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# Spin ordering and enhancement of electronic heat capacity in an organic system of $(\text{DI-DCNQI})_2(\text{Ag}_{1-x}\text{Cu}_x)$

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## Abstract

Thermodynamic measurements on the organic system of  $(\text{DI-DCNQI})_2(\text{Ag}_{1-x}\text{Cu}_x)$  ( $x = 0, 0.05, 0.71, 0.90$ ) were performed to study the change from the charge-ordered (CO) insulating state to the  $\pi$ -d hybridized metallic state. A thermal anomaly associated with the antiferromagnetic transition that occurred in the charge-ordered lattice was observed at 6.2 K from the temperature dependence of the heat capacity of  $(\text{DI-DCNQI})_2\text{Ag}$ . We have found that the magnetic entropy around the peak is only 1.5% of  $R \ln 2$ , corresponding to the full entropy expected for the formula unit of  $(\text{DI-DCNQI})_2\text{Ag}$ . This anomaly is suppressed down to about 3 K in the  $x = 0.05$  sample owing to the disorders induced in the CO lattice. In the metallic concentration of  $x = 0.90$ , the low-temperature electronic heat capacity coefficient,  $\gamma$  was found to be enhanced by up to about  $63.6 \text{ mJ K}^{-2} \text{ mol}^{-1}$  probably owing to the cooperative effect of  $\pi$ -d hybridization and intersite Coulomb interaction ( $V$ ).

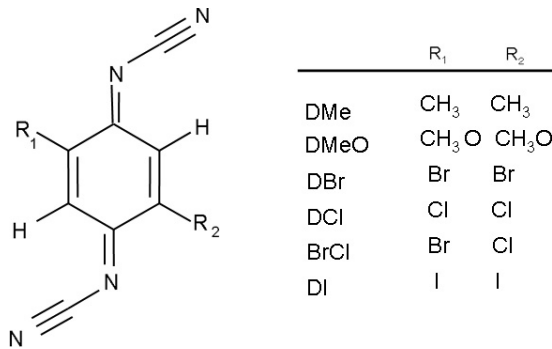
(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The charge transfer complexes consisting of organic donor or acceptor molecules with their counter ions give a fascinating stage for studying electronic properties in low-dimensional structures. In these systems, a rich variety of electronic and magnetic phases appear with the tuning of external parameters such as temperature, pressure, magnetic field, etc [1, 2]. The experimentally determined phase relations through various measurements are summarized as electronic phase diagrams which give a clue for developing new materials [3]. Although numerous organic molecules have been synthesized up to now with the purpose of producing novel properties, the series of DCNQI (dicyanoquinonediimine) molecules shown in figure 1 have been widely investigated acceptors over the last two

decades [4]. They form charge transfer complexes with metal cations and crystallize into a structure with space group  $I4_1/a$  [4–6]. The interesting point of DCNQI complexes is that  $\pi$  electrons have a strong electron–electron interaction and electron–phonon interaction in quasi-one-dimensional structures. In the case of monovalent cations like  $\text{Li}^+$ ,  $\text{Ag}^+$ , the system becomes a good candidate to study the electronic properties produced only by the  $\pi$ -electrons in the quarter-filled or effectively half-filled band. On the other hand, when the valence of cations is larger than one, as in the Cu complexes, d-electrons are known to hybridize to the  $\pi$ -band. Therefore, the DCNQI system is a unique system in which the strong Coulomb repulsions, giving the Mott or charge-ordered (CO) insulating states, electron–phonon interactions, and  $\pi$ -d coupling, compete or coexist in the same crystalline structures.

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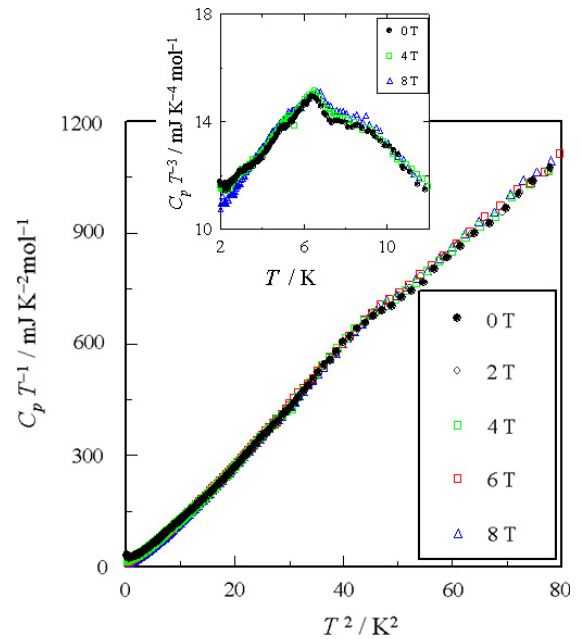
**Figure 1.** Molecular structure of ( $R_1$ ,  $R_2$ -DCNQI). The candidates for  $R_1$ ,  $R_2$  are shown in the right-hand table.

The complexes consisting of DI-DCNQI (diiodo-dicyanoquinonediimine) which has iodine in the  $R_1$ ,  $R_2$  are known to give most narrow electron band systems. The large radius of iodine reduces the intermolecular overlap in the stacking direction and therefore, the band energy,  $W$ , competes with the on-site or intersite Coulomb energy,  $U$ ,  $V$  [7, 8]. (DI-DCNQI)<sub>2</sub>Ag shows a non-metallic behavior below room temperature and has a charge order (CO) transition around 200–220 K [9]. A charge disproportionation with the [1010···] pattern in the stacking direction was observed by nuclear magnetic resonance (NMR) and x-ray diffraction experiments in [10, 11]. Recently, it was suggested that this CO pattern potentially has a frustration if one considers the helical structure of the DI-DCNQI arrangement in three-dimensional (3D) space [12]. The spin degree of freedom remains mainly on the electron-rich sites of DI-DCNQI molecules down to low temperatures and an antiferromagnetic order occurs around 5–6 K. On the other hand, (DI-DCNQI)<sub>2</sub>Cu is metallic down to the 10 mK region without showing any phase transition. In this salt, the average valence of the Cu cation is considered as +4/3 and the hybridization of  $\pi$ - and d-electrons in the metallic state produces the enhanced metal character which is reflected in the large paramagnetic susceptibility and the heat capacity coefficient  $\gamma$  [13, 14].

The systematic variation from the CO insulator in pure  $\pi$ -electrons to the hybridized metallic state has been studied by Ito *et al* through transport measurements of the substitution system of (DI-DCNQI)<sub>2</sub>(Ag<sub>1-x</sub>Cu<sub>x</sub>) [15, 16]. In order to extend the quantitative discussion of the variation of the electronic state produced by the substitution, thermodynamic measurements are required since they provide information from the standpoint of electronic entropy. Therefore, we have performed systematic heat capacity measurements of (DI-DCNQI)<sub>2</sub>(Ag<sub>1-x</sub>Cu<sub>x</sub>) in this work.

## 2. Experimental details

The samples used for this work were prepared by the electrochemical reduction method using a standard H-type cell with Pt electrodes. The yielded crystals were thin needles with a diameter of about 0.05–0.1 mm and a length of 0.5–2.0 mm. The concentration of the metal cations of each sample was determined by the electron probe



**Figure 2.** Temperature dependence of the heat capacity of (DI-DCNQI)<sub>2</sub>Ag shown in the  $C_p T^{-1}$  versus  $T^2$  plot. The data obtained under magnetic fields are also presented. The inset shows the  $C_p T^{-3}$  versus  $T$  plot around the thermal anomaly.

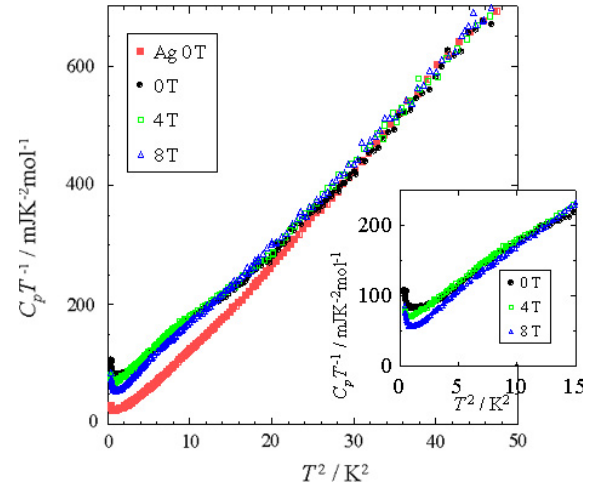
micro analyzer (EPMA) method as described in [15]. The heat capacity measurements were performed by a thermal relaxation calorimeter constructed for measuring small size samples like organic conductors. The detail of the calorimeter has been described in [17]. In each measurement, about 20 to 30 pieces of single crystals selected from the same batch are aligned and attached on the stage of the calorimeter using Apiezon N grease. The total masses of the samples used for each measurement are 1.13 mg, 0.592 mg, 0.834 mg, 0.352 mg, and 0.824 mg for concentrations of  $x = 0, 0.05, 0.71, 0.90,$  and  $1.0$ , respectively. The magnetic fields were applied perpendicular to the  $c$ -axis corresponding to the stacking direction of DI-DCNQI molecules. Prior to the sample measurements, we performed a blank measurement of the sample stage together with the correct amount of Apiezon N grease used for adhesion of the crystals. This blank heat capacity is subtracted from the total heat capacity to determine the absolute value of heat capacity of the sample. Hereafter, we show the molar heat capacity,  $C_p$  using the formula unit of (DI-DCNQI)<sub>2</sub>Ag.

## 3. Results and discussion

In figure 2, we show the temperature dependence of the heat capacity of (DI-DCNQI)<sub>2</sub>Ag in the  $C_p T^{-1}$  versus  $T^2$  plot, which shows a small anomaly at 6.2 K. The existence of the thermal anomaly is more clearly observable in the  $C_p T^{-3}$  versus  $T$  plot in the inset, since the lattice contribution obeying the Debye  $T^3$  law should give moderate temperature dependence in this plot. In our previous report, we did not see any thermal anomaly related to the magnetic transition in spite of the detection of the antiferromagnetic transition by the NMR experiment. Instead of the anomaly, a finite  $T$ -linear

term with a coefficient of  $32.6 \text{ mJ K}^{-2} \text{ mol}^{-1}$ , which is reduced by application of external fields, was observed [14]. In the present work, we have used a sample with improved quality without showing any Curie component in low-temperature magnetic susceptibility. The subtle anomaly has been revealed in this better quality sample. Although investigations of CO states in organic systems have been widely performed in this decade, thermodynamic confirmation of the spin ordering existing in the charge-ordered lattices has not been reported to the authors' knowledge. The separation of the spin and the charge degrees of freedom in CO systems is confirmed from the thermodynamic standpoint. As is shown in the inset, the observed thermal anomaly is insensitive to external magnetic fields up to 8 T, suggesting that the 3D magnetic order is stable against external fields. To explore a quantitative discussion on the thermal anomaly, a smooth background was determined by least squares fitting to the fourth polynomial function using the data below 4.0 K and above 7.0 K in the 0 T curve. We have subtracted this background curve from the raw data to evaluate the magnetic heat capacity  $\Delta C_{\text{mag}}$ . The magnetic entropy around the thermally anomaly is estimated as  $76 \text{ mJ K}^{-1} \text{ mol}^{-1}$  from the integration of  $\Delta C_{\text{mag}} T^{-1}$  with respect to temperature. This value is only 1.5% of  $R \ln 2$  expected for the full entropy of the  $S = 1/2$  spin systems. Even if we take into account the nature of the low-dimensional magnetic system characterized by the broad peak of 30–40 K in the static susceptibility, this value seems to be very small. The reduced magnetic entropy around the peak means that the quantum fluctuations in the charge-ordered states disturb the development of the long-range character of the phase transition. A similar situation is also inferred for the antiferromagnetic transitions of the quasi-2D Mott insulators of  $\kappa$ -(BEDT-TTF) $_2$ X. The antiferromagnetic orders of these systems were observed by NMR measurements but the thermal anomalies are absent around the corresponding temperatures [18]. The missing entropy problem of the magnetic insulating systems with strong electron correlation is also the case in several intermetallic compounds such as  $\text{La}_2\text{CuO}_4$  known as a mother material of high- $T_c$  superconductors [19] and Y-doped  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [20], etc. The local disorders due to the substitution, possible frustrations of competing interactions, and a coupling with other degrees of freedom seem to give a pronounced influence on the long-range character of the 3D magnetic transitions. The long-range nature and the quantum fluctuations in the magnetic state in these systems seem to be an interesting subject to be considered thermodynamically.

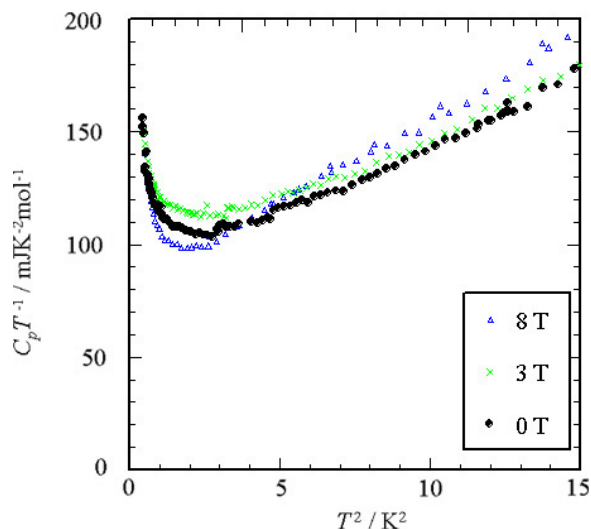
As is shown in figure 3, we can see that the low-temperature heat capacity of Ag salt still gives the  $T$ -linear term under 0 T. However, the value of the  $T$ -linear coefficient is  $5.85 \text{ mJ K}^{-2} \text{ mol}^{-1}$  and we have found that it decreases gradually with the increase of magnetic field and reaches  $0.78 \text{ mJ K}^{-2} \text{ mol}^{-1}$  under 8 T. The structural study by Kakiuchi *et al* using synchrotron radiation suggested that the charge order occurs also in the inter-column direction of DI-DCNQI molecules and a kind of frustration exists in the formation of the 3D CO structure [12]. The disorder sensitive behavior in the heat capacity may be related to this geometric



**Figure 3.**  $C_p T^{-1}$  versus  $T^2$  plot of  $(\text{DI-DCNQI})_2(\text{Ag}_{0.95}\text{Cu}_{0.05})$  under magnetic fields. The 0 T data of  $(\text{DI-DCNQI})_2\text{Ag}$  are shown for comparison.

frustration. This tendency is consistent with the result of the substitution system. Upon substituting  $x = 0.05$  of Cu in the Ag site, we have found that the magnetic order is suppressed. The peak at 6.2 K in  $(\text{DI-DCNQI})_2\text{Ag}$  is broadened and reduced down to about 3 K, as shown in figure 3. The application of a magnetic field of 8 T makes the peak-shape broaden further and suppresses the  $C_p T^{-1}$  values below 2.5 K. The induced reduction of  $T_N$  and peak broadening behavior are interpreted as glass-like freezing of the spins.

According to the transport measurements by Itou *et al*, the CO state produced by the intersite Coulomb repulsion melts gradually by the increase of the Cu substitution rate [15]. The charge-gap determined by a temperature dependence of the resistivity is reduced monotonically with the increase of  $x$  up to the concentration  $x = 0.3$ . In the intermediate concentration between  $x = 0.3$  and 0.7, which is assigned as the disorder-induced gapless region, electron localization appears at low temperatures. In the concentration  $x > 0.7$ , metallic behavior is shown in the whole temperature range below room temperature. These behaviors produced by the Cu substitution are summarized as a phase diagram in [15]. Figure 4 displays the results of the heat capacity measurements of the  $x = 0.71$  sample at 0 T and under magnetic fields. We can observe a subtle magnetic field dependence in the  $C_p T^{-1}$  versus  $T^2$  plot which demonstrates that traces of paramagnetic spins in the sample still exist in this concentration. From the data of the  $x = 0.90$  and 1.0 samples displayed in figure 5, we can see that such magnetic field dependence is absent. The 0 T data of the  $x = 1.0$  sample reproduces well the previous result in [14], claiming that the electronic heat capacity is enhanced due to the  $\pi$ -d hybridization in the electron bands. The  $\gamma$  value is evaluated as  $41.7 \text{ mJ K}^{-2} \text{ mol}^{-1}$  by the least square fitting to the formula of  $C_p = A/T^2 + \gamma T + \beta T^3$  that coincides well with the previous result [14]. Unexpectedly, the  $\gamma$  value of the  $x = 0.90$  sample becomes  $63.6 \text{ mJ K}^{-2} \text{ mol}^{-1}$ , which is 1.5 times larger than the  $x = 1.0$  sample. The increase of  $\gamma$  in spite of the decrease of the d-electron number is curious from the standpoint of the  $\pi$ -d hybridization. We

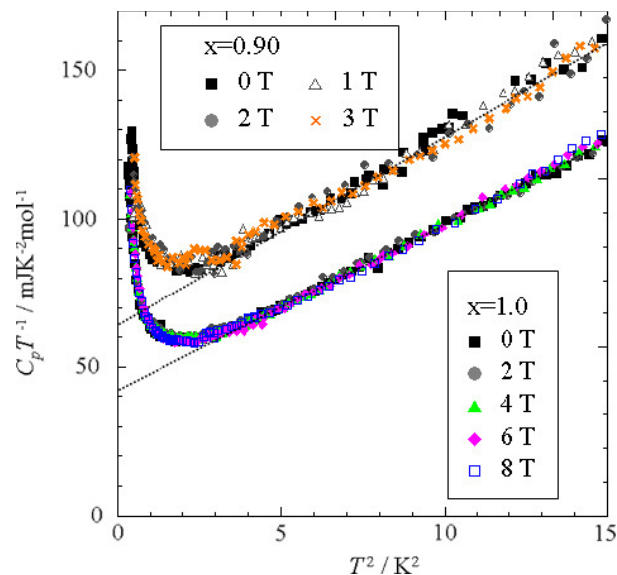


**Figure 4.**  $C_p T^{-1}$  versus  $T^2$  plot of  $(\text{DI-DCNQI})_2(\text{Ag}_{0.29}\text{Cu}_{0.71})$  under magnetic fields.

can exclude the possibility of the two-level system occurring by the distribution of localized paramagnetic impurities, often discussed in such kinds of substitution systems, because there is no magnetic field dependence in the  $C_p T^{-1}$  versus  $T^2$  plot. Furthermore, the almost parallel curvatures of the  $C_p T^{-1}$  versus  $T^2$  plot of the  $x = 0.90$  and  $1.0$  samples demonstrate that the lattice contributions do not differ so much between two concentrations and the observed enhancement is attributable to the increase of the electronic heat capacity.

The enhancement of  $\gamma$  in the low-temperature heat capacity is one of the interesting subjects in condensed matter physics, since the appearance of an anomalous Fermi liquid state is discussed in relation to the unconventional superconductivity. This subject is widely investigated in the heavy electron behavior in Ce and U based intermetallic compounds [21]. Realization of such a state in the organic conductors of which conduction carriers are usually  $\pi$ -electrons was one of the starting interests of the DCNQI investigation. In fact, the physical properties of  $(\text{DMe-DCNQI})_2\text{Cu}$  have been studied in relation to the Kondo problem [5, 6]. However, a drastic metal–insulator transition due to the cooperative mechanism of the electron correlation and  $\pi$ -d hybridization in 1D structures occurs, accompanied by a drastic increase of resistivity of the order of  $10^7$  times [22, 23]. The possibility of electron mass enhancement due to the  $\pi$ -d hybridization has been suggested by Tamura *et al* in  $(\text{DI-DCNQI})_2\text{Cu}$  [13]. Further increase of the  $\gamma$  value by introducing  $\text{Ag}^+$  may imply the existence of another factor to control the electron correlations in low-temperature electronic state.

In this paragraph, we discuss the possible mechanism of increasing  $\gamma$  in the substitution system. The role of d-orbital in the electronic state of the DCNQI system has been studied microscopically by band-selective NMR experiments through the chemical substitution of  $^{13}\text{C}$  and  $^{15}\text{N}$  in the DI-DCNQI molecules [24, 25]. In the Cu salt, the energy level of the  $d_{xy}$ -orbital is very close to the  $\pi$ -band of organic molecules



**Figure 5.**  $C_p T^{-1}$  versus  $T^2$  plot of the metallic sample of  $(\text{DI-DCNQI})_2(\text{Ag}_{0.10}\text{Cu}_{0.90})$  and  $(\text{DI-DCNQI})_2\text{Cu}$  under magnetic fields.

and hybridization occurs between them. This hybridization flattens the dispersion of the  $\pi$ -band as is explained in [24, 25]. The enhancement of the electronic heat capacity coefficient of  $(\text{DI-DCNQI})_2\text{Cu}$  is qualitatively explained by a kind of Stoner-type enhancement owing to the spin fluctuations in the flattened band [26]. However, the unexpected increase of  $\gamma$  in the metallic state of the  $x = 0.90$  sample demonstrates that the electron correlations in the  $\pi$ -electrons, which tend to make the CO state with antiferromagnetic character, work to enhance the static physical properties. The mechanism to increase such properties by the on-site Coulomb repulsion ( $U$ ) is known as the Brinkmann–Rice enhancement [27]. The electronic heat capacity coefficient  $\gamma$  and magnetic susceptibility  $\chi$  in the metallic region near the metal–insulator transition is enhanced with the increase of Coulomb repulsion as in  $\text{V}_2\text{O}_{3-y}$  [28] and  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  [29] systems. Similar enhancement of  $\gamma$  in  $\kappa$ -(BEDT-TTF) $_4\text{Hg}_{2-\delta}\text{X}_8$  ( $\text{X} = \text{Br}, \text{Cl}$ ) has been observed by single crystal calorimetry by Naito *et al* [30]. In this organic system,  $\gamma$  is enhanced up to  $52$ – $55$   $\text{mJ K}^{-2} \text{mol}^{-1}$  which is almost twice as large as the other  $\kappa$ -type salts due to the carrier doping near the Mott transition. Although the antiferromagnetic interaction in  $(\text{DI-DCNQI})_2\text{Ag}$  is considered to have arisen by the intersite Coulomb repulsion ( $V$ ) in the uniformly stacked column, similar competition between the band energy ( $W$ ) and electron correlation may well make the BR-like enhancement in the static properties. The cooperative effect of electron correlation and  $\pi$ -d hybridization may be the cause of this anomalous enhancement in the metallic state. Although the phase behavior, especially in the intermediate region, is not clear at present, the electronic state changes induced by the substitution of the cations contain interesting physics in the electron correlation of  $\pi$ -d system.



#### 4. Conclusion

We have performed a low-temperature calorimetric investigation to study the nature of the CO insulating state and a systematic variation from this insulating state to the  $\pi$ -d hybridized metallic state. The thermal anomaly related to the AF magnetic ordering was observed in the CO insulating state. The low-temperature thermodynamic behavior was found to be sensitive to the disorders in the sample. In the metallic region, an enhancement of electronic heat capacity was observed which arose by the strong electron correlation in  $\pi$ -electrons coupled with the  $\pi$ -d hybridization of this material.

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