New phase of (BEDT-TTF)(TCNQ)

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Abstract

A new phase of (BEDT-TTF)(TCNQ) has been obtained from a CH$_2$Cl$_2$ solution containing BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), TCNQ (tetracyanoquinodimethane), and tetraiodoethylene by slow evaporation of the solvent. The X-ray crystal structure analysis, electrical resistivity as well as ESR measurements, and tight-binding band calculation were performed on this phase. This phase shows metallic resistivity behaviour down to the lowest temperature with three anomalies around 170, 80 and 20 K. The ESR measurement suggests that the resistivity anomaly at 20 K is coupled with a magnetic ordering. The band calculation reveals that the Fermi surfaces have rectangular cross-sections.

Keywords: BEDT-TTF; TCNQ; Synthetic metal; Resistivity anomaly; Band calculation

1. Introduction

We have utilized iodine-containing neutral molecules as the third component of the conductive cation radical salts and formed supramolecular assemblies in those systems [1]. During our research on this multicomponent system, we have found another type of participation of the iodine-containing molecule in the process of crystal formation. That is a catalytic effect of tetraiodoethylene (TIE), and we obtained a new phase of (BEDT-TTF)(TCNQ) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; TCNQ = tetracyanoquinodimethane). As for (BEDT-TTF)(TCNQ), two different polymorphs were reported and their conducting properties are basically semiconductive below room temperature [2–5]. The third new phase, on the other hand, exhibits metallic character down to the lowest temperature. Here we report the preparation, crystal structure, resistivity, and ESR study on this new phase of (BEDT-TTF)(TCNQ).

2. Experiment

A CH$_2$Cl$_2$ (or CH$_2$Br$_2$) solution (20 ml) of BEDT-TTF (40 mg), TCNQ (40 mg), and TIE (500 mg) was placed at room temperature, and the solvent was allowed to evaporate slowly to dryness within 24 h. Several black elongated plates branched out from a single crystal of TIE. The crystallographic parameters are: triclinic, $P - 1$, $Z = 1$, $a = 7.118(2)$ Å, $b = 20.323(8)$ Å, $c = 4.105$ Å, $\alpha = 92.10(3)^\circ$, $\beta = 90.79(2)^\circ$, $\gamma = 84.72(3)^\circ$, $V = 590.8(3)$ Å$^3$, $R = 0.052$. The resistivity of the salt was measured by the standard four-probe method. The ESR signals were recorded on JES-A300 of JEOL and analyzed assuming Lorentzean shape of the absorption peak.

3. Results

The crystal structure of the salt is shown in Fig. 1. The unit cell contains only one BEDT-TTF and one TCNQ molecule, both of which are located on the inversion centers. The donor and acceptor molecules form separate layers parallel to the $ac$ plane. The donor molecules form pseudo-stack arrangement so-called the $\beta'_{00}$-type, while the acceptor layer is composed of parallelly aligned one-dimensional (1D) columns. A short H(BEDT-TTF)···N(TCNQ) contact (2.57 Å), indicated as a dotted line in Fig. 1, is observed between the donor and acceptor. The transferred charge from BEDT-TTF to TCNQ is estimated to be about 0.74e by the bond lengths analysis for the donor molecule [6]. The resistivity data exhibit metallic temperature dependence with three anomalies at 170, 80, and 20 K as shown in Fig. 2. The behaviour is somewhat dependent on the current direction. The results of the ESR measurement show an abrupt increase of the peak width and drop of spin susceptibility at 20 K.
4. Discussion

Although the detail of the crystal formation process is not clear as yet, TIE has a certain role in the formation of this new phase of (BEDT-TTF)(TCNQ). Without TIE, only the two phases reported in the literature are formed. In the presence of TIE, on the other hand, the crystals of the new phase grow on the TIE crystals. Several crystals are often formed on a single crystal of TIE, while the crystal of the new phase contacts only one TIE crystal. We therefore consider that the TIE crystals provide nuclei for the crystal formation. Because iodine atoms covalently bonded on the carbon atoms are known to interact with electronegative nitrogen atoms, it is plausible that the iodine atoms on the surface of the TIE crystal work as template for the new phase of (BEDT-TTF)(TCNQ) by anchoring the terminal nitrogen atoms of TCNQ in the initial stage of the crystal formation.

The tight-binding band calculation was performed on the basis of extended Hückel MO calculation. The overlap integrals between frontier orbitals ($S/10^{-3}$) are: $S_a = -8.29$; $S_c = -1.32$; $S_p = 1.16$; $S_d = 0.12$; $S_{ad} = 12.45$; $S_{pt} = 0.05$ (the intermolecular relations are designated in Fig. 1). The overlaps between the donor and the acceptor range from 0.1 to $0.2 \times 10^{-3}$. In the acceptor layer, the interaction in the stacking direction ($c$-axis) is dominant. In the donor layer, on the other hand, only weak overlap integral is observed in the pseudo-stacking direction. The interaction along the $a$-axis is dominant instead ($S_a = -8.29$). As a result, the Fermi surfaces associated with TCNQ layer are a pair of parallel planes normal to the $c$-axis, and those for BEDT-TTF layer are normal to the $a$'-axis. When the weak interactions between donor and acceptor are taken into account, however, the degeneracy at the crossing points is removed and rectangular Fermi surfaces are obtained as shown in Fig. 2.

The resistivity anomalies at 80 and 20 K may be explained on the basis of this band calculation. The strong 1D character of Fermi surfaces associated with the donor or acceptor layers tends to cause partial nesting of the Fermi surfaces and an increase of resistance parallel to the nesting vector. This seems to be the case of these two anomalies where the steep resistivity increases are observed along the $c$-axis (at 80 K) and the $a$-axis (at 20 K). Further discussion, however, needs other data such as low temperature X-ray diffraction. Below 20 K, 2D or 3D small Fermi surfaces originating from the round corners of the rectangular Fermi surfaces remain and maintain the stable metallic character. The ESR
measurement suggests that the resistivity anomaly at 20 K is coupled with a magnetic ordering. The higher resistivity along the $a$-axis compared to that along the $c$-axis can also be explained as the difference in overlap integrals; the overlap integral along the acceptor stack ($S_{ct}$) is 1.5 times larger than the side-by-side interaction in the donor layer ($S_{sa}$).

5. Conclusion

New phase of (BEDT-TTF)(TCNQ) was obtained by the use of TIE as a catalyst. This salt exhibited metallic resistivity behavior down to the lowest temperature with anomalies around 170, 80, and 20 K. Band calculation revealed Fermi surfaces with rectangular cross-sections.

References