnetic susceptibility of \(\beta'-(BEDT-TTF)_2ICl_2\) crystals with field perpendicular to the long side of crystals.
magnetic field is applied in a direction such that it is mostly perpendicular to the easy axis (presumably the long side of crystals, i.e., c-axis). These results, combined with the disappearance of the ESR signal accompanied with a sharp increase in the ESR linewidth below 20 K[12,14], gives a definite evidence for the nature of this magnetic phase transition at 20 K in \( \beta'-(\text{BEDT-TTF})_2\text{ICl}_2 \) as a transition to an antiferromagnetic ground state. Here again, we consider it inappropriate to call it a SDW state[14], since it is not a metal.

In summary, we have studied the temperature dependence of conductivity and static magnetic susceptibility of semiconducting \( \text{(BEDT-TTF)}_2 \) trihalides, and found various phase transitions accompanied with distinct change in the magnetic susceptibility, as well as anomalous temperature dependence of conductivity.

REFERENCES