Electrical Properties of the Organic Conductor, $(BEDT\text{-}TTF)_3(ClO_4)_2$

Kenichi Imaeda,* Toshiaki Enoki,† Gunzi Saito,†† and Hiroo Inokuchi
Institute for Molecular Science, Okazaki 444
††The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106

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Synopsis. Electrical conductivity and thermoelectric power have been measured for $(BEDT\text{-}TTF)_3(ClO_4)_2$. The electrical conduction is two-dimensional in the bc plane. The metal–insulator transition temperature is lowered by pressure at a rate of $-8\,K\,kbar^{-1}$. The negligible thermopower at high-temperatures indicates that $(BEDT\text{-}TTF)_3(ClO_4)_2$ is the system with large on-site Coulomb repulsion.

Since our presentation on a two-dimensional metallic conductivity for $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene),[1] BEDT-TTF radical salts have been actively investigated because they show a polymorphism and novel electronic properties due to the thermal vibrations of the ethylene groups. Interestingly, β-$(BEDT\text{-}TTF)_2I_3$ became a superconductor near 8 K.[2,3] Recently, Urayama et al. found a superconductivity at 10.4 K under ambient pressure in $(BEDT\text{-}TTF)_2Cu(NCS)_2$.[4] This transition temperature is the highest among organic superconductors hitherto known.

There are two crystalline phases in (BEDT-TTF)-ClO_4 salts, $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ and $(BEDT\text{-}TTF)_3(ClO_4)_2$. The former remaines metallic down to 0.8 K for a rapid cooling, while it shows a nesting transition at 25 K for a slow cooling, which is associated with the ordering of the $C_2H_3Cl_3$ molecules.[5,6] On the other hand, the latter shows a metal–insulator transition around 170 K.[7] As to $(BEDT\text{-}TTF)_3(ClO_4)_2$, the structural analysis presents that the BEDT-TTF molecules form a two-dimensional network with the face-to-face stacks along the $[0\bar{1}1]$ direction and the side-by-side arrangements along not only the [012] direction but also the [021] direction.[7,8] The band calculation suggests the semimetallic band structure and the two-dimensional intermolecular interactions with a small anisotropy of transfer integral ($t[012]/t[021]\approx 3$).[8] The polarized reflectance measurement gives the two-dimensional optical spectra.[9] ESR studies also suggest the two-dimensionality with large linewidth.[5] In this note, we report the experimental results of the anisotropy and pressure effect of electrical conductivity, and thermoelectric power for $(BEDT\text{-}TTF)_3(ClO_4)_2$.

Experimental

The black thin plate crystals of $(BEDT\text{-}TTF)_3(ClO_4)_2$ were prepared in $C_2H_3Cl_3$ solvent by a standard electrochemical technique. The anisotropy of electrical conductivity in the bc plane (see Ref. 7 for the definition of the crystal axes) was measured with a Montgomery method. Electrical conductivity under pressure up to 10 kbar along the c-axis was measured by a four-probe method in a BeCu clamp cell using Idemitsu Daphne oil #7373 as a pressure medium liquid. The pressure at room temperature was monitored with a manganin sensor. Thermoelectric power along the c-axis was measured with the method described by Chaikin and Kwak.[10]

Results and Discussion

Figure 1 shows the result of the anisotropy of the resistivity. The small anisotropy ($\rho_b/\rho_c\approx 2$) at room temperature means that electrical conduction is two-dimensional in the bc plane, which is consistent with the results of X-ray analysis, band calculation, optical and ESR experiments. ρ_b/ρ_c is entirely independent of temperature in the metallic region. Below the metal–insulator (M–I) transition at 172 K, ρ_b/ρ_c increases gradually and then increases abruptly below 110 K. The ESR study has presented that the g-value for the applied field parallel to the b′-axis changes from 2.002 to 2.006 below the metal–insulator transition temperature (T_{MI}).[5] The shift of $g_{b'}$ suggests the displacement of the BEDT-TTF molecules. Therefore, the increase of ρ_b below T_{MI} is considered to be associated with such a displacement unfavorable for electron transport along the b direction.

Figure 2 shows the result of the thermoelectric power S. The value of S is almost zero in the high-temperature region. Then, S falls off sharply below 172 K. The thermopower for intrinsic semiconductors depends on temperature with the relation of $S\propto -(k/|e|)((b-1)/(b+1))(E_g/2kT)$, where b is mobility ratio μ_e/μ_h between electron and hole carriers and E_g is

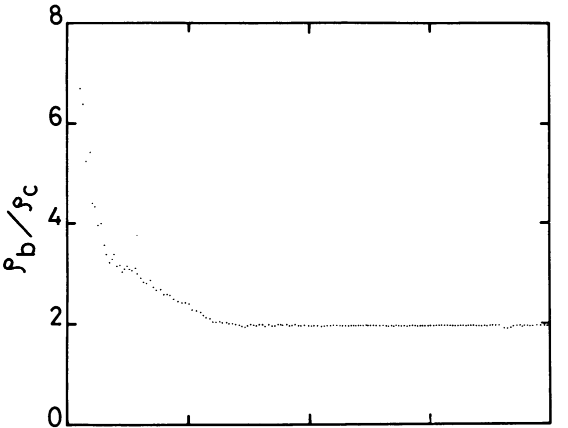

Fig. 1. Temperature dependence of the anisotropy ρ_b/ρ_c of the resistivity.

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† Present address: Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152.

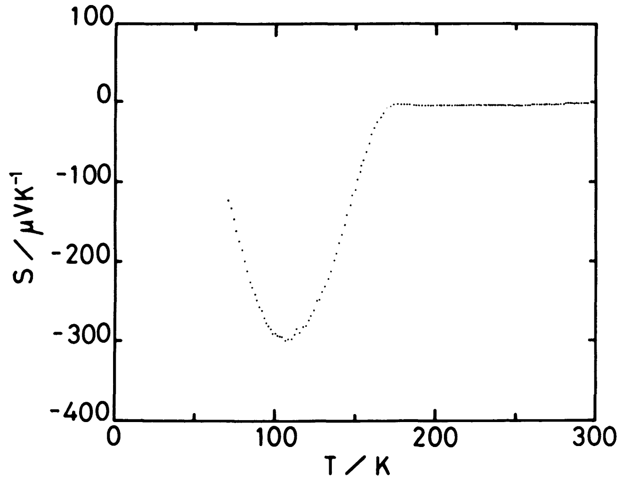

Fig. 2. Temperature dependence of the thermoelectric power.

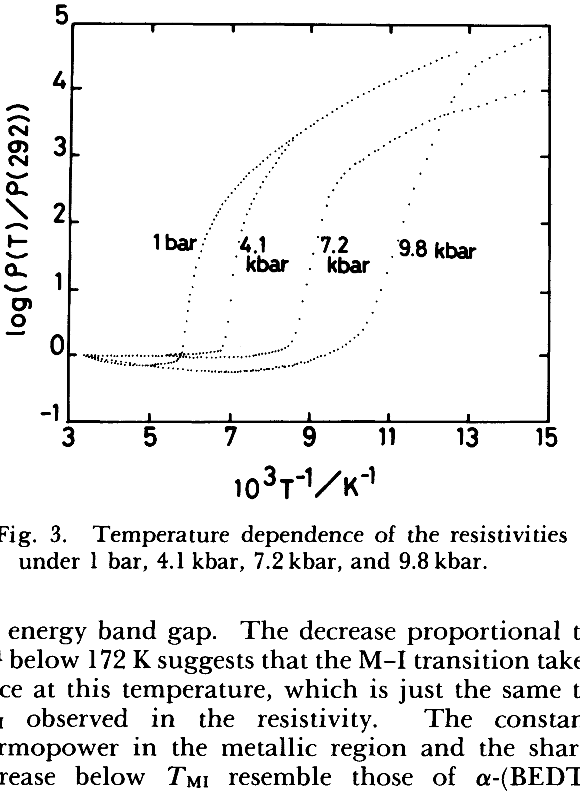

Fig. 3. Temperature dependence of the resistivities under 1 bar, 4.1 kbar, 7.2 kbar, and 9.8 kbar.

the energy band gap. The decrease proportional to T^{-1} below 172 K suggests that the M–I transition takes place at this temperature, which is just the same to T_{MI} observed in the resistivity. The constant thermopower in the metallic region and the sharp decrease below T_{MI} resemble those of α-(BEDT-TTF)$_2$I$_3$[11] and (BEDT-TTF)$_2$PF$_6$.[12] In the semiconducting region, S shows a minimum around 110 K with a large value of −300 μV K^{-1} and increases again with lowering temperature. The sign of the slope in the plot between S and T^{-1} depends on the magnitude of b (μ_e/μ_h). The negative slope above 110 K means that $b>1$, namely $\mu_e>\mu_h$, while the positive slope below 110 K means $\mu_e<\mu_h$. Therefore, the anomaly at 110 K, which corresponds to the temperature with a rapid increase in the anisotropy ρ_b/ρ_c, is considered to be caused by a some modulation in the electronic structure associated with the change in the magnitude of the mobility between electron and hole carriers.

Next, we present the result of the pressure effect on the M–I transition. Figure 3 shows the temperature dependence of the resistivities under several pressures. As the different samples are employed due to thin fragile crystals, the resistivity behaviors in the metallic region are somewhat different for each pressure. The M–I transition is suppressed as the pressure is increased. T_{MI} was determined to be the temperature with the maximum of $-\mathrm{d}\log\rho/\mathrm{d}T$. Figure 4 shows the correlation between T_{MI} and pressure. T_{MI} is lowered linearly with pressure at a rate of −8 K kbar^{-1}. This rate is approximately the same as those of other BEDT-TTF salts; $\mathrm{d}T_{\mathrm{MI}}/\mathrm{d}P=-10$ K kbar^{-1} for (BEDT-TTF)$_2$ReO$_4$[13] and −11 K kbar^{-1} for α-(BEDT-TTF)$_2$-I$_3$.[14] (BEDT-TTF)$_3$(ClO$_4$)$_2$ is expected to become a metal above ca. 22 kbar corresponding to the pressure at which T_{MI} is extrapolated to zero.

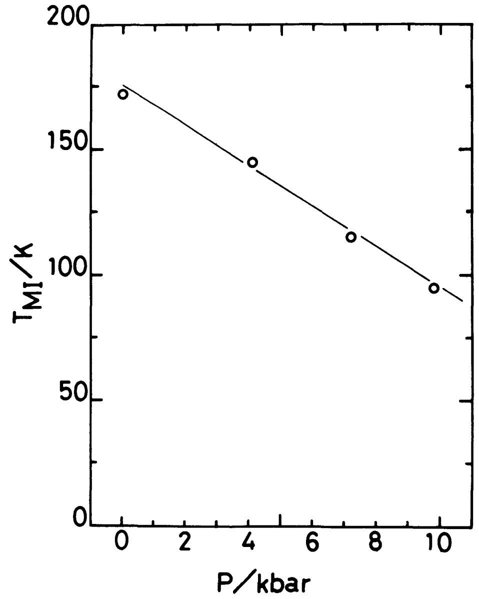

Fig. 4. Pressure dependence of the metal-insulator transition temperature (T_{MI}). The solid line corresponds to $\mathrm{d}T_{\mathrm{MI}}/\mathrm{d}P=-8$ K kbar^{-1}.

Finally, we mention the evidence of strong on-site Coulomb repulsion in the (BEDT-TTF)$_3$(ClO$_4$)$_2$ system. The thermopower in the high-temperature limit for a system with a strong on-site Coulomb repulsion U can be given by the following equation, according to the statistical-mechanical treatment by Chaikin and Beni;[15]

$$S = -\frac{k}{|e|}\ln\left(2(1-\gamma)/\gamma\right),$$

where γ is the degree of charge transfer. We obtain $S=0$ from the above equation using $\gamma=2/3$. The complete agreement of the magnitude of S with the experimental result suggests the importance of electron–electron Coulomb interactions in the present system. This fact is in good accordance with the result by Parkin et al.[16] They have reported that the spin susceptibility of (BEDT-TTF)$_3$(ClO$_4$)$_2$ is enhanced by Coulomb interactions beyond the Pauli paramagnetism expected for noninteracting electrons with $4t_{/\!/}=0.75$ eV and U is estimated to be 3—4 eV according to the formalism presented by Torrance et al. for

$U \gg 4t$.[17)]

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