Low-Temperature Heat Capacity Measurements of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$

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Abstract

Low-temperature heat capacity measurements of single crystals of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$, which is known as a strongly correlated organic system were performed. We observe an interesting behavior in lattice heat capacity associated with the chain structure of mercury atoms in the anion layers. The electronic heat capacity coefficient, γ was found to be about 2-3 times larger than those of well known 10 K class superconductors.

Key words: organic superconductor ; heat capacity ; electron correlation

The electronic states of organic charge transfer salts, especially those who have κ-type structure, is attracting considerable attention in condensed matter physics, since it contains important physics related to the strongly correlated electrons system in two dimension. Among various κ-type salts, (BEDT-TTF)$_2$Cu(NCS)$_2$ and (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br are known as 10 K class superconductors with strongly anisotropic character in their superconductive gap. In these salts, enhanced antiferromagnetic spin fluctuations which play an important role for the formation of the superconductivity are detected by ^{13}C-NMR on BEDT-TTF molecules [1]. The (BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ are also known to crystallize into the κ-type structure. The peculiar aspect of this salt as compared with 2:1 salts is reflected in the structure in the anion layers. Heavy mercury atoms form a chain structure along the a-axis as is reported in Ref.[2] and their own lattice periodicity is incommensurate with that of halogens and donor molecules. Due to this incommensurability, the electron filling of $p\pi$-band is shifted from the usual half-filled state of dimerized 2:1 salts, and a kind of hole-doped state is considered to be realized. Surprisingly, the antiferromagnetic fluctuations are much enhanced than those in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT- TTF)$_2$Cu(NCS)$_2$ and develop with decreasing temperatures without showing any long-range magnetic ordering [3]. The superconductive transition is known to occur at 4.3 K [2]. In order to study the low-temperature behavior of this salt from a thermodynamic standpoint, we performed heat capacity measurements between 0.3 K and 50 K.

Single crystals of this salt were grown by the standard electrochemical oxidation method. The heat capacity measurements were performed by the thermal relaxation technique. Typical crystals weighing about 0.5-0.6 mg were used for the measurements. They were adhered on the sample holder by small amount of Apiezon N grease.

In Fig.1, we show a temperature dependence of heat capacity of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ in a C_p vs T plot. As is usually the case in organic salts, the heat capacity gives large values due to the low-energy phonon

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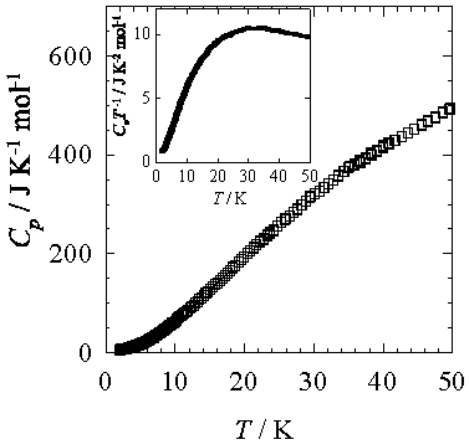

Fig. 1. Temperature dependence of heat capacity of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$. Inset shows a C_pT^{-1} vs T plot.

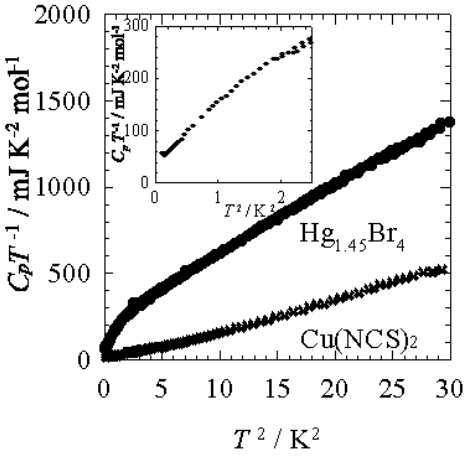

Fig. 2. C_pT^{-1} vs T^2 plot of the low-temperature data. The molar heat capacity are calculated using the chemical formula of (BEDT-TTF)$_2$Hg$_{1.45}$Br$_4$. The inset shows the data below 1.6 K.

contribution. The values at 20 K, 50 K are 188 J K^{-1} mol^{-1}, 486 J K^{-1} mol^{-1} respectively and are comparable to the typical BEDT-TTF salts. In the inset of the figure, we show C_pT^{-1} vs T plot. From the figures, we can notice that a broad heat capacity hump exist around 30-40 K. This is due to the optical phonon contribution originating from the librational vibrations of BEDT-TTF molecules.

In order to see the electronic contribution in details, we performed heat capacity measurements at low temperatures by a ^{3}He apparatus. Obtained data are shown in Fig.2 in a C_pT^{-1} vs T^2 plot. The molar heat capacity in this figure is normalized using the chemical formula of (BEDT-TTF)$_2$Hg$_{1.45}$Br$_4$ so as to compare them with other typical BEDT-TTF salts. We also plot the data of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in the same figure for comparison. Unexpectedly large values of C_pT^{-1} and curious temperature dependence are observed even at low temperatures below 2 K in the present salt. In general, typical 2:1 salts of BEDT-TTF show simple Debye's T^3 behavior below about 2 K and above this temperature they show upward deviation from the linear T^2 dependence of C_pT^{-1} [4]. The peculiar structural aspect in this system is an existence of chain structure of heavy mercury atoms in the anion layers. Due to this chain structure, a dimensional crossover phenomenon in phonon spectrum should appear in the temperature dependence of heat capacity. The one-dimensional character dominated at higher temperatures gradually varies to three-dimensional character below about 1.5 K. This tendency is also observed in $Hg_{3-\delta}AsF_6$, which also possesses similar type of incommensurate chains of mercury. To explain this behavior in lattice heat capacity, the Tarasov's model in which the crossover process from 1D to 3D phonon is taking into account is effective [5]. For the present κ-type salt, the characteristic Debye temperatures of Θ_{1D}= 150 K and Θ_{3D}= 7 K for the Tarasov's model are found to be well to reproduce the lattice heat capacity curvature.

Another important finding obtained from the present data is the existence of electronic contribution dominated by temperature linear term and a slight upturn of C_pT^{-1} retained even in the superconductive state. This is shown in the inset of Fig.2. Although we cannot estimate how much fraction of superconductivity is realized in the present sample, the C_pT^{-1} values shown in the inset is about 2-3 times larger than the normal state γ values of 10 K class κ-(BEDT-TTF)$_2$X salts. The enhancement of the electronic heat capacity coefficient γ may be induced by the strong fluctuations detected by ^{13}C-NMR experiment.

In conclusion, we have performed low-temperature heat capacity measurements of κ-type organic conductors (BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$. Interseting behaviors in electronic and lattice heat capacity are observed at low temperatures. The enhancement of temperature linear term of heat capacity may be related to the strong antiferromagnetic spin fluctuations.

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