Electrical Properties of an Organic Conductor, β'- (BEDT-TTF)$_2$ICl$_2$ up to 10 GPa

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Four-probe resistivity measurements were made on an organic semiconductor, β'-(BEDT-TTF)$_2$ICl$_2$ up to 10 GPa by using a diamond anvil high-pressure cell. The activation energy was decreased with increasing pressure and the metallic phase appeared around 8 GPa. When the pressure was kept around 10 GPa, the resistivity was gradually increased with time, indicating an irreversible pressure-induced solid state transformation.

The discovery of an organic superconductor, β-(BEDT-TTF)$_2$I$_3$ in 1984[1] aroused a large interest not only because the organic superconductor was very rare material at that time but also because the tight-binding band calculation on this system gave a two-dimensional large cylindrical Fermi surface (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene).[2,3] Soon after this discovery, an analogous conductor with smaller anions, (BEDT-TTF)$_2$ICl$_2$ was found to be polymorphic (β, β').[4,5] The simple tight-binding band calculation suggested that β'-(BEDT-TTF)$_2$ICl$_2$ with the modified β-type structure has an effectively half-filled narrow band owing to the strong dimeric nature of BEDT-TTF stacks, which is consistent with the semiconducting nature of the system.[3,4] The expected antiferromagnetic insulating ground state, characteristic of the highly correlated electron system has been found out afterward.[6,7] It is well known that the antiferromagnetic insulating phase (or spin density wave phase) of the first organic superconductor (TMTSF)$_2$PF$_6$ transforms to superconducting phase at high pressure.[8] Similarly, the antiferromagnetic insulating phase of κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Cl, which retains the highest T_c-record of organic superconductor since 1990, transforms to the superconducting phase by applying very soft pressure.[9] Therefore, the existence of the superconducting phase in β-(BEDT-TTF)$_2$I$_3$ and the antiferromagnetic insulating phase in β'-(BEDT-TTF)$_2$ICl$_2$ tempted us to examine the electrical properties of β'-(BEDT-TTF)$_2$ICl$_2$ at high pressure.

It is frequently observed that the high-pressure electronic properties of organic conductor (D$_2$X) resemble the ambient-pressure properties of analogous conductor (D$_2$X') with smaller anions (X > X')("chemical pressure effect").[10] From this viewpoint, the electronic state of β'-(BEDT-TTF)$_2$ICl$_2$ might correspond to the high-pressure state of β-(BEDT-TTF)$_2$I$_3$. On the other hand, considering the fact that the pressure tends to change a semiconductor into a metal and the existence of metallic modification [β-(BEDT-TTF)$_2$ICl$_2$],[5] it is difficult to foresee what pressure effect is realized in β'-(BEDT-TTF)$_2$ICl$_2$.

It is well known that the usual clamp-type high-pressure cell can be used for the resistivity measurement up to ca. 2 GPa. Since the preliminary high-pressure experiments showed that a fairly high pressure is required to examine the possibility of the pressure-induced transition in β'-(BEDT-TTF)$_2$ICl$_2$, we adopted a diamond anvil high-pressure cell. Despite that the resistivity measurements by the diamond anvil high-pressure technique have contributed to disclose many remarkable physical properties of various substances even above 100 GPa,[11] the technique of the resistivity measurements at extremely high-pressure is not applicable to the accurate measurement on the single crystal sample. Although the single crystal four-probe resistivity measurements can be performed up to 8 GPa by using the multi-anvil high-pressure apparatus,[12] more convenient high-pressure apparatus will be desirable. So far, many efforts have been paid to establish the method of diamond-anvil resistivity measurement.[13] We have recently succeeded to perform the resistivity measurements of β'-(BEDT-TTF)$_2$ICl$_2$ up to 10 GPa. To our knowledge, this is the first report on the four-probe resistivity measurement on single organic crystal above 8 GPa and down to 4 K.

Black needle crystals of β'-(BEDT-TTF)$_2$ICl$_2$ were prepared electrochemically. Typical size of the crystals used was *ca.* 0.28 x 0.08 x 0.04 mm^3 (Figure 1). Annealed gold wires (5 or 10 μφ) were bonded to the crystal by gold paint. The four leads were set in the four ditches engraved in the surface of metal gasket (Figure 1). Alumina and epoxy resin were used to keep the insulation between the leads and gasket. Mixed silicon oil was used as a pressure medium.[13] The applied pressure was determined by the standard ruby fluorescence method. The detailed procedure will be reported elsewhere.[14]

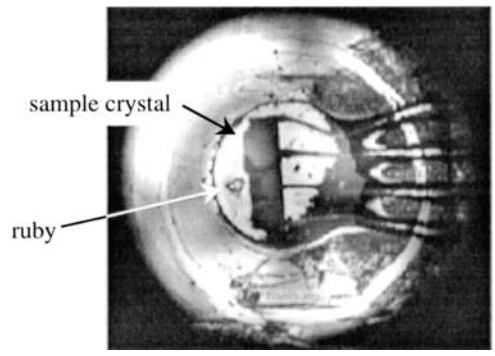

Figure 1. A crystal of β'-(BEDT-TTF)$_2$ICl$_2$ put in the hole of metal gasket (at 10.2 GPa).

As shown in Figures 2 and 3, the sufficiently accurate resistivity data comparable to those obtained by usual clamp-type cell were obtained up to ca. 10 GPa. At first, we imagined that the semiconducting state of β'-(BEDT-TTF)$_2$ICl$_2$ can be easily changed into the metallic state. However, to our amazement, the semiconducting state persisted up to about 7 GPa despite of the 2:1 stoichiometry of the complex. The inset of Figure 2 shows the pressure dependence of the activation energy determined at the temperature range of 300-150 K, which

decreases to zero around 7 GPa. The resistivity at 8.3 GPa showed the metallic behavior down to ca. 80 K. The room temperature resistivity was decreased to 10^{-2} Ω cm, which is about three orders of magnitude smaller than that at ambient pressure

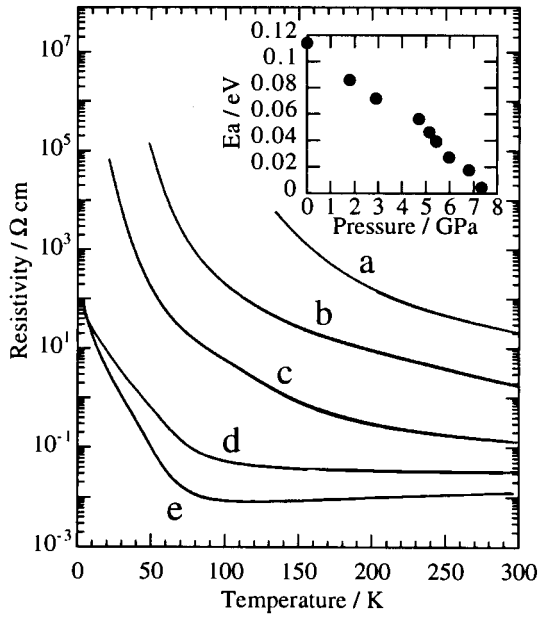

Figure 2. Resistivities of β'-(BEDT-TTF)$_2$ICl$_2$ up to 8.3 GPa. The inset shows the activation energy determined at 300-150 K. a:1 bar; b:2.9 GPa; c:5.1 GPa; d:7.3 GPa; e:8.3 GPa.

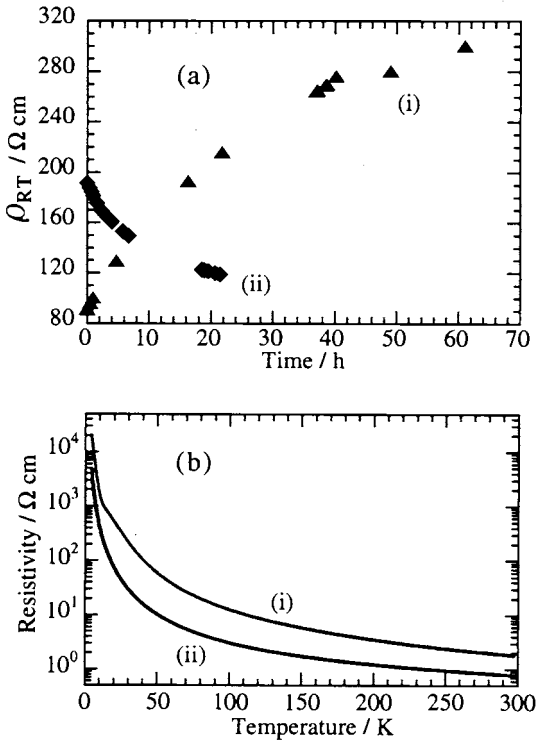

Figure 3. The time-dependence of the room-temperature resistivity (ρ_{RT}) (a) and the temperature dependence of the resistivity (b) at 10.4 GPa (i) and 8.1 GPa (ii) (ii: measured after decreasing pressure from 10.4 GPa).

(≈ 20 Ω cm). A metal-insulator transition (T_{MI}≈ 60 K) indicates that low-dimensional metal instability remains even at 8 GPa. These results show that the phase diagram of β'-salt is completely different from that of β-salt.

Anomalous resistivity behavior was observed when the pressure was increased up to 10.4 GPa. Although the pressure was kept constant at room temperature, the resistivity increased with time. At first, we suspected some accident such as crack of the crystal or trouble in the leads. But any accidental situation could not be detected by the close microscope observation (see Figure 1) and the resistivity satisfied completely an ohmic relation. After keeping the crystal for 60 h at room temperature, the resistivity measurement was made (Figure 3). The room-temperature resistivity was more than 10^4 larger than that at 8.3 GPa. The measurements took about 6 h including cooling and heating processes. A semiconducting behavior was observed throughout the temperature range (E ≈ 0.03 eV). The gradual increase of the resistivity suggests the occurrence of some solid state transformation. If some solid state reaction takes place, the metallic properties will not be restored by decreasing pressure. To confirm this, the pressure was lowered down to 8.1 GPa and the resistivity was measured after keeping the crystal for 24 h. As was expected, the semiconducting behavior was observed. The partial recovery of the resistivity suggests that the (irreversible) solid state transformation around 10 GPa had not been completed (see Figure 3).

In summary, we have performed the four-probe resistivity measurements of organic semiconductor, β'-(BEDT-TTF)$_2$ICl$_2$. Around 8 GPa, the metallic phase was stabilized down to about 80 K. Around 10 GPa, the resistivity increased with time and the system became semiconducting. It becomes clear that β'-(BEDT-TTF)$_2$ICl$_2$ with an antiferromagnetic ground state at ambient pressure has not a superconducting phase at any pressure region.

References and Notes

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