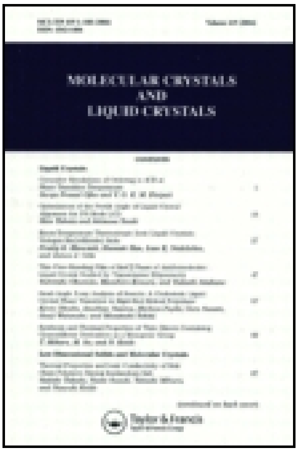

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Methyl Rotation and Reentrant Metal-Insulator Transition in Deuterated (DMe-DCNQ1) 2 Cu System

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Methyl Rotation and Reentrant Metal-Insulator Transition in Deuterated $(DMe\text{-}DCNQ1)_2Cu$ System

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We studied the thermal property of metal complex salts $(DMe\text{-}DCNQI)_2Cu$ formed of DMe-DCNQI molecules of which some of hydrogen atoms are substituted by deuterium atoms. In those systems, we have discovered peaks in the specific heat originating from the orientation freedom of deuterated methyl groups. In systems containing methyl groups with one deuterium atom (CH_2D), we found Schottky type of specific heat. In system with CHD_2, we observed peaks not of Schottky type. To find out the origin and mechanism of these anomalies, we carried out the thermal study of the mixed crystals composed of molecules with CH_2D and those with CHD_2. We clarified the conformational ordering of CHD_2 molecular along c axis in the DCNQI-Cu system.

Keywords: Methyl Rotation, Thermal properties, Order-disorder transition, M-I transition, Phase Transition, Mott Transition, CDW, Specific heat, Deuteration.

INTRODUCTION

An organic conductor $(DMe\text{-}DCNQI)_2Cu$ is known to exhibit reentrant phase transitions when it is placed under certain pressures. As it is cooled, it changes from a metallic state at high temperatures to an insulating state at intermediate temperatures and then returns to a metal again at low temperatures. In these phase transitions, mixing of π band formed of electrons on DMe-DCNQI molecule and a d band of electrons on Cu atom plays an essential role, since mixing of $2p\pi$ and 3d bands reduces the low dimensional nature of 2pπ band and, thus, stabilizes the metallic state. The mixing rate can be controlled by applying pressures on the sample [1]. The same effect is obtained when we use crystals with DMe-DCNQI molecules containing deuterated methyl groups. Since size of the methyl groups can control lattice constant along DCNQI stacking direction (c axis) that determine the distortion of crystal field surrounding a Cu atom, the deuteration of methyl group reduces its size and change the hybridization between 3d and DCNQI π band.

In the thermal experiments done to clarify the origin of the reentrant phase transition [2], we found the anomalous specific heat ascribable to the tunneling assisted rotation of methyl groups. This phenomenon was observed when there are methyl groups of which hydrogen atoms are partially substituted by deuterium atoms.

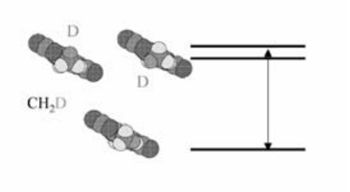
EXPERIMENTAL RESULTS AND DISCUSSION

In the present studies, the specific heat of $(DMe\text{-}DCNQI)_2Cu$ systems are measured by the thermal relaxation method. 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 number of deuterium in each of two methyl basis, and b in six-membered ring. The number $n(=a_1+a_2+b)$ denotes the total of deuterium in a molecule.

$[CH_2D]_{1-x}[CHD_2]_x$ system ($d_2[1,1;0]_{1-x}\, d_4[2,2;0]_x$)

In this experiment, specific heat of mixed crystals of $d_2[1,1;0]$ and $d_4[2,2;0]$ were examined. Several crystals with different ratios of $d_4[2,2;0]$ were used. They are denoted as $d_2[1,1;0]_{1-x}\, d_4[2,2;0]_x$ (x=0, 0.25, 0.50, 0.75, 0.84, 1.0). In all of these crystals, peaks in the specific heat are observed. To deduce the peak component from the raw data, we used data of undeuterated $(DMe\text{-}DCNQI)_2Cu$ as the background to be subtracted. The resultant data after subtraction are shown in Fig.1. The curves in Fig.1 are classified into two groups. First, between x=0 and x=0.5, the peak position does not change. Peak height , on the other hand, decreases with increasing x. Between x=0.75 and 1.00, on the other hand, we find the change in the shape of the specific heat curve. It becomes apparent above x=0.75. For x=0.75, a new peak appears at the higher temperature side of the initial peak. As x increases, this new peak grows and the peak position shifts towards higher temperatures. Finally, for x=1, the low temperature peak disappears. We found that in the small x region ($x \leqq 0.50$), the curves in Fig.1 can be well fitted by superposition of two different Schottky type functions. In the higher x region (x>0.5), on the other hand, the shape of the specific heat curve varies from the Schottky type to the phase transition type.

To understand these changes of the specific heat, first, we pick up two extreme cases (x=0 and 1) and discuss the origin of the anomalous peak.



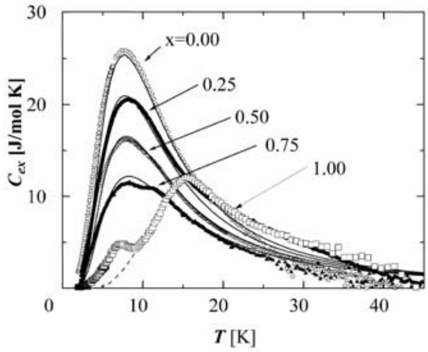


FIGURE 1 Excess specific heat of mixed crystal $d_2[1,1;0]_{1-x}\,d_4[2,2;0]x$ (x=0, 0.25, 0.50, 0.75, 1.0). Solid lines represent the Schottky function. Inset figure indicates energy scheme of three different configulation of CH_2D in DMe- DCNQI molecular.

CH_2D systems (x=0)

As will be discussed in Ref [3], the origin of the specific heat peak in this system is due to the rotation of methyl groups of which one of three hydrogen atoms is substituted by a deuterium atom (CH_2D). Because there exists high potential barrier (500K) for rotation, rotation at low temperatures can occur only through the quantum tunneling process. By systematic studies using crystals with several different CH_2D densities [3], we have clarified one CH_2D molecule add $k_B\ln3$ to the entropy. The factor ln3 indicates that there are three different stable positions for a CH_2D group.

Based on this picture, we carried out the fitting of the data by a two level Schottky function as follows,

$C(g_o, g_1, \Delta, T) = Nk_B(\Delta/k_BT)^2(g_o/g_1)\exp(\Delta/k_BT)/[1+(g_o/g_1)\exp(\Delta/k_BT)]^2$, (1)

where g_o, g_1 and Δ are the degeneracy of the energy levels for the ground (g_o) and the first excited states (g_1), and the energy difference between them (Δ). The best fitting was achieved by using g_o=1, g_1=2 and Δ/k_B=22[K] (see solid curve marked with x=0.00 in Fig.1). A possible orientations of CH_2D group in the lowest energy state and the first excited states are shown in inset of Fig.1. The configuration with the deuterium atom in the plane of the DCNQI molecule has the lowest energy, and those with deuterium atom out of plane are the doubly degenerated excited states. Another important information is obtained from the fact that the specific heat is expressed as a Schottky function. It implies that the rotation of each methyl group is independent.

CHD_2 system (x=1.00)

Sample of x=1.00 is d_4[2,2;0]. It is composed of DMe-DCNQI molecules each containing two CHD_2 groups. We see two peaks of specific heat at 7K and 15K. The small peak around 7K is ascribed to the antiferro-magnetic (AF) transition of the Cu^{2+} spins. After subtracting the specific heat due to the AF ordering, we obtain the specific heat we are interested in here (dashed curve). Two things should be noted. First, the shape of this curve is quite different from the Schottky curve shown in Fig.1. Secondly, the entropy of this excess specific heat is estimated to be 12.6J/mol K. This value is only one third of 4Rln3=36J/molK observed in the d_2[1,1;0] with CH_2D molecule. In the next part, we discuss the entropy change with the ratio x.

Mixed crystals (0<x<1)

1. entropy

Figure 2 illustrates the entropy as a function of x. Reduction of the entropy occurs linearly with increasing x from 36J/molK for x=0 to 12.6J/molK for x=1. This behavior is explained as follows: As mentioned in a previous paragraph, substitution of H atom in a CH_3 group by a D atom varies the energy scheme of the group. If we assume that substitution of a H atom located out of plane of DMe-DCNQI molecule lifts the energy of the methyl group more than the substitution of in-plan H atom, we may expect that the energies of a methyl group in the configurations (b), (c) are equal to each other and lower than that of (a). It means that the ground states of CHD_2 are doubly degenerated and the exited state is not degenerated. In this situation, entropy of ln 2 per CHD_2 will not appear in the studied temperature region (T>1.5K) and we will observe the entropy 4R(ln3-ln2). Agreement between this prediction (solid line) and the experimental results is good (see Fig.2). Note that the data for d_4[2,2,0] is also on the line. This result supports that the origin of the anomalous specific heat not of the Schottky type found in d4[2,2,0] is also ascribable to the freedom in deuterated methyl groups.

2. Shape of excess term

Next, we will discuss the shape of the curve. As shown in Fig.1, the specific heat for the samples with $x \leqq 0.5$ have a maximum around 8K, of which the peak height is a decreasing function of x. We found that each curve in this region is well fitted by a function $C(x,T) = f_1(T)\ (1\text{-}x) + f_2(T)\ x$, ($x<0.75$). Here, $f_1(T) = C(g_o=1,\ g_1=2,\ \Delta/k_B=22\text{K},T)$ and $f_2(T) = C(2,\ 1,\ 22\text{K},\ T)$ are the Schottky functions given by equation (1). As demonstrated in Fig.3 for the sample x=0.5, agreement is fairly well.

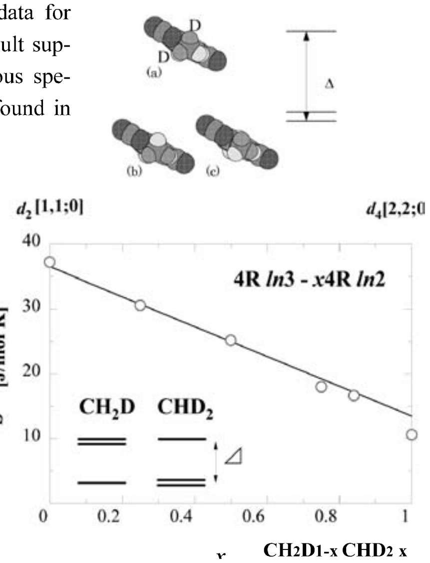


FIGURE 2 The excess entropy vs. CHD_2 concentration. Solid line indicate the expected entropy variation of 4R(ln3-$x$ln2).

Between x=0.75 and x=1, on the other hand, a drastic change occurs. In Fig.4, we plotted the excess specific heat C' of the samples of x=0.75, 0.84, 1. Solid curves shows the Schottky functions $C(x,T)=f_1(T)(1\text{-}x)+f_2(T)x$. Agreement between Schottky curves and the experimental results is bad. In the curve for the sample of x=0.75, we find a small hump at 11K on top of the Schottky curve. Increasing x up to 0.84, the Schottky component reduces to half of the expected value (solid curve), and higher temperature hump grows to a well defined peak with the maximum at 14K. Finally, for x=1, the Schottky type component disappears and the peak position of the specific heat shifts to 16K.

A possible mechanism that determines the shape of the curve of anomalous specific heat of the sample for x=1 is the phase transition due to order-disorder in the orientation (configuration) of CHD_2 system. Since deuteration reduces the lattice constant of the crystal along the c axis [4], the mean distance between the neighboring CHD_2 decreases with increasing x. It will enhance the interaction between the methyl groups.

For the case of x=1 (d_4[2,2;0]), we expect that the system of CHD_2 drops in to the ordered state at the critical temperature 15K due to the interaction between them. Doping of CH_2D, on the other hand, reduces the interaction and suppresses the phase transition. Figure 4 shows that this changes occurs between x=1 and x=0.75.

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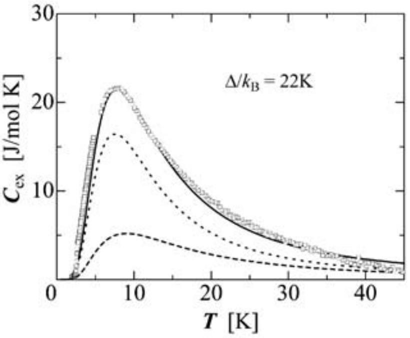

FIGURE 3 Excess specific heat of $d_2[1,1;0]_{1-x}$ $d_4[2,2;0]x$ (x=0.5). Dashed line, dotted and solid lines indicate the Schottky functions with g_1=1 and g_2=2: $f_1(T)$x0.5 (dash), g_1=2 and g_2=1:f_2(T)x0.5 (dot) and their combination $f_1(T)$x0.5+f_2(T)x0.5 (solid).

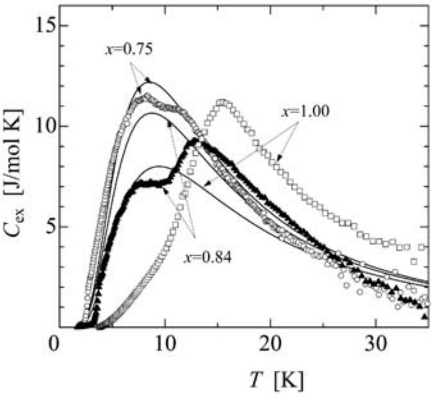

FIGURE 4 Excess specific heat of $d_2[1,1;0]_{1-x}$ $d_4[2,2;0]x$ (x=0.75, 0.84 and 1.00). Solid lines represent their addition using $C(x,T)=f_1(T)(1-x)+f_2(T)x$.