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Heat capacities of antiferromagnetic dimer-Mott insulators in organic charge-transfer complexes

S. Yamashita · Y. Nakazawa

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Abstract Heat capacity measurements of quasi-two-dimensional Mott insulating compounds consisting of BEDT-TTF (bisethylendithiotetrathiafulubalene) donor molecules and counter anions were performed by the thermal relaxation calorimetry technique for single crystal samples. No distinct thermal anomalies at the predicted antiferromagnetic transition temperatures in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl ($T_N = 27$ K) and β′-(BEDT-TTF)$_2$ ICl$_2$ ($T_N = 22$ K) were observed. These results demonstrate that the Mott insulating state of the organic salts which are dominated by the strong two-dimensional intra-layer antiferromagnetic interactions between neighboring $S = 1/2$ spins shows somewhat different features from the simple quasi-two-dimensional Heisenberg model with $S = 1/2$. The strong quantum fluctuations produced by the electron correlations suppress the long-range character of the spin correlations, which seems to be an important aspect of this kind of Mott insulating materials.

Keywords Heat capacity · Organic conductor · Mott-insulator · Antiferromagnetic transition

Introduction

The electronic states of charge-transfer salts (BEDT-TTF)$_2$X, where BEDT-TTF is an abbreviation of bisethylendithiotetrathiafulubalene and X represents counter anions are attracting wide interests in the area of condensed matter physics, since they give various kinds of strongly correlated electrons systems with quasi-two-dimensional structure. The donor molecule of BEDT-TTF and the counter anion crystallized to form segregated layered structures and they are inclined to form metallic state due to the imperfect filling of electron band. It is now well-known that some of these salts show 10 K class superconductivity at ambient pressure [1, 2]. Existence of several insulating salts which show antiferromagnetic transitions [3, 4], charge order transitions [5] and a crossover to the spin liquid states [6, 7] with similar layered structures are also known up to now. The important parameters which dominate the electronic properties are coulomb energies expressed by U, V and the width of quasi-two-dimensional bands W. When the dimerization of the donors are strong enough and an approximation to consider each dimer as a structural unit is held, the electron filling is 1/2 and the simple Mott–Hubbard physics determined by competition of the on-dimer U and W appears. If the value of U is larger than that of W, the system becomes a Mott insulating state. As a matter of fact, the pressure–temperature phase diagram in which the antiferromagnetic phase is neighboring to the superconducting phase is reported by Kanoda et al. [8] According to this diagram, the strongly correlated Mott insulating salts where effectively 1/2 filling transforms into superconductors with rather high-T_c when external pressures are applied. The interesting physics related to the phase separation in the mesoscopic levels, spin liquid state, and field-induced transitions or reentrant transitions are being discussed [6, 7, 9, 10] around this Mott boundary.

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is a typical Mott insulator [3]. Since the value of U/W of this salt is closed to the boundary, it has been studied in details under hydrostatic pressures. A systematic appearance of the ground state from antiferromagnetic insulator, superconductor, normal metal states [3, 11, 12] is realized with a pressure range up

S. Yamashita (✉) · Y. Nakazawa
Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan
e-mail: sayamash@chem.sci.osaka-u.ac.jp

to a few hundred bars. The intra-layer magnetic interactions $J/k_B = -2t^2/U$, where t is a transfer energy between neighboring dimers is one order of magnitude larger than the inter-layer magnetic interactions. Therefore, it is generally believed that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl should be a model material of quasi-two-dimensional Heisenberg system with $S = 1/2$. In fact, the long-range ordering is observed at 27 K [3] in spite of the much larger intra-layer interaction J/k_B is in the order of 10^2 K. However, the thermal anomaly around the ordering temperature was not observed in the previous thermodynamic reports except for the kink of thermal expansion measurements performed by Müller et al. [13, 14].

The salt of β'-(BEDT-TTF)$_2$ICl$_2$ which also has a strongly dimerized structure shows Mott insulating behavior at ambient pressure. Although the donor packing is different from κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, the electronic state of this compound is phenomenologically resembles to the κ-type salts. The long-range antiferromagnetic ordering is reported to occur at 22 K [4] and the superconductivity with the critical temperature of 14.2 K appears under pressure of 8.2 GPa [15]. The intra-layer magnetic interaction is estimated as $J/k_B = -59$ K from the magnetic susceptibility measurement which is nearly 3 times larger than the ordering temperature.

In this paper, the heat capacity measurements of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl were performed with better resolution using high-quality single crystal in order to examine the existence or absence of the transition anomaly in heat capacity. We also compared the results with the measurements of dimer-Mott insulating salt of β'-(BEDT-TTF)$_2$ICl$_2$.

Experimental

The low-temperature heat capacity measurements were performed by our homemade relaxation calorimeter constructed for measuring single crystals of molecular compounds. We have used two calorimetry cells which covers the temperature region between 0.7–10 K and 5–70 K. The stage of the higher temperature cell is consisting of a cernox thermometer (LakeShore) and a strain gauge heater (Tokyo Sokki). For the low-temperature cell, we have used a ruthenium oxide sensor of which resistance is 1 kΩ at room temperature. The sample stage was linked to the heat sink through six constantan wires of which diameters are 25 µm. The heat leak is adjusted so as to attain appropriate time constant of the temperature relaxation (typically 10^{1-2} s) in the whole temperature range. We used a single piece of crystals of 3.88 mg for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl salt and 0.724 mg for β'-(BEDT-TTF)$_2$ICl$_2$ salt which are adhered on the stage using proper amount of Apiezon N grease. The background heat capacities including the Apiezon N grease were determined by different measurement performed before mounting the sample. The absolute values of the heat capacity are obtained by subtracting the background values from the total heat capacity. To characterize the samples, we studied temperature dependences of magnetic susceptibility of two salts for sample characterization using a SQUID magnetometer. The magnetic anomaly owing to the three-dimensional ordering were observed at the reported temperatures in both of samples [3, 4].

Results and discussion

In Fig. 1, we show temperature dependence of the heat capacity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl under different magnetic fields, where the heat capacity data between 0.7 and 40 K are plotted in a C_p/T versus T plot. The data between 24 and 34 K are expanded in the inset of Fig. 1. There is no distinct thermal anomaly in the whole temperature range including around 27 K where the clear antiferromagnetic transition accompanied with the formation of internal magnetic fields was observed by ^{1}H-NMR experiments performed by other group [3]. The absence of thermal anomaly is consistent with the previous work [13]. The resolution of the heat capacity data is greatly improved in the present experiments from the data in Ref. [13] and therefore the absence of thermal anomaly is confirmed to be intrinsic for this material. Furthermore, we could not detect any systematic differences between C_p under 8 and 0 T. In order to further investigate the existence of thermal anomalies, we measure the heat capacity around 27 K in more details. In general, thermal relaxation method can not

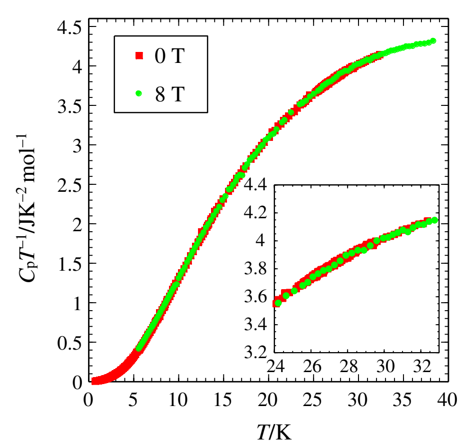

Fig. 1 C_pT^{-1}versus T plot for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl at fields of 0 and 8 T. The *inset* shows C_pT^{-1} versus T plot around antiferromagnetic transition temperature (27 K)

detect the first order transition accompanied with the release of latent heats. If a thermodynamic transition occurs accompanied by a release of latent heats with narrow temperature region, our measurement might fail to detect the anomaly. To exclude this possibility, the relaxation method with small ΔT values corresponding to 0.5% of the sample temperature has been performed. However, we could not see any anomaly in this condition.

We also show the low-temperature data obtained for the identical crystal in C_p/T versus T^2 plot in Fig. 2 under different magnetic fields. From the data shown in the inset of Fig. 2, we can confirm a clear T^3 contribution in heat capacity below 2 K. Although a spin-wave contribution due to the three-dimensional ordering may be included in the T^3 contribution, the linear extrapolation using the formula of $C_p = \beta T^3 + \gamma$ down to 0 K gives a vanishing electronic heat capacity coefficient. This behavior is consistent with the typical insulator with antiferromagnetic ordering and previous report. In the case of the typical low-dimensional magnets, several experimental results [16] and theoretical calculations [17] suggest the small anomaly around the three-dimensional ordering temperatures, although much of the magnetic entropy is consumed by the low-dimensional short-range ordering.

In order to confirm this behavior in a similar Mott insulating system with quasi-two-dimensional structure, we have examined the similar dimer-Mott insulating system of β'-(BEDT-TTF)$_2$ICl$_2$. This salt has open Fermi surfaces in band calculations [18], however, the semiconductive behavior below the room temperature and antiferromagnetic transition at 22 K were observed in this salt [4]. In this salt, a linear relation of C_pT^{-1} against T^2 and a vanishing electronic heat capacity coefficient was observed in the low temperature heat capacities [19]. These results are similar to those observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. In Fig. 3, we show C_p/T versus T plot between 5 and 40 K for

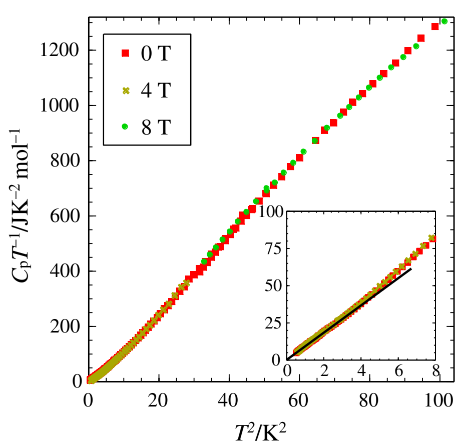

Fig. 2 C_pT^{-1} versus T^2 plot for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl below 10 K at fields of 0, 4, and 8 T

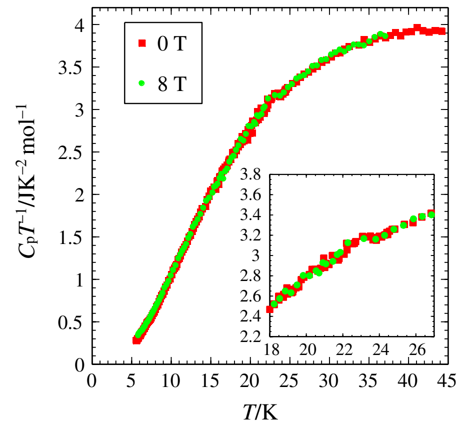

Fig. 3 C_pT^{-1} versus T plot of β'-(BEDT-TTF)$_2$ICl$_2$ at fields of 0 and 8 T. The *inset* shows C_pT^{-1} versus T plot around antiferromagnetic transition temperature (22 K)

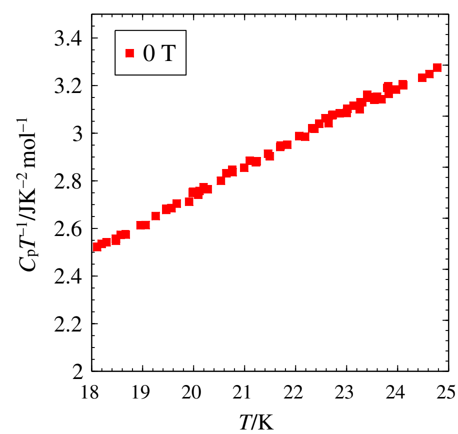

Fig. 4 C_pT^{-1} versus T plot for β'-(BEDT-TTF)$_2$ICl$_2$ around antiferromagnetic transition temperature (22 K)

β'-(BEDT-TTF)$_2$ICl$_2$ salt. Here again, we cannot observe distinct anomaly related to the magnetic ordering as well as the magnetic field dependence between 5 and 40 K. The small hump may be seen in Fig. 3, but it is difficult to conclude within the present resolution. To exclude the possibility of existence of the anomaly with transition, again we measure heat capacity of β'-(BEDT-TTF)$_2$ICl$_2$ using different detection system independently. From the result of this measurement shown in Fig. 4, we can conclude that the thermal anomaly is considered to be very small.

The intra-layer magnetic interactions of β'-(BEDT-TTF)$_2$ICl$_2$ salt J/k_B is estimated as—59 K from the analysis of two-dimensional Heisenberg analysis of the magnetic susceptibility [4]. Therefore, the transition temperature is relatively close to the J/k_B value and magnetic entropy may remain around 22 K, if a simple low-dimensional magnet picture is assumed. We consider that the absence of thermal anomaly in these Mott insulating system should be considered from the standpoints of electron correlations. The magnetic behavior of the Mott insulator is produced by the strong coulomb interactions which is expressed by the Hubbard Hamiltonian where both charge and spin degrees of freedom coexists. Although the magnetic ordering evidenced by the static internal magnetic fields appears below the transition temperature, the antiferromagnetic states still have strong quantum fluctuations produced by the residual charge-degrees of freedom at low temperatures. The long-range character should be suppressed by these fluctuations and consequently no thermodynamic peak appears in the heat capacity. In this sense, the similar situations may occur in duetrated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, β'-(BEDT-TTF)(TCNQ), etc., and other quasi-two-dimensional compounds. Although this is a speculative discussion, the absence of the thermal anomaly around the long-range ordering temperature has been reported in La_2CuO_4 in the initial stage investigation of high-T_c cuprates by Sun et al. [20]. The reduced magnetic entropy problem around the long-range ordering temperatures are also discussed in the charge-ordered system which is also the long-range ordering occurs in the strongly correlated low-dimensional systems. The three-dimensional ordering of (DI-DCNQI)$_2$Ag shows a small peak corresponding to about 1.5% of Rln2 and similar behaviors are observed in several intermetallic compounds such as Y-doped $La_{0.7}Ca_{0.3}MnO_3$ [21, 22]. The long-range nature and the quantum fluctuations in the magnetic state in these systems seem to be an interesting subject to be discussed thermodynamically. The NMR measurements and μSR measurements which can detect information in the shorter time domain can detect the existence of the internal magnetic fields, but the present thermodynamic data demonstrates that it's not still in a static limit and short-range fluctuations are important in characterize the electronic state of the Mott insulating salts.

Conclusions

In conclusion, we have measured the heat capacities of charge-transfer salts κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and β'-(BEDT-TTF)$_2$ICl$_2$ by thermal relaxation method under magnetic fields. We have detected an absence of thermal anomaly with antiferromagnetic transition and no magnetic field dependences in both salts. The typical behavior of insulating state was observed in the low temperature heat capacity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. These results are consistent with previous study [13] and suggest that the entropy associated with these transitions is quite small. We consider this character is not only about these salts but also about many of Mott insulators, because the difference of the value of *U/W* between two salts is quite large. Furthermore, these results suggest the possibility of common feature of strongly correlated electron systems.

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