Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 435–438

CALORIMETRIC STUDY OF MOLECULAR SUPERCONDUCTOR κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O WHICH CONTAINS WATER IN THE ANION LAYERS

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Thermodynamic investigation of an organic superconductor κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O in which the BEDT-TTF dimers are arranged in the κ-type structure in the donor layers is performed by the relaxation calorimetric technique at low temperatures and under magnetic fields. A thermal anomaly related to the superconductive phase transition was observed at 5 K. The existence of residual γ^* in the superconductive state is about 18% of the normal state γ value, which is larger than those of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt. The lattice heat capacity reflected on the β-term in the low-temperature heat capacity was found to be affected by the cooling rate. The disorder produced in the network structure constructed by hydrogen bond in the insulating layer is considered to give low-energy phonon excitations reflected in the heat capacity.

Keywords: *electronic heat capacity coefficient, organic superconductor, strongly correlated electrons system, relaxation calorimetry*

Introduction

Molecular compounds consisting of organic donors and their counter anions give an interesting series of materials to discuss fundamental problems of electronic states with low-dimensional structures [1]. The segregated stacking of donors and anions produces a separation of conducting columns or layers and insulating ones in the crystals. Therefore, they sometimes give an alternative arrangement of conducting layers or columns and insulating ones in the crystal. The TMTSF and TMTTF based salts, which are known to give the first generation superconductors of organics are understood as a strongly correlated electron system with one-dimensional character. The existence of on-site and inter-site coulomb interactions gives various anomalous characters related to spin and charge degree of freedoms [2]. The two-dimensional system consisting of BEDT-TTF and BETS molecules are most widely studied materials since some of them tend to make dimmer-based packing in the donor layers. In such cases, the electronic state becomes an effectively half-filled state, if the donor dimmers are considered as a structural unit. One electron can be localized on each dimmer, when the electron correlation on the dimmer is strong enough. The typical example is the κ-type salts in which such electron correlations produces interesting physical properties like unconventional superconductivity. The pressure *vs*. temperature phase diagram of the κ-type salts proposed by Kanoda *et al.* is explained by the Mott–Hubbard physics dominated by the competition of U and W [3, 4]. This conceptual phase diagram proposed in the initial stage is confirmed by the experiments under gas pressure by Kagawa *et al.* [5]. The nature of the Mott insulating phase and superconductive phase including their phase relations is systematically investigated in terms of the localized and itinerant superconductivity.

In discussing the electronic state, especially the superconductivity of the κ-type salt of these systems, thermodynamic measurements are helpful. The pairing symmetry of the superconductivity can be characterized by the temperature dependence of heat capacity through the analysis of low-energy excitations over the energy gap around the Fermi surface. The famous material of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br of which superconducting transition temperature is 9.4 and 10.6 K, respectively were studied by several groups. The magnitude of the heat capacity jump at T_c is considered to be consistent with the strong coupling model [6–8], but the low-temperature heat capacity gives a residual γ^* term and T^2 dependence if the lattice heat capacity is assumed from the thermodynamic data of the insulating salts [9]. The normal state γ value changes drastically in the phase diagram if the partially deuterated

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1388–6150/$20.00

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BEDT-TTF molecules are measured to evaluate the chemical pressure effects of the superconductive phase. Such curious behavior demonstrates that the superconductive phase of this 2D strongly correlated system contains novel features characteristic of the 2D electron correlation system.

κ-$(BEDT\text{-}TTF)_2Ag(CN)_2H_2O$ was synthesized by Mori *et al.* in 1990 [10, 11]. The unique point of this material is that water molecules are contained in the anion layers of the $Ag(CN)_2^-$ to construct the coordination network structure through the hydrogen bond. The content of the water is not varied from the stoichiometric concentration if we keep the sample in the atmospheric condition. The superconductive transition temperature of about 5.0 K is reported by the resistivity measurement, which is consistent with the magnetic susceptibility measurement performed later. Since this compound can be classified into the middle-T_c compounds among various dimer-based organic salts, the comparison with the thermodynamic behavior with 10 K class salts is interesting to get a systematic view of the superconductivity of organic salts. Thus, we performed heat capacity measurements of the single crystal of κ-$(BEDT\text{-}TTF)_2Ag(CN)_2H_2O$ under magnetic fields up to 8 T.

Experimental

The crystals used for this work was grown by the electrochemical oxidation methods using H-type cell. The BEDT-TTF molecules and counter anions are dissolved in the 1,1,2-trichloroethane (nacalai tesque). The constant electric current is applied to the solution through the Pt electrodes. The grown crystals are black plates with the sample mass of about 1–3 mg. The heat capacity measurements are performed by our original relaxation calorimeter constructed to measure single crystals of molecular compounds. The calorimetry cell is mounted on the home made ^{3}He cryostat. The thermometer used for the calorimetric cell is the ruthenium oxide chip sensor (KOA Co. Ltd.) of which magnet resistance is calibrated against the standard thermometer.

Results and discussion

In Fig. 1, we show temperature dependence of heat capacity of κ-$(BEDT\text{-}TTF)_2Ag(CN)_2H_2O$ in a C_pT^{-1} *vs.* T^2 plot. The heat capacity values between 0.7 and 6 K is close to the values of other κ-$(BEDT\text{-}TTF)_2X$ salts, which demonstrates that the lattice heat capacity is not so much different among various κ-type salts. The thermal anomaly associated with the superconductive transition temperature is observed around T=5 K, which is consistent with the electron transport experiments. To investigate how the superconductivity is suppressed by external magnetic fields, we have performed the heat capacity measurements under magnetic fields. We have used the crystal weighing 3.32 mg in this experiment. The crystal was the black plate and the inter-plane direction was found to be parallel to the largest surface of the crystal. This is in fine contrast with usual BEDT-TTF salts. Therefore, the application of magnetic fields perpendicular to this surface gives the mixed information of in-plane and out-of-plane configuration. The induced vortex state contains the information of the Josephson vortices and the upper critical field, H_{c2} becomes relatively larger than the perpendicular direction in the present data. If we see the heat capacity data under 0.5 and 8 T, the thermal anomaly disappears which means that these fields are large enough to destroy superconductivity. The magnitude of heat capacity jump ΔC_pT^{-1} at the transition temperature is determined as 30 mJ K^{-2} mol^{-1}, if we assume that the 8 T data is the summation of the lattice heat capacity and electronic heat capacity. The temperature dependence of the electronic heat capacity is shown in the inset of Fig. 1. The peak structure is a typical mean-field type and the fluctuation region that is observed in 10 K class superconductors, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2Br]$ is not so clear in this compound. This behavior is close to the κ-$(MDT\text{-}TTF)_2AuI_2$ with the similar magnitude of T_c.

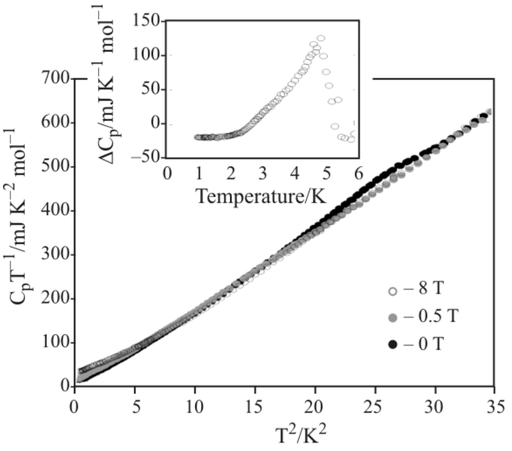

Fig. 1 Temperature dependence of heat capacity of κ-$(BEDT\text{-}TTF)_2Ag(CN)_2H_2O$ in a C_pT^{-1} *vs.* T^2 plot. The inset shows the temperature dependence of the electronic heat capacity around the superconducting transition assuming that the 8 T curve is consisting of the lattice contribution and normal state electronic contribution (γT)

The low-temperature heat capacity below 2 K under 0 T and several magnetic fields are shown in Fig. 2. In this figure, we show the data in C_pT^{-1} *vs.* T^2

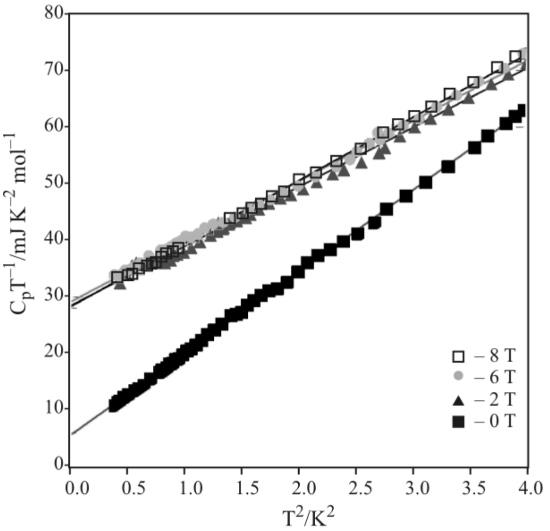

Fig. 2 C_pT^{-1} *vs.* T^2 plot of κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O obtained under 0 T and under magnetic fields

plot to see the electronic heat capacity coefficient γ and lattice heat capacity coefficient β obtained as the low-temperature approximation of Debye models. In the molecular conductors with softer crystal lattices than those of inter-metallic compounds or alloys, the temperature region obeying the simple formula of Debye approximation is limited at low temperatures below about 2–3 K. The 0 T data shown in Fig. 2 indicates that this material gives a distinct γ^* value of 5.2 mJ K^{-2} mol^{-1} even in the superconducting state. If the isotropic superconducting gap is formed around the Fermi surface, the electronic heat capacity which reflects on the quasi-particle excitations over the gap should give an exponentially temperature dependent contribution. Therefore, the electronic heat capacity coefficient is expected to be 0 mJ K^{-2} mol^{-1}. However, the large residual γ^* value on the order of several mJ K^{-2} mol^{-1} suggests that a normal electron density of states survives at low temperatures below T_c. Such behavior is sometimes observed in unconventional superconductors which possesses the line-nodes in the superconducting gap. The low-temperature heat capacity of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br are known to give γ^* of about 2 mJ K^{-2} mol^{-1} [9, 12, 13]. The observation of similar magnitude of γ^* without showing large sample dependence in the same salt seems to be intrinsic, that means the existence of the residual γ^* is a common feature of κ-type superconductors.

The normal state γ value of the present salt can be estimated by analyzing the data under magnetic fields shown in Fig. 2. As is shown in the figure, the data under magnetic fields of 2, 6 and 8 T coincide well. This fact demonstrates that the superconductivity is completely destroyed if we apply magnetic fields larger than 2 T even in the parallel orientation. The linear extrapolation of the data down to 0 K gives the normal state γ of 28.3 mJ K^{-2} mol^{-1} in the present salt. This value is 10–20% larger than the well known salts of 10 K class superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. This is almost comparable with κ-(MDT-TTF)$_2$AuI$_2$ which has similar magnitude of T_c. The superconductive phase of κ-(BEDT-TTF)$_2$X, namely the dimer system of D$_2$X is understood as a strongly correlated superconductor neighboring to the insulating phase [3, 4]. Although the 10 K class superconductor is located very close to the boundary region of Mott transition, the present material is mapped in the inside region of the metallic region of the phase diagram. Therefore, the Mott–Hubbard character which split the electron band to upper and lower bands by electron correlations is not so strong as compared with the 10 K class superconductor. In such case, a competition of band character and Mott–Hubbard character coexist to give rise to an intrinsic inhomogeneity in the electronic system. The relatively large ratio of γ^*/γ in the lower T_c sample may imply the manifestation of this possibility.

Another interesting observation for this material is the existence of cooling rate dependence in lattice heat capacities and superconductive transition temperatures. In Figs 3 and 4, we show C_pT^{-1} *vs.* T^2 plot of the same sample cooled down from 300 K to liquid helium temperature with the rate of 0.5 and 10 K min^{-1}. From the figures, we can notice that there is no drastic change in both γ and γ^* values. In the case of 0.5 K min^{-1}, γ and γ^* are evaluated as 28.0 and 5.1 mJ K^{-2} mol^{-1}, respectively. The data of 10 K min^{-1} case gives the values of 28.5 and 5.5 mJ K^{-2} mol^{-1}. However, the temperature dependence of heat capacity of 10 K min^{-1} shows unexpected change, which is reflected in the slope of C_pT^{-1} *vs.* T^2. As we have mentioned above, the H$_2$O molecules forms a polymeric

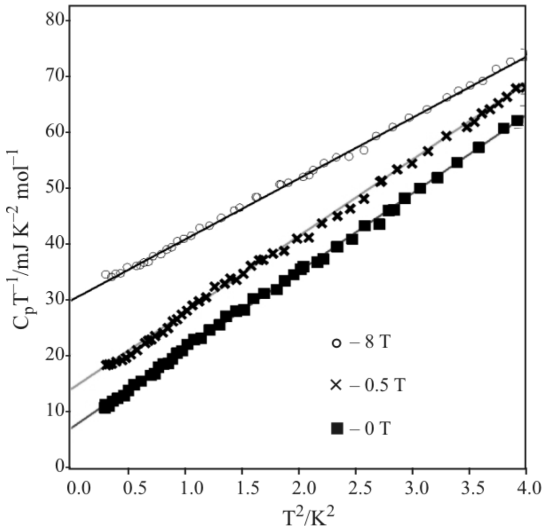

Fig. 3 C_pT^{-1} *vs.* T^2 plot of κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O cooled down from 300 to 4.2 K with the cooling rate of 0.5 K min^{-1}

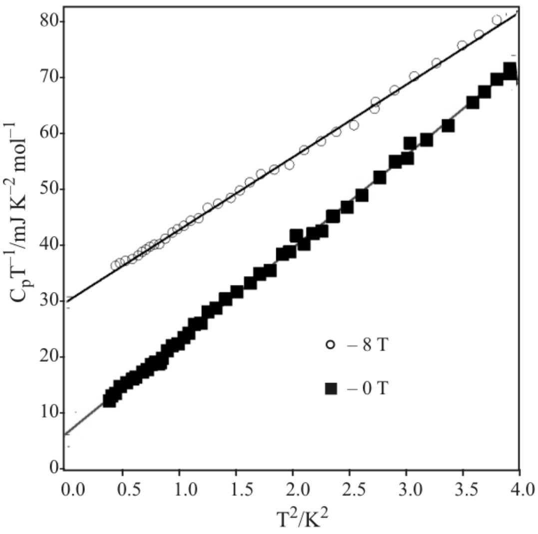

Fig. 4 C_pT^{-1} *vs.* T^2 plot of κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O cooled down from 300 down to 4.2 K with the cooling rate of 10 K min^{-1}

network structure in the anion layers. The lattice disorder observed in the rapid cooling case can be explained by the disorder in the hydrogen-bonded networks. Mori *et al.* precisely studied the deuteration effect of the ethylene groups in the BEDT-TTF molecules and observed an increase of transition temperature of about 1 K [14], which is an unexpectedly large and inverse isotope effect, if we considered the BCS type superconductors. This fact may be related to the softer and more variable crystal lattice of this material due to the existence of hydrogen-bonds network in the anions. In the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$Br], Akutsu *et al.* has observed that a glass like freezing of molecular motion of ethylene groups in the BEDT-TTF molecules exists around 90 K [15]. The difference of cooling rate around these temperatures gives rise to the slight volume change. However, in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$Br], the volume change was not large enough to give systematic variation of lattice heat capacity at extremely low-temperature region in question. The observed difference of the lattice heat capacity in the present material implies that the hydrogen-bonded network in the anions can give further interests in the lattice dynamics.

Acknowledgements

This work was partially supported by a Grant-in-Aid on Priority Area ‘Novel Functions of Molecular Conductors under Extreme Conditions’ from the Ministry of Education, Science, Sports and Culture of Japan, and a Grant-in-Aid for Scientific Research (No. 18340103) from JSPS. One of the authors, Y. Nakazawa thanks the Ikenaka Science and Technology Foundation for financial support.

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DOI: 10.1007/s10973-007-8966-y