Thermodynamic study of $\kappa$-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O under pressures and with magnetic fields

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Abstract. A low-temperature thermodynamic investigation on an organic superconductor $\kappa$-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O is performed under pressure and with magnetic fields. Using the ac-modulation technique available under pressures, we have succeeded to detect the thermal anomaly being associated with the superconducting transition. The thermal anomaly was found to be sensitive to the external magnetic fields at ambient pressure. We have observed that this anomaly disappears under pressure of 0.4 GPa which suggests that the superconducting ground state is transformed into the normal metallic state by the application of the pressure. The observed feature is consistent with the scenario of Mott-Hubbard physics realized due to the strong electron correlations in the dimerized BEDT-TTF salts.

1. Introduction

Low-temperature electronic properties of organic superconductors are attracting wide interests of researchers in the area of condensed matter chemistry and physics, since the superconductivity realized in the π-electron band has low-dimensional and strongly correlated electron characters. This is a typical feature of molecular compounds which usually have an anisotropic stacking of molecules and possess relatively soft lattices. In these molecular systems, strong electron-phonon interactions and electron-electron interactions play an important role to determine the phase relation around superconductive phases. A variety of electronic phases appear at low temperatures and interesting electronic phase diagrams are reported so far as is summarized in [1]. The most widely studied organic superconductors are charge transfer complexes based on the donor molecules of TMTSF/TMTTF and BEDT-TTF. The salts consisting of former molecules and their counteranions give a typical one-dimensional system, where the donor molecules stack along the $a$-axis of the crystal. On the other
hand, the latter molecule forms two-dimensional structure with a variety of molecular packing patterns [2]. The physical properties of these complexes are summarized as pressure versus temperature phase diagram, and relation between crystal packing and phase diagrams are intensively studied [3-5].

Among various kind of superconducting complexes reported up to now, the κ-type BEDT-TTF complexes are known to give 10 K class superconductors which have relatively high-$T_c$ among the organic systems. The BEDT-TTF molecules form a strongly dimerized structure through the face to face contact of π-electrons and each dimer is arranged in zigzag structure to form square lattice in the plane. For the dimer-Mott salts with two-dimensional structures, the conceptual phase diagram was proposed by K. Kanoda [4,5] and the detailed structure of the phase diagram was determined by the transport experiments under gas pressure [6]. According to this phase diagram, the superconducting phases are known to appear as a high pressure phase of Mott insulating phase. The electron correlation based on the Mott-Hubbard physics in low-dimensional lattice is discussed in relation to the possible mechanism and peculiar character of the superconductivity.

We have been interested in the thermodynamic properties of κ-(BEDT-TTF)$_2$X. (X= monovalence anions). The nature of the Mott insulating phase and superconductive phase including the phase relations have been studied by our relaxation calorimetry [7]. The insulating salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl gives a clear charge-gap due to the localization of electrons through the on-dimer Coulomb interactions [8], while the superconducting salts of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ reveal low-energy excitations demonstrating a nodal structure in the superconductive gap in the dilution temperature region [9-10,13]. In spite of numerous and intensive efforts from experimental and theoretical sides, to understand the mechanism of the organic superconductors is still an open question [9-13]. Since the pressure is the important parameter to directly control the phase relation, the systematic thermodynamic study under pressures is required to grasp the overall picture of superconductivity inevitable to discuss the mechanism. We have recently developed an ac-calorimetric system to obtain thermodynamic information of tiny single crystal of molecular compounds under pressure up to about 1.0 GPa [14]. In this work, we report the result of thermodynamic measurement using this high-pressure technique for κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O whose superconducting transition temperature is 5 K [15,16]. We trace the change of thermodynamic character of the electronic state under pressures using the high-pressure system.

2. Experimental

The crystals used for this work was grown by the electrochemical oxidation method. The BEDT-TTF molecule and the counteranion were solved in the 1-1-2 trichloroethane (nacalai tesque Co., Ltd.). We used H-type electro-chemical cells with 100mL in volume for crystal growth. The constant electric current was applied to the solution through the Pt electrodes with a diameter of 1.0 mm. The grown crystals are black plate with a typical weight of 0.2-3 mg. The crystal used for the experiment was a
single piece weighing 1.323 mg and 1.5×0.6×0.2 mm$^3$ in size.

The ac heat capacities under pressures were measured by the home-made apparatus constructed for detecting small temperature modulation arisen in a single crystal of molecular compounds. Small ruthenium oxide chips with 100 $\Omega$ and 1 k$\Omega$ at room temperature were used as a thermometer and a heater, respectively. These chips are commercially available (KOA Co., Ltd.) and known as a low temperature thermometer available under strong magnetic fields. The magneto-resistance of the chip is typically 5% at 100 mK and 2-3% at 4.2 K and these values are similar to those of the Cernox thermometer. The single crystal sample was sandwiched by the two chips with thin lead wires ($\phi$0.06 mm) as is shown in figure 1. The sample with the chip resistances were coated by small amount of epoxy (Stycast 1266) and sealed inside the teflone capsule with the pressure medium of Daphne 7373 oil (Idemitsu Co., Ltd). The sample cell was set in the Cu-Be piston cylinder and clamped using Cu-Be screws from both sides. To produce a proper temperature oscillation around the sample, square wave currents with an amplitude of 80-100 $\mu$A and a frequency of 20-35 Hz was applied to the heater chip by the DC current source. The temperature oscillation, $T_{ac}$, was detected by the ac resistance bridge and the error signal from the setpoint value was amplified by the analogue Lock-in amplifier. The high-pressure calorimetry system was mounted on the $^3$He cryostat at Osaka university. The temperature was determined by another ruthenium oxide chip sensor adhered on the pressure cell holder made of high-purity Cu. The magnetoresistances were calibrated against the standard thermometer. The detailed description of the system including the typical data is reported in ref. [14]. Although it is very difficult to determine the absolute value of the heat capacity by the present system, high sensitivity on the relative change of heat capacity is available for such kind of investigations to see small heat capacity anomaly. To confirm the validity of the obtained signals, we have compared the result with that of the relaxation calorimeter result for similar size of single crystals.

![Figure 1. A schematic view of the arrangement around the sample and the chip resistances in the thermodynamic measurement system under pressure.](image-url)
3. Results and Discussion

In figure 2, we show temperature dependence of the heat capacity at ambient pressure. In general, the ac calorimetry should be performed in the frequencies to satisfy the validity criterion of the measurement. This criterion is determined as $\omega_1 < \omega < \omega_2$, where $\omega_1$ and $\omega_2$ corresponds to external and internal time constant. A systematic study on checking the appropriate frequencies has been performed using the similar type of molecular compounds in reference [14] and it is concluded that the $\omega = 20$ Hz is an appropriate frequency for these molecular compounds. The amplitude of ac temperature modulation detected by the Lock-in amplifier can be transformed into the heat capacity using the relation of $C_p = \frac{Q_0}{\omega T_{ac}}$. The data are plotted in $C_pT^{-1}$ vs $T^2$ in figure 2 by an arbitrary unit. In this figure, we plotted the data between 3.8 K and 5.5 K in order to see the behavior around the superconducting transition temperature. Also shown in Fig.2 are the data obtained under 2 T for comparison. The discrepancy between 0T and 2 T data clearly demonstrates that a broad thermal anomaly corresponding to the superconductive transition exists around 5 K in the 0 T curve. The direction of magnetic fields was adjusted to be parallel to the largest surface of the plate-like crystal. However, this configuration implies the averaged information of the in-plane and out-of-plane directions. Since the magnetic field of 2 T is larger than the $H_{c2}$ value of both directions taking account of the previous heat capacity measurements in [17], the thermal anomaly reflects on the superconductive transition of this compound. It is difficult to quantitatively evaluate the extra

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure2}
\caption{\(C_pT^{-1}\) vs. $T^2$ plot of $\kappa$-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O at ambient pressure. The data of 0 T and 2 T are shown to clarify the behavior around the transition temperature.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure3}
\caption{Temperature dependences of $\Delta C_pT^{-1}(H) = C_pT^{-1}(H) - C_pT^{-1}(2T)$ for $H=0$ T, 0.05 T, 0.1 T, and 0.3 T.}
\end{figure}
contributions of the background heat capacity owing to the contribution on chips and the epoxy surrounding the sample. The heat release through the pressure medium also gives an ambiguous factor for the measurements. However, the temperature dependence of the discrepancy between 0 T and 2 T curve should mean the change of electronic heat capacity correctly. To see the behavior of this electronic heat capacity around the superconducting transition temperature, we have plotted $\Delta C_p = C_p(0 \, \text{T}) - C_p(2 \, \text{T})$ as a function of temperature in figure 3. The existence of peak structure around 5 K is clearly observable, which seems to be a typical shape of the thermal anomalies of the organic superconductors. The data shown in figure 4 is the heat capacity obtained by the thermal relaxation calorimeter, which were reported in reference [17]. The crystals used for both measurements are similar size and they are selected from the same batch. The nature of superconducting transition and its suppression by strong magnetic fields of 8 T is more clearly observable. The magnitude of the heat capacity jump $\Delta C_p / T_c$ is 25 mJ K$^{-2}$ mol$^{-1}$. Using these data, it is possible to calibrate the vertical axis of figure 3. The data obtained under external magnetic fields of 0.05 T, 0.1 T and 0.3 T are also shown in figure 3 in a $\Delta C_p T^{-1}$ vs $T$ plot. We can observe that the peak-shape is gradually suppressed with the increase of magnetic fields. This tendency is again consistent with the feature of the organic superconductors when the magnetic fields are applied parallel to the conducting plane. The result ensures that we have succeeded to detect the behavior of superconductive transition of this material.

The temperature dependence of heat capacity obtained under a pressure of 0.4 GPa is shown in figure 5. By the application of the external pressure, the chip resistance values decrease about 5-7% from the ambient pressure values at room temperature since the resistive part is made of sintered ceramics. However, this decrease does not seriously change the characteristic temperature dependence of the resistance. Therefore we have performed the correction of this resistive change, and the plotted

![Figure 4. Temperature dependences of the heat capacity of $\kappa$-(BEDT-TTF)$_2$$\text{Ag(CN)}_2\text{H}_2\text{O}$ under 0 T and 8 T which were obtained by the relaxation calorimetry technique (see details in reference[17]).]
data already reflect on this behavior. Contrary to the ambient pressure data in figure 2, there is no noticeable discrepancy between 0T and 2 T. This tendency is more clearly observable in the plot of $\Delta C_p T^{-1}$ as a function of temperature shown in the inset of the figure. The result means that the superconductive transition has been suppressed completely and the ground state of this compound at 0.4 GPa has been transformed into the normal metal region as is expected from the phase diagram. It is very difficult to determine the electron density of states from this experiment, and the next important task for this material is to see the systematic variation of $\gamma$ with the increase of the pressure.

The disappearance of the thermal anomaly related to the superconductive transition is consistent with the scenario of the two-dimensional strongly correlated electron system of organics. In the conceptual $p$-$T$ phase diagram for the $\kappa$-type organic system, the Mott insulating phase and relatively high-$T_c$ phase are neighboring each other. The superconducting transition temperature shows the maximum value of 13.4 K in the boundary region and decreases with the increase of pressure [4,5]. By further pressurizing, the ground state of the system changes to a good metal which possesses a definite Fermi surface of effectively quarter-filled electron band. Since the present salt of $\kappa$-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O is located on the higher pressure side from the10 K class superconductors, the application of 0.4 GPa is sufficient to suppress the superconductivity completely. Some experiments aiming to see the pressure effects in the superconductive phase through heat capacity measurements have been performed by changing the size of anions or partial deuteration of BEDT-TTF molecules. An interesting change of physical properties has been observed by thermodynamic parameter such as $\gamma$-term [18]. However, the chemical pressure usually produces an ambiguity of introducing the change of other parameters than the pressure, for example disorders etc. Our present result is meaningful in that such kind of pressure effects in thermal property can be obtained directly using single piece of crystal, although the resolution and the calibration ways should

![Figure 5](image)

**Figure 5.** Temperature dependences of the heat capacities under pressure of 0.4 GPa. The inset shows the difference between 0 T data and 2 T data.
be much improved. The detailed pressure dependence including lower-temperature region is required for the further discussion.

4. Summary
We have performed a thermodynamic measurement in the low temperature region between 3.5 K and 6 K in order to observe the suppression of superconductive phase by applying pressure. Using the newly constructed high-pressure ac-calorimeter for detecting thermal anomaly for tiny single crystals, we have confirmed the superconducting phase transition at ambient pressure and its disappearance under pressure of 0.4 GPa. The result is consistent with the idea of the two-dimensional strongly correlated superconductivity of the dimer-Mott organic superconductor.

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