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UNUSUAL LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF PELLET SAMPLES OF (DMe-DCNQI)$_2$M (M=Li, Ag)

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We have performed low-temperature heat capacity measurements on pellet samples of (DMe-DCNQI)$_2$M (M=Li, Ag) which is known to show spin-Peierls transitions at 51 and 86 K, respectively. A linearly temperature-dependent term in the low-temperature heat capacity has been observed for both the samples: It is attributable to the spin-wave excitations induced by the inhomogeneous pressure effects produced in the pellet forming process. Although the temperature dependences of the magnetic susceptibility in both materials are almost the same, the coefficient of T-linear term of the Ag salt becomes three times larger that that of the Li salt. The peculiar electronic state originating from the competition of the spin-Peierls mechanism and the Coulomb repulsion is suggested.

Keywords: *electron correlation, organic conductors, spin-Peierls transition*

Introduction

In the field of condensed matter physics, there is increasing interest in studying the electronic states and phase transitions in organic charge transfer salts consisting of donors and acceptors with their respective counter ions. These salts are known to give various kinds of electronic phases even though their electronic structures are very simple as is well expressed by the overlap of the molecular orbital using the extended-Hückel approach [1]. A well known acceptor molecule of 2,5-R_1,R_2-dicyanoquinodiimine abbreviated as R_1,R_2-DCNQI forms a charge transfer salts with metal cations such as Cu, Li, Ag, etc. They have been giving hot topics in this decade, since series of materials show interesting variety of ground states such as CDW, spin-Peierls, enhanced metal and charge ordered (CO) ones in the identical crystal structure [2–4]. The possible candidate for R_1 and R_2 are CH_3, CH_3O, Br, Cl, I, etc. Among them, 2,5-dimethyl-N,N'-dicyanoquinonediimine with R_1 and R_2=CH_3 (DMe-DCNQI) are most widely studied, because of their interesting phase transitions cooperatively produced by electron correlations, electron-lattice couplings and π–d hybridization in quasi-one-dimensional band [5].

In this work, we will study an unusual thermodynamic property of (DMe-DCNQI)$_2$M (M=Li, Ag), which give exactly 1/4 filled electronic state in strongly 1D band. The DMe-DCNQI molecules are stacked along the c-axis and form a column structure in this direction. The metal cations are coordinated by four different DMe-DCNQI molecules each of which belongs to different columns neighboring each other. The crystal symmetry is tetragonal with space group $I4_1/a$ [3]. In this system, the competition between the bandwidth (W), electron correlation (U and V), and electron-phonon coupling gives rise to interesting electronic phases related to the spin and charge degree of freedom. Although conducting at room temperature, they undergo a broad metal-insulator transition with decreasing temperature in association with dimerization of the DMe-DCNQI molecules in the stack direction. With further decreasing temperature, a $2k_F$ lattice modulation appears and spin-Peierls transition takes place at 83 K for the Ag salt and 50 K for the Li salt.

In the previous paper, some of the authors have reported the results of ac calorimetry and thermally relaxation calorimetry for these materials. The novel finding was that the (DMe-DCNQI)$_2$Ag show two distinct heat-capacity peaks at about 71 and 86 K, while (DMe-DCNQI)$_2$Li have a single peak at 52 K in association with the spin-Peierls transition. Although the fully gapped nature characteristic of the usual spin-Peierls ground state was confirmed by the low-temperature heat capacities of high quality single crystal measurement of (DMe-DCNQI)$_2$Li, unusual behaviors in the case of compacted pellet samples were indicated simultaneously. The thermal anoma-

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lies due to the spin-Peierls transition have been diminished and 1D spin-wave excitations arisen by the strong magnetic couplings in the column direction was suggested by the preliminary experiments [6]. In this work we report the detailed experimental results on this point so as to extract what is intrinsic to explain low-energy excitations of the spin-Peierls system with 1/4 filling band. The possibility of electron correlation effects is also discussed for these materials. To compare the overall temperature dependence of the heat capacity, we also measured the heat capacity of (DMe-DCNQI)$_2$Cu between 2 and 230 K.

Experimental

Single crystals of the (DMe-DCNQI)$_2$M salts were yielded as thin needles by an electrochemical method. The typical size of the crystals was about 0.005×0.003×1 mm^3 for Ag and Cu salt and 0.02×0.01×0.2 mm^3 for Li salt. Therefore, to do thermodynamic measurements, we have formed pellet samples from multi-pieces of crystals using two kinds of stainless cylinders with diameters of ϕ1 and 2 mm. The heat capacity measurements were performed with two different thermal relaxation-calorimeters. One is the thermal property measurement option of the PPMS system (Quantum Design model RO-6000) and the other is a ^{3}He relaxation calorimetry apparatus constructed by ourselves for the measurement only with small amount of samples. The total mass of the sample used for the PPMS was about 1 mg, and those for ^{3}He apparatus were 80 and 120 μg. In each measurement, we performed the addenda measurement with proper amounts of Apiezon N grease and then adhered the samples onto the addenda to obtain sample heat capacities. The molar heat capacity is determined by subtracting the addenda heat capacity from the total heat capacity. The accuracy of the data is estimated as ±3–10% in each measurement. The crystals of the (DMe-DCNQI)$_2$Li and (DMe-DCNQI)$_2$Ag salts were picked up from the identical batches with those used for the previous experiments.

Results and discussion

Figure 1 shows temperature dependences of molar heat capacity of (DMe-DCNQI)$_2$Li, (DMe- DCNQI)$_2$Ag, and (DMe-DCNQI)$_2$Cu in a C_p *vs.* T plot. We can point out that the absolute values of heat capacities in the low-temperature region are smaller than those of typical organic conductors consisting of BEDT-TTF and TMTSF molecules. For example, heat capacities of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ known as a 10 K class superconductor are about 2 J K^{-1}mol^{-1} at 5 K and 15 J K^{-1}mol^{-1} at 10 K. These are roughly three times larger than those of the present (DMe-DCNQI)$_2$M systems. The second point we can suggest from Fig. 1 is that the temperature region where so-called Debye's T^3 law holds reaches to about 8 K in all compounds of (DMe-DCNQI)$_2$M. This is also in contrast to the behavior of the typical organic salts based on TTF-type electron donor molecules. This discrepancy can be explained by the librational phonon modes typically present in the TTF type salts. These phonons give an additional contribution to the acoustic phonons. In the case of the present salts, this contribution seems to be absent and the lattice heat capacity is dominated mainly by the acoustic modes only. The linear extrapolation of C_pT^{-1} *vs.* T^2 curve below about 4 K to estimate the γ term in the initial stage by Nishio *et al.* [7] seems to be quite reasonable. In fact, we can reproduce almost the same γ value with that determined by Nishio *et al.* for (DMe-DCNQI)$_2$Cu system. Although the overall tendency between the (DMe-DCNQI)$_2$Li and (DMe-DCNQI)$_2$Ag salts are explained by the difference of Debye temperatures, the temperature dependent behavior of the (DMe-DCNQI)$_2$Cu is different. Since the (DMe-DCNQI)$_2$Cu is metallic, the origin of this difference can partially be attributable to the contribution of electronic heat capacity determined by $C_{el}=\gamma T$ which increases in proportion to the temperature. In addition to this the valence of cations in the (DMe-DCNQI)$_2$Cu is +4/3 in an average and hybridization of *d*-electrons to the π-electrons is existent in this salt [3, 5]. The discrepancy in the temperature dependence of heat capacity is attributed to the difference of hybridization effect by the metal cations that influences the lattice vibrations. It is important to mention that the similar tendency is also observed in the difference of overall temperature dependence of

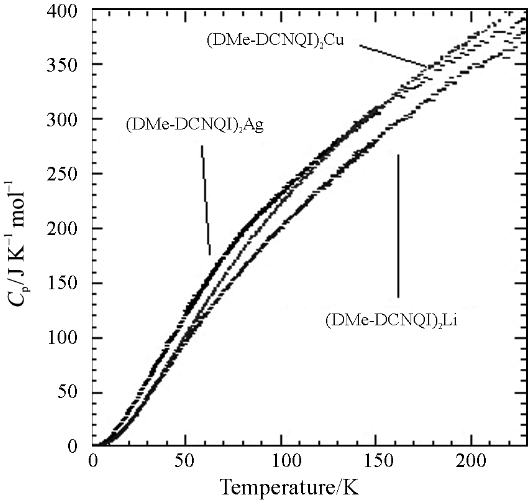

Fig. 1 Temperature dependence of heat capacity of (DMe-DCNQI)$_2$M (*M*=Li, Ag, Cu)

(DI-DCNQI)$_2$Ag and (DI-DCNQI)$_2$Cu salts in the temperature range between 2 and 240 K, where the latter salt is known to show characteristic features of enhanced metal.

Some of the authors have mentioned in the previous work that the spin-Peierls transition in the (DMe-DCNQI)$_2$Ag and (DMe-DCNQI)$_2$Li salts has disappeared in the measurements of pellet samples. The isotropic gap due to the formation of spin-singlets by the spin-Peierls state has been broken and low-energy excitations represented by a T-linear temperature dependence appears. We now turn to discuss the low-temperature behavior of the pellet samples. The heat capacities of (DMe-DCNQI)$_2$Li and (DMe-DCNQI)$_2$Ag are shown in Fig. 2. The coefficient of T-linear term, γ in the low-temperature heat capacity is estimated as 11.3 and 30.8 mJ K^{-2} mol^{-1}, respectively. From the magnetic susceptibility measurements performed by Hiraki *et al.* [8], (DMe-DCNQI)$_2$Li and (DMe-DCNQI)$_2$Ag are found to have almost similar magnetic behavior. Magnetic susceptibility shows almost the same temperature dependence above 100 K. A drastic decrease of magnetic susceptibility due to the spin-Peierls transition occurs at about 50 and 80 K, and below these temperatures non-magnetic state is established except for the few % of Curie component. Above the transition temperatures, the temperature dependences of magnetic susceptibility can be explained by the 1D antiferromagnetic Heisenberg chain. The J/k_B value in the 1D chains is estimated as –205 K for (DMe-DCNQI)$_2$Li by Sakurai *et al.* [9] and the similar analysis for (DMe-DCNQI)$_2$Ag salt gives the J/k_B value of about –244 K. According to the model calculation on thermodynamic feature of 1D antiferromagnetic Heisenberg model performed by Bonner and Fisher, the low temperature heat capacity is expressed by C_pT^{-1}=$0.35Rk_B/|J|$ [10] and if we use this J/k_B value determined above, the γ should be 14.2 mJ K^{-2} mol^{-1} for the Li salt and 11.9 mJ K^{-2} mol^{-1} for the Ag salt. For the Li salt, the coincidence with the experimental value of 11.3 mJ K^{-2} mol^{-1} is well if we consider the effects of disorders and concomitant paramagnetic spins produced in the pellet formation process. However, the large discrepancy in the Ag salt is serious. To check the reproducibility of the data of the Ag salt, we have performed another heat capacity measurement with different sample and different calorimeter and the data obtained are plotted in Fig. 3 together with the previous data. Although it is very difficult to derive accurate γ on account of the existence of small upturn below 1.7 K and data scattering due to the experimental resolution [11], reproducibility of the above tendency has been confirmed within the resolution of the present calorimeter. We consider that the peculiar aspect of the (DMe-DCNQI)$_2$Ag is the appearance of the intermediate state during the spin-Peierls transition. This originates from the competition between the spin-Peierls mechanism to form the $2k_F$ modulation and the long-range Coulomb repulsion to form charge disproportionation inside the dimmers. From this standpoint, the anomalous enhancement of the T-linear term means the increase of low-energy excitations related with this competitive mechanism. It is important to remind that the charge-ordered (CO) system of BEDT-TTF and TMTSF salts shows several anomalous features such as γ term remaining even in the charge-ordered insulating state and the long thermal relaxation time to get equilibrium state at low temperatures [12].

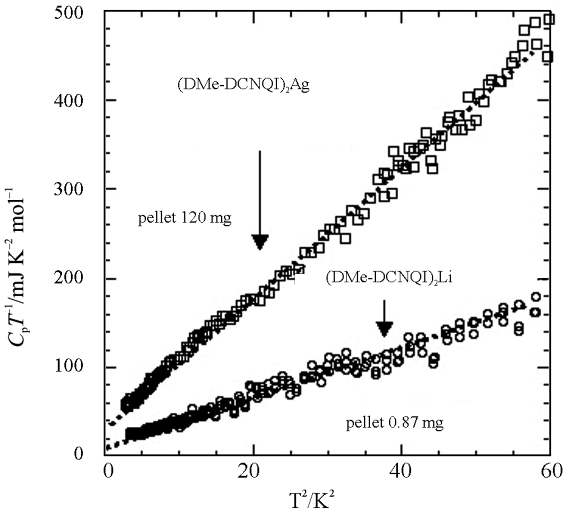

Fig. 2 C_pT^{-1} *vs.* T^2 plot of (DMe-DCNQI)$_2$Li and (DMe-DCNQI)$_2$Ag obtained for compacted pellet samples. The dashed line represents the linear extrapolation of the data

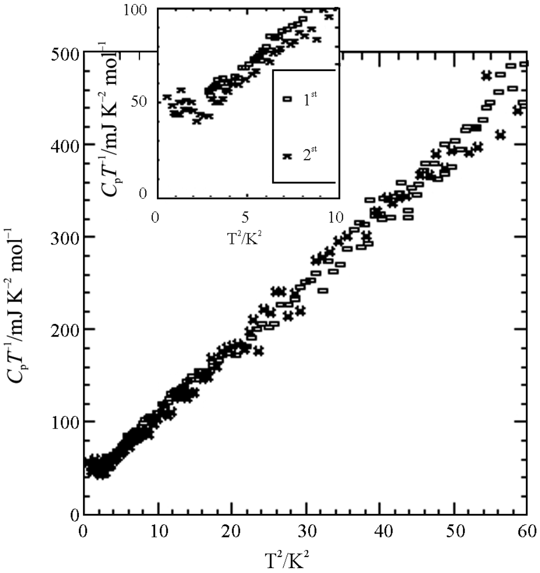

Fig. 3 C_pT^{-1} *vs.* T^2 plot of (DMe-DCNQI)$_2$Ag for two different samples

Conclusions

We have measured low-temperature heat capacities of pellet samples of $(\text{DMe-DCNQI})_2\text{M}$ (M=Li, Ag, Cu) between 0.8 and 230 K. Temperature linear term in the low temperature heat capacity was observed in M=Li and Ag samples due to the suppression of long-range effects to form the spin-Peierls ground state by the pellet forming process. However, the magnitude of the T-linear contribution of the $(\text{DMe-DCNQI})_2\text{Ag}$ sample is unexpectedly larger than the $(\text{DMe-DCNQI})_2\text{Li}$ sample, although the susceptibility behavior in both the compounds are almost the same. The possibility of long range Coulomb repulsion which makes charge disproportionation in the column direction may be related to the unusual spin-Peierls state of this material.

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