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Thermodynamic behavior of the 10 K class organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ studied by relaxation calorimetry

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Abstract

Heat capacities of single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, which is known as an organic superconductor with T_c = 9.5 K, were measured with a recently constructed ^{3}He-calorimeter of a relaxation type. A large heat capacity jump of about $\Delta C_p T^{-1}$ = 65 mJ K^{-2} mol^{-1} was observed in association with the superconductive transition. The characteristic behavior of the thermal anomaly is compared with the previous results reported. Only slight change was found between the heat capacity peaks for the slowly cooled and rapidly cooled samples. This demonstrates that the degree of disorder left in the cooling process is not so serious in this material.

Keywords: Heat capacity; Organic superconductor; Electron correlation

1. Introduction

Bis-(ethylenedithio)tetrathiafulvalen, abbreviated as BED T-TTF, is a well known electron–donor molecule which yields many charge transfer complexes with counter anions such as I_3, AuI_2, IBr_2, PF_6, ClO_4, etc. [1]. Since the discovery of (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$ salt [2], the BEDT-TTF complexes have widely been recognized as ideal systems to give molecular-based conducting compounds. In these materials, donor molecules and counter anions are stacked separately in the crystal and form a layered structure as shown in Fig. 1. The donor layers and anion layers are piled up alternately. The electronic properties are usually determined by the character in the donor layers and the anion layers work as an insulating space. Thus, an ideal two-dimensional electronic system is constructed. Since the composition of these charge transfer complexes is usually 2:1, chemical formula is expressed as (BEDT-TTF)$_2$X, where X denotes the anion molecules. These compounds are known to give a rich variety of electronic ground states originating from electron–phonon interaction and strong electron–electron interaction occurring in the 2D plane. The electronic phases such as metallic, superconductive, spin/charge density wave, antiferromagnetic insulating phases, etc. appear due to the variation of the molecular arrangements in the donor layers. The difference of donor arrangements is usually denoted with Greek characters such as α, β, κ, θ, etc. [1].

Among various BEDT-TTF based organic salts, the κ-phase family attracts great interest in the area of condensed matter physics, because their ground state becomes either superconducting state with relatively high-T_c or antiferromagnetic insulating state due to the difference of anions. The X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts are superconductors with T_c = 9.5 and 11.4 K, respectively, while the X = Cu[N(CN)$_2$]Cl and Cu$_2$(CN)$_3$ salts are antriferromagnetic insulators. The crystallographic peculiarity in the κ-phase family is understood as the donor molecules form a dimerized structure and are arranged in nearly orthogonal coordination to construct a zigzag network as is shown schemat-

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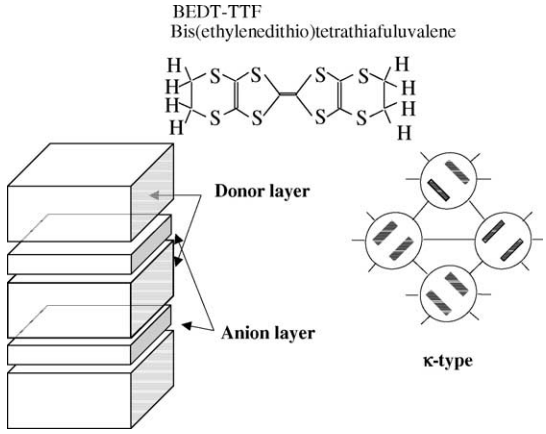

Fig. 1. Molecular structure of BEDT-TTF (upper portion), schematic illustration of layered structure consisting of organic donors and anions (lower left side), and the donor arrangement of the κ-type materials (lower right side). The longer axis of donor molecules is arranged perpendicularly to the paper sheet in the lower right drawing.

ically in Fig. 1. When the intra-dimer electron transfer t_{dimer} is larger than other inter-dimer transfer t_{inter}, a dimerization gap appears in the center of the highest occupied molecular orbital (HOMO) bands. They split into upper-HOMO and lower-HOMO bands. The originally third-quarter filling of electronic state determined by the 2:1 composition is, therefore, considered as effectively half-filling of the upper-HOMO band. This dimerization effect also enhances the on-site Coulomb interaction (U) inside the dimers and the magnetic character is enhanced for example in the κ-type systems. The competitive picture between metallic (superconductive) and magnetic characters in this phase is, therefore, considered within the framework of the Mott–Hubberd physics [3]. The intrinsic parameter is, therefore, the ratio of U/W, where W denotes the band-width. The strong spin fluctuations which make the Néeel ordering in the Mott insulating phase remain in the normal state of superconductive phase and thus, the pairing symmetry of superconductivity is considered as an unconventional d-wave [4,5].

Concerning the superconductivity of the κ-(BEDT-TTF)$_2$X system, several groups have studied by different calorimetric techniques, for example, relaxation, ac and adiabatic ones. The thermal anomalies have been successfully observed for X = Cu[N(CN)$_2$]Br salt by Andraka et al. [6], Elsinger et al. [7], and Kovalev and Ishiguro [8], and for X = Cu(NCS)$_2$ salt by Andraka et al.[9], Graebner et al. [10], and Müller et al. [11]. The so-called heat capacity jump $\Delta C_p T_c^{-1}$ determined by these experiments shows scattering in a range of 40 and 60 mJ K^{-2} mol^{-1}. In addition, the low-temperature heat capacity below 2 K always gives residual γ^* term of about 2–3 mJ K^{-2} mol^{-1}, even though the superconductive gap is established. This point is discussed from the standpoint of an unconventional superconductivity with nodal gap structure in Ref. [5].

In the molecular superconductors, it is not unusual that sample dependence due to the disorders in the molecular packing is observed. In the κ-phase salts of BEDT-TTF (κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br), the physical properties usually show cooling rate dependence. Since these salts are located near the critical boundary of Mott transition, these extrinsic factors sometimes affect the superconductive volume and transition temperature T_c. The aim of the present work is to pursue how the heat capacity peak of superconductive transition changes by the difference of cooling sequence in X = Cu(NCS)$_2$. Although a lot of works which deal with this cooling rate dependence have been performed up to now, there is no thermodynamic data to discuss these effects in terms of entropic information.

2. Experimental

A single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ was prepared by the usual electrochemical oxidation method in 1,1,2-trichloroethane. The large plate-like crystal of 0.996 mg was characterized by the SQUID magnetometer (QD-MPMS system) and the existence of perfect Meissner signal was confirmed. The heat capacity measurements were performed with a thermal relaxation calorimeter, which had been constructed by ourselves. We used two different relaxation calorimetry cells the details of which are described elsewhere. Ruthenium oxide (KOA model RX73 series) and Cernox (Lake Shore CX1080) were utilized as the thermometers for low (0.5–14 K) and high (5–50 K) temperature calorimeter cells, respectively. Typical time constant (τ) in the temperature relaxation process was 20 s at 5 K and 50 s at 10 K.

3. Results and discussion

Fig. 2 shows low-temperature heat capacities of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt in the C_pT^{-1} versus T^2 plot. The data are consistent with the reported results obtained with the dilution

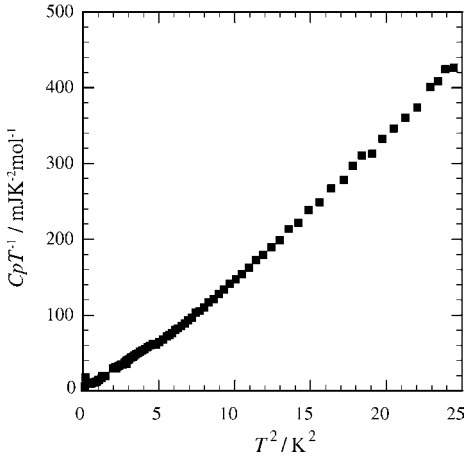

Fig. 2. Low-temperature heat capacity data of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ shown in C_pT^{-1} vs. T^2 plot.

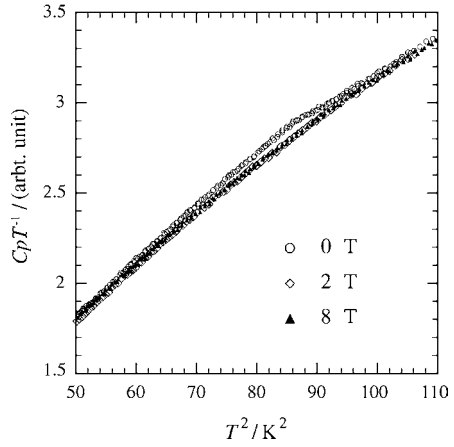

Fig. 3. Heat capacities of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ around the superconductive transition temperature obtained under 0, 2 and 8 T.

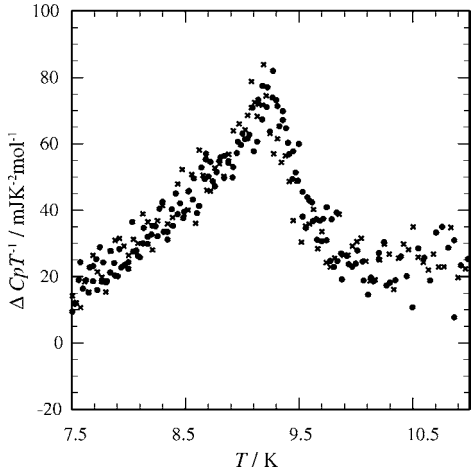

Fig. 4. Temperature dependence of the electronic heat capacity near T_c: (●), slowly cooled; (×), rapidly cooled sample. ΔC_pT^{-1} was determined by the analytic subtraction of $C_p(8\,T)T^{-1}$ data from $C_p(0\,T)T^{-1}$ data.

refrigerator in Ref. [12]. It is notable from the temperature dependence that finite γ^* remains, even though the perfect Meissner signal has been observed and bulk superconductivity is established. This value corresponds to about 10% of the normal state value $\gamma = 25\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ estimated by applying a magnetic field higher than $H_{c_2} = 6$ T.

Fig. 3 shows the T^2 dependence of C_pT^{-1} in a temperature range between 7.1 and 10.5 K. In this plot, a thermal anomaly due to the superconductive transition is clearly found. The transition temperature T_c is estimated as 9.5 K, which is consistent with the magnetic susceptibility result. In the figure, we also show the data obtained under magnetic fields of 2 and 8 T which are applied perpendicular to the metallic plane. Since 8 T is higher than the critical field H_{c_2} in the perpendicular direction, the C_pT^{-1} versus T^2 curve at this field should correctly reflects the lattice heat capacity plus the electronic heat capacity of the conduction electrons. The subtraction of the fitted result of $C_p(8\,T)T^{-1}$ from the $C_p(0\,T)T^{-1}$ makes it possible to discuss how the electronic heat capacity behaves as a function of temperature. The data shown in Fig. 4 is ΔC_pT^{-1} versus T plot thus obtained, where ΔC_p corresponds to $C_p(8\,T)$–$C_p(0\,T)$. The value of heat capacity jump is estimated as $65\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ and this value is larger than the reported value of $55\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ by Müller et al. [11]. The value of $\Delta C_p\gamma^{-1}T_c{}^{-1}$ amounts to about 3 and this is 2.1 times larger than that expected by the BCS strong coupling theory. The sharp peak-shape and large $\Delta C_p\gamma^{-1}T_c{}^{-1}$ sometimes lead us to consider the strong coupling electron–phonon behavior as was suggested by Andraka et al. in the initial paper [9] and more recently for X = Cu[N(CN)$_2$]Br by Elsinger et al. [7]. However, this sharp peak gives a close resemblance to the superconductive transition of high-T_c cuprates of YBCO [13] in which the unconventional superconductivity due to the strong electron correlation has been established. As a matter of fact, the discrepancy between $C_p(8\,T)$ and $C_p(0\,T)$ seems to exist up to higher temperatures than the bulk T_c as is shown in Fig. 4. The fluctuation analysis based on 2D superconductive transition is necessary. Another serious factor we have to take into account is that the normal metallic state obtained by applying magnetic field of 8 T may have relatively strong magnetic fluctuations existing above 20 K. They gradually crossover to the Fermi liquid state with the decrease in temperature. The electronic heat capacity in such a sate may not be expressed by simple γT term determined from the low-temperature behavior below 1 K.

To see the influence of the structural disorder, we warmed the sample up to 300 K and then cooled again rapidly down to the liquid helium temperature. The cooling rate from 300 to 30 K was $6.5\,\mathrm{K\,min^{-1}}$, which was high enough to give rise to the broadening of superconductive transition in this system. The obtained data are also shown in Fig. 4 as the ΔC_pT^{-1} versus T plot. Although slight decrease (−0.05 K) in the transition temperature is observed, no drastic broadening and discrepancy in the peak shape appear between slowly cooled and rapidly cooled samples. This result demonstrates that the disorder in the donor arrangement is not so serious in this material. The broadening of the transition width and the slight decrease of Meissner fraction are produced by the local effects for example at the surface or dislocation in the sample.

For several organic salts consisting of BEDT-TTF and DMET molecules, Akutsu et al. have performed a systematic ac calorimetry and observed a glass transition related to the conformational ordering of the ethylene groups at the edge of these molecules [14,15]. They explained that the electronic state is affected by this order–disorder arrangement of the ethylene groups through a chemical pressure effect in the crystal. In the case of κ-phase salts, the conformational disorders left in the rapid cooling process increases the unit-cell volume and the magnetic character is enhanced accordingly. The slowly cooled samples stayed at the metallic region. According to their detailed experiments, the glass transition which clearly has a frequency dependence is observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt and its dueterated salt, but not in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

salt. The almost negligible change in $\Delta C_p T^{-1}$ versus T is consistent with their ac calorimetry results, although a recent high-resolution dilatometry work by Müller et al. [16] clearly detected the glass like behavior even in the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. To study relation between the superconductivity and the freezing of ethylene groups, the similar study in the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt is required.

4. Conclusion

We carried out low-temperature heat capacity measurements on the superconductive transition of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and studied how the difference in the cooling rate affects the peak structure. The behavior of the electronic heat capacity estimated from $\Delta C_p = C_p(0\,\mathrm{T}) - C_p(8\,\mathrm{T})$ shows no drastic cooling rate dependence. This suggests that the conformational disorder in the ethylene groups is not so seriously affects on the bulk superconductivity in this material.

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