AC heat capacities of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ measured by microchip calorimeter

Y Muraoka$^1$, S Yamashita$^2$, T Yamamoto$^1$ and Y Nakazawa$^{1,*}$

$^1$Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, JAPAN
$^2$RIKEN, Hirosawa 2-1, Wako, Saitama 351-0198, JAPAN

E-mail: nakazawa@chem.sci.osaka-u.ac.jp

Abstract. Thermodynamic measurements of an organic spin liquid compound of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene were performed by the ac calorimetry technique using a microchip device of TCG3880. This technique is effective to measure relative temperature and magnetic-field dependences of heat capacity for tiny single crystal samples less than 1μg. Broad hump structures in $C_p$ vs $T$ which are known as so-called 6 K anomaly were observed in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and its deuterated compound. The hump temperatures are evaluated as 5.7 K in both compounds. This result demonstrates that the TCG3880 is useful for performing thermodynamic investigations of such kind of organic charge transfer complexes with much reduced sample quantity than the conventional techniques and that the existence of hump structure is intrinsic for κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The in-plane angular dependence of the magnetic field of 7 T applied parallel to the two dimensional layer is also studied and absence of in-plane anisotropy of the hump structure is discussed in both pristine and deuterated compounds.

1. Introduction

There are increasing interests on low-temperature magnetic properties of organic triangular lattice compounds, since realization of quantum liquid state and appearance of novel physical properties peculiar for molecule-based materials are expected in them [1-2]. Up to now, two compounds are known as candidates of the organic spin liquid. The first compound is κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ of which absence of long range ordering nor glass-like freezing down to 30 mK was reported by Shimizu et al. by magnetic susceptibility and $^{13}$C-NMR experiments [3]. This compound has a similar molecular arrangement as the famous 10 K class superconductors consisting of BEDT-TTF donor molecules. The other is an acceptor and cation compound of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ whose frustrated character was suggested by magnetic susceptibility measurement by Tamura et al. in 2002 [4]. Quite recently, detail $^{13}$C-NMR experiments [5] revealed that this compound also do not show any long-range orderings down to 19 mK and the ground state is a spin-liquid state which are also confirmed by thermal conductivity measurement [6]. The possibility of electronic structure change around 1 K was suggested by $^{13}$C-NMR experiments [7]. The two compounds are dimer based Mott insulators in which one electron/hole localizes on each dimer site owing to strong electron correlations in two-dimensional (2D) layer.

Concerning on κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, we performed a low temperature heat capacity measurement down to dilution temperature region and reported absence of thermal anomalies related to a long range ordering. Instead of the formation of magnetically ordered structures, the fluctuating spins give a distinct $T$-linear contribution in heat capacity with a finite electronic heat capacity coefficient $\gamma$ at low temperatures[8]. The $\gamma$ value is reported as 12.6 mJ K$^{-2}$mol$^{-1}$ from the measurement in the dilution temperature range, which scales to the magnetic susceptibility $\chi(0)$ extrapolated down
to $T=0$. This fact indicates that the formation of spin-liquid ground state in 2D $S=1/2$ triangular system is really established in this material and the excitations from the ground state are gapless as is suggested by theories [9,10] for example long-range resonance valence bond (RVB) theory which predicts Fermionic excitations. However, a possibility of small gap opening at extremely low temperature region below 0.5 K was reported by thermal transport measurement [11]. In addition to the gapless or tiny gapped excitations, this compound shows a broad anomaly around 6 K, which is insensitive to external magnetic fields up to 8 T applied perpendicular to the 2D layer. The thermal expansion measurements by Manna et al. observed a clear kink in lattice parameters at this temperature [12]. Furthermore, a curious dielectric property which may be related to the internal degrees of freedom in each dimer has been observed by Abdel-Jawad et al. [13]. The origin of the hump structure in the thermodynamic properties is still an unsolved problem and probably gives profound physics which have not been discussed within spin-liquid theories.

$\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ sample whose ethylene groups in BEDT-TTF molecule are all substituted by deuterons is known to show almost the same spin-liquid behaviors as pristine compound, although some $\kappa$-(BEDT-TTF)$_2$X compounds are known to show drastic isotope effects by deuteration of ethylene groups. We reported that $\mathcal{C}$ the heat capacity of deuterated sample shows similar $\gamma$ value and temperature dependence of heat capacity below 5K is almost the same as pristine compound [14]. Since the deuterated samples used for the previous heat capacity measurements are thin plates, to unveil precise temperature dependence of heat capacity around the hump temperature was difficult in the previous work in Ref. [14]. We have recently developed a microchip calorimetry system by which we can analyze relative change of heat capacity using tiny piece of crystal less than 1$\mu$g [15]. It is an aim of the present work to report capability of the calorimeter for the study of organic charge transfer salts and discuss the magnetic fields dependence of the broad hump of hydrogenated and deuterated samples. We also discuss angular dependence of external magnetic fields in the in-plane configuration.

2. Experimental

2.1 Experimental apparatus for ac heat capacity measurements

For the measurements of thermodynamic properties of tiny single crystal, we used a micro-chip device of TCG3880 supplied by Xensor company [16]. This chip is utilized for high-speed thermal analysis with a temperature scanning rate of $10^4$ to $10^5$ K s$^{-1}$ in order to study melting, recrystallization, and glass formation for polymer substances in inequilibrium condition by H. Huth and C. Schick and their collaborators [17-18]. A photo picture and a schematic view of the chip is displayed in Fig.1.

![Figure 1. Schematic view of the microchip device TCG3880.](Image) The chip consist of SiN membrane surrounded by Si frame. In the centre of the membrane a small heater and hot junctions of thermopiles are fabricated.
This chip consists of a Si frame and a SiN membrane with nearly 20 μm thickness. In the centre of the membrane, small resistance heater with approximately 600 Ω at room temperature is fabricated. The resistance of the heater decreases about 20% at liquid helium temperature, but the temperature dependence is moderate enough to be fitted by a simple polynomial formula. Surrounding this heater part, six hot junctions of a thermopile sensor are fabricated. The cold junction of the thermopile is on the Si frame and therefore detection of the temperature difference between sample part and Si frame is possible by measuring the output voltage of the thermopile. The Si frame is thermally linked to the heat sink made of Cu block on which calibrated thermometers are mounted. The sensitivity ($S$) of the thermopile is reported as 0.75 mV K$^{-1}$ at room temperature and decreases down to about 5% of the room temperature value at 15 K. Since the sensitivity decreases with the decrease of temperatures especially below 100 K, we have constructed a signal-amplify unit consisting of low-noise DC amplifiers (YOKOGAWA 3132) and low pass filter. By this unit, we can amplify small signal efficiency up to 100 times and low temperature experiments down to liquid helium temperature are possible. The sample was adhered on the resistance heater and the hot junctions by small amount of Apiezon N grease. The temperature of the Cu block with a diameter of 25 mm was controlled accurately by a temperature controller (LakeShore 340). We used a calibrated Pt (PT-111 Lake Shore) sensor and a cernox (Cx1030 Lake Shore) sensor to determine temperature of the chip. The temperature ranges of 30-350 K and 0.5-30 K were covered by Pt sensor and cernox sensor, respectively. The block diagram of the measurement system is shown in Fig.2.

The Cu block with TCG3880 was mounted on a $^3$He cryostat which is available in a VTI (variable temperature insert) system. By a 7T split pair magnet, we can apply magnetic field just parallel to the donor layers and therefore angular dependence of in-plane heat capacity is measurable. In order to detect small signal efficiently, we used the ac calorimetric technique to perform thermodynamic experiments. By studying the frequency dependence of the temperature oscillation signal, we have determined a proper frequency of 3.3Hz at which $T_{ac}/\omega$ gives the largest peak in the high vacuum condition.

### 2.2 Sample preparation

The hydrogenated sample used for this study is selected from the same batch as those used in previous reports. The deuterated samples were synthesized by electrochemical oxidation technique using Pt electrode according to the procedure reported by Komatsu et al. [19]. Small dc current with 1 μA was applied by a constant current source to oxidize the donor molecule solved in organic solvent. Since it was very difficult to measure sample mass of tiny crystals used in this study, we roughly...
estimated the magnitude of sample mass from the dimension of the crystals estimated by microscope and density of the sample. The mass of the pristine sample was about 1μg and that of deuterated sample was about 20-30% of the pristine sample.

3. Results and Discussion

In Fig.3, we show ac heat capacity data of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ in a $C_p$ vs $T$ plot. In general, the ac calorimetry is known as a high-resolution technique to detect relative change of heat capacity. Thermodynamic nature of small thermal anomalies and their frequency dependences are studied widely by this technique. However, it is difficult to determine absolute values of heat capacity especially in the case of tiny sample measurement as in the present case. Therefore, the vertical axis in Fig.3 is shown in arbitrary unit to discuss only relative change of heat capacity as a function of temperature. It is noteworthy from the figure that a broad hump structure ranging from 3 to 7 K in $C_p$ vs $T$ plot exists in this compound [8]. The peak of the hump is estimated to be 5.7 K and this temperature coincides well with the previous work, although the experimental technique in previous reports was relaxation calorimetry technique and was different from the present method. It is emphasized that the broadness and peak position are almost the same as that reported in the previous work obtained by the relaxation technique which usually use $10^3$-$10^4$μg samples. This fact demonstrates that micro-chip device TCG3880 is effective tool to detect thermal anomaly of organic compound. By this chip calorimetry technique, we have also succeeded to detect thermal anomaly related to superconductive transition and glass freezing of ethylene groups in BEDT-TTF molecules in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [20], but the observation of such kind of broad hump structure can expand further possibility of the chip devices. The data of the deuterated sample is also shown in Fig.3. Since the deuterated sample was very thin plate (with the thickness of about 20 μm), the resolution of the data was worse than that of hydrogenated sample. As is observed in Fig.3, the deuterated sample also shows the similar hump structure with exactly the same temperature as pristine sample. The thermodynamic properties including both $\gamma$ and the hump structure are almost the same in both compounds and therefore the chemical pressure effect is confirmed to be not so serious in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. 

Figure 3. Temperature dependences of heat capacity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and its deuterated compound.
Our next interest on this broad thermal anomaly of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is how the magnetic field affects on the hump structure. In our first heat capacity report of this compound in Ref.[8], thermodynamic data up to 8 T with $H \perp$ plane configuration were presented and negligibly small magnetic field dependence was reported. The ratio of two kind of transfer integrals between neighbouring dimers is evaluated as $t'/t = 1.06$ by extended Hückel calculation which claims that 6% distortion from regular triangular structure exists in this compound [3]. Therefore, small in-plane anisotropy against external magnetic fields may appear in thermodynamic properties. In order to examine whether the in-plane anisotropy exists or not, especially between of $H //a$-axis and $H \perp a$-axis configurations, we have performed heat capacity measurements under magnetic fields applied parallel to the plane. Using a split pair magnet, we applied magnetic field of 7 T from three different directions shown schematically in Fig. 4. The application of magnetic field in all directions did not show any difference in both hydrogenated and deuterated compounds which means that the hump structure is insensitive to magnetic fields. The clear kink in temperature dependence of thermal expansion and existence of dielectric anomaly related to the intradimer charge fluctuations reported in Ref. [12, 13] demonstrates that the 6 K anomaly contains the entropy related to the charge and lattice degrees of freedom. The absence of anisotropic behaviour even in the in-plane direction is consistent with these experiments. At present, it is not clear how these degrees of freedom affect on the liquid-like magnetic property appears at the lowest temperature region. In discussing the spin-liquid behaviour of organic dimer systems, the role of these freedoms should be taken into account in addition to spin degrees of freedom.

4. Summary

AC heat capacity measurements using tiny single piece of crystal were performed for the spin liquid compound of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The thermodynamic hump structure around 5.7 K corresponding to so-called 6 K anomaly was observed. Substitution of deuterons for eight hydrogen atoms in an ethylene group of BEDT-TTF molecule did not show any systematic change for the formation of hump structure. The effects of magnetic fields applied parallel to the two-dimensional layer did not show any angular dependence in heat capacity, which means that the magnetic fields

---

Figure 4. Temperature dependences of heat capacity of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and its deuterated compound obtained under magnetic fields of 7 T applied from three different directions.
dependence of the hump structure is very small due to the strong magnetic interactions dominated by large $J/k_B$. The results presented here demonstrate that the present chip calorimeter is effective to detect small thermodynamic anomaly of molecule based conducting materials even though their single crystals are small.

Acknowledgements
This work was supported by a Grant-in-Aid on Priority Area “Novel States of Matter Induced by Frustration (22014007)” and a Grant-in-Aid for Scientific Research (No. 20654033) from JSPS.

References
[1]  Lee P A 2008 Science 321 1306-1307
[2]  Balents L 2010 Nature 464 199-208
[3]  Shimizu Y, Miyagawa K, Kanoda K, Maesato M and Saito G 2003 Phys. Rev. Lett. 91 1007001
[4]  Tamura M and Kato R 2002 J. Phys. Condens. Matter. 7 L729-734
[5]  Itou T, Oyamada A, Maegawa S, Tamura M and Kato R 2009, J. Phys. Conference Series 145 012039
[6]  Yamashita M, Nakata N, Senshu Y, Nagata M, Yamamoto H M, Kato R, Shidauchi T and Matsuda Y 2010 Science 328 1246-1248
[7]  Itou T, Oyamada A, Maegawa S and Kato R 2010 Nature Phys. 6 673-676
[8]  Yamashita S, Nakazawa Y, Oguni M, Oshima Y, Nojiri H, Shimizu Y, Miyagawa K and Kanoda, K 2008, Nature Phys. 4 459-462
[9]  Anderson P W 1973 Mater. Res. Bull. 8 153-160
[10]  Grover T, Trivedi N, Senthil T and Lee P A 2010 Phys. Rev. B 81 245121
[11]  Yamashita M, Nakata N, Kasahara Y, Sasaki T, Yoneyama N, Kobayashi N, Fujimoto S, Shibauchi T and Matsuda Y 2009 Nature Phys. 5 44-47
[12]  Manna R S, de Souza M, Brühl A, Schlueter J A and Lang M 2010 Phys. Rev. Lett. 104 016403
[13]  Abdel-Jawad M, Terasaki I, Sasaki T, Yoneyama N, Kobayashi N, Uesu Y and Hotta C 2010 Phys. Rev. B 82 125119
[14]  Yamashita S, Yamamoto T and Nakazawa Y 2010 Physica B 405 S240-243.
[15]  Inoue Y, Nakazawa Y 2009 Thermochimica Acta, 492 85-88
[16]  http://www.xensor.nl/pdfiles/sheets/xen-tcg3880.pdf
[17]  Minakov A A, Roy S B, Bugoslavsky Y V, Cohen L F 2005 Rev. Sci. Instrum. 76 043906
[18]  Huth H, Minakov A A, Schick C 2006, J. Polym. Sci. Part B Polymer Physics 44 2996-3005
[19]  Komatsu T, Matsukawa N, Inoue T and Saito G 1996 J. Phys. Soc. Jpn. 65 1340-1354
[20]  Muraoka Y, Yamashita S, Yamamoto T and Nakazawa Y 2011 Thermochimica Acta in press