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Thermal Study of DCNQI-Cu using a High Accuracy Specific Heat Measurement System

Ayaka Matsui, Yui Takaoka, Yutaka Nishio, Reizo Kato and Koji Kajita

1Department of Physics, Toho University, miyama 2-2-1, 274-8510, Chiba, Japan
2Condensed Molecular Materials Lab. RIKEN, 2-1, Hirosawa Wako, Saitama, 351-0198, Japan

E-mail: nishio@ph.sci.toho-u.ac.jp

Abstract. DCNQI-Cu system exhibits a mysterious metal-insulator-metal (M-I-M) phase transition. Deuteration of methyl basis can control critical temperatures of these peculiar phase transitions. We have been studying a mechanism of the transitions by measuring thermal properties. To quantitatively discuss the phase transitions, we have developed specific heat measurement system in a wide temperature range between 5 K and 200 K for the sample with the weight of less than 0.3mg. We have succeeded in an observation of the specific heat jump and latent heat at this first order phase transition in the cooling and heating processes.

1. Introduction

For a high accurate measurement of small samples, we have improved a differential thermal analysis (DTA) method in the wide temperature range from 5 K to 200 K. This method is based on a simple principle and has advantages over the other methods in a high accuracy and detection of latent heat. We can measure the specific heat and the latent heat of (DMe-DCNQI)\textsubscript{2}Cu system, in which the metal-insulator-metal transition undergoes by a combination of the Charge Density Wave (CDW) with the Mott insulator [1].

We have studied (DMe-DCNQI)\textsubscript{2}Cu system, which exhibits the metal-insulator-metal transition as lowering temperatures by the thermal relaxation method [2]. We had reported the specific heat anomaly, the latent heat ascribed to the M-I-M transition and Schottky anomaly caused by the deuterium degrees of freedom [3].

2. Experimental

In this study, we used a new technique developed by Schilling et al. [4] on specific heat measurement. Some improvements to this technique were made in order to achieve a sufficiently accurate measurement of specific heat for small samples with a weight of less than 0.3 mg. In this method, we use two samples connected to a thermal bath by weak heat links as shown in figure 1. One of them is the studied sample, while the other is a standard reference material whose heat capacity \( C_r \) is well known. The measurement is performed by slowly scanning the temperature of the heat bath. When the temperature of heat bath \( T_B \) is changed, heat flows between the bath and the sample and reference. This heat flow in turn causes changes in the sample temperature \( T_s \) and reference temperature \( T_r \), given by the equations below as,

\[
\begin{align*}
C_s T_s &= K_s(T_B - T_s) \\
C_r T_r &= K_r(T_B - T_r).
\end{align*}
\]
where \( C_s \) is the heat capacity of sample; \( C_r \), heat capacity of the reference; \( K_s \), the heat conductance between the sample and the bath; and \( K_r \), heat conductance between the reference and the bath. From these equations, we have

\[
C_s = C_r \left( \frac{K_s}{K_r} \right) \frac{T_r}{T_s} \left( \frac{T_B - T_s}{T_B - T_r} \right) \tag{2}
\]

We chose Polystyrene as the reference sample. Change et al. [5] precisely determined the absolute value of the specific heat of this material. It is also important that the heat capacity of polystyrene is of the same order of magnitude as that of our sample in the entire temperature region. In our experiment, we measured \( T_B \) using a Cernox resistance thermometer, and \( T_B - T_s \) and \( T_B - T_r \) using Chromel-Constantan thermocouples. In the present study, we scanned the temperature of the heat bath at a rate of \( dT_s/dt = 7 \text{ mK/s} - 20 \text{ mK/s} \). In order to isolate the thermal radiation from the surroundings, all the measurement assemblies were placed in a sample chamber made of copper that was connected tightly to the thermal bath.

![Figure 1](image.png)

**Figure 1** Schematic view of DTA measurements system.

We can determine the heat capacity of sample \( C_s \) by measuring the temperature differences \( T_B - T_s \) and \( T_B - T_r \) if we know the temperature dependence of \( K_r/K_s \). Before the heat capacity measurement for the studied sample, we determined the temperature dependence of the ratio of \( K_r/K_s \) done by measurements of two polystyrenes, one of which was measured as the sample and the other as the reference.

It is noted that at the lowest temperature, \( T_B - T_s \) does not become zero under the thermal equilibrium condition with zero scanning rate. We can calculate the thermal bath temperature correction \( \Delta T_B \) by suggesting that \( \Delta T_B \) has the same value in the cooling and heating processes. Equation (1) can be corrected by,

\[
C_s \frac{T_{s|1}}{T_{s|1} + \Delta T_{Bs}} = K_s \left( T_{B|1} - T_{s|1} + \Delta T_{Bs} \right)
\]

\[
C_s \frac{T_{s|1}}{T_{s|1} + \Delta T_{Bs}} = K_s \left( T_{B|1} - T_{s|1} + \Delta T_{Bs} \right) - \Delta T_{Bs} \frac{T_{s|1}}{T_{s|1} + \Delta T_{Bs}} \tag{3}
\]

From these equations, we can calculate \( \Delta T_{Bs} \) assuming that \( C_s \) corresponds in both processes except in the first order transition region. We can estimate \( \Delta T_{Bs} \) to calculate \( C_s \) in both cooling and heating processes by

\[
\Delta T_{Bs} = \frac{\Delta T_{s|1}}{T_{s|1} - \Delta T_{Bs}} - \frac{\Delta T_{s|1}}{T_{s|1} + \Delta T_{Bs}} \left( T_{s|1} - T_{s|1} \right) + \Delta T_{Bs} \frac{T_{s|1}}{T_{s|1} + \Delta T_{Bs}} \tag{4}
\]

where \( \Delta T_{s|1} \) and \( \Delta T_{s|1} \) are defined as \( \Delta T_{s|1} = T_{s|1} - T_{B|1} \) and \( \Delta T_{s|1} = T_{s|1} - T_{B|1} \), respectively. Using this correction, we can obtain the heat capacity in the heating process \( C_{s|1} \) and cooling process \( C_{s|1} \).

Samples are 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, while \( b \) is the number of deuterons in six-membered-ring. The number \( n \) (\( n = a_1 + a_2 + b \)) denotes the total of deuterons in a molecule. In this
system, the effective pressure can be varied by changing the rate of the deuterium. Kato estimated the effective pressures $P_{\text{eff}}$ as $P_{\text{eff}} = 80[a_1+a_2+0.2b]$ bar. Fig. 2 shows the $P_{\text{eff}}-T$ phase diagram of the deuterated (DMe-DCNQI)$_2$Cu system.

![Figure 2 Phase diagram of (DMe-DCNQI)$_2$Cu.](image)

### 3. Results and discussions

![Figure 3. Specific heat for the sample of $h_8=d_0$ ($P_{\text{eff}}=0$ bar), $d_{2}[1,1;0](160)$, $d_{2}[2,0;0](160)$, $d_{3}[1,1;1]$ (176), $d_{4}[1,1;2](192)$, $d_{5}[3,0;0](240)$, $d_{4}[2,2;0](320)$ $d_{6}$ [3, 3; 2](496) in the cooling(red line) and heating(blue line). The origin of vertical axis for each sample is shifted by 100 J/mol·K.](image)

![Figure 4. At the phase transition, specific heat of $d_{3}[2,0;0]$ (a) and $d_{4}[2,2;0]$ (b) in the cooling (blue line) and heating (red line) process, respectively.](image)

Fig.3 shows the plot of the heat capacity and latent heat of $h_8=d_0$, $d_{2}[1,1;0]$, $d_{2}[2,0;0]$, $d_{3}[1,1;1]$, $d_{4}[1,1;2]$, $d_{5}[3,0;0]$, $d_{4}[2,2;0]$ and $d_{6}$ [3, 3; 2] under various chemical pressures. Specific heat shows the rapidly standing up and linear temperature dependence above 30 K. We can not detect the anomalous peak or excess part for $h_8$ whose metal phase is stabilized in entire studied temperatures.
As increasing the chemical pressure, the critical temperature $T_c$ of metal-insulator in higher temperature above 50 K shifts to higher temperature, while insulator-metal transition below 50 K is suppressed as shown in Fig.3. The medium temperature insulator phase is stabilized as increasing the chemical pressure. Specific heat of $d_2 \ [2,0;0]$ shows the sharp peaks at 20 K (metal-insulator transition) and 60 K (insulator-metal transition) in the heating and cooling processes accompanying clear temperature hysteresis as shown in figure 4(a). These hystereses are the key features suggesting that these metal-insulator transitions are the first order phase transitions.

Another point we should mention about the data in Fig.4 is the background specific heat. As shown in the figure, the background can be approximated by two dotted straight lines with slightly different slopes. The system changes from high temperature metallic phase to insulating phase at low temperatures Therefore, two lines represent the specific heat of the metallic phase and insulating phase. In this figure, we can estimate the specific heat difference $\Delta C$ between metal and insulator phases to be 2.7 $\text{J/mol-K}$ at 60K for $d_2 \ [2,0;0]$ and 3.1 $\text{J/mol-K}$ at 72 K for $d_4[2,2;0]$. These values are good accordance with $\gamma^*T$ with $\gamma^* = 0.040 \text{mJ/molK^2}$ reported in previous paper [2].

The temperature dependence of $\gamma^*T$ looked to suggest that it originated from the free electrons. The value $\gamma^* = 0.040 \text{mJ/molK^2}$, however, was different from the coefficient of electronic specific heat $\gamma = 0.025 \text{mJ/molK^2}$ we found at low temperatures below 4 K [2]. A way to explain this difference was to assume a temperature dependence in the density of state $N(E_F)$ at the Fermi surface. According to magnetic susceptibility measurements, however, $N(E_F)$ was 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 believed the lattice vibration was responsible. From the data of the entropy, we estimated the temperature dependence of the free energy and discussed the origin of the metal-insulator-metal transition in this system. The stability of the phase was primarily determined by the balance between entropies of free electron gas in the metallic phase and of localized spins in the insulating phase.

4. Summary
We have built up a new type of the specific heat measurements system based on the DTA method. This method can detect the high accuracy specific heat both in the cooling and heating processes for the sample with the weight of less than 0.3 mg in the temperature region from 200 K to 5 K. At the phase transition, we can observe the latent heat, which gives the information concerning change of the entropy. These measurements can discuss the mechanism of the phase transition varying the sweep rate.

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