Thermodynamical Study of (DMe-DCQNI)$_2$Cu System
- Mechanism of Reentrant Metal-Insulator Transition -

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We have experimentally studied the mechanism of reentrant metal-insulator-metal transition of DCNQI-Cu system. Measurements of specific heat and latent heat were carried out by thermal relaxation (0 < T < 40 K), adiabatic pulse (20 < T < 100 K) and Differential Thermal Analysis (DTA) methods on samples under various chemical pressures. From the experimental results, we determined the Gibbs free energy difference between metallic and insulating phases and succeeded to draw the phase diagram that reproduces the experimental result quite well. We conclude that the free energy change of free electrons (metallic phase) to localized electrons with spin 1/2 (insulating phase) is essential to drive the anomalous phase transition in this system. Contribution of lattice system is also clarified.

KEYWORDS: DCNQI-Cu, CDW, reentrant metal-insulator transition, specific heat

§1. Introduction

Under the ambient pressure, the organic conductor (DMe-DCNQI)$_2$Cu is a good metal:1) It is metallic from the room temperature down to the liquid helium temperatures. Its conductivity at low temperatures is the highest among the organic conductors. The metallic state, however, is fragile against pressure.2-4) Even a weak pressure makes the metallic state unstable. For example, a sample under a pressure of about 200 bar undergoes a metal-insulator transition at about 70 K (refer to Fig. 1).

Entering into the insulating phase, three-fold lattice distortion due to the CDW formation appears5-7) and the conductivity drops by 6-8 orders of magnitude within a few Kelvin. Among many drastic changes, an important modification of the insulating phase is the appearance of localized spins. In the insulating phase, one third of copper ions is found to be in the Cu$^{2+}$ states with spin $S = 1/2$.8-11)

On further cooling, the behavior of the system depends on the pressure. A sample under pressures above 240 bar remains insulating to the lowest temperatures. On the other hand, under intermediate pressures (75 < P < 240 bar), it exhibits a jump of the conductivity by several orders of magnitude and returns to a metal again. We refer to those successive transitions (metal to insulator transition followed by insulator-metal transition) as the reentrant M-I-M (metal-insulator-metal) transitions.

To clarify the mechanism of this M-I-M transition has been one of the main theme of the physics of organic conductors. Theoretically, it was discussed based on both phenomenological12) and microscopic models.13) No experimental attempts, however, were made to approach this problem directly. In this article, we focus on the mechanism of these reentrant phase transitions. Thermodynamical analysis is done based on the results of thermal measurements.

To escape from difficulties inherent in thermal measurements under pressures, we carried out the measurements, using the samples under "chemical pressures". The "chemical pressure" is recognized in samples in which constituent (DMe-DCNQI)$_2$Cu molecules are replaced by molecules with some modifications. Some of them show the M-I or M-I-M transitions under zero pressure. Therefore, these systems under zero pressure can be regarded to be in the same state with a (DMe-DCNQI)$_2$Cu system under pressures. In such cases, we

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Fig. 1. P-T phase diagram of (DMe-DCQNI)$_2$Cu system.
use a term “chemical pressure”. The “chemical pressure” of a specific material is estimated from the critical temperatures of phase transitions of the material. We find the “physical pressure” under which the (DMe-DCNQI)$_2$Cu system exhibits phase transitions at the same critical temperatures with the given material, and define it as the “chemical pressure” on the material.

Among several modifications of molecules that are effective to apply chemical pressure, deuteration of DMe-DCNQI molecule was found to be the best.\textsuperscript{14-18} In this system, DMe-DCNQI molecules are substituted by those in which hydrogen atoms at some selected positions are replaced by deuterium atoms. As we show below, different configuration of deuterium gives different chemical pressure. Being free from inhomogeneities and imperfections, this system allows us to study the various physical quantities under uniform chemical pressures.

Table I summarizes the samples we used. A sample is denoted as $d_n[a_1,a_2;b]$ by the numbers of deuterium atoms in the molecule. Here, $a_1$ and $a_2$ are the numbers of deuterons in each of two methyl groups, and $b$ in six-member-ring. The number $n (= a_1 + a_2 + b)$ denotes the total of deuterons in a molecule. In this system, the effective pressure can be varied by changing the rate of the deuteration. As the number of deuterium atoms increases, the lattice constant and unit volume decrease and the coordination angle $\alpha$ around Cu increases.\textsuperscript{17,18} These observations support the phenomenological equivalence of the deuteration to the application of the physical hydrostatic pressure. Kato estimated the effective pressures $P_{\text{eff}}$ as $P_{\text{eff}} = 80[a_1 + a_2 + 0.2b]$ bar.\textsuperscript{18}

We performed specific heat and latent heat measurements on samples under various chemical pressures. From the temperature dependence of the entropy, we quantitatively estimate the Gibbs free energy, which gives the information concerning the stabilization of the phase. The results were used to discuss the mechanism of the phase transitions.

In §3, we present the experimental results. First, in §3.1 we determine the temperature dependence of specific heat and entropy in the insulating phase. In this phase, we find spins on Cu$^{2+}$ ions are important. In §3.2, we investigate the specific heat in the metallic phase. It gives the information concerning the free electrons. From these observations, we conclude that the phase transitions in this system are determined mainly by the competition of these two freedoms. However, to discuss the transitions quantitatively, we have to examine a role of the lattice system.

In §3.3.1, we describe the measurements of DTA that give the latent heats $\Delta Q$ released or absorbed at the phase transitions. These experiments give us the entropy difference between metallic and insulating phases in a wide temperature region. It is also important in giving us the information on the contribution of the lattice system. In §3.3.2, we describe the measurement of the specific heat both in metallic and insulating phases on the same sample. We succeeded in doing that utilizing a large hysteresis of the lower temperature phase transitions. This experiment was also used to determine the temperature and pressure dependence of entropy difference in both phases. These entropies enable us to evaluate the free energy in both phases. In §3.3.2 and §3.3.3, we present detail investigations of the difference of specific heat in both phases $\Delta C = C_M - C_I$. Finally, §4 is devoted to the discussion of the phase transitions. We evaluate the Gibbs free energy difference using experimental results and discuss the critical temperature as a function of the pressure.

§2. Experiments

We measured the specific heat using single crystals with the weight of about 0.2-0.5 mg. The thermal relaxation method\textsuperscript{19,20} is used in the temperature region $0.5 < T < 40$ K and pulse method in the region $20$ K $< T < 100$ K. We also carried out the Differential Thermal Analysis (DTA) to measure the latent heat associated with the transition. We used a Cernox 1050 as the thermometer. For both the electrical leads and thermal contact lead between the sample and the heat bath, we used stainless wires with 15 $\mu$m diameter.

§3. Results

3.1 Entropy in the insulating phase (Spin freedom of Cu$^{2+}$)

In this section, we describe specific heat measurements in the insulating phase. Our purpose here is to determine the entropy of the system in the insulating phase. The results of this section will be used in the §4 for the thermodynamical discussion on the M-I-M transitions.

Two samples $d_0[3,3;2]$ and $d_0[3,0;0]$ were used for these experiments. These samples undergo a metal-insulator transition at about 80 K and remain insulating below this temperature. Since no reentrant transition to the metallic state occurs, they provide us a good testing ground of the insulating phase over a wide temperature region including low temperatures.

An example of the result is shown in Fig. 2(a). The specific heat shown in this figure consists of two components: One component is characterized by a peak around 6.8 K. We ascribe this component to the magnetic phase transition of spins on Cu$^{2+}$ ions. The reason is as follows. First, the peak position (6.8 K) coincides with the temperature where AF (antiferromagnetic) ordering of the
spins is reported to occur.\textsuperscript{21,22} Secondary, the shape of this peak has a character common to second order phase transitions of spin systems.

The remainder is the second component that is due to the lattice vibration. At low temperatures, this component is small and is submerged under the large peak of the first component, but it becomes apparent at higher temperatures (10 < T < 18 K). It obeys well-known \( T^3 \) law.

Using the first component of the specific heat, we calculated the entropy of the spin system. The spin component \( S' \) (the first component) is derived from subtracting the lattice component \( (\beta T^3) \) from the total specific heat \( (C - \beta T^3) \). Then, the entropy is calculated by integrating \( C'/T \) over temperature.

The resulting entropy is shown in Fig. 3. It monotonically grows as the temperature goes from 2 K to 18 K and stays constant above 18 K where the spin system is considered to be completely random. The saturated value of the entropy is about 1.8 J/mol K.

The number of spins participating in this phenomenon is estimated from the saturated value of entropy. Since the spin on a Cu\( ^{2+} \) ion is 1/2, the entropy well above the AF transition temperature is given by \( S_o = k_B N \ln 2 \), where \( N \) is the number of Cu\( ^{2+} \). Putting \( S_o = 1.8 \) J/mol K, we have \( N = N_o/2.8 \), where \( N_o \) is the Avogadro’s number. It indicates that about one third of Cu atoms is in the Cu\( ^{2+} \) states, which is in good agreement with other estimates.\textsuperscript{8-11} \( S_o = 1.8 \) J/mol K is somewhat underestimated, because the integration of the \( C' \) is restricted between 1.4 K and 15 K. In the discussion in \S4, we use \( S_o = 1.9 \) J/mol K, which corresponds to \( N = N_o/3 \).

Another important experimental observation is the ineffectiveness of the chemical pressure on the spin system. It is demonstrated in Fig. 2(b). Here, the specific heat of spin system for two samples with different chemical pressures (240 bar for \( d_3[3,0;0] \) and 512 bar for \( d_8[3,3;2] \)) are illustrated. Apparent coincidence of two curves proves that the temperature dependence of the specific heat due to Cu\( ^{2+} \) spins is independent of pressure.

This section is summarized as follows.

1) The entropy of the insulating phase \( S_1 \) consists of two components; lattice component \( S_{1L} \) and the spin component \( S_{1S} \): \( S_1 = S_{1L} + S_{1S} \).

2) At low temperatures, spins are in an ordered state with low entropy. Passing through the phase transition at \( T_N = 6.8 \) K, the spin component of entropy grows from zero to 1.9 J/mol K. Above 18 K, it stays constant.

3) The spin entropy is independent of the “chemical pressure”. Therefore, \( S_{1S}(T, P_{\text{eff}}) \) can be expressed by a function, \( S_{LS}(T) \), which depends on temperature but is independent of \( P_{\text{eff}} \): \( S_{1S}(T, P_{\text{eff}}) = S_{LS}(T) \).

3.2 Thermal property of the metallic phase

In this section, we deal with the metallic state. The discussion is based on specific heat data of the samples \( d_0[0,0;0] \), \( d_1[1,0;0] \), \( d_2[1,1;0] \) and \( d_2[2,0;0] \) which are metallic at low temperatures. For all of them, specific heat obeys the \( \gamma T + \beta T^3 \) relation in the region \( 0.5 < T < 2 \) K. What we are interested in, here, is the \( \gamma T \)-term that originates from the electrons near the Fermi energy. The parameter \( \gamma \) known as the Sommerfeld constant gives a direct information on the density of states at the Fermi level, \( N(E_F) \).

Table II lists the values of \( \gamma \). Insulating samples \( d_0[3,0;0] \) and \( d_8[3,3;2] \) have \( \gamma = 0 \) as is expected. Metallic samples, on the other hand, have finite values of
γ. They are about 25 mJ/molK² for all metallic samples. The entropy $S_{\text{M, e}}$ due to electrons in the metallic state is calculated as $S_{\text{M, e}} = \int \frac{\gamma}{T} \, dT$. The resulting entropy $S_{\text{M, e}}$ is given by $S_{\text{M, e}} = \gamma T$ with $\gamma = 25$ mJ/molK². Adding the entropy, $S_{\text{M, L}}$, due to lattice vibration, we can write the total entropy of the metallic phase, $S_{\text{M}}$, as $S_{\text{M}} = (S_{\text{M, L}} + S_{\text{M, e}}) = S_{\text{M, L}} + \gamma T$.

Note that γ values are the same for all four metallic samples. It implies that the chemical pressure does not affect the entropy of the electron system in the metallic states.

As a summary,

1) The entropy of the metallic phase $S_{\text{M}}$ is given as a sum of $S_{\text{M, e}}$ due to the conduction electron and $S_{\text{M, L}}$ due to lattice: $S_{\text{M}} = S_{\text{M, L}} + S_{\text{M, e}}$.

2) The entropy of the electron system is given as $S_{\text{M, e}} = \gamma T$ with $\gamma = 25$ mJ/molK².

3) The Sommerfeld parameters $\gamma$ are independent of the material (or the chemical pressure).

So far, we studied the thermal properties both of the metallic states and of the insulating state at low temperatures. In the metallic state, conduction electrons as well as the lattice system play a key role in the thermal behavior. In the insulating state, conduction electrons disappear. Instead, there come up spins. The phase transition of this system, thus, is expected to be determined by these two freedoms together with the contribution of the lattice system.

The experiments mentioned in §3.1 and §3.2 were done at low temperatures below 20 K. In order to discuss the full phase transition of the system, however, it is necessary to have information in a wider temperature region. In the higher temperature region, it is hard to determine the entropy of the electron system because the specific heat of electrons is on top of a very large specific heat of lattice. A possible way to determine that in higher temperature is to utilize latent heat at the phase transition. From the latent heat, we have the entropy difference between two phases.

### 3.3 Measurement of the entropy difference between metallic and insulating phases

#### 3.3.1 Latent heat

In this section, we describe the determination of the entropy difference between metallic and insulating phases. It was done utilizing the latent heat at the phase transitions. This opened a way to estimate the Gibbs free energy in a wider temperature region than we examined in §3.1 and §3.2.

Latent heat can be determined by Differential Thermal Analysis (DTA) method. In the experiment, jump of the sample temperature at the M-I transition is observed which indicates the appearance of finite latent heat. The latent heat ($\Delta Q$) is estimated by integrating $\Delta T \times K$ over the time for the system to complete the phase transition. Here, $\Delta T$ and $K$ are the temperature difference and thermal conductivity between the sample and the thermal bath, respectively. The latent heats observed for three samples $d_2$, $d_4$ and $d_6$ are listed in Table II. The latent heat $\Delta Q$ is related to the entropy difference $\Delta S = S_M - S_I$ between metallic and insulating phases through an equation, $\Delta S = \Delta Q / T_C$.

In discussing the phase transition, we utilize the difference of Gibbs free energy between two phases. It is calculated by integrating the entropy difference $\Delta S$ over temperature. Since different material has different chemical pressure, each sample has, in general, different curve of $\Delta S(T)$. Therefore, in order to discuss the phase transition of a sample, we need data of $\Delta S$ of that sample as a function of $T$. In experiments, however, we have $\Delta S$ only at the transition temperature ($T_C$) of the sample as shown in Fig. 3. There seems no way to draw the curve of the temperature dependence of $\Delta S$. But we can do it as follows.

Look at three points in Fig. 3 that are indicated by (■). They are obtained on the same sample, $d_2[1,1,0]$. This sample undergoes reentrant metal-insulator-metal transitions. Utilizing three transitions at 61 K, 37 K (heating process) and 20 K (cooling process), we could determine $\Delta S$ at three different temperatures. A clue to

### Table II. Effective pressure $P_{\text{bar}},$ Latent heat $\Delta Q,$ entropy difference $\Delta S (S_M - S_I),$ Sommerfeld constant $\gamma$ and lattice specific heat coefficient $\beta$.

<table>
<thead>
<tr>
<th>sample</th>
<th>$P_{\text{bar}}$</th>
<th>$\Delta Q_{/ \text{Jmol}^{-1}}$</th>
<th>$\Delta S_{/ \text{Jmol}^{-1} \text{K}^{-1}}$</th>
<th>$\gamma_{/ \text{mJmol}^{2}}$</th>
<th>$\beta_{/ \text{mJmol}^{4}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_2[0,0,0]$</td>
<td>0</td>
<td>0</td>
<td>$25 \pm 2$</td>
<td>$3.4 \pm 0.1$</td>
<td></td>
</tr>
<tr>
<td>$d_2[1,1,0]$</td>
<td>160</td>
<td>42</td>
<td>$0.70$</td>
<td>$22 \pm 3$</td>
<td>$4.0 \pm 0.5$</td>
</tr>
<tr>
<td>$d_2[2,0,0]$</td>
<td>160</td>
<td>42</td>
<td>$0.70$</td>
<td>$22 \pm 3$</td>
<td>$4.0 \pm 0.5$</td>
</tr>
<tr>
<td>$d_3[1,1,0]$</td>
<td>192</td>
<td>76</td>
<td>$1.02$</td>
<td>$0 \pm 3$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
<tr>
<td>$d_3[0,0,0]$</td>
<td>240</td>
<td>—</td>
<td>—</td>
<td>$0 \pm 3$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
<tr>
<td>$d_4[3,3,2]$</td>
<td>512</td>
<td>122</td>
<td>$1.45$</td>
<td>$0 \pm 3$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
</tbody>
</table>
draw the curve of $\Delta S(T)$ is given by these data. The curve for this sample should pass these points. Among possible curves of $\Delta S(T)$, we take the simplest one; a line connecting the points. Although this is only a hypothesis here, in §3.3.2 and §3.3.3, we give evidence indicating $\Delta S(T)$ of this sample is a linear function of $T$.

Another point we should note in Fig. 3 is that all data of $\Delta S(T_c)$ of different samples are located on the line of $\Delta S(T)$ for the sample $d_2$. This fact strongly suggests that 1) the curves of $\Delta S(T)$ are independent of sample (or chemical pressure) and that 2) they are expressed as a line connecting points $\Delta S(T_c)$ in Fig. 3. The suggestion 1) can be approved because it is consistent with what we found in the experiment mentioned in §3.1 and §3.2. There, we found that the thermal property of the present systems is independent of the chemical pressure both in metallic and insulating phases.

Accepting the picture that $\Delta S$ is independent of chemical pressure, we are led to a conclusion that the temperature dependence of $\Delta S$ is given by the line shown in Fig. 3 for all the samples with different chemical pressures. Hence, we can write $\Delta S(T, P_{eff}) = \gamma T - S_o$, with parameters $\gamma$ and $S_o$ which are independent of chemical pressure $P_{eff}$. From the slope of the line, we get $\gamma = 40 \text{ mJ/molK}^2$. The constant $S_o$, on the other hand, is found to be equal 1.9 mJ/molK. This is the same value with $S_o$ we estimated in §3.1 as the entropy of the spin system at temperatures above 18 K.

On the left ordinate of Fig. 3, we plot $\Delta S + S_o = -\gamma T$. The meaning of this value is as follows. Using the notations mentioned in the summary of §3.1 and §3.2, we obtain $\Delta S = \Delta S_M - S_I = S_M - (S_{IM} + S_{IL})$ and $S_o = S_{IL}$ at $T > 18$ K. Combining these equations, we have $\Delta S + S_o = S_M - S_{IL}$. Therefore, $\Delta S + S_o$ is considered to be the entropy of the metallic phase that is measured on the base of the entropy of lattice in the insulating phase ($S_{IL}$). On the other hand, $S_{IL} = S_I - S_{IL}$ is the entropy of the insulating phase measured on the same base $S_{IL}$. In Fig. 3, we plot both $\Delta S + S_o$ and $S_{IL}$ (refer to the left ordinate).

Lastly, we give another expression for $\Delta S + S_o$ to use in §4 in the discussion of the origin of $\gamma$. Substituting $S_M = S_{Me} + S_{ML}$ into $\Delta S + S_o = S_M - S_{IL}$, we obtain $\Delta S + S_o = \gamma T = S_{Me} + S_{IL}$. Here, $S_{Me}$ is the entropy due to electrons in the metallic phase and $\Delta S_{IL}$ is the entropy difference of lattice between metallic and insulating phases $(\Delta S_{IL} = S_{ML} - S_{IL})$. We use this expression in the discussion in the §4.1.

In the next two subsections, we mention other experiments indicating that $\Delta S$ is given as $\Delta S = \gamma T - S_o$.

### 3.3.2 Direct determination of the temperature dependence of specific heat difference $\Delta C$

In this subsection, we give further evidence indicating that $\Delta S$ is written as $\gamma T - S_o$. Experiments were made using the sample of $d_2[1,1;0]$. As shown in the inset of Fig. 4, the phase transition of this system exhibits a large hysteresis in the cooling and heating processes. For example, when the sample is cooled, it changes from a metal to an insulator at about 61 K, and returns to a metal at $T_{CC} = 20$ K. When heated, on the other hand, the phase transition to an insulator does not occur at 20 K, but the system remains metallic up to $T_{CH} = 37$ K. This large hysteresis allows us to measure the specific heat both of the insulating and metallic phases on the same sample in the temperature region between $T_{CC} = 20$ K and $T_{CH} = 37$ K. Experiments were done using the thermal relaxation method.

Figure 4 illustrates the specific heat data in cooling and heating processes for the sample $d_2[1,1;0]$. Above 37 K and below 20 K, coincidence of two curves is good. In the intermediate temperatures, on the other hand, curves apparently separate. It is because the sample is in the insulating phase in the cooling process, and in the metallic phase in the heating process.

The difference of the specific heat between heating pro-
cess and the cooling process \( (\Delta C = C_H - C_C) \) is shown in Fig. 5. In the region of 25-37 K, it is well fitted by \( \Delta C = \gamma^* T \) with \( \gamma^* = 40 \text{ mJ/molK}^2 \). The entropy difference estimated from this specific heat is written as \( \Delta S_{\Delta C} = \gamma^* T - \text{const} \). The constant cannot be determined in this experiment. However, combining the data with those mentioned in the previous sections, we can expect \( \text{const} = S_0 = 1.9 \text{ J/mol K} \).

### 3.3.3 Measurements of \( \Delta C \) and \( \Delta S \) at higher temperature phase boundary

Experiments mentioned so far are done at temperatures below 40 K. Here, we give an experimental result that shows that \( \Delta S_{\Delta C} = \gamma^* T - \text{const} \) also in higher temperatures. It is given in the experiment measuring the specific heat in the vicinity of higher temperature M-I transition for the sample \( d_2[1,1;0] \). Experiment was made using the adiabatic method. This method is powerful in detecting a small signal change on top of large lattice specific heat.

We found a discrepancy in data obtained in the heating process and cooling process. In the heating process, we observed a peak at the transition temperature as shown in Fig. 6(a). This peak does not mean the existence of anomaly in the specific heat, but it is due to latent heat.

It appears only when the system crosses the phase boundary from low temperature to high temperature. In the cooling process, latent heat does not affect the measurement for the following reason. Imagine two successive measurements in the cooling process; one just above the transition temperature and one below it. The experiment is done as follows: i) After the measurement at the temperature above \( T_C \) is completed, the sample temperature is set to a lower value below \( T_C \) by decreasing the bath temperature. ii) Then, the sample is heated to have a small temperature difference between the bath, and the heat introduced into the sample is measured.

In this process, the sample crosses the phase boundary in the procedure i). The latent heat appears during this process. However, it is not measured. Latent heat affects the measurement in case that the sample crosses the phase boundary again from low temperature to high temperature in the procedure ii). However, it never happens, because once the sample enters into the insulating state, it is stabilized and the phase boundary shifts to a much higher temperature. The system can not cross the new phase boundary in the procedure ii) in which the temperature is raised only a little. Therefore, we don’t meet the latent heat in this measurement. Such a behavior of the latent heat is a characteristic of the first order phase transition with a wide hysteresis.

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**Fig. 6.** Specific heat in the region of the higher temperature M-I phase boundary, in the heating process (a) and cooling process (b).

(a) The measurement in the heating process is affected by the absorption of the latent heat at the transition temperature that appears as peaks in the figure. (b) In the cooling process, latent heat does not affect the specific heat measurement. In this process, we clearly see a jump of the specific heat by an amount of \( \gamma^* T \) at the phase transition at about 60 K. The dotted line indicates the temperature dependence of \( C_1 \). The dashed line, on the other hand, draw \( C_1 + \gamma^* T \). Data in the metallic phase fit well to this line.
Another point we want to emphasize in Fig. 6 is the discontinuous change of the specific heat at the phase boundary (Fig. 6(b)). The specific heat in the metallic phase is larger than that in the insulating phase. From this curve, we can determine the specific heat difference between two phases. Dashed line in Fig. 6(b) plots $C_I + \gamma^* T$, where $C_I$ is the specific heat in the insulating phase. Note that it is connected to the line of $C_M$ (the specific heat in the metallic phase) without discontinuity or a kink. Therefore, we reasonably expect that this line gives the specific heat that the sample in the metallic phase will have, if it is realized in this temperature region. As the result, we have $\Delta C = C_M - C_I = \gamma^* T$.

Since $\Delta C = T (\frac{d\Delta S}{dT})$, the temperature dependence of $\Delta S_{d2}$ is of the form $\Delta S_{d2} = \gamma^* T - \text{const}$. As a conclusion, we find in the high temperature region around 61 K, $\Delta S_{d2}$ has the same form with that we find at lower temperatures.

§4. Discussion

4.1 The origin of the term $\gamma^* T$

In the above experiments, we found that the entropy difference between metallic state and insulating state is written as $\Delta S = \gamma^* T - S_o$. Before going into the discussion of the phase transition, we analyze the origin of this entropy difference especially of the term $\gamma^* T$.

We derived in §3.3.1, $\gamma^* T = \Delta S + S_{I,S} = S_{M,e} + \Delta S_L$. Here, $\Delta S_L$ is the entropy difference of lattice between metallic and insulating phases and $S_{I,e}$ is the entropy due to electrons in the metallic state. Since $S_{M,e} = \gamma^* T$ ($\gamma$ is the Sommerfeld constant), $\gamma^* T = S_{M,e} + \Delta S_L = \gamma^* T + \Delta S_L$.

The temperature dependence of $\gamma^* T$ looks to suggest that it originates from the free electrons. Actually, if $\Delta S_L = 0$ (i.e., if the difference in the phonon modes between insulating and metallic phase is small), $\gamma^* T$ is identical to $S_{I,e}$. In that case, the coefficient $\gamma^*$ should be equal to the Sommerfeld constant $\gamma$. The value $\gamma^* = 40 \text{ mJ/molK}^2$ however, is too much different from the one ($\gamma = 25 \text{ mJ/molK}^2$) we found at low temperatures below 4K (refer to §3.2).

A way to explain this difference is to assume a temperature dependence in the density of state $N(E_F)$ at the Fermi surface. According to magnetic susceptibility measurements, however, $N(E_F)$ is constant over high and low temperature metallic states. Thus, the difference could not be ascribed to the change in $N(E_F)$. There must be other freedom participating in $\gamma^*$.

We believe the lattice vibration is responsible. In the temperature region, 20 K $< T < 100$ K, the specific heat of lattice was found not to be proportional to $T^3$ but roughly proportional to $T$ both in insulating and metallic phases. Since the slope of the temperature dependence of it may be different between two phases, a term $\Delta S_L = \alpha T$ will be added to the specific heat difference when the system crosses the M-I phase boundary. We believe that $\gamma^* = \gamma + \alpha$: the sum of the Sommerfeld constant $\gamma$ and $\alpha$ which comes from lattice.

4.2 Mechanism of the reentrant phase transition

In the experiment, we found 1) In the insulating phase, the entropy due to spins on Cu$^{2+}$ ions is important. Above 18 K, the entropy coming from this freedom is constant, $S_o = 1.9 \text{ mJ/molK} (-\frac{N_B}{2} \ln 2$).

2) In the metallic phase, the free electron system having a Fermi surface appears. The entropy is given as $\gamma T$, where $\gamma = 25 \text{ mJ/molK}^2$.

3) The entropy difference $\Delta S$ between two phases is the sum of the difference of these two entropies and the difference of lattice entropies. $\Delta S$ was determined experimentally. At temperatures above 18 K, $\Delta S$ is written as $\Delta S = \gamma^* T - S_o$, with $\gamma^* = 40 \text{ mJ/molK}^2$.

4) All these properties were found to be independent of the chemical pressure.

In this section, we discuss the origin of the phase transitions based on the observation mentioned above. For a system placed under a constant pressure, the phase that has the lowest Gibbs free energy $G(=U - TS + PV)$ is realized. What we need, thus, is $\Delta G(=G_M - G_I)$, the free energy difference between metallic and insulating phases. It is calculated from the experimental results as follows. In the quantitative discussions, we use parameters, $S_o = 1.9 \text{ mJ/molK}$ and $\gamma^* = 40 \text{ mJ/molK}^2$.

The derivative of $\Delta G$ is given as $d\Delta G = -d\Delta SdT + \Delta VdP$, where $\Delta S(=S_M - S_I)$ and $\Delta V(= V_M - V_I)$ are differences of each quantity between metallic and insulating phases. Since our sample is placed under a pressure close to zero, $d\Delta G = -\Delta SdT$. Therefore, $\Delta G$ is given by integrating $\Delta S$ over temperature. By integrating $\Delta S = \gamma^* T - S_o$, we obtain

$$\Delta G = -\frac{1}{2}\gamma^* T^2 + S_o T + \Delta G_o. \quad (1)$$

Since $\Delta S = \gamma^* T - S_o$ applies only for $T > 18$ K where $S_o$ is constant, the integration is done over $T > 18$ K. All that occurs below this temperature is included in the constant of integration $\Delta G_o$. As a result, eq. (1) is valid only in the high temperature region above 18 K. As we found in the experiments, the first two terms of the right hand side of eq. (1) are independent of the sample or, in other words, “chemical pressure”. The difference of the sample appears only through the last term, $\Delta G_o$. In the following, we discuss the stability of phases using eq. (1) and show that eq. (1) can explain the reentrant (M-I-M) phase transitions observed in this system.

As is mentioned above, the stability of a phase is determined by the Gibbs free energy. A phase having the lowest free energy among the possible phases is realized. In the present system, the metallic state appears in the region where $G_M < G_I$, i.e., $\Delta G < 0$ and the insulating state does where $\Delta G > 0$. When we vary parameters such as temperature, a phase transition may take place. It occurs at a point where two phases have an identical free energy. In the present system, the critical temperature $T_C$ is given by the condition $\Delta G(T_C) = 0$. This quadratic equation for $T_C$ has the solutions:

$$T_C = (S_o \pm \sqrt{S_o^2 + 2\gamma^* \Delta G_o})/\gamma^*.$$

The solutions are classified into three types according to the values of $\Delta G_o$. The first case is for $\Delta G_o$ with a large negative value ($\Delta G_o < -S_o^2/2\gamma^*$). In that
case, we have no real $T_C$ and $\Delta G$ is negative all over the temperature. It means that the metallic state is stable everywhere. We meet this case in the sample with low chemical pressures ($d_0$).

The second case comes up when $\Delta G_o$ is negative and its absolute value is not so large ($-S_o^2/2\gamma^* \leq \Delta G \leq 0$). Here, we have two real positive solutions. Let them be $T_{C1}$ and $T_{C2}$ ($T_{C1} > T_{C2}$). They divide the temperature into three regions with different sign of $\Delta G$.

$$\Delta G = \begin{cases} <0 & (T > T_{C1}) \quad \text{Metal} \\ \geq 0 & (T_{C1} \geq T \geq T_{C2}) \quad \text{Insulator} \\ <0 & (T < T_{C2}) \quad \text{Metal} \end{cases}$$

According to the change in the sign, this system experiences two phase transitions. At high temperatures, the metallic state is stable. When the temperature is decreased, the first phase transition occurs at $T_{C1}$ where the system changes from a metal to an insulator. On further cooling, the second transition takes place at $T_{C2}$. Below this temperature, a metallic state becomes stable again. This behavior is just what we found in the experiment for samples under intermediate chemical pressures ($d_2[1,1,0]$ and $d_3[1,1,2]$). We called it the reentrant M-I-M transition.

The third case is for positive $\Delta G_o$. In this case, we have two real $T_C$. However, one of them is negative and has no physical meaning. The system is metallic above $T_C$ and insulating below it. The samples under high chemical pressures are classified in this case ($d_3[3,0,0]$ and $d_3[3,3,2]$).

Now, we have come to a stage where we can discuss why this system shows such a rich set of phase transitions. The Gibbs free energy difference $\Delta G$ in eq. (1) is composed of two temperature dependent terms ($-\frac{1}{2}\gamma^*T^2 + S_oT$) and a constant $\Delta G_o$. Among the $T$-dependent terms, $S_oT$ comes from the spin system in the insulating phase. The remainder is included in the term $-\frac{1}{2}\gamma^*T^2$. The main part of it is due to conduction electrons in the metallic phase, but the phonon freedom partly incorporates with it. The difference in the temperature dependence of these two terms plays an essential role in giving rise to the interesting phase transition of this system.

### 4.3 Chemical pressure and the phase diagram

As mentioned in §1, the chemical pressure is a parameter characteristic of the material. It is defined as the physical pressure on a sample of undeuterated (DMe-DCNQI)$_2$Cu ($d_0$) in which the phase transition occurs at the same critical temperatures with a given sample under the ambient pressure. In the discussion of the previous section, we found a clue suggesting the chemical pressure is related to the parameter $\Delta G_o$. Based on this finding, we discuss the origin of the chemical pressure as follows.

We rewrite $\Delta G_o$ as

$$\Delta G_o = -G_o + P_{\text{eff}}\Delta V.$$  \hspace{1cm} (2)

Here, the first term $-G_o$ represents $\Delta G_o$ for the sample $d_0$ that is under zero "chemical pressure", i.e., $P_{\text{eff}} = 0$. Since metallic state is stable in $d_0$ at $T = 0$, $\Delta G_o$ for this material should be negative ($\Delta G_o < -S_o^2/2\gamma^*$) as discussed in previous section. Therefore, we write it as $-G_o$ using a positive quantity $G_o$.

We express the remainder as $P_{\text{eff}}\Delta V$ where $\Delta V$ is the volume difference between metallic and insulating phases. Of cause $\Delta V$ is not a constant but depends both on temperature and material. However, we treat it as a constant (independent of temperature nor material), because the change was found to be small.\(^{15,17}\) On the other hand, $P_{\text{eff}}$ is a parameter that depends on the material. (According to the definition, $P_{\text{eff}} = 0$ for the sample $d_0$.) The character of the material appears only through this parameter. We define $P_{\text{eff}}$ as the chemical pressure.

Combining eq. (1) and (2), we have

$$\Delta G(T, P = 0) = -\frac{1}{2}\gamma^*T^2 + S_oT + P_{\text{eff}}\Delta V - G_o. \quad (3)$$

The solutions of the equation $\Delta G(T_C) = 0$ is

$$T_C = (S_o \pm \sqrt{S_o^2 + 2\gamma^*(P_{\text{eff}}\Delta V - G_o)})/\gamma^*. \quad (4)$$

Most parameters in this equation are experimentally determined: $S_o = 1.9\, \text{J/molK}$, $\gamma^* = 40\, \text{mJ/molK}^2$ and $\Delta V = 4\, \text{A}^3$.\(^{17}\) One exception is $G_o$. Unfortunately, we cannot directly determine $G_o$ by thermal experiments. Here instead, we treat it as a fitting parameter to reproduce the phase diagram. We chose the value of $G_o$ so that the critical chemical pressure $P_C$, above which two critical temperatures $T_C$ appears, is equal to the corresponding critical physical pressure (75 bar) in the $d_0$ system. The value of $G_o$ is given from eq. (4) as $G_o = P_C\Delta V + S_o^2/2\gamma^*$. Putting $P_C = 75$ bar, and the values of $\Delta V$, $S_o$ and $\gamma^*$ we have $G_o = 62\, \text{J/mol}$. With those parameters, we can draw the phase diagram. The result is shown in Fig. 7. It reproduces the phase diagram in Fig. 1 quite well.

### 5. Summary

We have performed a systematic study of thermodynamical properties of selectively deuterated DCNQI-Cu system, which exhibits the mysterious reentrant M-I-M transition. In the experiments, we determined the entropy difference between the insulating and metallic
phases. Based on these results, we discussed the mechanism of the phase transition of this system. The entropy of these systems is composed of two components, one is of the lattice and the other one is from the electron system.

At lowest temperatures \( T < 18 \text{K} \), we measured the specific heat of free electrons in the metallic region, and of spins in the insulating phase and calculated the entropy. At higher temperatures, on the other hand, we could not make separate measurements of these contributions of the insulating and metallic phases. Here, we determined the entropy difference between two phases, from the latent heat emitted or absorbed at the M-I transition. We also determined the temperature dependence of the entropy difference of two phases utilizing a large hysteresis of phase transition.

From the data of the entropy, we estimated the temperature dependence of the free energy and discussed the origin of the reentrant M-I-M transition in this system. The stability of the phase is primarily determined by the balance between entropies of free electron gas in the metallic phase and of localized spins in the insulating phase. We also succeeded in drawing the phase diagram. It reproduces the experimentally obtained phase diagram quite well.

We emphasize that the phenomena we encountered in this system are universal to phase transitions of Fermion particles in which free Fermion particles localize to have spin freedom. An example of this type of transition is the liquid to solid phase transition of \(^3\text{He}\). In the liquid phase, \(^3\text{He}\) atoms behave as free Fermion particles. Entering into the solid phase, they are localized on lattice sites and a new freedom due to nuclear magnetic moments appears.\(^{25-27}\)

The mechanism of the phase transition is similar in these two systems. The situation, however, is somewhat complicated in the DCNQI system than in \(^3\text{He}\) system. The \(^3\text{He}\) system is composed of only \(^3\text{He}\) atoms. In the DCNQI system, on the other hand, electrons move on the background of the lattice of DCNQI molecules. Therefore, we have two independent systems, electrons and lattice, which cooperate to determine the phase transition. Moreover, the electron system itself is complicated, because \(\pi\)- and \(d\)-electrons coexist. Such inner structure of the system gives rise to the interesting character of this material.

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