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A NOVEL BEHAVIOR OF ELECTRICAL RESISTIVITY IN A NEW TWO-DIMENSIONAL ORGANIC METAL, $(BEDT\text{-}TTF)_2ClO_4(1,1,2\text{-}TRICHLOROETHANE)_{0.5}$

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An unusual temperature dependence of the resistivity along the least conductive axis of a new two-dimensional organic metal, $(BEDT\text{-}TTF)_2ClO_4(1,1,2\text{-trichloroethane})_{0.5}$, is presented and discussed in terms of the crystal structure.

The organic cation radical salt, [bis(ethylenedithiolo)tetrathiafulvalene(abbreviated to BEDT-TTF, Fig.1)]$_2ClO_4$[1,1,2-trichloroethane(TCE)]$_{0.5}$, is the first organic metal which exhibits two-dimensional(2D) transport property($\rho_\perp : \rho_\parallel : \rho_b = 1 : 1\sim 2 : 10^2 \sim 10^3$, where $\rho_\perp$ is along the elongated direction of a leaf-like crystal and $\rho_\parallel$ is normal to it in the a-c plane and is nearly parallel to the stacking axis). Moreover, a remarkable suppression of a metal to semiconductor(MS) transition is achieved and a quasi-metallic character is observed down to 1.4K, i.e. $\rho_\perp$ for a best sample decreases monotonically from $3.8\times10^{-2}\,\Omega$cm at room temperature to minimum($1.0\times10^{-3}\,\Omega$cm) at 16K, then increases very gradually to $1.5\times10^{-3}\,\Omega$cm at 1.4K.$^{1)}$

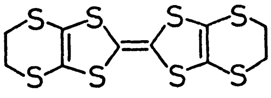
Fig.1. BEDT-TTF

In the crystal, BEDT-TTF molecules are stacked along the c axis with zig-zag configuration and the stacks are making an array along the a axis(Fig.2).$^{2)}$ The S-S distances between the neighboring BEDT-TTF's are considerably shorter than the van der Waals radius(3.7Å) as is indicated as $\gtrsim$ 3.34Å along the interstack direction(a axis) and $\gtrsim$ 3.58Å along the intrastack direction(c axis). As compared with those, the closest S-S intrastack distance in $(TMTTF)_2Br$, which has been claimed to be an organic 'high pressure' superconductor, is considerably big, 3.7Å.$^{3)}$

In this letter we report a unique behavior of the temperature dependence of the electrical resistivity of the BEDT-TTF salt. The resistivity of single crystals was measured along the elongated axis($\sim$a axis) between 300K and 1.4K by a four probe method. The crystals from the same batch of the best sample were used and they were apt to show several minor resistivity jumps due to the thermally produced microfissures between 260K and 40K. In Fig.3 errors caused by these small jumps are smoothed for rectification then the resistivities are normalized at 1.4K. Figure 3-1-a represents the observed resistivity thus modified(ρ_{obsd}) on the first cooling, where several resistivity jumps into less conductive states were noticed below 200K. Between 300K and 100K, ρ_{obsd} follows approximately T^1 instead of T^2 dependence observed for the best sample which was free from the microfissures(Fig.3-1-b). Below 100K this sample exhibits resistivity minimum at 15K which is well compared with the best one. This fact indicates that a Peierls distortion which shows resistivity minimum above 30K in usual organic metals is suppressed in this salt whether it has microfissures or not.[4)] The suppression of a Peierls distortion may be an important factor for the purpose of designing new organic metals leading to superconductors. Below 15K the resistivity increases gradually and the increase seems to be an activated process where the estimated activation energy(0.41K) is less than kT. This apparent activation energy is too small to be considered as that for the semiconduction.

On heating(Fig.3-2) the aspect between 50K and 250K changes drastically, whereas the behavior at lower temperatures is unchanged except slight broadening of the minimum. There is a rapid increase of resistivity above 50K and a huge hump appeared with a maximum around 180K. Then ρ_{obsd} seems to return to the initial state above 260K. On this heating process, resistivity jumps only into more conductive states were observed a few times between 230K and 250K(see insert, Fig.3-2). These jumps may indicate the recovery of the current channels along the elongated axis.

Figure 3-3 shows the second cooling process in which the jumps into less conductive states were seen again below 200K frequently. There is a small bump at around 180K which was not seen in Fig.3-1-a but is reminiscent of the maximum in Fig.3-2. This is suggestive that enough number of microfissures are generated to reveal the resistivity maximum hidden in the case of the first cooling. Below 50K the feature is almost the same as that observed in Fig.3-2. The second heating process(Fig.3-4) reproduces that observed in the first one(Fig.3-2) roughly.

A microscopic investigation of the samples after the resistivity measurements shows several small microfissures on the a-c crystal surface, but does not show any big cracks which might destroy the electrical contacts. The generation of microfissures and/or a possible incorrect alignment of the electrical contacts pick up the transport properties along the less conductive directions. Therefore we can conclude that ρ_{obsd} in Fig.3 includes not only $\rho_{\perp}$ but also $\rho_{\parallel}$ and ρ_b.

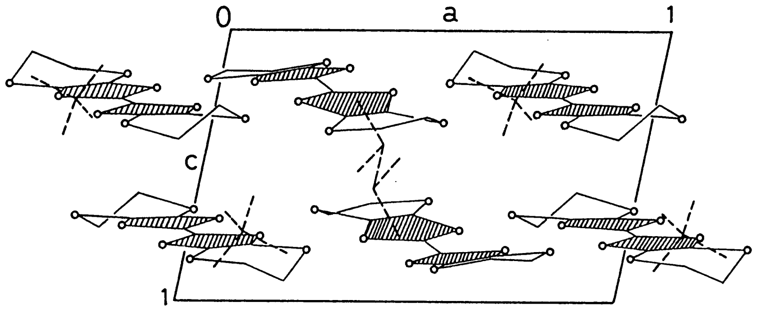

Fig.2. Preliminary result of crystal structure of $(\mathrm{BEDT\text{-}TTF})_2\mathrm{ClO}_4\mathrm{TCE}_{0.5}$:projection along the b-axis.[2)] TTF moieties in BEDT-TTF are hatched and sulfur atoms are indicated by open circles. Below and above the sheet of BEDT-TTF on the a-c plane, the ClO_4 ions and TCE's(both indicated by broken lines) are making sheets(only one of them is depicted). There are four indistinguishable positions for the chlorine atoms of TCE. The ClO_4 ions, TCE's, and the methylenes of BEDT-TTF are disordered.

Generally the inclusion of the resistivity along the less conductive directions does not change the total aspect of the temperature dependence of a one-dimensional organic metal drastically. However, Jacobsen et al.[5)] have found a resistivity maximum around 80K in addition to an MS transition due to SDW at ca.20K in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ along the axis perpendicular to sheets of TMTSF stacks(the least conductive direction), but the former anomaly was absent in the temperature dependence of the resistivity along the other directions completely. Moreover, it has been known that thermally produced microcracks have big effects on the resistivity behaviors of the 'zero pressure' superconductor, $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, such as masking transport anomaly just above the superconducting transition or broadening the transition.[4)] Consequently the electrical resistivities along the stacking(or the most conductive direction) will be considerably influenced by the inclusion of the properties along less conductive directions or by the formation of a small number of microcracks in some cases. An unusual behavior of the resistivity as a result of the generation of microfissures in Fig.3 can deduce the real temperature dependence along the least conductive direction from the following considerations.

It is found that both $\rho_\perp$ and $\rho_\parallel$ do not exhibit any anomaly down to 3K except the faint minimum at around 16K.[1)] This fact leads to the consequence that the queer behavior of ρ_{obsd} is attributable mainly to the inclusion of ρ_b component. Considering the fact that ρ_b is $10^2\sim10^3$ times bigger than the other components, the inclusion of ρ_b may be extremely small, but has big effects on the behavior of the observed temperature dependence. The actual temperature dependence of ρ_b is strongly reflected in ρ_{obsd} of Fig.3-2 below 230K, since in this temperature range there was no generation of new microfissures nor recovery of the current channels in this heating process. While, the metallic behavior between 250K and 300K in Fig. 3-2 may be mainly ascribed to the behavior of $\rho_\perp$ because of the recovery of the current channels, so we can deduce ρ_b is in semiconductive region down to 180K then a metallic region down to ca.15K followed by a gradual increase down to 1.4K.

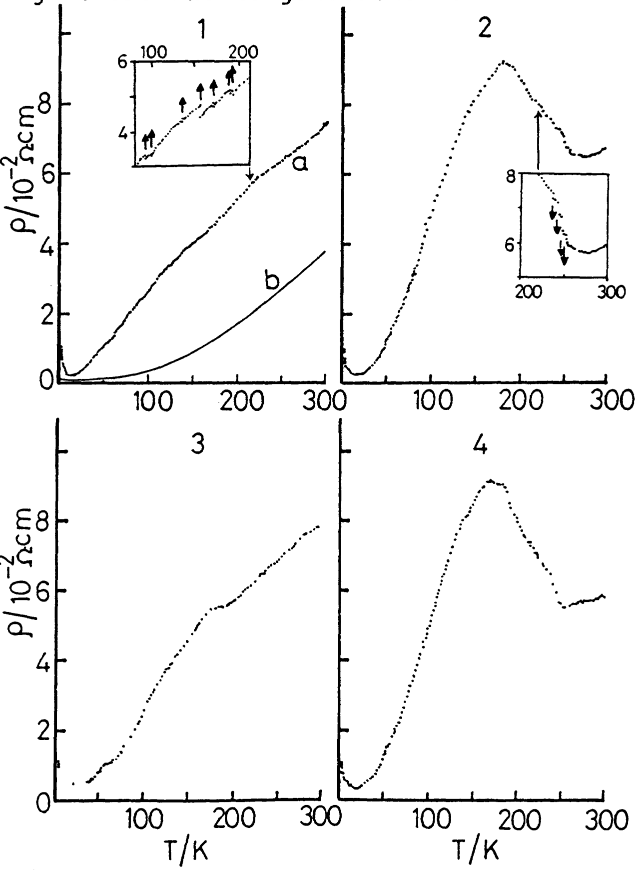

Fig.3. Hysteresis of the temperature dependence of ρ_{obsd} of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$: 1-a) the first cooling, 2) the first heating, 3) the second cooling, and 4) the second heating process. The inserts are the observed resistivity before the rectification and arrows indicate the resistance jump. Curve 1-b) represents $\rho_\perp$ of the best sample (microfissure free) after Ref.1.

The feature of ρ_b is quite abnormal but is not an unknown phenomenon. To our knowledge, this kind of extraordinary temperature dependence has been reported for five organic metals out of more than one hundred fifty already in hand. Only one of those is two column system; highly conductive charge-transfer complex, TMTSF·2,5-dimethylTCNQ, at high pressure.[6)] A cation radical salt, $TTF(BF_4)_{0.55}$, is another example to show double MS transitions at 341K and 180K.[7)] The aforementioned salt, $(TMTSF)_2PF_6$, also belongs to those. Very recently structural phase transitions corresponding to order-disorder(o-d) transitions involving the counter anions were found in $(TMTSF)_2X$; $X=NO_3$ and ReO_4.[8)] These o-d transitions were characterized by anomalous conductivity changes at or below these transition temperatures (T_{o-d}).[9-11)] $(TMTSF)_2NO_3$ at 6.5kbar exhibits double MS transitions with one at ca.40K(T_{o-d}) and the other maybe due to SDW below 10K.[10)] On the other hand, $(TMTSF)_2ReO_4$ at ca.11kbar shows an MS transition at ca.80K(T_{o-d}) then a metallic behavior takes place down to 1K, where this salt falls into superconducting state.[11)]

The resultant behavior of ρ_b can be understood in terms of the crystal structure. The b axis is nearly perpendicular to the electrically 2D a-c plane(the angle between b and b^* is 21.7°). Along this direction, each sheet of the donor molecules is separated from the next one by intervening a sheet composed of ClO_4 ions and TCE molecules (Fig.2). In the latter sheet, these anions and molecules are disordered with large thermal motion at room temperature. Therefore a charge carrier going this direction must hop from a donor sheet to the next donor sheet via the barrier producing insulating sheet. Furthermore, as the long molecular axis of BEDT-TTF is parallel(but not precisely, tilted ca.22°) to the b axis, a charge carrier also feels a barrier produced by the thermal motion of the methylenes of BEDT-TTF. As a result, activated hopping process dominates in the semiconductive region down to 180K. Then a metallic behavior takes place indicating a transition around 180K. This transition may be caused by an ordering and/or freezing of motion of the counter ions or TCE molecules. Other possibility is a stop of vibration of the methylenes of BEDT-TTF. The existence of only one maximum suggests that these barrier extinguishing changes occur cooperatively. These changes reduce the scattering process and increase the carrier mobility, so that ρ_b will result in a metallic behavior. The reason why the anomaly at 180K is not observed on $\rho_\perp$ and $\rho_\parallel$ may be that the nonperiodicity produced by disorderness of ClO_4, TCE, or the methylenes of BEDT-TTF does not affect strongly enough the electronic state in the electronically 2D sheet along the a-c plane. We expect that this kind of anomaly is rather common in organic metals of one column system with components of low symmetry.

References

1) G.Saito, T.Enoki, K.Toriumi, and H.Inokuchi, Solid State Commun., 42,557(1982). $\rho_\perp$ and $\rho_\parallel$ in this reference are corresponding to $\rho_\parallel$ and $\rho_\perp$ in the text, respectively.

2) H.Kobayashi, A.Kobayashi, G.Saito, T.Enoki, and H.Inokuchi, unpublished results.

3) S.Flandrois, C.Coulon, P.Delhaes, D.Chasseau, C.Hauw, J.Gaultier, J.M.Fabre, and L.Giral, Mol. Cryst. Liq. Cryst., 79, 307(1982).

4) K.Murata, T.Ukachi, H.Anzai, G.Saito, K.Kajimura, and T.Ishiguro, J. Phys. Soc. Japan, 51, 1817(1982).

5) C.S.Jacobsen, K.Mortensen, M.Weger, and K.Bechgaard, Solid State Commun., 38, 423(1981).

6) A.Andrieux, P.M.Chaikin, C.Duroure, D.Jerome, C.Weyl, K.Bechgaard, and J.R.Andersen, J. Physique, 40, 1199(1979).

7) P.Kathirgamanathan, S.A.Mucklejohn, and D.R.Rosseinsky, J. Chem. Soc.Chem. Commun., 1979, 86.

8) J.P.Pouget, R.Moret, R.Comes, and K.Bechgaard, J. Physique Lett., 42, L543(1981), J.P.Pouget, R.Moret, R.Comes, K.Bechgaard, J.M.Fabre, and L.Giral, Mol. Cryst. Liq. Cryst., 79, 129(1982), and C.S.Jacobsen, H.J.Pedersen, K.Mortensen, G.Rindorf, N.Thorup, J.B.Torrance, and K.Bechgaard, J. Phys. C: Solid State Phys., 15, 2751 (1982).

9) S.S.P.Parkin, M.Ribault, D.Jerome, and K.Bechgaard, J. Phys. C: Solid State Phys., 14, 5305(1981).

10) C.Coulon, P.Delhaes, S.Flandrois, R.Lagnier, E.Boujour, and J.M.Fabre, to be published, and A.Mazaud, Thesis University of Paris-Sud(1981) unpublished, through references 8 and D.Jerome, Mol. Cryst. Liq. Cryst., 79, 155(1982).

11) S.S.P.Parkin, D.Jerome, and K.Bechgaard, Mol. Cryst. Liq. Cryst., 79, 213(1982).

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