Reflectance Spectra and Electrical Resistivity of
(Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub>

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We systematically study transport and optical properties of charge-transfer salts, (Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> (0 ≤ x ≤ 1). The temperature dependence of electrical resistivity exhibits semiconducting behavior at x = 0, a metal-semiconductor transition for 0.08 ≤ x ≤ 0.29, and metallic behavior down to 4.2K for x ≥ 0.39. A semiconductor-semiconductor transition is observed around 60K for x ≤ 0.14. The reflectance spectra at room temperature reveal two optical excitations in the infrared region. The first excitation appears in salts with x ≠ 0 far below 650 cm⁻¹. The second excitation is the so-called mid-infrared band, which appears around 3000 cm⁻¹ for 0 ≤ x ≤ 0.14, and shifts downward for x ≥ 0.17. We propose a hypothesis which provides an explanation both for the metallic conduction and for the mid-infrared band in a one-dimensional conductor having a quarter-filled band.

KEYWORDS: molecular conductors, one-dimensional conductors, electronic properties, reflectance spectra

§1. Introduction

It is well known that a one-dimensional molecular conductor having a quarter-filled π-band exhibits the so-called mid-infrared band (an intense absorption band in the infrared region), although it exhibits metallic conduction around room temperature. This phenomenon was aroused an interest of many researchers, since the mid-infrared band does not appear within a framework of a simple band theory, and since there is no appropriate explanation on the metallic conduction in a salt exhibiting the mid-infrared band. In the article written by Jacobsen, he reviewed several theoretical models which explain the mid-infrared band and concluded that the phenomenon has not been explained yet.¹)

From the experimental point of view, the difficulties in the study of the phenomenon are as follows: At first most of one-dimensional molecular conductors have dimerized columnar structure which results a gap in the middle of the π-band. Thus the effect of lattice distortion is not negligible in most cases. Secondary, the control of the carrier density is impossible in most of molecular conductors. Thus the mechanism of electrical conduction is difficult to study.

In this paper we present our detailed studies on reflectivity and electrical resistivity for (Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> alloys intending to clarify the phenomenon. For this purpose, the advantages of this system over other one-dimensional molecular conductors are as follows:

i) Based on X-ray diffraction study, Me₂-DNCQI molecules form one-dimensional regular columns at room temperature.²,3) This means the effects of lattice distortion is negligible in this system.

ii) The valence of the cation is Li⁺ and Cu⁻⁴/³⁺ in (Me₂-DNCQI)₂Li and (Me₂-DNCQI)₂Cu, respectively.⁴) Therefore, by substituting Cu for Li, we can change the filling of the π-band from a quarter to approximately one-third.

As for the second advantage we should note that (Me₂-DNCQI)₂Cu is a three-dimensional conductor due to the coordination bond between Cu and Me₂-DNCQI, although (Me₂-DNCQI)₂Li is a one-dimensional conductor. Thus, for the relatively large x, (Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> is no more a one-dimensional conductor but a three-dimensional conductor. However, for relatively small x, we expect that the three-dimensional character is significantly small. In fact, this expectation is ascertained in the following studies.

Up to now, several experiments (resistivity,⁵,⁶) magnetic susceptibility,⁷,⁸) NMR⁹,¹⁰) are reported for (Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> and the related (R₁R₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> alloys. However optical studies has not been reported yet except for the cases of x = 0 and x = 1.¹⁰) Moreover previous experiments are restricted around x = 1, where the alloys are expected to be three-dimensional conductor,⁵,⁹) or mainly intended to investigate the crossover from the one-dimensional conductor to the three-dimensional conductor.⁶) The study around x = 0 has not been reported yet.

§2. Sample Preparation and Characterization

Single crystals of (Me₂-DNCQI)₂Li were prepared by the diffusion method from Me₂-DNCQI and LiI in acetonitrile as a solvent. The typical size of the crystals thus prepared is 0.2 mm×0.2 mm×1 mm.

The alloyed crystals (Me₂-DNCQI)₂Li<sub>1−x</sub>Cu<sub>x</sub> (x ≠ 0) were synthesized by the chemical reduction using (n-Bu₄N)I from acetonitrile solution saturated with Me₂-DNCQI and containing a mixture of (Et₄N)₂CuBr₄ and LiClO₄.¹⁰) From the molar content of (Et₄N)₂CuBr₄ (M<sub>Cu</sub>) and that of LiClO₄ (M<sub>Li</sub>), the value of...
and x_{\text{prep}}. For this purpose, the values of x in several crystals were determined by the first method, and were related with the corresponding values of x_{\text{prep}}. The obtained relation is shown as a solid line in Fig. 1. A similar relation is also reported by Hiraki as a result of ICP analyses.\(^6\) It should be noted that significant deviation from this relation was observed when the reactant solution was not fully saturated with Me\textsubscript{2}-DCNQI.

[Method (III)] An x-value was determined by using a reflectance spectrum obtained in this study. This method is useful for samples with small x. The details on this method will be described in the later section.

[Method (IV)] An x-value was deduced from the x-value of another crystal synthesized simultaneously in the same batch. The latter x-value was determined by the first method. This method was mainly applied for the batches, where reactant solutions were not fully saturated with Me\textsubscript{2}-DCNQI.

The inhomogeneity effect in (Me\textsubscript{2}-DCNQI)\textsubscript{2}Li\textsubscript{1-x}Cu\textsubscript{x} crystals synthesized by the same method was examined by Hiraki.\(^6\) On the basis of NMR measurements, he concluded that there is no serious inhomogeneity in crystals. In our experiments, we examined this effect by measuring the resistivity and reflectivity on several crystals grown in one batch. We found that the effect is serious for x_{\text{prep}} < 0.05, but allowable for x_{\text{prep}} ≥ 0.05. Thus we concluded that the methods (II) and (IV) are not reliable for x_{\text{prep}} < 0.05, since these methods assume the homogeneity of crystals grown in one batch.

§3. Electrical Resistivity

Figure 2 shows the temperature dependence of the electrical resistivity for (Me\textsubscript{2}-DCNQI)\textsubscript{2}Li\textsubscript{1-x}Cu\textsubscript{x} (0 ≤ x ≤ 1) crystals. The resistivity was measured by the standard four probe method. The x-values in this figure were deduced by the methods (II) and (IV). Since these methods are not reliable for x_{\text{prep}} < 0.05, the x-value of 0.01 is written in parentheses. For x ≈ 0, the resistivity curves exhibit semiconducting behavior in all the temperature range.\(^{11}\) For x ≥ 0.08, the curves exhibit metallic behavior around room temperature and metallic-semiconductor transition on lowering the temperature. With a further increase in x, the semiconducting behavior in the curves is gradually suppressed. For x ≥ 0.39, the curves exhibit metallic behavior in whole the temperature range measured.

The inset of Fig. 2 shows the x-dependence of resistivity at room temperature. The resistivity decreases with an increase of x. The figure demonstrates that the resistivity data at x = 0, shown as white-centered circles, show large statistical variance. We investigated the origin of this variance by examining the resistivity data at x = 0 both in temperature dependences and in absolute values. As a result, we found a sample having smaller absolute value exhibits the temperature dependence similar to that of x = 0.01. Thus we concluded that the smaller values of resistivity are due to extrinsic effects such as impurities, and that the intrinsic x-dependence of resistivity is singular at x = 0. The variance is attributable to the difference of impurity concentrations in samples with x = 0.
to 60 K, below which it exhibits an inflection due to a semiconductor-semiconductor (S-S) transition. This S-S transition is also observed in the magnetic susceptibility, NMR, and X-ray measurements, being attributable to the freezing of $2k_F$, CDW $^{5,12,13}$ With increasing $x$, the curves gradually deviate from the activation-type. However, the inflection still survives for $x \leq 0.14$. Interestingly, all the curves in this range exhibit an inflection around 60 K. Just above this temperature the curves take almost the same slope giving the activation energy about 270 K. With an increase in $x$ above 0.17, the S-S transition shifts downwards in temperature, and is gradually smeared out of the resistivity curve.

Figure 4 shows the summary of the resistivity data. In this diagram, $x_{c1}$ represents the critical $x$-value above which the S-S transition temperature shifts downwards, and $x_{c2}$ represents the $x$-value above which the system exhibits metallic behavior down to 4.2 K. These values are depicted by shaded zones in the figure in order to represent uncertainties in the values.

§4. Reflectance Spectra

Table I shows the list of samples used in the reflectivity measurements. The four methods described in §2 were used to deduce $x$-values in (Me$_2$-DCNQI)$_2$Cu$_2$Li$_{1-x}$ alloys. More than two methods among four were applied to most of samples. The most reliable values of $x$ are determined based on the following criteria:

i) Method (I) is most reliable in the range of $x$.

ii) For $x_{prep.} < 0.05$, method (III) is reliable next to method (I).

iii) For $x_{prep.} > 0.05$, the reliability is in the order of method (I)>method (IV)>method (II).

The reflectance spectra between 650 cm$^{-1}$ and 5000 cm$^{-1}$ were measured by use of JASCO FTIR microspectrophotometer with 16 cm$^{-1}$ resolution. The spectra between 4400 cm$^{-1}$ and 25000 cm$^{-1}$ were mea-
Fig. 5. The reflectance spectra of \((\text{Me}_2\text{DCNQI})_2\text{Li}_{1-x}\text{Cu}_x\) for the light polarized parallel to the crystallographic \(c\)-axis, which is the stacking axis of \(\text{Me}_2\text{DCNQI}\). Note the scale offset between the different spectra. A, B and C denote A-, B- and C-band. (See the corresponding description in §5.) A-band appears below the frequency range measured (650–25000 cm\(^{-1}\)).

Fig. 6. The reflectance spectra of \((\text{Me}_2\text{DCNQI})_2\text{Li}_{1-x}\text{Cu}_x\) for the light polarized parallel to the crystallographic \(c\)-axis, which is perpendicular to the stacking axis of \(\text{Me}_2\text{DCNQI}\). Note the scale offset between the different spectra.

Reflected by use of OLYMPUS MMSP microspectrophotometer.

Figure 5 shows the reflectance spectra of \((\text{Me}_2\text{DCNQI})_2\text{Cu}_x\text{Li}_{1-x}\) for the light polarized parallel to the crystallographic \(c\)-axis, which is the stacking axis of \(\text{Me}_2\text{DCNQI}\) molecules. The spectrum of \(x = 0\) is not Drude-like. This optical behavior is often observed in organic conductors such as \((\text{TMTTF})_2X\), being ascribed to the formation of a band gap by strong electron-electron correlation. The vibrational structures (~940 cm\(^{-1}\), ~1140 cm\(^{-1}\), ~1500 cm\(^{-1}\), ~2090 cm\(^{-1}\)) and a broad dispersion (~14 \times 10^3 cm\(^{-1}\)) are respectively attributable to the \(a_g\) vibrational modes induced by electron-molecular vibration (e-mv) couplings, and to the lowest intramolecular excitation of \(\text{Me}_2\text{DCNQI}^-\).\(^{10}\) The latter exhibits a structure due to a phonon sideband. With an increase in \(x\) both the vibrational structures and the intramolecular excitation band gradually smear out of the spectra.

Figure 6 shows the reflectance spectra for the light polarized parallel to the \(\alpha\)-axis, which is perpendicular to the stacking axis of \(\text{Me}_2\text{DCNQI}\) molecules. The Drude dispersion appears below 1500 cm\(^{-1}\) in samples with \(x \geq 0.75\), suggesting the three-dimensional nature of electrical properties in these samples. For \(x \leq 0.49\), the spectra do not exhibit Drude dispersion in the frequency range studied. Thus we concluded that the present alloy system is highly anisotropic at least for \(x \leq 0.49\).

In order to examine the Cu-substitution effect on the reflectance spectra, \((R_x - R_{Li})/R_{Li}\), where \(R_x\) and \(R_{Li}\) represent the reflectivity of \((\text{Me}_2\text{DCNQI})_2\text{Cu}_x\text{Li}_{1-x}\) and that of Li-salt. If the substitution effect is significantly small, the differential reflectance spectrum is given by

\[
(R_x - R_{Li})/R_{Li} = \alpha(e_1, e_2)\Delta\varepsilon_1 + \beta(e_1, e_2)\Delta\varepsilon_2, \tag{1}
\]

where \(\Delta\varepsilon_1\), \(\Delta\varepsilon_2\) are the differential dielectric constants; \(\alpha(e_1, e_2), \beta(e_1, e_2)\) are functions of dielectric constants.\(^{14}\) In our case, the substitution effect is too large to apply this relation. Nevertheless the differential reflectance spectra still help us qualitatively to find subtle changes associated with the Cu-substitution.

From the data shown in Fig. 7, we found the spectral change occurs mainly in three regions below 2000 cm\(^{-1}\), around 8000 cm\(^{-1}\), and around 16000 cm\(^{-1}\). In these regions, the spectral changes are spread over the width of 1000 cm\(^{-1}\). Thus we concluded that these changes are attributable to some changes in electronic transitions. The Cu-substitution has following effects on these spectral changes:

i) The spectral change in the region below 2000 cm\(^{-1}\) is considerably sensitive to the small deviation of \(x\) from \(x = 0\) but rather insensitive with a further increase of \(x\). In other words, even a slight replacement of Li with Cu is critical for this change.

ii) In contrast to the spectral change below 2000 cm\(^{-1}\), the spectral change around 8000 cm\(^{-1}\) grows continuously with an increase of \(x\).

iii) The spectral change around 16000 cm\(^{-1}\) also grows continuously with an increase of \(x\). This change is smaller than the spectral change around 8000 cm\(^{-1}\). Since the data of Fig. 7 indicate correlation between \(x\)
and the peak area around 8000 cm\(^{-1}\) (\(A\)), we plotted them in Fig. 8. The figure shows an explicit relation between these parameters. Based on this finding, we devised a method to determine the \(x\)-value in a crystal. This is the method (III) which we have already mentioned in §2. In this method, an appropriate relation between \(A\) and \(x\) are assumed and are obtained by use of the data shown in Fig. 8. The relation is shown as a solid line in the figure. Once this relationship is established, we can inversely determine \(x\) from \(A\). The most remarkable feature of this method is that \(A\) at \(x = 0\) is guaranteed to be zero in the relation. Thus, this method is useful when \(x\) in a sample is expected to be small.

§5. Analyses of the Reflectance Spectra

Based on the results given by Fig. 7, the reflectance spectra of Fig. 5 were analyzed in the following way. At first, we tried Kramers-Kronig transformation of the reflectance spectra by extrapolating constant reflectivity below 650 cm\(^{-1}\). However, this analysis failed to give physical results: the resulting conductivity spectra is negative below about 1000 cm\(^{-1}\) for \(0 < x \leq 0.17\). Thus we concluded that there is some electronic transition hidden below 650 cm\(^{-1}\). Hereafter we refer to this transition as A-band.

Then, we applied the dispersion analysis to the reflectance spectra. In this analysis, we assumed the complex dielectric function given by

\[
\varepsilon(\omega) = \varepsilon_\infty - \sum_m \frac{\Omega_m^2}{\omega^2 - i \Gamma_m \omega},
\]

where \(\varepsilon_\infty\) stands for the frequency-independent dielectric constant, and \((\Omega_m, \Gamma_m, \Omega_{pm})\) are a set of parameters for the Lorentz oscillator which simulates the \(m\)-th optical transition. In the analyses we assumed the following optical transitions:

i) A-band (\(\Omega_1\)).

This is the above-mentioned transition hidden below 650 cm\(^{-1}\). Since just a tail of this transition appears in the spectra, we could not determine its excitation energy. We tentatively assumed the transition has zero-excitation energy, and obtained its intensity.

As a result of the dispersion analyses, we found that the transition does not exist in the salt with \(x = 0\) and appears in salts with \(x \neq 0\). Although this conclusion is rather surprising, it is consistent with the spectral change appearing below 2000 cm\(^{-1}\) in Fig. 7.

ii) Transitions due to e-mv couplings (\(\Omega_2 \sim \Omega_4\)).

We analyzed three vibrational transitions induced by e-mv couplings. The structures due to these transitions appear at \(\sim 940\) cm\(^{-1}\), \(\sim 1140\) cm\(^{-1}\), and \(\sim 2090\) cm\(^{-1}\). With an increase of \(x\), they become less distinct.

iii) B-band (\(\Omega_5\)).

This is the so-called mid-infrared band. The excitation energy of this transition is about 3000 cm\(^{-1}\) for \(0 \leq x \leq 0.14\) and decreases for \(x \leq 0.17\).

iv) C-band (\(\Omega_6\)).

This transition is most easily observed in the spectrum of Cu-salt above 7000 cm\(^{-1}\). The structure around 8000 cm\(^{-1}\) and 16000 cm\(^{-1}\) in the differential spectra are associated with this transition. Since these structures grow continuously with an increase of \(x\), we concluded that the intensity of this transition increases with an increase of \(x\). This behavior suggests that transition C is a charge transfer excitation between Cu and Me\(_2\)DCNQI.

v) Intramolecular transitions of Me\(_2\)DCNQI (\(\Omega_7, \Omega_8\)).

We analyzed an intramolecular electronic transition and its phonon side-band, both appearing in the visible region (at \(\sim 14000\) cm\(^{-1}\)). Intramolecular transitions having higher excitation energies are neglected. With an increase of \(x\), the structures due to these transitions become less distinct.

Figure 9 shows the observed data of reflectivity (circles) and the simulated curves (solid lines). The parameters of the Lorentz oscillators for simulating the A- and B-bands are shown in Fig. 10. Although the simulated curves almost perfectly reproduce the experimental curves, it is difficult to uniquely determine the Lorentz
parameters especially for $x \geq 0.75$. This is because $\Omega_{p1}$ and $\Omega_{p5}$ are interacting on each other. In this range of $x$, $\Omega_{p1}$ determined in the simulation may be taken as its lowest limit.

Figure 11 shows the conductivity spectra derived from the reflectance spectra of Fig. 5 through the Kramers-Kronig transformation. In this transformation we extrapolated the reflectivity data below 650 cm$^{-1}$ by using the parameters determined in the dispersion analyses. The conductivity spectra show that the peaks attributable to the transition B shift downwards at some $x$ between 0.14 and 0.17. This is consistent with the results of dispersion analyses shown in Fig. 9.

By comparing the spectrum of $x = 0$ with $x < 0.01$, we can see some extra absorption appearing in the spectra of $x = 0$ around 1000 cm$^{-1}$. A similar conclusion is also reached by the dispersion analyses. This absorption may be a substitute for the A-band in the case of $x \neq 0$. As for this absorption, detailed studies should be done in the future.

6. Summary and Discussion

The resistivity and reflectivity data obtained in this study are summarized as follows:

i) $x = 0$

Temperature dependence of resistivity is activation-type for the entire measured temperature range. A semiconductor-semiconductor transition occurs around 60 K. The reflectance spectrum does not exhibit any trace of the A-band. The B-band appears around 3000 cm$^{-1}$.

ii) $0.14 \geq x > 0$

Temperature dependence of the resistivity deviates from activation type. The semiconductor-semiconductor

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Fig. 9. The least-squares fit to the reflectance spectra using eq. (2). Note the scale offset between the different spectra.

Fig. 10. The parameters of Lorentz oscillators for simulating A- and B-band. Here, $x_{c1}$ and $x_{c2}$ denote the critical $x$-values determined by resistivity measurements. Dotted lines are guides for eyes.

Fig. 11. Conductivity spectra obtained through Kramers-Kronig transformation of the reflectance spectra illustrated in Fig. 5. Note the scale offset between the different spectra. Arrows in the figure represent peak positions of B-band determined by the dispersion analyses. The B-band shift downwards at some $x$ between 0.14 and 0.17.
transition around 60 K still exists. The reflectance spectrum exhibits the A-band with excitation energy far below 650 cm\(^{-1}\). The plasma frequency of the A-band is \(\sim 2800\) cm\(^{-1}\) and does not depend on x. The B-band still appears around 3000 cm\(^{-1}\).

iii) \(0.29 \geq x \geq 0.17\)

The semiconductor-semiconductor transition around 60 K becomes smeared and disappears. The plasma frequency of the A-band is still \(\sim 2800\) cm\(^{-1}\) and does not depend on x. The B-band shifts downwards below \(\sim 2500\) cm\(^{-1}\).

iv) \(1.00 \geq x \geq 0.39\)

Temperature dependence of the resistivity is metallic all the temperature range measured. The plasma frequency of the A-band increases with an increase in x.

Hereafter we discuss the properties of (Me\(_2\)DCNQI)\(_2\)Li\(_{1-x}\)Cu\(_x\) for \(0 < x \leq 0.29\), where the salts exhibit one-dimensional properties. One may be tempted to view the x-dependence of the resistivity in terms of charged carriers injected into an intrinsic semiconductor. If this is the case, the A-band is attributable to the intraband transition associated with the injected carriers. However, such an explanation is not plausible for the salts in this range of x, since the plasma frequency of the A-band does not increase so much in the range of \(0 < x \leq 0.29\).

Moret et al. found \(4k_F\) superstructure at room temperature in (Me\(_2\)DCNQI)\(_2\)Ag.\(^{13}\) By using a NMR spectrum Hiraki and Kanoda recently revealed a \(4k_F\) superstructure due to charge-disproportionate state below 220 K in (I\(_2\)-DCNQI)\(_2\)Ag, whose crystal structure is similar to that of (Me\(_2\)DCNQI)\(_2\)Ag and (Me\(_2\)DCNQI)\(_2\)Li.\(^{15}\) Such a charge-disproportionate state is often called the Wigner crystal and discriminated from a CDW state, since instead of electron-phonon coupling nearest neighbor and higher-order Coulomb repulsion is necessary to realize this state. In fact, Seo and Fukuyama theoretically proved such charge- (and spin-) disproportionate states become stable for relatively large values of nearest neighbor Coulomb repulsion by use of the extended Hubbard Hamiltonian and a mean-field approximation.\(^{16}\) We followed their approximation and calculated the optical conductivity spectra. Then we found: i) a mid-infrared band similar to the B-band appears in a spectrum in the charge- (and/or spin-) disproportionate state; ii) the degree of the disproportionation in charge (and/or spin-) determines the excitation energy of this absorption band.\(^{17}\) These results suggest that (Me\(_2\)DCNQI)\(_2\)Li\(_{1-x}\)Cu\(_x\) (\(x < 0.29\)) is in a charge- (and/or spin-) disproportionate state even at room temperature and that the shift of the B-band between \(x = 0.14\) and \(x = 0.17\) is due to some change in charge (and/or spin-) distribution in a crystal. One may find some discrepancy between this conclusion and the NMR experiments,\(^{15}\) where a charge-disproportionate state is not found around room temperature. However, this discrepancy is solved by assuming that at a high temperature a Wigner crystal melts into a “Wigner liquid” formed by a large number of charge- (and/or spin-) disproportionate domains, and that each domain moves over the speed of NMR frequency. In such a “Wigner liquid”, current should be carried by collective excitations associated with domain boundaries rather than by single particles. The A-band may be assigned to such collective excitations, and this assignment may explain our observed result that the plasma frequency of the A-band does not increase so much in the range of \(0 < x < 0.29\).

On the basis of the discussion given above we finally reached the following hypothesis which provides an explanation both for the metallic conduction and for the mid-infrared band in the one-dimensional conductors having a quarter-filled band:

i) The ground state of the one-dimensional conductor having a quarter-filled band is a charge- (and/or spin-) disproportionate state formed by electron-electron correlation (U and V) rather than CDW state formed by electron-phonon coupling. In this state, the formed gap (here we call it as a correlation gap) is significantly larger than the CDW gap and survives even around room temperature. The mid-infrared band is attributable to the single-particle excitation across such a correlation gap. In other words, the appearance of the mid-infrared band indicates that the salt is essentially a semiconductor.

ii) The electric conduction in this charge (and/or spin-) disproportionate state is due to some collective mode associated with domain boundaries. When the excitation energy of the collective mode is comparable to the thermal energy a salt exhibits metallic behavior, and when the energy is smaller than that it exhibits semiconducting behavior. In this context the metal-insulator transition defined by transport properties is not the phase transition thermodynamically defined.

Although the A-band observed in the present study support the above hypothesis, more evidences are necessary to prove it. Detailed studies are still under way.

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6) K. Hiraki: Dr. Thesis, Graduate University for Advanced Studies and Institute for Molecular Science, Okazaki, Japan, 1996.

11) In this article we refer to the state of $dp/dT < 0$ ($\rho$: resistivity) as semiconducting and that of $dp/dT \geq 0$ as metallic. A metal-insulator transition in this definition does not indicate the phase transition thermodynamically defined.
17) H. Tajima et al.: to be published.