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DRASTIC COOLING RATE DEPENDENCE OF THERMAL ANOMALY ASSOCIATED WITH THE SUPERCONDUCTING TRANSITION IN κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$

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Using a thermal relaxation calorimetry technique, we have measured heat capacities of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ system under magnetic fields between 0 and 6 T. With the increase of cooling rate from room temperature to liquid helium temperature, we have observed a remarkable but systematic tendency that the thermal anomaly associated with the superconductive transition shifts to the lower temperatures. The course of this phenomenon is attributable to the degree of disorder in the mercury chains which give an incommensurate potential to the superconducting planes.

Keywords: *cooling rate, incommensurate lattice, organic superconductor*

Introduction

Since the discovery of superconductivity in organic charge transfer salt of (TMTSF)$_2$PF$_6$ in 1980 [1], a large number of molecular superconductors have been observed up to now [2]. The transition temperature, T_c, of these salts ranges from low temperatures below 100 mK up to the highest value of 14.2 K recently recorded in β'-(BEDT-TTF)$_2$ICl$_2$ under high pressures of 8.6 GPa [3] . These salts consist of electron donor molecules (denoted by D) with TTF frame and monovalent counter anions (denoted by X), and the chemical formula is usually D$_2$X. The donors and anions have segregate stacking in the crystal lattice and form a layered structure in which the donor and anion layers are arranged alternately. The electronic structure is usually determined by the donor packing in the conducting layer.

The most extensively studied materials in terms of superconductivity are those classified into the κ-type salts, in which the donor molecules are arranged to form a strongly dimerized structure. The T_c's for the typical materials of κ-(BEDT-TTF)$_2$C u[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$, κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O and κ-(MDT-TTF)$_2$AuI$_2$ are reported as 11.4, 9.6, 5.0 and 4.1 K, respectively [2]. These temperatures are relatively high as compared with other salts which do not have dimerized structures. In them, the intra-dimer coupling expressed by t_{dimer} is larger than other inter-dimer couplings and a dimerization gap appears in the center of HOMO band. If the electron correlation is enough large, the competitive relation between the band metals and Mott insulators makes interesting phenomenon that is discussed based on the electronic phase diagram [4, 5]. The relatively high transition temperatures of these salts are considered to be related with the strong correlation effect understood in the framework of the Mott-Hubberd physics.

κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ which was developed by Lubovskaya *et al*. in 1987 is known as a unique κ-type salt [6]. The mercury ions in the anions layers form a chain structure of it's own and their periodicity becomes incommensurate with that of the donors and halogens. Thus, the chemical composition of mercury becomes non-stoichiometric with other components. The superconductive transition temperature determined by the onset of resistivity was reported as 4.3 K. With a purpose of studying the bulk thermodynamic properties of this compound, we have previously performed a thermodynamic investigation especially at low temperatures in [7, 8]. We have observed

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an interesting behavior in the lattice heat capacity associated with the dimensional crossover of 1D phonon to 3D phonon with lowering temperature. We also observed that the electronic heat capacity coefficient is enhanced up to about 55 mJ K^{-2} mol^{-1} which is 2-2.5 times larger than that of typical κ-type superconductive salts of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The thermal anomaly in association with the superconductive phase transition has been found to be broadened and large residual electronic heat capacity coefficient remains in the gap was also observed [8].

To gain information on the thermodynamic aspect of the superconductivity of this material, we have performed a systematic heat capacity measurements around the superconductive transition. In this work, we focus on how the superconductive fraction and transition temperature change with the difference in the cooling rate of the sample, since many organic salts are known to show cooling rate dependence in their phase transitions due to the volume effects linked with the molecular arrangement.

Experimental

Single crystals of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ were grown electrochemically. Thick plate crystals with typical mass of 0.1–0.6 mg were yielded using the standard H-type cells with Pt electrodes by applying an electric current of 0.1 μA for nearly one month. Since the existence of some polymorphic phases is known [6], the magnetic susceptibility measurements by SQUID magnetometer (Quantum Design MPMS system) were performed prior to the thermodynamic measurements. The reproducibility of the reported χ *vs.* T behavior was confirmed. The heat capacity measurements were performed with a thermal relaxation-calorimeter constructed by ourselves. The crystals used for the present work were 0.45 and 0.55 mg. The calorimetry cell was equipped with a ^{3}He refrigeration system and magnetic fields up to 6 T were applicable with a superconducting magnet (Cryogenics Ltd.). The calibration of the thick-film chip of ruthenium oxide (KOA Japan) thermometer was performed under magnetic fields.

Results and discussion

Figure 1 shows temperature dependences of the heat capacity of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ measured under different magnetic fields between 0 and 6 T which were applied perpendicularly to the conducting layers. In this experiment, the cooling rate from room temperature down to the liquid helium temperature was controlled at 0.2 K min^{-1} in an average. If we consider the non-stoichiometric concentration due to the incommensurate periodicities of donors and mercury chains, the electronic state of the conducting layers is altered from the effectively half-filled state realized in the typical κ-(BEDT-TTF)$_2$X system. When the valence of mercury is divalent as in the electrolytes in the starting material of electrochemical growth, nearly 10% of holes are doped into the conducting donor layers. For the comparative discussion with other κ-phase salt, the molar heat capacity in Fig. 1 is calculated using the chemical formula of κ-(BEDT-TTF)$_2$Hg$_{1.45}$Br$_4$ as we have also done in the previous report [7, 8]. When only the heat capacity data under 0 T is seen, the existence of the thermal anomaly related to the superconductivity is not clear since the unusual temperature dependence of lattice heat capacity is observed. However, if we compare the 0 T data with those obtained under magnetic fields, the gradual suppression of thermal anomalies observed around 3 K is noticeable. In accordance with the decrease of superconductive anomaly, the electronic contribution at low-temperature side in Fig.1 increases with the increase of magnetic fields. The relatively large change of C_pT^{-1} as is observed in the electronic heat capacity is consistent with the large normal state γ of 55 mJ K^{-2} mol^{-1} determined from the data obtained with the dilution refrigerator.

The low-temperature heat capacities were also measured for the samples cooled down at different cooling rates as are shown as C_pT^{-1} *vs.* T^2 curves in Figs 2 and 3. The averaged cooling rates were 0.4 and

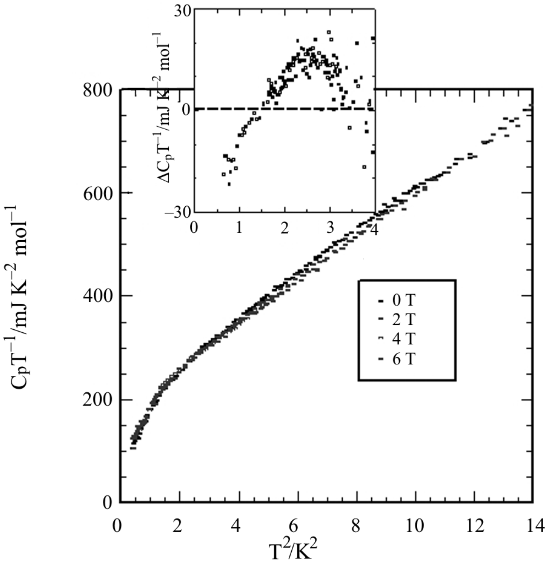

Fig. 1 Temperature dependence of heat capacity of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ in a form of C_pT^{-1} *vs.* T^2 plot. The cooling rate 0.2 $Kmin^{-1}$ The inset shows the temperature dependence of $\Delta C_pT^{-1}=C_pT^{-1}$ (0 T)-C_pT^{-1} (6 T)

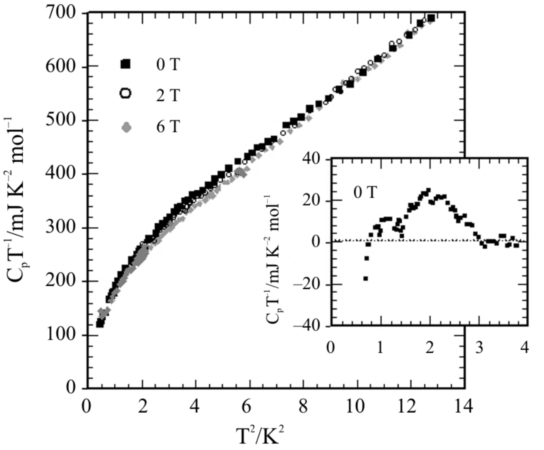

Fig. 2 C_pT^{-1} *vs.* T^2 plot for κ-(BEDT-TTF)$_2$Hg$_{1.45}$Br$_4$ cooled at a rate of 0.4 K min^{-1}. The inset shows the temperature dependence of $\Delta C_pT^{-1}=C_pT^{-1}$ (0 T)–C_pT^{-1} (6 T)

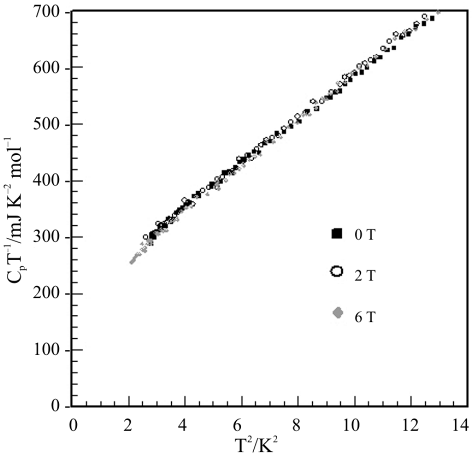

Fig. 3 C_pT^{-1} *vs.* T^2 plot for κ-(BEDT-TTF)$_2$Hg$_{1.45}$Br$_4$ cooled at a rate of 0.8 Kmin^{-1}

0.8 K min^{-1}, respectively. In these measurements also magnetic fields up to 6 T were applied perpendicularly to the conducting layers. By comparing the data shown in Figs 1–3, one can notice that the thermal anomaly related to the superconductive transition shifts towards the lower-temperature side with the increase of the cooling rate. The inset of Fig. 2 displays $\Delta C_pT^{-1}=C_pT^{-1}$(0T)–$C_pT^{-1}$(6 T) as a function of temperature. Since 6 T is large enough to reduce the critical temperature below 100 mK, this plot shows the change of electronic heat capacity around T_c. The broad peak with its maximum at 2 K is observable in the figure. In the case of 0.8 K min^{-1} as shown in Fig. 3, we cannot observe any difference between 0 T data and those obtained under magnetic fields, which means that the thermal anomaly has been reduced down to the lower temperature than the present measurement. Since the reported transition temperature of 4.3 K is close to that of the elemental mercury, the possibility of the superconductivity of mercury has been suspected for this salt. As sometimes happens in the intermetallic compounds, a filamental participation of elements at the grain boundaries or surface regions gives extrinsic superconductive behaviors. However, judging from the magnitude of the heat capacity jump at T_c ($\Delta C_pT_c^{-1}$=20 mJ K^{-2} mol^{-1}) and relatively higher critical magnetic fields to suppress superconductivity, the possibility of participation of mercury is excluded.

Our next interest is directed to consider why such cooling rate dependences in the bulk level appear in this material. In the 10 K class superconductors of κ-(BEDT-TTF)$_2$X (X=Cu[N(CN)$_2$]Br, Cu(NCS)$_2$), the existence of cooling rate dependence of the superconductive character has been discussed. The conformational ordering of ethylene groups at the edge of BEDT-TTF molecules induces a kind of volume effect in the crystal. If they are cooled down rapidly, disorder remains in the arrangement of the ethylene groups and induces an additional expansion effect in the unit cell. This effect works to decrease the width of the electron bands. The nature of these phenomena was discussed using a frequency dependence in the ac calorimetry by Akutsu *et al.* [9] and by the dilatometry measurements by Müller *et al.* [10]. In the case of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$, the thermal anomaly related to conformational order-disorder effects of the ethylene groups are not observed in both ac and relaxation calorimetry. Therefore, the drastic cooling rate dependence observed here is not directly associated with the ethylene groups. The most plausible candidate to make structural difference by the difference of cooling rate is the mercury chain in the anion layers. Disorders in the mercury chains seem to give a similar kind of influence as that of ethylene groups in the donor molecules. As a matter of fact, the crystallographic study by X-ray diffraction by Ruiming Li *et al.* [11] has observed the gradual variation in the chain structure even at low temperatures around 40 K. Another important factor to be considered for explaining the broadening of the thermal anomaly is the structural peculiarity originating from incommensurate relation between donors and mercury. In the case of the present salt, due to the difference of periodicities of the layers, the conducting plane feels complicated electrostatic potentials. The Fermi surface should experience a multiple folding by this potential effect, and a similar kind of broadening of electronic bands is expected. The broad thermal anomalies in question may probably be related with this effect. It is reasonable to consider that a small amount of disorder may obscure the Fermi surface and enhance the broadening of superconductive phase transition through a kind of random potential effect on the conducting donor layers.

Conclusions

We have measured heat capacity around the superconductive phase transition of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ salt. The suppression of the transition temperature with increasing cooling rate was clearly observed by comparing the 0 and 6 T data. The drastic influence by the external magnetic fields may be related with the peculiar electronic state of the incommensurate relation between mercury and donors. The course of the broadening of thermal anomaly is attributable to a kind of random potential effect produced by the structural incommensurability.

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