Infrared Reflectance Spectra of (Me₂DCNQI-d₇)₂Cu

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The temperature dependence of polarized infrared reflectance spectra was investigated on the single crystal of (Me₂DCNQI-d₇)₂Cu whose electrical resistivity was continuously monitored by the four-probe method. Above 77 K, the resistivity decreases on lowering the temperature, and the reflectance spectra exhibit Drude-like dispersion for both polarizations parallel and perpendicular to the crystallographic c-axis. Between 77 K and 75 K, the resistivity increases more than 10⁶ times that of 77 K, and the reflectance spectra exhibit drastic change suggesting dimensionality crossover from a three-dimensional conductor into a one-dimensional insulator. Based on the reflectivity data it was concluded that the metal-insulator transition in this salt is accompanied by discontinuous formation of CDW.

DCNQI, organic conductors, reflectance spectra, infrared spectra

§1. Introduction

After the pioneer work by Aumüller and Hünig¹) considerable efforts have been devoted to the studies of \((R₁, R₂-DCNQI)_₂X\) \([X=\text{Cu}, \text{Ag}, \text{Li}, \text{Na}, \text{K}, \cdots; R₁, R₂-DCNQI: 2,5-disubstituted dicyanoquinodimine}]²⁻⁷)⁸ Early works revealed that these salts can be classified into three categories according to their electrical behavior.⁷) The first category is one-dimensional metals which exhibit a broad metal-insulator transition. All the salts having the cation other than Cu fall into this category. The second and third categories are composed of salts having Cu cation. The crystal structures and electrical properties of these salts are similar to each other at room temperature. The difference in these two categories is that the salts of the second category keep metallic behavior down to a low temperature while those of the third category exhibit a metal-insulator transition on lowering the temperature.

At almost the same time, \(T-P\) phase diagram was investigated on \((\text{Me}_₂\text{DCNQI})₂\text{Cu}⁸) belonging to the second category, and its metallic state was proved not so stable: the temperature dependence of resistivity exhibits a metal-insulator-metal transition (reentrant transition) under a slightly-applied pressure, and a metal-insulator transition as the pressure increases more.⁹) This phenomenon suggests that a salt of the third category can be considered in a pressurized state of that of the second category. In other words it suggests the possibility of constructing the universal \(T-P\) phase diagram on \((R₁, R₂-DCNQI)₂\text{Cu}\) through the study of \((\text{Me}_₂\text{DCNQI})₂\text{Cu}\) (or another typical copper salt of \(R₁, R₂-DCNQI\) over a wide range of pressure. Furthermore, it was recently found that selective deuteration of \((\text{Me}_₂\text{DCNQI})₂\text{Cu}\) brings it to the state which is almost the same as that under applied pressure \((P \leq 500 \text{ bar})\).¹⁰,¹¹) By use of this technique various kinds of measurements has now come into use in the study of \(T-P\) phase diagram of \((\text{Me}_₂\text{DCNQI})₂\text{Cu}\). In this report we will present our spectroscopic study on \((\text{Me}_₂\text{DCNQI-d₇})₂\text{Cu}[\text{Me}_₂\text{DCNQI-d₇}; \text{see Fig. 1}], whose electronic structure is expected to be almost the same as that of \((\text{Me}_₂\text{DCNQI})₂\text{Cu}\) under the pressure of 500 bar.
§2. Experimental

Single crystals of (Me₂DCNQI-d₇)₂Cu were synthesized by the same procedure described elsewhere. Polarized infrared reflectance spectra were measured by use of FTIR microspectrophotometer (Jasco FTIR8900μ). We chose the two polarization directions parallel and perpendicular to the crystallographic c-axis. The c-axis is the unique optical axis in the I₄₁/a crystal symmetry of (Me₂DCNQI-d₇)₂Cu, and corresponds to the direction in which Me₂DCNQI-d₇ stacks. We measured two kinds of reflectance spectra with different resolutions (16 cm⁻¹ and 4 cm⁻¹) at each temperature. The higher-resolution spectra were mainly used for the study of vibrational absorption in the region between 800 cm⁻¹ and 2250 cm⁻¹.

Temperature was controlled by a cryostat manufactured at Oxford Ltd. (CF1104). This cryostat cools a sample down by the heat transfer to a cold plate through solids. The cold plate is made of copper and its temperature is measured by a thermocouple. In our usual measurement whole one side of a sample is adhered to the cold plate with a small amount of grease in order to secure good thermal contact, and then the sample is cooled down in a vacuum. In this process the sample is expected to be gradually stressed with a decrease in temperature, because of the difference in the thermal expansion coefficient between the sample and copper. However, thus generated stress is usually presumed to be too small to affect the electronic structure of the sample. (Me₂DCNQI-d₇)₂Cu (n=0~8) is the rare exception for the above presumption. The electronic structure of this salt is quite sensitive to the stress. So that we attempted another method of attaching a sample, in order to minimize the stress as possible during an experiment. Figure 2 shows the method where a thermal contact is prepared with carbon paste between one end of the crystal and a plate made of epoxy-fiber composite, which plate is adhered to the cold plate. We chose a long crystal (3 mm × 0.15 mm × 0.15 mm) for measurements and took a long distance between the thermal contact and the microspot on which reflectivity was measured, so that the effect of the stress generated at the thermal contact could be neglected. The main disadvantage of this method is poverty of the thermal conduction between the sample and cold plate. This results in inaccurate estimation of the sample temperature. In order to compensate this inaccuracy we measured the electrical resistance by use of the four-probe method throughout the reflectivity measurements. This resistance measurement allows us to know whether the sample is in a metallic state or in an insulating state.
§3. Results and Discussion

3.1 Infrared reflectance and conductivity spectra in the range between 650 cm\(^{-1}\) and 5000 cm\(^{-1}\)

Figure 3 shows the temperature dependence of polarized reflectance spectra of a \((\text{Me}_2\text{DCNQI-d}_{\text{7}})_2\text{Cu}\) single crystal for the polarizations parallel and perpendicular to the c-axis, and Fig. 4 shows the temperature dependence of the resistance obtained in the same cooling run when the reflectance spectra were measured. The resistivity measurements on the same compound, reported elsewhere,\(^{12}\) exhibit the resistivity jump around 83 K when the sample is cooled down. The corresponding jumping temperature of Fig. 4 is 76 K, 7 degrees lower than that. This deviation should arise from poor thermal contact between the sample and cold plate. By taking this deviation of 7 degrees into account, the real temperature of the sample is roughly estimated 7 degrees higher than the temperature shown in Figs. 3 and 4 around the phase transition temperature.

From room temperature down to 80 K, Drude-like dispersion appears in both \(E//c\) and \(E\perp c\) spectra. In this temperature range, the electrical resistance monotonously decreases and the reflectivity at a lower frequency increases. These facts indicate that the scattering rate of a carrier decreases with a decrease in the temperature. From 80 K down to 77 K the resistance gradually increases. However, the Drude-like dispersion remains almost unaltered in both \(E//c\) and \(E\perp c\) spectra. Between 77 K and 75 K, the resistance jumps by a factor more than 10\(^6\). The corresponding changes of reflectance spectra are drastic: i) the Drude-like dispersion com-

![Fig. 3. Temperature dependence of the polarized reflectance spectra of (Me\(_2\)DCNQI-d\(_{7}\))\(_2\)Cu single crystal. The resolution of the spectra is 16 cm\(^{-1}\) and the sample was set by the method shown in Fig. 2. The value of \(R/R_{\text{SSK}}\) in the figure represents the resistance normalized by that of 85 K. Note that the temperature shown in the figure has some ambiguity, arising from poor thermal contact between the sample and thermometer. (See the text.)](image1)

![Fig. 4. Temperature dependence of the resistance obtained in the same cooling run when the spectra shown in Figs. 3, 5–7 were measured. Note that the temperature shown in the figure has some ambiguity, arising from poor thermal contact between the sample and thermometer. (See the text.)](image2)
pletely disappears in both $E//c$ and $E\perp c$ spectra; ii) a dispersion due to charge-transfer excitation appears in the $E//c$ spectrum; iii) sharp peaks due to electron-molecular vibration coupling (EMVC) appears in the $E//c$ spectrum (see §3.2). Similar drastic change of reflectance spectra were found in the previous study on (MeBrDCNQI)$_2$Cu.\textsuperscript{14,15} Below 75 K, the resistance became so high that we could not measure it. The spectral change is quite small in this temperature range.

Figure 5 shows the conductivity spectra obtained through Kramers-Krönig transformation of the reflectance spectra of Fig. 3. From room temperature down to 77 K, the conductivity spectra do not exhibit optical gap, corresponding to the Drude-like line shape of the reflectance spectra. The weak absorption around 1100 cm$^{-1}$, becoming apparent in the $E//c$ spectrum below 150 K, may be attributable to an inter-band transition. Below 75 K, the $E//c$ spectrum exhibits optical gap around 2000 cm$^{-1}$. (Here we defined the optical gap as the wavenumber at which the conductivity curve takes half of the maximum value of the CT absorption band.) Similar values of optical gaps were obtained for insulating phases of (MeBrDCNQI)$_2$Cu and (Me$_2$DCNQI)$_2$Na.\textsuperscript{14} This suggests that the optical gap originate from electron-electron correlation effects.

\subsection*{3.2 Vibrational structure}

Figure 6 shows the conductivity spectra for the polarization parallel to the $c$-axis obtained through the Kramers-Krönig transformation of the reflectance spectra with 4 cm$^{-1}$ resolution. The peak energies appeared in the conductivity spectra are listed in the Table I.

Only broad band due to electronic transition is present in the spectra above 79 K, while strong vibrational bands appear in the spectra below 75 K. The spectrum at 77 K exhibits a broad electronic band, on which very weak vibrational bands are superposed. The vibrational bands are attributable to $a_1$ modes\textsuperscript{46} induced by EMVC. The intensity of the EMVC modes little change below 75 K. This fact is somewhat inconsistent with the earlier work, where gradual change in the intensity of EMVC modes was pointed out on the powder absorption spectra of (Br$_3$DCNQI)$_2$Cu.\textsuperscript{17} One of the possible origin for this inconsistency is the local-stress effect which should be inevitable in the powder absorption spectroscopy. We will discuss this effect later.

The appearance of EMVC mode indicates that the Me$_2$DCNQI-d$_1$ molecules deviate from inversion symmetry points in the crystal.\textsuperscript{18} In the present study it is obvious that the deviation comes from the CDW formation accompanying metal-insulator transition. Thus we concluded from the temperature dependence of the EMVC mode that CDW is almost discontinuously formed below 75 K. This behavior on CDW formation is apparently differ-
ent from that of typical quasi-one-dimensional conductors such as (Me$_2$DCNQI)$_2$Ag, where CDW is formed at a temperature much higher than that of a metal-insulator transition.

Figure 6 shows the conductivity spectra for the polarization perpendicular to $c$-axis. The peak energies appeared in the conductivity spectra are listed in the Table I. The vibrational bands at 1476 and 1529 cm$^{-1}$ can be attributable to molecular vibration with $b_u$ mode.$^{19}$ Below 75 K these bands disappear and new vibrational bands appear at 1437, 1456, and 1496 cm$^{-1}$.

All the vibrational bands appearing in the range between 2050 cm$^{-1}$ to 2250 cm$^{-1}$ are associated with CN stretching. Above 77 K only a weak vibrational band centered around 2140 cm$^{-1}$ exists in this frequency range, being attributable to $b_u$ mode. Below 75 K several strong vibrational bands appear instead of this band. This phenomenon was not pointed out in the previous optical studies on $R_1$, $R_2$-DCNQI salts. Taking into account the intensity of these band, they should be attributable to vibrational modes of a certain kind, coupled with a charge-transfer excitation. However, they can be discriminated from the ordinary EMVC mode since the modes associated only with CN-stretching exhibit this enormous increase of absorption intensity in the $E \perp c$ spectra. Hereafter, we will call these modes anomalous EMVC (AEMVC) modes, and discriminate them from ordinary EMVC

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**Table I.** Peak energies observed in the conductivity spectrum of (Me$_2$DCNQI-$d_2$)$_2$Cu.

<table>
<thead>
<tr>
<th>$E // c$</th>
<th>No vibrational band</th>
</tr>
</thead>
<tbody>
<tr>
<td>85 K</td>
<td>967(vs; OEMVC), 1127(s; OEMVC), 1160(s; OEMVC), 1196(s; OEMVC), 1243(vs; OEMVC), 1293(vs; OEMVC), 1349(w; OEMVC), 1367(w; OEMVC), 1594(vs; OEMVC), 2098(w), 2119(w), 2132(vs; OEMVC), 2147(w), 2162(m; OEMVC), 2183(m; OEMVC)</td>
</tr>
<tr>
<td>15 K</td>
<td>1476(s; $b_1$), 1529(w; $b_2$), 2140(w; $b_1$)</td>
</tr>
</tbody>
</table>

| $E \perp c$     | 1274(w & br), 1326(w & br), 1437(m; $b_1$), 1456(m; $b_3$), 1496(s; $b_1$), 2109(w), 2122(s; AEMVC), 2137(w), 2148(s; AEMVC), 2165(w), 2177(w) |

In units of cm$^{-1}$

OEMVC: A band attributable to ordinary electron-molecular-vibration coupling mode.

AEMVC: A band attributable to anomalous electron-molecular-vibration coupling mode.

vs: very strong, s: strong, m: medium, w: weak, br: broad, $b_i$: $b_i$ mode
(OEMVC) modes.

Based on the Rice's climer model, the absorption intensity due to EMVC mode should depend on EMVC constants, each of which is a unique parameter of each vibrational mode, and on the intensity of charge transfer absorption. This model can be easily extended to a multi-dimensional system. Although a solution against the extended Rice's model is missing, we can still predict something based on this model by taking the uniqueness of coupling constants into account: the intensity order among various EMVC mode in one polarization is almost kept in another polarization, i.e. strong (weak) EMVC mode should be also strong (weak) in another polarization. However, this prediction is not true in (Me₂DCNQI-d₃)₂Cu as can be seen from the appearance of EMVC modes of different kinds (OEMVC and AEMVC). So that, we considered that there are two types of important EMVC constants for each vibrational mode of Me₂DCNQI-d₁. One is derived from the modulation of LUMO's energy of Me₂DCNQI-d₁ itself due to the molecular vibration of Me₂DCNQI-d₁. The other is derived from the modulation of coordination energy of Cu cation due to the molecular vibration Me₂DCNQI-d₁. A coupling constant of the former type is the one commonly known and non zero only for the a₂ mode molecular vibration. This is related to OEMVC band. A coupling constant of the latter type is exceptional one in the organic conductors. This type of the constant should be large only for the vibrational mode associated with CN groups, since CN-groups coordinate to copper cation. We consider this type of coupling constant related AEMVC. Since the change of coordination energy should result in charge transfer between Cu and Me₂DCNQI-d₁, the EMVC absorption band associated with this coupling constant should be polarized along the direction of coordination bond. This is consistent with the observation of AEMVC mode polarized perpendicular to the c-axis. Similar discussions were given by Lunardi et al on the Fano-type lineshape of the vibrational band observed in (Me₂DCNQI)₂Cu.

3.3 Local-stress effect on the spectra

Figure 8 shows the typical reflectance spectra of (Me₂DCNQI-d₁)₂Cu, whole one side of which is adhered to the copper block with a small amount of grease. In this measurement the sample is expected to be gradually stressed as decreasing temperature, because of the difference in thermal expansion coefficient between the sample and copper. The characteristic features of the spectra shown in Fig. 8 are as follows: 1) they exhibit EMVC bands below 100 K; 2) the EMVC bands become intense on lowering the temperature and decrease the intensity at 30 K; 3) Drude-like dispersion do not completely disappear all the temperature range down to 30 K. These features contrast

![Graph showing conductivity vs wave number](image-url)

Fig. 7. Vibrational structure in the conductivity spectra of (Me₂DCNQI-d₁)₂Cu for the polarization perpendicular to the c-axis. The conductivity spectra are obtained through the Kramers-Kronig transformation of reflectance spectra with 4 cm⁻¹ resolution. Note that the temperature shown in this figure has some ambiguity, arising from poor thermal contact between sample and thermometer. (See the caption of Fig. 4 and the text.)
with the spectra shown in Fig. 3. This indicates how large local stress affect the optical spectra in (Me₂DCNQI-d₁)₂Cu. Based on the interpretations described previously the first feature can be explained by the partial CDW formation below 100 K, while the third feature by the existence of free carriers down to 30 K. The most plausible explanation on this spectral change is to consider that the metallic and insulating phase inhomogeneously coexist in the stressed sample, although we can not completely exclude the possibility that the sample is in a new state which is different from both the metallic and insulating state, described previously.

Local-stress effect is not usually observed in organic conductors. However, the metal-insulator transition of DCNQI salt is so sensitive that particular attention should be paid to the optical study of these salts. Especially, a care should be taken on the interpretation of powder absorption spectra, since microcrystals used in measurements should be stressed when they are formed into KBr Disk, etc. In fact the EMVC absorption bands of the (Me₂DCNQI-d₈)₂Cu reported in ref. 21 exhibit temperature dependence of absorption intensity similar to that shown in Fig. 8.

§4. Summary and Conclusion

We have measured the temperature dependence of the infrared polarized reflectance spectrum of (Me₂DCNQI-d₁)₂Cu single crystal under almost stress-free condition. We observed several phenomena associated with the metal-insulator transition. They are 1) disappearance of Drude-like absorption for both E//c and E⊥c polarizations; 2) appearance of charge transfer absorption for E//c polarizations; 3) appearance of EMVC mode for E//c spectrum; 4) split and shift of b₀ vibrational mode; 5) appearance of anomalous EMVC (AEMVC) associated with CN stretching mode. The discontinuity of the spectra at the phase transition suggests that the phase transition is first-order.

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References

8) Hereafter we definitely note the degree of deuteration as $\text{Me}_2\text{DCNQI-d}_n$, where $d_n$ represent that $n$ deuterium atom is included in a $\text{Me}_2\text{DCNQI}$ molecule. $\text{Me}_2\text{DCNQI-d}_n$, i.e. $\text{Me}_2\text{DCNQI}$ which do not include deuterium, is simply noted by $\text{Me}_2\text{DCNQI}$.
16) Hereafter we neglect the unsymmetrical effect arising from deuteration.