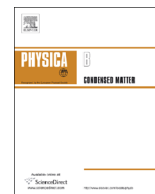




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Antiferromagnetic fluctuations and proton Schottky heat capacity in doped organic conductor κ -(BEDT-TTF)₄Hg_{2.78}Cl₈ [☆]

Ryo Yoshimoto, Akihito Naito, Satoshi Yamashita, Yasuhiro Nakazawa ^{*}

Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan

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ABSTRACT

Low temperature heat capacity measurements of hole-doped organic conducting compound of κ -(BEDT-TTF)₄Hg_{2.78}Cl₈ were performed by the ac calorimetry and the thermal relaxation technique. It was observed that low temperature electronic heat capacity at 0 T can be fitted by a kind of spin fluctuations model for two-dimensional (2D) itinerant electrons. The enhancement of electronic heat capacity is originated from these magnetic fluctuations occur at extremely low temperature region. We also observed that the low temperature heat capacity under magnetic fields show large additional contribution explained by the two-level Schottky model of protons located on the edge of BEDT-TTF molecules. The strong spin fluctuations peculiar for 2D electrons in this hole-doped organic compound influence the relaxation process of proton spins to get thermal equilibrium state. This is the first example among organic conducting systems where magnetic fluctuations of itinerant electrons affect on the relaxation of proton spins. Similar tendency was observed in another hole-doped system of κ -(BEDT-TTF)₄Hg_{2.89}Br₈ of which magnitude is reduced down to 20–25% of that of κ -(BEDT-TTF)₄Hg_{2.78}Cl₈.

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1. Introduction

Organic radical salts consisting of BEDT-TTF (bisethylenedithio-tetrathiafulvalene) molecule and its counter anions provide fascinating research stages for studying fundamental physics in condensed matter, because they give variety of electronic states due to the difference of molecular packing [1–3]. The electron correlation of κ -electrons manifests in 2D lattices give unique and complementary information for 3d and 4f electrons systems extensively studied in intermetallic compounds [4]. Possible unconventional superconductivity dominated by electron correlation [5–7], spin-liquid states appear in dimer Mott triangle system [8,9], and drastic charge disproportionation/charge ordering in simple structures [10,11] etc. are discussed as major topics in such organic compounds. In various BEDT-TTF salts, it is recognized that rigid dimerization in donor arrangements tend to form an effectively half-filling state. The compounds possessing κ -, β' -, and λ - type structure are known to have rigidly dimerized donor arrangements and tend to have strongly correlated metallic states or Mott insulating ground states which convert to conducting state by applying pressures. The κ -(BEDT-TTF)₂Cu(NCS)₂ and κ -(BEDT-TTF)₂Cu[N(CN)₂]Br are ambient pressure superconductors with $T_c=10.4$ K [12] and $T_c=11.6$ K [13].

The pressure induced superconductivity at $T_c=14.2$ K appears in κ QJ; β' -(BEDT-TTF)₂Cl₂ under 8.2 GPa [14].

The κ -(BEDT-TTF)₄Hg_{2.78}Cl₈ and κ -(BEDT-TTF)₄Hg_{2.89}Br₈ (abbreviated as κ -HgCl, κ -HgBr hereafter), containing divalent mercury ions in the counter anion layers are recognized as hole-doped organic compounds for dimer-Mott systems [3,4]. Since the mercury ions form a one-dimensional chain structure of which periodicity is incommensurate with that of the donors, the chemical compositions of them are non-stoichiometric as was reported by Lyubovskaya et al. in 1985 [15–17]. The hole doping rates from the effectively half-filling state were evaluated as 11% for κ -HgCl and 5–6% for κ -HgBr. The electronic properties are studied by transport measurements under pressures by Taniguchi et al. [18] and NMR experiments by Furuta et al. [19] and Kurosaki et al. [20]. Anomalously large spin fluctuations in two-dimensional donor layers were reported by them. The thermodynamic measurements by Naito et al. suggested enhancement of electronic heat capacity coefficient, γ due to these spin fluctuations [21,22]. It is the aim of the present paper to study the nature of the low temperature heat capacity of κ -HgCl (and κ -HgBr) precisely at 0 T and under magnetic fields upto 8 T. We have observed the appearance of nuclear Schottky contribution of protons in heat capacity and analyzed their typical behaviors in terms of peculiar spin fluctuations occur in them.

2. Experimental

The samples used for this study were grown by standard electrochemical method. The block type single crystals were obtained in

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^{*} Corresponding Author. Tel.: +81 6 6850 5396; fax: +81 6 6850 5396.

E-mail address: nakazawa@chem.sci.osaka-u.ac.jp (Y. Nakazawa).

H-type cell with Pt electrodes. For performing heat capacity measurements by single crystal samples at low temperature region, we used two types of thermal relaxation calorimeters constructed for measuring heat capacity of single crystals in the dilution temperature region and ^3He temperature region [23,24]. In order to attain good resolution in temperature relaxation curvatures, we used ruthenium oxide chip sensor ($1.0 \times 0.5 \times 0.2 \text{ mm}^3$) of which room temperature resistance was $1 \text{ k}\Omega$. The chip sensor adhered on the sample stage was calibrated against standard thermometers. The sample used for this work was 0.43 mg for $\kappa\text{-HgCl}$ and 0.62 mg for $\kappa\text{-HgBr}$. Temperature dependences of the ac heat capacity above 15 K were recorded by light-chopped ac heat capacity measurements system with a frequency of 2 Hz .

3. Results and discussion

In Fig. 1(a),(b), we show temperature dependences of the ac heat capacity of $\kappa\text{-HgCl}$ and $\kappa\text{-HgBr}$. The smooth curvatures of C_p vs T from room temperature down to about 15 K demonstrate that the two compounds do not show any structural phase transitions in this region. Therefore, incommensurate structure of mercury chains is retained even at low temperatures. The data between

20 K and 120 K are shown in Fig. 1(b) with $C_p T^{-1}$ vs T plot. Neither the glass like freezing nor hysteretic behaviors related to ethylene conformation of BEDT-TTF molecules typically observed in $\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{X}$ ($\text{X}=\text{Br}, \text{Cl}$) [25] and $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ [26] was observed by the present ac heat capacity measurements with 2 Hz . In Fig. 2(a),(b), we show low temperature heat capacities of $\kappa\text{-HgCl}$ and $\kappa\text{-HgBr}$ obtained by the thermal relaxation technique. In order to compare absolute values of heat capacity with typical 2:1 salts with $(\text{BEDT-TTF})_2\text{X}$ ($\text{X}:\text{monvalent anions}$), we calculated the molar heat capacity with a formula of $\kappa\text{-(BEDT-TTF)}_2\text{Hg}_{1.39}\text{Cl}_4$ and $\kappa\text{-(BEDT-TTF)}_2\text{Hg}_{1.45}\text{Br}_4$ following to the analyses in the previous reports [21–22,27]. We also show heat capacity data under magnetic fields upto 8 T for $\kappa\text{-HgCl}$ and upto 6 T for $\kappa\text{-HgBr}$. The temperature dependences of the heat capacities under 0 T coincides with those reported previously, which reported that the $C_p T^{-1}$ vs T^2 plot gives large T -linear term [21,22]. The electronic heat capacity coefficient γ larger than $50 \text{ mJ K}^{-2} \text{ mol}^{-1}$ was confirmed in the present measurements. Since these γ 's were determined from extrapolation of higher temperature data down to 0 K , it is necessary to discuss temperature dependence at low temperature region in details. The electron correlation in the itinerant electron systems tends to show enhancement of electronic heat capacity with decreasing temperatures.

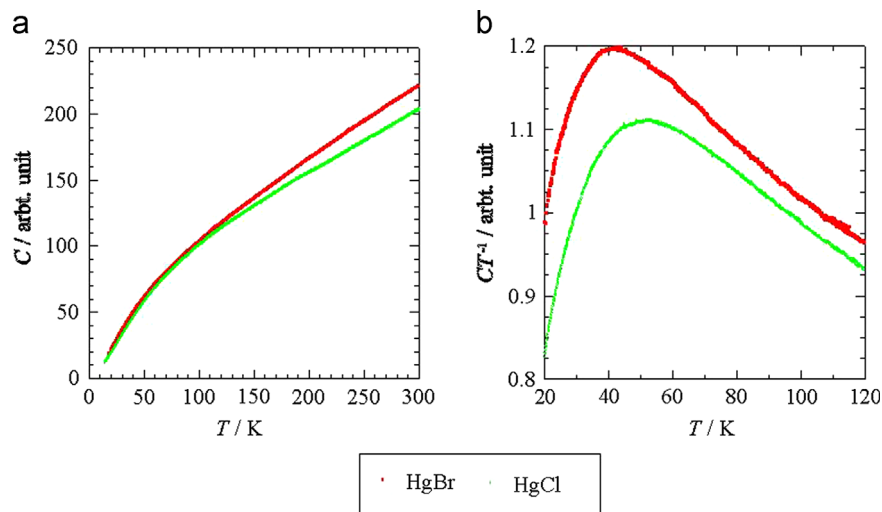


Fig. 1. (a) Temperature dependences of the ac heat capacities of $\kappa\text{-(BEDT-TTF)}_4\text{Hg}_{2.78}\text{Cl}_8$ and $\kappa\text{-(BEDT-TTF)}_4\text{Hg}_{2.89}\text{Br}_8$. The data between 15 K and 300 K are shown in C_p vs T . (b) Temperature dependences of the ac heat capacities shown by $C_p T^{-1}$ vs T plot of $\kappa\text{-(BEDT-TTF)}_4\text{Hg}_{2.78}\text{Cl}_8$ and $\kappa\text{-(BEDT-TTF)}_4\text{Hg}_{2.89}\text{Br}_8$ between 20 K and 120 K .

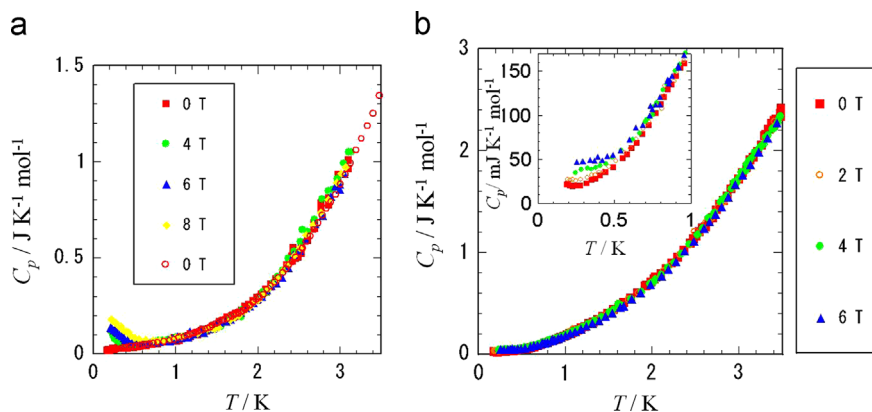


Fig. 2. (a) (Left) Temperature dependences of heat capacity of $\kappa\text{-HgCl}$ obtained under magnetic fields of 0 T , 4 T , 6 T and 8 T . The data under magnetic fields are obtained by the dilution refrigerator. The 0 T data shown by red open circles are obtained by the ^3He refrigerator. The molar heat capacity was calculated using a chemical formula of $\kappa\text{-(BEDT-TTF)}_2\text{Hg}_{1.39}\text{Cl}_4$ so as to compare the low temperature heat capacity values with typical 2:1 salts of BEDT-TTF. (b) (Right) Temperature dependences of heat capacity of $\kappa\text{-HgBr}$ obtained under magnetic fields of 0 T , 2 T , 4 T and 6 T . The inset shows the low temperature part in C_p vs T plot. The molar heat capacity was calculated using a chemical formula of $\kappa\text{-(BEDT-TTF)}_2\text{Hg}_{1.45}\text{Br}_4$ similar to the case of $\kappa\text{-HgCl}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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