

Magnetic susceptibility of low-dimensional organic conductors with bis(ethylenedithio)tetrathiafulvalene: $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ and $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$

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The magnetic susceptibilities, χ , have been measured for 2 two-dimensional metallic bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) perchlorate salts under slow or rapid cooling conditions. $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ shows a semimetal-insulator transition due to a Peierls instability at 175 K which is independent of the cooling rate. $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$ shows a semimetal-semimetal transition associated with nesting of a part of the Fermi surface at 25 K under slow cooling. Under rapid cooling this transition disappears. The dependence of the transition observed for χ on the cooling rate is confirmed by resistivity measurements. The properties and the origin of anomalies observed for χ with the two salts are discussed in connection with the motion of ethylene groups and $\text{C}_2\text{H}_3\text{Cl}_3$ molecules.

I. INTRODUCTION

Since the discovery of superconductivity in the tetramethyltetraselenafulvalenium (TMTSF) cation radical salt $(\text{TMTSF})_2\text{PF}_6$, many investigations have been carried out to clarify the origin of the superconductivity in such organic compounds.¹ This has renewed the interest in the syntheses and properties of organic metals. The important principles in designing a new organic conductor that can lead to a superconductor are to increase the dimensionality of the electronic system and to reduce the on-site Coulomb repulsion in order to suppress the metal-insulator transition. Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), which was employed on such principles, is a TTF derivative containing two additional fused dithiocyclohexane rings. BEDT-TTF molecules form cation radical salts $(\text{BEDT-TTF})_n\text{-X}$ with inorganic anions: $\text{X} = \text{PF}_6^-$, ClO_4^- , ReO_4^- , I_3^- , Br_2I^- , AuI_2^- , etc. Superconductivity in $(\text{BEDT-TTF})_2\text{ReO}_4$ was observed near 2 K under pressures above 4 kbar for the first time among the sulfur donor compounds.² Moreover, β -(BEDT-TTF)₂I₃,³ $(\text{BEDT-TTF})_2\text{Br}_2\text{I}$,⁴ and $(\text{BEDT-TTF})_2\text{AuI}_2$ (Ref. 5) were found to become superconductors under ambient pressure at about 1.5, 2.7, and 5 K, respectively. β -(BEDT-TTF)₂I₃ was recently found to become a superconductor at 8 K under ambient pressure.^{6,7}

Differing from $(\text{TMTSF})_2\text{X}$ or tetramethyltetrathiafulvalenium (TMTTF) cation radical salts, BEDT-TTF complexes show a multiplicity of stoichiometries and crystal structures and inclusion of solvent molecules because the structure of BEDT-TTF molecules can be easily deformed by the thermal vibrations of the ethylene groups. A great variety of physical properties results from this behavior. Schirber *et al.*⁸ discussed the sensitivity of the superconducting transition temperature T_c to the disorder in donors and anions. They accounted for the high- T_c phase in β -(BEDT-TTF)I₃ by the effect of shearing strain gen-

erated by the cooling processes on the ordering of the ethylene groups.

As to the ClO_4 complexes, BEDT-TTF is known to give four kinds of complexes.⁹ The first two are $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$ [(2:1:0.5) phase] and $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_4\text{H}_4\text{O}_2)$ which include solvents (1,1,2-trichloroethane and dioxane, respectively). The third is $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ [(3:2) phase]. The fourth is a blue salt with no data on its physical properties because of its explosive nature.

The crystal structure and the electrical resistivity of the (3:2) phase investigated by Kobayashi *et al.*¹⁰ suggested quasi-one-dimensionality in the electronic system and a sharp metal-insulator transition at 170 K. The electrical resistivity and the crystal structure of the (2:1:0.5) phase investigated by Saito *et al.*¹¹ and by Kobayashi *et al.*¹² showed two-dimensional metallic behavior which was preserved even at low temperatures down to 1.4 K, though the resistivity showed a small increase below 15 K. In the (2:1:0.5) phase of BEDT-TTF the molecules have a side-by-side arrangement with very short intermolecular S-S atomic contacts (3.34 Å) along the *a* axis. The strong transverse intermolecular interaction originating from these S-S atomic contacts together with the interaction along the stacking axis gives the two-dimensional character to the electronic properties.

As to the magnetic properties of the ClO_4 complexes, the previous papers reported ESR results¹³ and preliminary results on the static magnetic susceptibility^{9,14} for the (3:2) phase and the (2:1:0.5) phase. Recently, Parkin *et al.* reported the results from static magnetic susceptibility and ESR measurements for the (3:2) phase.¹⁵ In this paper we report the temperature dependence of the static magnetic susceptibility for both phases in the temperature range between 2 and 250 K. In addition to the effect of the thermal motion of ethylene groups and $\text{C}_2\text{H}_3\text{Cl}_3$ molecules on the electronic properties of these

compounds is made clear by changing the cooling conditions. The electrical resistivity for the (2:1:0.5) phase is also investigated in the temperature range between 0.8 and 290 K, and the results are discussed in connection with those from the susceptibility measurements.

II. EXPERIMENTS

Single crystals of the (3:2) phase and the (2:1:0.5) phase were prepared by a standard electrochemical technique. A 2×10^{-4} mol quantity of BEDT-TTF was reacted with $(1.8-3.7) \times 10^{-3}$ mol of $(C_4H_9)_4NClO_4$ in 100 ml of $C_2H_3Cl_3$ under a constant current (5 or 10 μA) for one week. Two kinds of lustrous black crystals were simultaneously produced in the electrochemical cell. The assignment of the structures was determined by means of x-ray diffraction. At 10 μA , thin plates of $(BEDT-TTF)_3(ClO_4)_2$ were mainly obtained. At 5 μA , thick plates of $(BEDT-TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ were mainly obtained. Typical dimensions of the crystals were $2 \times 5 \times 0.05$ mm³ for the (3:2) phase and $1 \times 1 \times 0.3$ mm³ for the (2:1:0.5) phase, respectively.

The magnetic susceptibilities χ of these two phases were measured by use of a Faraday magnetic balance (Oxford Instruments Co.) in the temperature range between 2 and 250 K under a magnetic field of 5 T. Approximately ten crystals mounted in a quartz cell with Apiezon-*N* grease were used in one measurement, because the volume of a single crystal was too small to measure χ . The accuracy of the following measurements is within 1×10^{-8} cgs emu/g. χ was measured between 4 and 2 K in a cooling run just after cooling the sample down to 4 K from room temperature, while it was measured between 4 and 250 K in a heating run just after the measurement between 4 and 2 K. The temperature was monitored by a carbon resistor (2–30 K) and a platinum resistor (30–250 K). Two kinds of cooling rates were taken in order to investigate the effect of the cooling rates on the electronic properties; a rapid cooling condition (–5 K/min between room temperature and 4 K) and a slow cooling condition (–5 K/min between room temperature and 205 K, –5 K/h between 205 and 160 K, and –5 K/min between 160 and 4 K).

The electrical resistivity of the (2:1:0.5) phase was measured by use of a standard four-probe technique applying silver paint (Dupont 4817) in a ³He refrigerator (Torisha Co.) for a cooling run and a subsequent heating run between 0.8 and 290 K at a measuring-current value of 100 μA . The absence of a Joule-heating effect of the measuring current was confirmed by comparing the measurement at 10 μA . The temperature was monitored by two calibrated germanium resistors (0.8–45 K) and a calibrated platinum resistor (45–290 K). The same two cooling conditions as used for the susceptibility measurements were used here.

Figure 1 shows the temperature dependence of the magnetic susceptibility χ for the (3:2) phase under rapid cooling. The external magnetic field H was applied perpendicular or parallel to the a^* axis, which is normal to the thin plate of the sample. Above 175 K, χ decreased gradually with decreasing temperature. The temperature

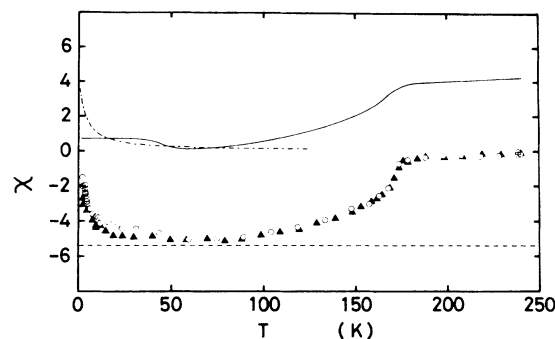


FIG. 1. Temperature dependence of χ for the (3:2) phase under the rapid cooling condition (in units of 10^{-7} cgs emu/g). The symbols \odot and \blacktriangle denote the measurements with $H||a^*$ and $H||a^*$, respectively. The dashed, dash-dotted, and solid lines show the values of χ_c , χ_1 , and χ_s , respectively (see text), all three of which contribute to χ represented by the symbol \odot .

dependence of χ showed an exponential decrease below 175 K. Below 30 K, χ had a Curie tail. Further, the temperature dependence of χ with $H||a^*$ under the slow cooling condition was measured and the same results as those shown in Fig. 1 were obtained. No anisotropy in χ was found for either direction except for a small increase with $H||a^*$ below about 50 K. These small increases appeared only with $H||a^*$ and the increments ranged from 2×10^{-8} to 5×10^{-8} cgs emu/g depending on the samples and the cooling conditions.

Figure 2 shows the temperature dependence of χ for the (2:1:0.5) phase under rapid cooling conditions. The magnetic field was applied perpendicular or parallel to the b^* axis which is normal to the thick plate of the sample. χ decreased slowly with decreasing temperature above 50 K. The slope in the χ -versus- T curve became steep below about 180 K, and then leveled out below about 90 K. A Curie contribution became apparent at temperatures below about 10 K.

Figure 3 shows the temperature dependence of χ with $H||b^*$ for the (2:1:0.5) phase under slow cooling conditions. The sample was heated from 2 to 90 K in the first run. Then the sample was cooled again down to 4 K at a cooling rate of –12 K/min, and the second run was taken from 4 to 2 K and then 4 to 250 K. The temperature dependence of χ showed an exponential decrease below 25 K. Above 25 K, χ showed a similar temperature dependence to that observed under the rapid cooling condition. A Curie contribution appeared in the low-temperature region below about 10 K. Changes of slope seemed to appear around 180 and 90 K, but were not so clear as those in Fig. 2. A small increase in χ appeared below about 50 K with $H||b^*$ in Fig. 2 and for the first run in Fig. 3, while it disappeared for the second run in Fig. 3. Further, the temperature dependence of χ with $H||b^*$ was measured under various cooling conditions, where the temperature region of the rapid cooling was changed; (i) –5 K/h between 300 and 4 K; (ii) –5 K/h between 300

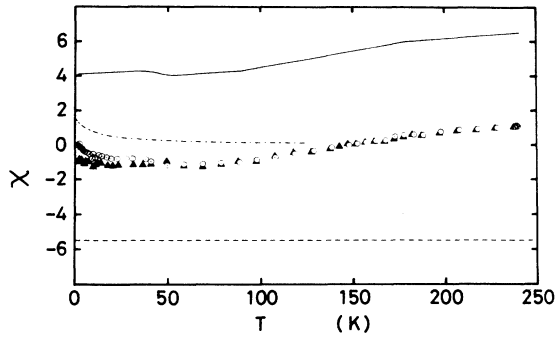


FIG. 2. Temperature dependence of χ for the (2:1:0.5) phase under the rapid cooling condition (in units of 10^{-7} cgs emu/g). The symbols \odot and \blacktriangle denote the results with $\mathbf{H}\parallel\mathbf{b}^*$ and $\mathbf{H}\perp\mathbf{b}^*$, respectively. The dashed, dash-dotted, and solid lines show the values of χ_c , χ_1 , and χ_s , respectively (see text), all three of which contribute to χ represented by the symbol \odot .

and 70 K, -5 K/min between 70 and 4 K; (iii) -5 K/h between 300 and 105 K, -5 K/min between 105 and 4 K. Results similar to those in Fig. 3 were obtained independently of the cooling conditions.

In order to estimate the core diamagnetic contribution, the value of χ for powdered neutral BEDT-TTF, $(\text{C}_4\text{H}_9)_4\text{NClO}_4$, and $\text{C}_2\text{H}_3\text{Cl}_3$ were measured and found to be -5.7×10^{-7} cgs emu/g (250 K), -7.1×10^{-7} cgs emu/g (250 K), and -5.6×10^{-7} cgs emu/g (200 K), respectively.

Figure 4 shows the temperature dependence of electrical resistivity for the (2:1:0.5) phase under the slow and the rapid cooling conditions. For slow cooling, the resistivity which was of metallic character at higher temperatures increased below about 50 K and then it became a constant below about 10 K. The inflection point was 22

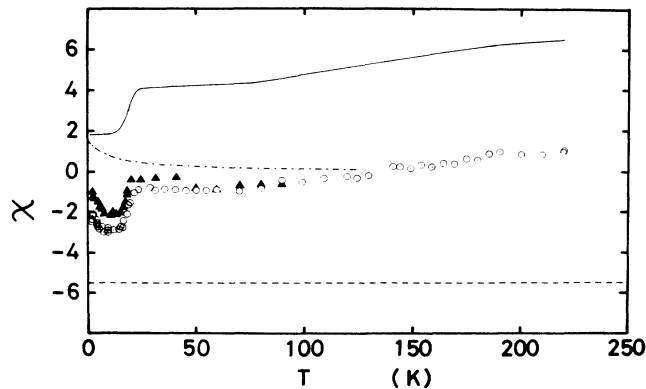


FIG. 3. Temperature dependence of χ for the (2:1:0.5) phase with $\mathbf{H}\parallel\mathbf{b}^*$ under the slow cooling condition (in units of 10^{-7} cgs emu/g). The symbols \blacktriangle and \odot are the results for the first run and the second run, respectively. The dashed, dash-dotted, and solid lines show the values of χ_c , χ_1 , and χ_s , respectively (see text), all three of which contribute to χ represented by the symbol \odot .

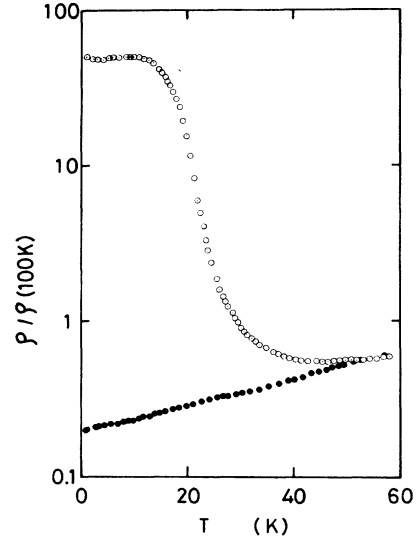


FIG. 4. Temperature dependence of resistivity perpendicular to \mathbf{b}^* axis for the (2:1:0.5) phase under the slow cooling condition (\odot) and the rapid cooling condition (\bullet).

K and close to the transition point observed in χ , while under rapid cooling the resistivity persisted as metallic resistivity down to 0.8 K without any anomalous change.

III. DISCUSSION

The observed total magnetic susceptibility can be separated into three terms,

$$\chi = \chi_1 + \chi_c + \chi_s,$$

where χ_1 is the contribution related to the Curie tail at low temperatures, χ_c the temperature-independent diamagnetic core contribution, and χ_s the contribution associated with charge carriers. The dash-dotted lines in Figs. 1–3 show the contribution from χ_1 . The concentrations of localized spins derived from χ_1 were estimated to be about 0.2% of BEDT-TTF molecules for both phases. The contributions from χ_c and χ_s will be discussed separately in the following section.

A. The diamagnetic core contribution

χ for neutral BEDT-TTF and $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ were -5.7×10^{-7} and -7.1×10^{-7} cgs emu/g, respectively. χ for ClO_4^- is found to be -3.6×10^{-7} cgs emu/g by subtracting the $(\text{C}_4\text{H}_9)_4\text{N}$ contribution from χ for $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ using tabulated values.¹⁶

χ for $\text{C}_2\text{H}_3\text{Cl}_3$ was -5.6×10^{-7} cgs emu/g. From these values the core contributions χ_c can be calculated to be -5.4×10^{-7} and -5.5×10^{-7} cgs emu/g for the (3:2) and (2:1:0.5) phases, respectively. These values are slightly different from the calculated susceptibilities for Pascal's diamagnetism derived from tabulated values:¹⁶ -4.7×10^{-7} cgs emu/g for the (3:2) phase and -4.8×10^{-7} cgs emu/g for the (2:1:0.5) phase. The above results are listed in Table I. The respective

TABLE I. Comparison of the calculated and the observed diamagnetic core susceptibility for neutral BEDT-TTF, ClO_4^- , $\text{C}_2\text{H}_3\text{Cl}_3$, the (3:2) phase, and the (2:1:0.5) phase (in units of 10^{-7} cgs emu/g).

	Calculated	Observed
BEDT-TTF	-4.9	-5.7
$(\text{C}_4\text{H}_9)_4\text{NClO}_4$		-7.1
ClO_4^-	-3.4	-3.6
$\text{C}_2\text{H}_3\text{Cl}_3$	-5.7	-5.6
(3:2) phase	-4.7	-5.4
(2:1:0.5) phase	-4.8	-5.5

discrepancies are attributable to the contribution from neutral BEDT-TTF component. Though these may be in part associated with the extended π -electron system of neutral BEDT-TTF, we neglect its contribution. Moreover, the contributions associated with the extended π -electron system and the Landau diamagnetism for both the (2:1:0.5) phase and the (3:2) phase are suggested to be negligibly small, because the anisotropies in χ for both phases disappeared within experimental error in the high-temperature region. Therefore, the derived values using the measured ones can be used for the values of χ_c in the following discussions. The dashed lines in Figs. 1–3 show the values.

B. Spin paramagnetic contribution for charge carriers

1. $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$

BEDT-TTF molecules are stacked along the $[0\bar{1}1]$ direction in the bc plane, and have a considerably large side-by-side interstack overlapping through S-S atomic contacts along the $[012]$. The intrastack and the side-by-side interactions give a quasi-two-dimensional conducting sheet in the bc plane. The long axis of the BEDT-TTF molecule is nearly parallel to the a^* axis. The two-dimensional network of the BEDT-TTF molecules in the bc plane is separated from the adjacent one by ClO_4^- anions.

The solid line in Fig. 1 shows the temperature dependence of χ_s for the (3:2) phase with $\mathbf{H}\parallel\mathbf{a}^*$ under the slow cooling condition, where χ_s is obtained by subtracting both the core diamagnetic susceptibility (-5.4×10^{-7} cgs emu/g) and the Curie susceptibility from the observed susceptibility. A nearly constant spin susceptibility χ_s above $T=175$ K suggests a metallic character, consistent with the resistivity measurement.¹⁰ The susceptibility for Pauli paramagnetism χ_s in a two-dimensional metal can be expressed by the free-electron model as shown in the following equation:

$$\chi_s = \mu_B^2 N_0 / \pi t, \quad (1)$$

where μ_B is the Bohr magneton, N_0 is Avogadro's number, and t is an intrasheet transfer integral. The observed χ_s provides an estimation of $t=0.045$ eV at 200 K, though t will be modified by a fairly large on-site

Coulomb interaction $U=1.3$ eV.¹³ This small magnitude of t is consistent with the semimetallic character of the (3:2) phase suggested by theory¹⁷ and optical reflectance results.¹⁸ Taking into account the behavior of χ_s and the resistivity, a semimetal-insulator transition takes place at $T_c=175$ K, below which χ_s shows a singlet ground state in the insulating phase. An exponential decrease of χ_s gives an activation energy of $E_a=0.061$ eV. The $2E_a/T_c$ ratio is 8.0, larger than 3.5 which is derived from the mean-field theory.

X-ray analysis showed that the (3:2) phase had the threefold periodicity of the BEDT-TTF molecules at room temperature,¹⁰ and a large U was expected to cause a semimetallic character.¹⁷ The observed g shift at about T_c in the ESR spectrum reveals that the BEDT-TTF molecules are displaced in the critical region of the transition point.¹³ X-ray diffraction gives evidence that the thermal vibrations of the ethylene groups on the BEDT-TTF molecules are suppressed below T_c .¹⁹ The semimetal-insulator transition at 175 K can be explained as resulting from the Peierls instability with the $4k_F$ distortion.¹³ The flexibility of the structure for the BEDT-TTF molecule seems to have an important role in this transition. The thermal vibration of ethylene groups disturbs the occurrence of the transition in the high-temperature region. The deformation of the BEDT-TTF molecule becomes more well defined with decreasing temperature due to the suppression of the thermal motion in ethylene groups. At 175 K it becomes significant enough to cause the transition. This may be why the transition occurs well below room temperature where the lattice already has the threefold periodicity. The effect of thermal motion of ethylene groups on the crystal structure was also found in other BEDT-TTF salts. As for β - $(\text{BEDT-TTF})_2\text{I}_3$, Leung *et al.* found an incommensurate superstructure below ~ 200 K from x-ray analysis.²⁰ Maniwa *et al.* showed that the thermal motion of ethylene groups in BEDT-TTF started to freeze at ~ 195 K from pulsed ^1H NMR measurement.²¹

A small increase in χ_s was observed below about 50 K only with $\mathbf{H}\parallel\mathbf{a}^*$. In the case of the similar compound, $(\text{TMTTF})_2\text{ClO}_4$, the ClO_4^- anions have significant thermal motion down to about 70 K, below which long-range ordering is developed in the anion lattice.²² Since the temperature at which this small increase becomes apparent is close to the temperature for the ordering of ClO_4^- anions in $(\text{TMTTF})_2\text{ClO}_4$, this increase might be related to the motion of the ClO_4^- anions. The details of the features that give rise to this increase have not been made clear yet due to the lack of the structural information at low temperatures.

2. $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$

The BEDT-TTF molecules are stacked along the $[102]$ direction, and the cooperation between the face-to-face and the relatively large side-by-side intermolecular overlappings gives rise to a two-dimensional conducting sheet in the ac plane, which is separated from the adjacent sheets by ClO_4^- anions and $\text{C}_2\text{H}_3\text{Cl}_3$ molecules. The long axis of the BEDT-TTF molecule is nearly parallel to

the b^* axis.

The solid lines in Figs. 2 and 3 show the temperature dependence of χ_s for the (2:1:0.5) phase with $\mathbf{H}\parallel\mathbf{b}^*$ under rapid and slow cooling, respectively. It should be emphasized that the appearance and the disappearance of the transition at 25 K are found to depend only on the cooling rate between 205 and 160 K.

The spin susceptibility shows the Pauli paramagnetism at high temperatures above 180 K, which is independent of the cooling rate. Though the (2:1:0.5) phase is regarded as a two-dimensional semimetal, we adopt Eq. (1) to estimate t . The observed magnitude of χ_s at 200 K provides an estimated value for t of 0.035 eV, which is consistent with the semimetallic character suggested from the band calculation²³ and the optical reflectance measurement,²⁴ though t will be modified to some extent by U .

The changes of slope in χ_s are observed at about 90 and 180 K independently of the cooling rate. Kagoshima *et al.* found, in an x-ray diffuse scattering experiment,²⁵ that peak intensity of the $2a \times b \times 2c$ satellite gradually increased below 225 K, rapidly increased below about 150 K, and almost saturated below about 20 K independently of the cooling (heating) speed of 250 K/h or 10 K/h. They concluded that the increase of the intensity might be due to an orientational order-disorder transition of $\text{C}_2\text{H}_3\text{Cl}_3$ molecules. The distance between a $\text{C}_2\text{H}_3\text{Cl}_3$ molecule and the ethylene group of a BEDT-TTF molecule is so close that there is a correlation in the motion between the $\text{C}_2\text{H}_3\text{Cl}_3$ and the BEDT-TTF molecules. Therefore, the development of the order-disorder transition of $\text{C}_2\text{H}_3\text{Cl}_3$ molecules will deform the BEDT-TTF molecules. The ordering in $\text{C}_2\text{H}_3\text{Cl}_3$ molecules starts to develop at about 180 K and tends to be completed below about 90 K, judging from the existence of the inflection points at around 180 and 90 K.

χ_s decreased with decreasing temperature above T_c and changed its slope slightly at 180 and 90 K. According to Eq. (1), this decrease suggests that t will increase with decreasing temperature. The development of the ordering in $\text{C}_2\text{H}_3\text{Cl}_3$ molecules with decreasing temperature can suppress thermal vibrations of the ethylene groups via the interactions between the ethylene groups and the $\text{C}_2\text{H}_3\text{Cl}_3$ molecules. This leads to the reduction of the interplanar distance between adjacent BEDT-TTF molecules and/or the deformation of the structure, which increases the electron hopping rate between adjacent BEDT-TTF molecules.

At low temperatures below 25 K, the situation depends on the cooling rate. For rapid cooling, a metallic state remains even at the lowest temperature without any transition, while slow cooling introduces a phase transition. Since thermal vibrations of ethylene groups on BEDT-TTF molecules at high temperatures correlate with motions of $\text{C}_2\text{H}_3\text{Cl}_3$ molecules, the situation for the quenching of the vibrations depends on how the order-disorder transition is developed. The rapid cooling will cause the transition to be incomplete, and this incompleteness generates random deformation of BEDT-TTF molecules which have an effect on the electron hopping rate in the BEDT-TTF sheets. The introduction of the random distribution of transfer integrals under the rapid cooling

suppresses the phase transition at low temperatures if the magnitude of the randomness overwhelms the gap generated by the transition. On the other hand, the slow cooling induces no random distribution in transfer integrals since the order-disorder transition is completed. In this case, a clear transition can be expected. The speculations discussed here are reinforced by the experimental results that show, in order to obtain the phase transition, the slow cooling condition is needed only for the temperature region between 205 and 160 K, where the order-disorder transition starts to be developed.

Under slow cooling the phase transition appeared at $T_c = 25$ K, below which a part of the Pauli paramagnetic contribution is suppressed. The magnitude of the remnant susceptibility of the Pauli paramagnetism at $T = 0$ K is 1.8×10^{-7} cgs emu/g, which is 44% of that under the rapid cooling condition, 4.1×10^{-7} cgs emu/g. An exponential decrease of χ_s below T_c gives an activation energy $E_a = 0.013$ eV and the ratio $2E_a/T_c = 12$, which is considerably larger than 3.5 from the mean-field theory. The electrical resistivity becomes larger in a relatively wide critical region between about 50 and 15 K, in spite of its metallic behavior at higher temperature, while well below $T_c = 25$ K it shows almost constant value down to 0.8 K. The transition at $T_c = 25$ K is suggested to be a semimetal-semimetal transition from the above results. From the theoretical calculation, the (2:1:0.5) phase is suggested to be a two-dimensional semimetal, and its Fermi surface consists of both small electron and hole parts. Further, under a slow cooling condition, the thermoelectric power shows an abrupt shift to the positive side below T_c .²⁶ The reduction of the χ_s by 56% at T_c seems to be associated with the disappearance of the electron or the hole Fermi surface through a nesting instability. The considerably large change observed in the resistivity at around 25 K as shown in Fig. 4 seems to be inconsistent with the disappearance of the electron or the hole part (only a half of the carriers). This may be interpreted by the deviation of the direction for the actual resistivity measurement from that of the nesting and by the decrease of the carrier mobility due to the development of long periodicity. A semimetal-semimetal transition observed here is reminiscent of the case for one-dimensional $(\text{TSeT})_2\text{Cl}$, where the metallic phase below T_c has been suggested to be associated with the splitting of the conduction band into two subbands by the presence of two pairs of nonequivalent stacks of TSeT molecules.²⁷

The small increase in χ_s was observed below about 50 K with $\mathbf{H}\parallel\mathbf{b}^*$ in Fig. 2 and in the first run in Fig. 3. Further, the increase was not clear in the second run in Fig. 3, while for the (3:2) phase it was always observed with $\mathbf{H}\parallel\mathbf{a}^*$. The exact mechanism that gives rise to this increase has not been made clear and is left open to further investigations.

IV. SUMMARY

The magnetic susceptibilities of two $(\text{BEDT-TTF})-\text{ClO}_4$ salts, $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ and $(\text{BEDT-TTF})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$, have been measured by the use of a Faraday magnetic balance under two kinds of cooling

rates. The spin paramagnetic contribution for charge carriers, χ_s , was derived by subtracting both the core diamagnetic susceptibility and the Curie susceptibility from the observed susceptibility.

χ_s for the (3:2) phase has shown a semimetal-insulator transition at 175 K with an activation energy of 0.061 eV through Peierls instability regardless of the cooling condition. The increase in χ_s below 50 K appeared only with $\mathbf{H}\parallel\mathbf{a}^*$.

Anomalies in χ_s have been observed at 180, 90, and 50 K for the (2:1:0.5) phase under the rapid cooling condition. The increase in χ_s below 50 K appeared only with $\mathbf{H}\parallel\mathbf{b}^*$. The ordering in $\text{C}_2\text{H}_3\text{Cl}_3$ molecules starts to develop at about 180 K and tends to be completed below about 90 K. Under the slow cooling condition, χ_s showed a phase transition at 25 K with an activation energy of $E_a=0.013$ eV. The completeness of the ordering of $\text{C}_2\text{H}_3\text{Cl}_3$ molecules was responsible for the transition.

The value of χ_s that remains far below 25 K suggested the transition to be a semimetal-semimetal one with the nesting of the electron part or the hole part of the Fermi surface. Furthermore, the appearance and the disappearance of the transition were confirmed by the resistivity measurement.

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