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Superconducting and Normal State Properties of Organic Metals (BEDT-TTF)$_2$X

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Recent progress in the superconducting and normal state properties of BEDT-TTF based organic metals, including β-(BEDT-TTF)$_2$X and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, are presented. In addition to the low- and high-T_c states, with T_c=1 K and 8 K, respectively, a new superconducting state with T_c=2 K was found in β-(BEDT-TTF)$_2$I$_3$. DC Hall effect of the low-T_c state of β-(BEDT-TTF)$_2$I$_3$ has been studied. Tunneling spectroscopy on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals by a low-temperature scanning tunneling microscope (STM) is reported. In addition to the Shubnikov-de Haas and de Haas-van Alphen effects, a new oscillatory phenomenon, discovered in the angular dependence of magnetoresistance in β-(BEDT-TTF)$_2$IBr$_2$ and θ-(BEDT-TTF)$_2$I$_3$, is shown to be a new powerful tool to study Fermi surfaces of quasi two-dimensional electronic systems.

KEYWORDS: organic superconductor, (BEDT-TIF)$_2$X, T_c, Hall effect, STM, magnetoresistance, Fermi surface

§1. Introduction

Superconductivity of BEDT-TTF based organic metals has been found to be quite sensitive to defects, disorders and impurities. In quasi-one dimensional metals, such as (TMTSF)$_2$X, the conduction path of electrons along the stacking donors can be seriously disturbed by the presence of defects or disorder. However, in two-dimensional system like BEDT-TTF salts, electronic conduction path forms a two-dimensional network so that the presence of point defects cannot cause a serious effect on the electrical conduction. Therefore it is not obvious why the superconductivity of BEDT-TTF based organic metals are so sensitive to the presence of non-magnetic impurities and defects. Two outstanding characteristics of the BEDT-TTF based organic superconductors, i.e. superconductivity at ambient-pressure and relatively high-T_c, are advantageous features for an extensive and quantitative study of superconducting properties in these organic metals.

In this paper we report on the progress made in the FY 1989 at Electrotechnical Laboratory in the study of the superconducting and normal state properties of organic superconductors (BEDT-TTF)$_2$X.

§2. Correlation between T_c and Resistivity in β-(BEDT-TTF)$_2$X[24,25]

First, we show some typical examples where superconducting transition temperature (T_c) and resistivity seems to be closely related with each other in β-(BEDT-TTF)$_2$X, which forms an isostructural family of organic metals. An important structural feature of β-(BEDT-TTF)$_2$I$_3$ is an incommensurate lattice modulation,[1] which appears below 175 K at ambient pressure. The presence of this incommensurate superstructure is considered to suppress its T_c from 8.1 K to 1.1–1.5 K. Another important feature in β-(BEDT-TTF)$_2$I$_3$ is the presence of disordered ethylene group as designated as A-type vs B-type[2] (or staggered vs eclipsed[3]) at one end of the molecule and the ordered group at the opposite end. The latter additional structural disorder can possibly be eliminated, as was confirmed in β-(BEDT-TTF)$_2$IBr$_2$ and β-(BEDT-TTF)$_2$I$_2$Br,[4] where the former superstructure is also absent.

The best example which demonstrates a high correlation between T_c and resistivity is seen in β-(BEDT-TTF)$_2$ trihalide mixed crystal system. The substitution of anions in β-(BEDT-TTF)$_2$I$_3$ was found to produce a series of isostructural crystals of β-(BEDT-TTF)$_2$X. Complete substitution of I$_3$ with IBr$_2$[5] and AuI$_2$[6] was found to suppress the incommensurate superstructure and realized the high-T_c state in β-(BEDT-TTF)$_2$X. However, substitution of I$_3$ with asymmetric anion I$_2$Br[7] did not give a superconductivity[8] although the "lattice pressure" model[8] predicted higher T_c and both the incommensurate superstructure and the disorder of the ethylene group were missing.[4] Partial substitution of anions corresponds to alloying in metals. It was found that we can prepare β-(BEDT-TTF)$_2$ trihalide mixed crystals, namely β-(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$, β-(BEDT-TTF)$_2$(IBr$_2$)$_{1-x}$(I$_2$Br)$_x$ and β-(BEDT-TTF)$_2$(I$_2$Br)$_{1-x}$(I$_3$)$_x$, for a wide composition range.[9] Temperature dependence of electrical resistance in these β-(BEDT-TTF)$_2$ trihalide mixed-anion crystals indicates that the mixed crystals of β-(BEDT-TTF)$_2$-trihalides constitute a clean alloy system, where the scattering of conduction electrons are predominantly due to phonons at temperatures above around 100 K even in high concentration (1:1) mixed crystals. The effect of alloying on the resistivity appears as a difference in the residual resistance ratio or residual resistivity at very low temperatures. From the residual conductivity (σ_R), which is inverse of residual resistivity, and T_c in β-(BEDT-TTF)$_2$ trihalide mixed crystals, we can see a clear correlation between T_c and residual conductivity (σ_R) for a wide range of composition,[10] that is, as we increase the

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amount of substituent (x or $1-x$), the residual conductivity decreases and the T_c decreases accordingly. Another interesting feature is the presence of a clear boundary, at $\sigma_R=6000$ S/cm, between the superconducting and non-superconducting samples, indicating the presence of *minimum conductivity* (6000 S/cm) required for realization of superconductivity in this system.[11] This value obtained from the above experimental results was found to be in fair agreement with a theoretical estimation based on the weak localization effect.[12] Also, this empirical rule explains why β-(BEDT-TTF)$_2$I$_2$Br does not show superconductivity.

The second example which shows a correlation between T_c and resistivity is β-(BEDT-TTF)$_2$I$_3$ itself in which two superconducting states are known to exist at ambient pressure, i.e. the low-T_c state (T_c=1.1–1.5 K) and the high-T_c state (T_c=7–8 K). The difference between the two states is considered to be the *incommensurate lattice modulation*[1] which appears below 175 K, where temperature dependence of resistance changes its slope or derivative.[11,13] Figure 1(a) shows a temperature dependence of resistance (R), and Figure 1(b) shows a temperature derivative of resistance (dR/dT) of β-(BEDT-TTF)$_2$I$_3$. At 175 K a crossover between the crystal structures with and without the incommensurate lattice modulation takes place. The former (β_L) is stable at lower temperature while the latter (β_H) is stable at higher temperature. And from Fig. 1(a), β_L state with the incommensurate superstructure seems to have higher resistance than β_H state without the superstructure at temperatures below 175 K.

The high-T_c state without the incommensurate superstructure (β_H) can be realized by releasing the pressure at low temperature after cooling under pressure.[14,15] A more direct difference in resistivity between β_H and β_L states were reported by Hamzic *et al.*[13] in which they observed an abrupt resistance increase due to a first order structural phase transition from the metastable β_H state to β_L state when the β_H sample was warmed up to about 130 K, although they do not mention the difference in residual resistivity at low temperature. A difference in residual resistivity at low temperature between the two states was reported by Ginodman *et al.*[16] The result shows that the resistivity of metastable β_H state is much lower than that in β_L state at low temperatures, indicating that correlation between T_c and residual resistivity also holds in this case.

§3. DC Hall Effect of the Low-T_c state of β-(BEDT-TTF)$_2$I$_3$[26]

The Hall effect was studied in β-(BEDT-TTF)$_2$I$_3$ in order to survey the problem of the low-T_c and the high-T_c states and the general interest to the Fermi surface of this material. i) Our measurement revealed that this material is a metal with almost constant hole numbers down to 20 K. By the estimate of $R_H=1/\text{nec}$, the hole number seems to be less than one per unit cell. ii) In the temperature dependence of R_H in detail, we found a pronounced stepwise decrease by 8% in Hall voltage when temperature is lowered through 175 K but not through 110 K. iii) Further, below 20 K, Hall voltage was found to decrease.

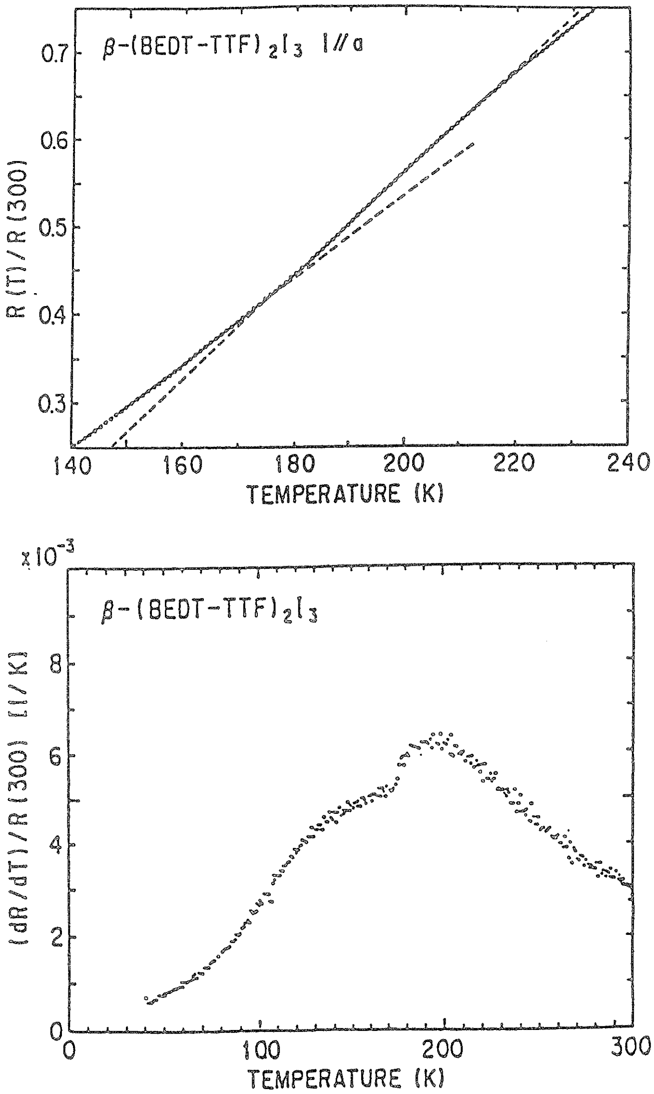

Fig. 1. (a) Temperature dependence of resistance (R) of β-(BEDT-TTF)$_2$I$_3$. (b) Temperature dependence of dR/dT of β-(BEDT-TTF)$_2$I$_3$.

As shown in the inset of Fig. 2, the current terminals were placed at both ends in full width to achieve a uniform current along the a-axis. The Hall voltage was taken by the difference in voltage in fields between + and −5 T during cooling. Part of the results are shown in Fig. 2. Figure 3 shows the temperature dependence of the Hall voltage, which is the difference between 5 T and −5 T. Two distinct transitions are noticeable. One is a stepwise decrease in R_H below 175 K. The other one is depicted by the sudden start of decrease in the Hall voltage below 20 K.

The absolute value of the Hall coefficient of β-(BEDT-TTF)$_2$I$_3$ is consistent with the crude model of metals, which consists of one electron charge transfer from two BEDT-TTF molecules to one I$_3$. However, upon more precise examination, the absolute value of the apparent carrier number itself seems to be smaller than 1 per unit cell. By lowering temperature through 175 K, where the structural transition takes place, the Hall coefficient decreases by 8% in a stepwise way. This result proved that the 175 K transition is accompanied by a transition

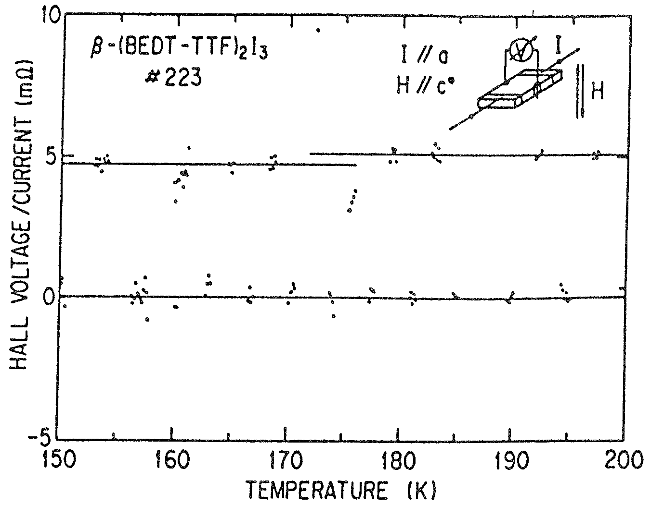

Fig. 2. Hall voltage/current of β-(BEDT-TTF)$_2$I$_3$ as a function of temperature. The difference in the vertical scale between the higher dots(in field of 5 T) and the lower dots (in fields of −5 T) is the Hall voltage signal. Inset shows the configuration of current and fields. The value above 175 K corresponds to 0.50±0.05 holes per unit cell for this sample, when $n=1/R_H ec$ is used.

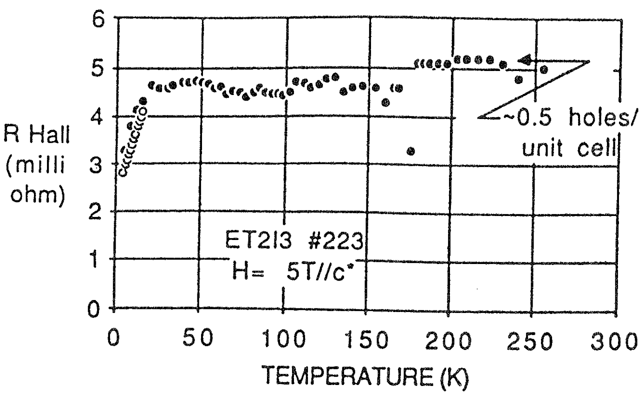

Fig. 3. Hall coefficient, R_H, of β-(BEDT-TTF)$_2$I$_3$ as a function of temperature. Stepwise reduction of R_H through 175 K, and steep decrease below 20 K are significant. Closed circles were taken by reversing fields during cooling. Open circles are the difference in R_{xy} voltage between those at 5 T and −5 T of the temperature sweep.

in the electronic state. The decrease in Hall coefficient is contradictory to the suppression of T_c from 8 K to 1 K, if we recognize the difference of the high-T_c and low-T_c states as a difference of the density of states and if the association of carrier number with density of states is allowed. At temperatures below 20 K, the Hall coefficient starts to decrease significantly. The possibility of a fluctuating phase below 20 K is proposed.

§4. 2 K Superconducting State in β-(BEDT-TTF)$_2$I$_3$[19,25]

Recently, annealing at about 110 K was found to result in a change of the incommensurate superstructure.[17] It was also found that a new superconducting state with T_c=2 K appears as a result of annealing,[18,19] although its origin or structural difference responsible to the change of T_c has not been identified yet. Annealing at 110 K is also accompanied by a decrease in resistance in addition to the change of incommensurate superstructure and appearance of the 2 K state. Figure 4. shows time dependence of resistance ($i/\!/c^*$) of β-(BEDT-TTF)$_2$I$_3$ due to annealing. The resistance decrease by as much as 10%, indicating that the new 2 K state has lower resistivity than the original low-T_c state. Figure 5 shows temperature dependence of resistance of β-(BEDT-TTF)$_2$I$_3$ before (···) and after annealing (——). A vertical line at 106 K in the figure indicates the decrease in resistance by annealing. This annealed 2 K state with lower resistance is also metastable, and gradually goes back to the original low-T_c (1.1–1.5 K) state with higher resistance when the sample is warmed up to about 120 K as seen in Fig. 5.

Now, what about the residual resistance at low temperature? Surprisingly, the temperature dependence of resistance in Fig. 5 shows that the difference in the resistance between the two states, which is as much as 10% at around 100 K, completely disappears as temperature goes down to below 40 K. More or less the same temperature dependence was observed for resistance with current flowing parallel to the conducting plane ($i/\!/a$).[20] It

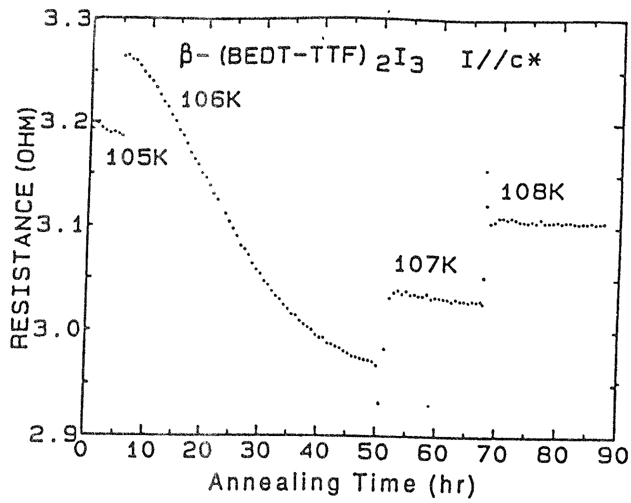

Fig. 4. Time dependence of resistance ($i/\!/c^*$) of β-(BEDT-TTF)$_2$I$_3$ due to annealing.

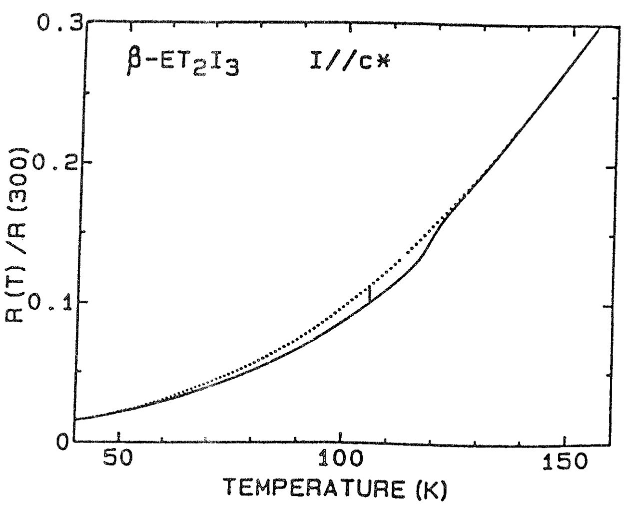

Fig. 5. Temperature dependence of resistance of β-(BEDT-TTF)$_2$I$_3$ before (···) and after annealing (——). A vertical line at 106 K in the figure indicates the decrease in resistance by annealing.

is, however, consistent with the ESR linewidth result as shown in Fig. 6. It is well known that structural disorder in β-(BEDT- TTF)$_2$X provides an additional scattering mechanism for the carriers which increases the residual (low-temperature) ESR linewidth.[21] It is also reported that in β-(BEDT-TTF)$_2$I$_3$, the linewidth in β_H state is much narrower than that of β_L state.[22] Figure 6 indicates that annealing at 100 K causes an appreciable decrease of the ESR linewidth at high temperature, but the reduction of linewidth due to annealing is much smaller at low temperatures, in contrast to the case of high-T_c (8 K) state.[22] These observations seem to indicate that the change of T_c is not accompanied by the change of the low-temperature residual resistance, or scattering, in the case of 2 K superconducting state. These results suggest that we must look for other reasons which can be relafed to the change of T_c in this case. The reduction of the critical field anisotropy in 2 K state[20] could give us a clue to obtain a better understanding of the effect of annealing. The anisotropy of H_{c2}, $H_{c2/\!/}/H_{c2\perp}$, is reported to show a significant decrease from 20.9 to 14.5, caused by annealing.[23]

It has been found by recent magnetization measurement that an extended annealing at about 110 K results in appearance of appreciable amount of the "high-T_c" state with T_c=7.5 K, while the bulk 2 K state gradually loses its volume fraction.[19] Figure 7 shows annealing conditions, i.e. annealing temperature (T_a) and annealing time, for each step of annealing. The effect of annealing performed in 17 steps in total can be classified into three stages. In the first stage, i. e. steps 1 through 7 where 107 K$\leq T_a \leq$111 K, we observed coexistence of two superconducting states with T_c=2 K and 7.5 K, as shown in Fig. 8. The diamagnetic shielding of the 2 K state is quite large ($\sim 1.3\times 10^{-1}$ emu/g·Oe) corresponding to the whole sample volume. In the second stage, i. e. steps 8 through 12 where 112 K$\leq T_a \leq$118 K, we observed only the 7.5 K state as shown in Fig. 9. In the third stage, i.e. steps 13 through 17, where 120 K$\leq T_a \leq$126 K, further annealing started to ruin the 7.5 K state and decrease the superconducting volume fraction without appreciable decrease in T_c. The structural difference between these superconducting states with different T_c has not been clarified yet, and needs further study on the superstructure and ethylene ordering.

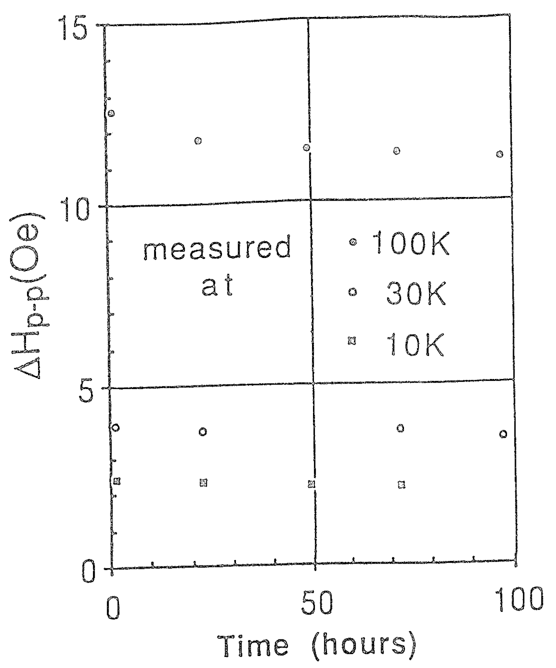

Fig. 6. Peak-to-peak ESR linewidth of β-(BEDT-TTF)$_2$I$_3$ at 100 K and at low temperatures versus annealing time after each annealing process at 100 K.

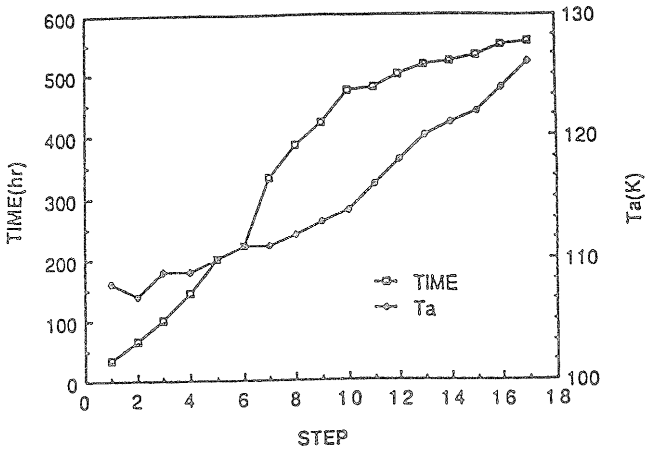

Fig. 7. Annealing temperature (T_a) and annealing time for each step.

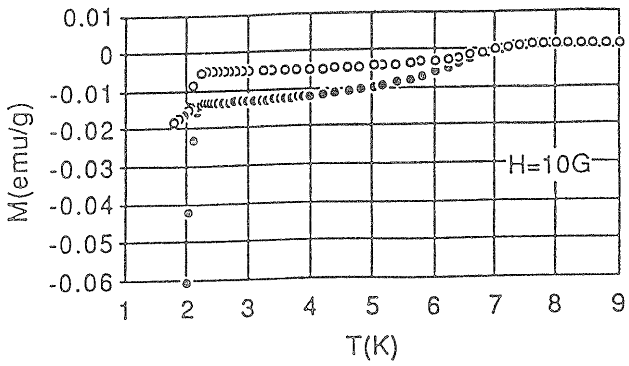

Fig. 8. Diamagnetic shielding (⊛) and Meissner effect (○) of β-(BEDT-TTF)$_2$I$_3$ after the annealing of step 5.

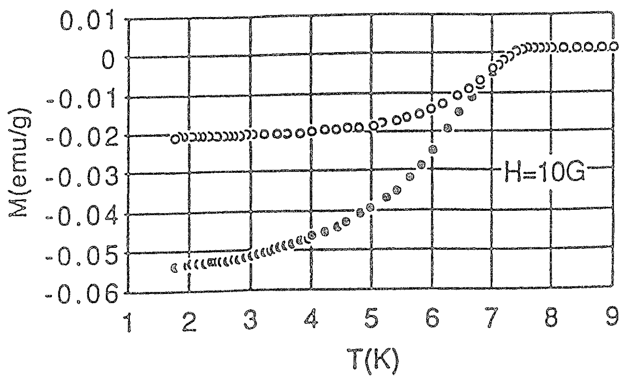

Fig. 9. Diamagnetic shielding (⊛) and Meissner effect (○) of β-(BEDT-TTF)$_2$I$_3$ after the annealing of step 8.

§5. STM Measurements of Superconducting Properties in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[27,28]

Tunneling spectroscopy on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals by a low-temperature scanning tunneling microscope (STM) was studied. The superconducting gap at 1.9 K, estimated from Fig. 10, was $2\Delta=4.8\pm1.1$ meV. Both its magnitude and temperature dependence, as shown in Fig. 11, were consistent with the BCS theory. The line shape of $\mathrm{d}I/\mathrm{d}V-V$ characteristics deviated from the BCS theory, indicating some distribution in the energy gap magnitude. We suppose it is possible to interpret the previously reported results of tunneling spectroscopy[29,30] if they sensed subsets of the distribution according to the configurations.

§6. Angle-Dependence of Magnetoresistance in Organic Superconductors[33,35]

The newly discovered angle-dependent oscillation of magnetoresistance in the β-(BEDT-TTF)$_2$IBr$_2$[31] and θ-(BEDT-TTF)$_2$I$_3$[32] has been found to arise from a nearly complete discretization of Landau levels or two-dimensionalization of Landau level distribution in the vicinity of the Fermi energy. This feature occurs since the Landau levels lose the dependence on the wave number, determined only by the Landau quantum number. This is shown by a semiclassical argument to occur at special angles for a weakly corrugated cylinder form of Fermi surface, as shown in Fig. 12. These angles are approximately given by

$$ck_{\mathrm{F}}\tan\varphi=\pi(n-1/4),\quad n=1,2,3,\cdots. \tag{1}$$

where φ defines the angle by which the applied magnetic field is tilted from the normal of the conducting plane.[33] At these special angles the magnetoresistance makes peaks, since almost all one-electron states become localized in the vicinity of the Fermi energy in the two-dimensionalized situation due to the same reason why the two-dimensional system loses conductivity in the quantum Hall state. Theoretical values of the angles are in good agreement with the observed peak angles, as shown in Fig. 13, including the value of the slope of the fitting line. This success gives a support to the validity of the tight-binding bands based on a single HOMO of the BEDT-TTF molecule for BEDT-TTF based superconductors.[34] We have also treated the case of the general form of in-plane Fermi surface and compared the results with experiments, finding a reasonable agreement between theory[35] and experiment.[36,37] These findings open a new

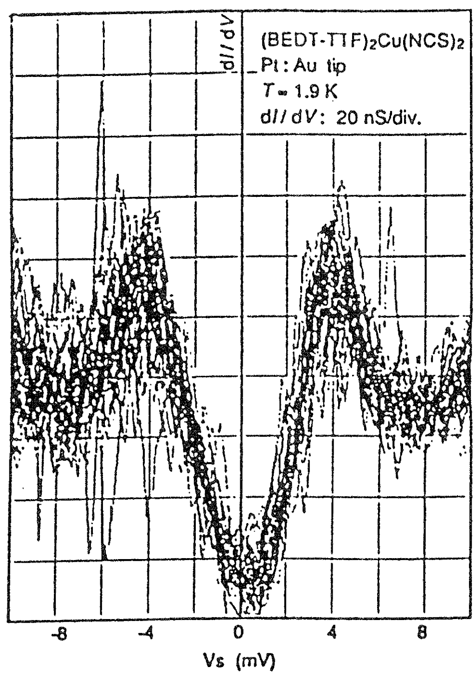

Fig. 10. Differential conductance of κ-(BEDT-TTF)Cu$_2$(NCS)$_2$ measured at 1.9 K. Traces of $\mathrm{d}I/\mathrm{d}V-V$ characteristics of 60 continuous sweeps were plotted.

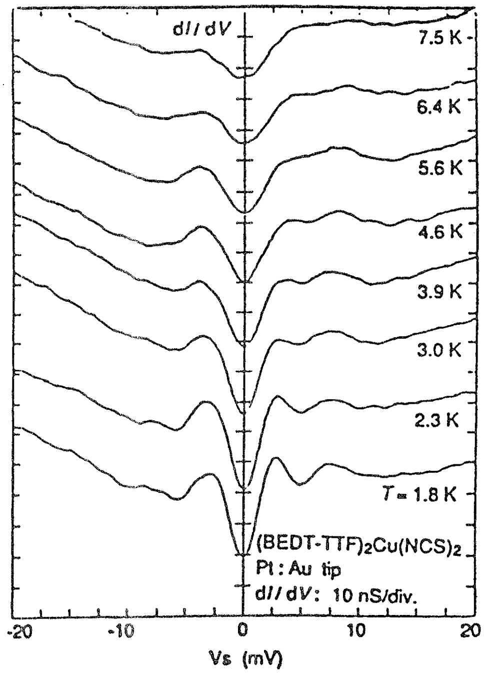

Fig. 11. Temperature dependence of differential conductance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

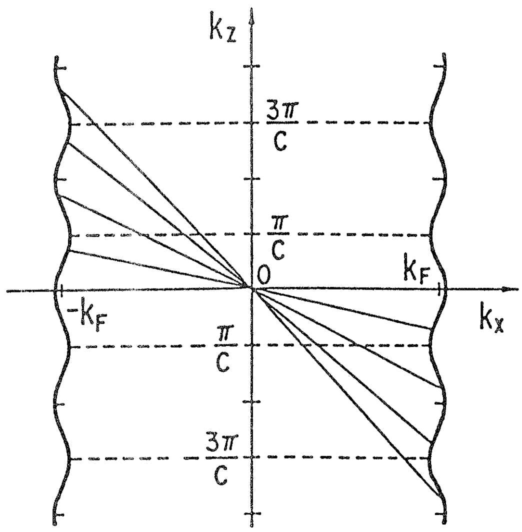

Fig. 12. Semiclassical-orbital planes satisfying (1) are shown by oblique lines. Here the special angle φ corresponds to the angle between the oblique and horizontal lines.

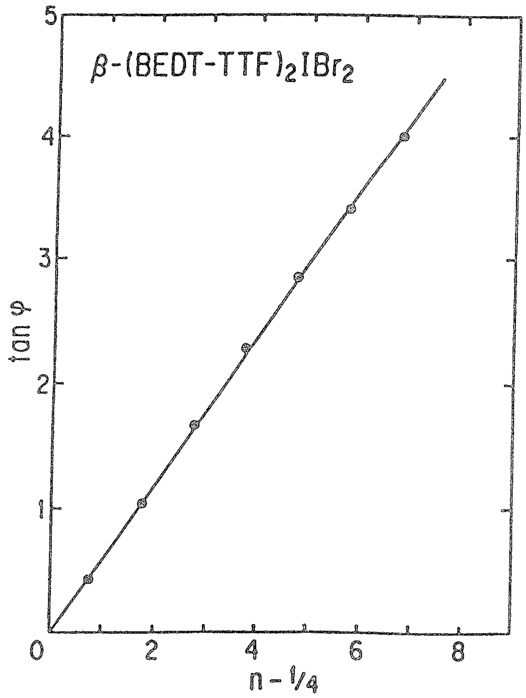

Fig. 13. Values of tan φ at peaks of the magnetoresistance (curve 1 in Fig. 1 of ref. 31) versus $n-1/4$ where n numbers the peaks from the $\varphi=0$ side. Here φ is the tilt angle of the magnetic field in the ac^* plane from the normal c^* of the conducting plane in β-$(ET)_2IBr_2$.

method to determine the form of the Fermi surface of quasi two-dimensional metals, the first target of which is the organic superconductors.

§7. Summary

Recent progress in the superconducting and normal state properties characteristic to the BEDT-TTF based organic metals, including β-$(BEDT\text{-}TTF)_2X$ and β-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, are presented. In addition to the low- and high-T_c states, with $T_c=1$ K and 8 K, respectively, a new superconducting state with $T_c=2$ K was found in β-$(BEDT\text{-}TTF)_2I_3$. DC Hall effect of the low-T_c state of β-$(BEDT\text{-}TTF)_2I_3$ was studied. Tunneling spectroscopy on κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ single crystals by a low-temperature scanning tunneling microscope (STM) is reported. In addition to the Shubnikov-de Haas and de Haas-van Alphen effects, a new oscillatory phenomenon characteristic to a quasi two-dimensional electronic system has been shown to be a new powerful tool in the study of Fermi surface in quasi two-dimensional metals.

Acknowledgments

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