

# Thermodynamic properties of a spin-1/2 spin-liquid state in a $\kappa$ -type organic salt

SATOSHI YAMASHITA<sup>1</sup>, YASUHIRO NAKAZAWA<sup>1,2\*</sup>, MASAHARU OGUNI<sup>3</sup>, YUGO OSHIMA<sup>2,4</sup>, HIROYUKI NOJIRI<sup>2,4</sup>, YASUHIRO SHIMIZU<sup>5</sup>, KAZUYA MIYAGAWA<sup>2,6</sup> AND KAZUSHI KANODA<sup>2,6</sup>

<sup>1</sup>Department of Chemistry, Osaka University, Toyonaka, Osaka 560-0043, Japan

<sup>2</sup>CREST-JST, Kawaguchi, Saitama 332-0012, Japan

<sup>3</sup>Department of Chemistry, Tokyo Institute of Technology, Meguro-Ku, Tokyo 152-8550, Japan

<sup>4</sup>Institute for Material Research, Tohoku University, Aoba-Ku, Sendai, Miyagi 980-8577, Japan

<sup>5</sup>RIKEN, Wako, Saitama 351-0198, Japan

<sup>6</sup>Department of Appl. Physics, The University of Tokyo, Bunkyo-Ku, Tokyo 113-8656, Japan

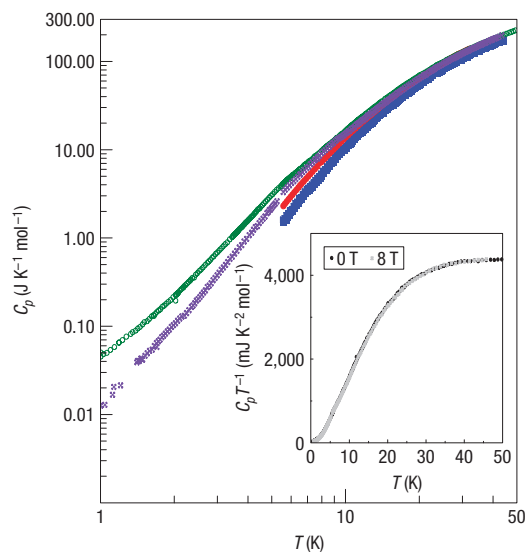
\*e-mail: nakazawa@chem.sci.osaka-u.ac.jp

Published online: 27 April 2008; doi:10.1038/nphys942

In two-dimensional triangular lattices, geometric frustration prohibits the formation of ordering even at the lowest temperatures, and therefore a liquid-like ground state is expected. The spin-liquid problem has been one of the central topics of condensed-matter science for more than 30 yr in relation to the resonating-valence-bond model<sup>1</sup>. One of the characteristic features proposed is the existence of a linear temperature-dependent contribution to the heat capacity, as the degeneracy of the energy states should give rise to gapless excitations. Here, we show thermodynamic evidence for the realization of a spin-liquid ground state through a single-crystal calorimetric study of the dimer-based organic charge-transfer salt  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, with a triangular lattice structure down to 75 mK. In addition, we report an unexpected hump structure in the heat capacity around 6 K, which may indicate a crossover into the quantum spin liquid.

The formation of a spin-liquid ground state is possible when the system has strong quantum character, and a high-order exchange such as ring-type exchange is involved in the model hamiltonian<sup>2</sup>. This is a widely discussed problem of the quantum magnetic system and the strongly correlated electron system, because such kinds of quantum effect may have some relation to the mechanism of high-temperature superconductivity<sup>3,4</sup>. Although numerous theoretical studies have been made on the triangular system, relevant experiments have been limited because of the absence of model materials. Well-known examples studied so far include ANiO<sub>2</sub> (A = Li, Na, Rb) (refs 5,6), Cs<sub>2</sub>CuCl<sub>4</sub> (ref. 7) and thin films of solid <sup>3</sup>He (ref. 8). However, in real compounds, especially intermetallic ones such as the two former examples, lattice disorder or appreciable interlayer coupling induces a kind of glassy freezing or a three-dimensional ordering of spins. The orbital degree of freedom also perturbs the spin states through spin-orbit coupling in inorganic materials. Hence, the intrinsic nature of the ground state of the spin  $S = 1/2$  two-dimensional triangular lattice is still unclear.

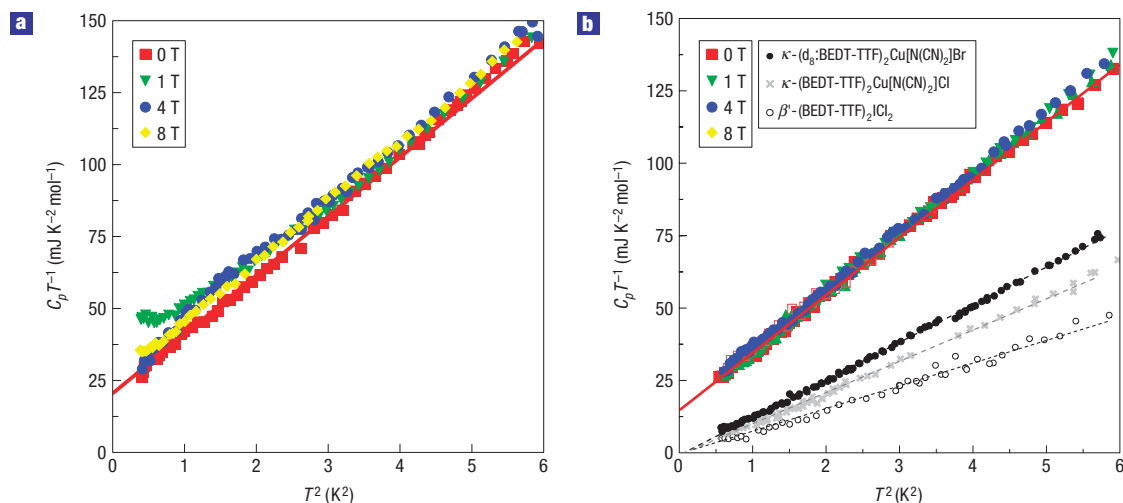
The  $\kappa$ -type salts consisting of BEDT-TTF donors show an interesting phase diagram, explained by Mott-Hubbard physics, dealing with competition between electron kinetic energy and correlation<sup>9-11</sup>. The Mott insulating phase and the superconductive



**Figure 1** Temperature dependence of heat capacities of BEDT-TTF-based salts.

The data of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> (green),  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> (red),  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl (purple) and  $\beta'$ -(BEDT-TTF)<sub>2</sub>Cl<sub>2</sub> (blue) are plotted on a logarithmic scale. The contribution of the lattice heat capacity is large but the overall temperature dependencies are similar to each other. Low-temperature deviation of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is notable, which demonstrates that large entropy exists in the low-temperature region. The inset shows the  $C_p T^{-1}$  versus  $T$  plot of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> under 0 and 8 T. The effect of magnetic field is very small.

phase are adjacent to each other in the effectively half-filled band originating from the donor dimers. The nature of the two phases and the transition between them by external pressure have been systematically investigated<sup>12</sup>. In  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, Shimizu *et al.* took notice of a triangular spin arrangement, considering that each BEDT-TTF dimer in the donor layers accommodates a spin of  $S = 1/2$  (ref. 13). Through nuclear



**Figure 2** Low-temperature heat capacities of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. **a, b**, Data obtained for two samples under magnetic fields up to 8 T in  $C_p T^{-1}$  versus  $T^2$  plots. **b** contains the data of the typical antiferromagnetic insulators  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, deuterated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br and  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> for comparison. The existence of a  $T$ -linear contribution even in the insulating state of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is clearly observed.

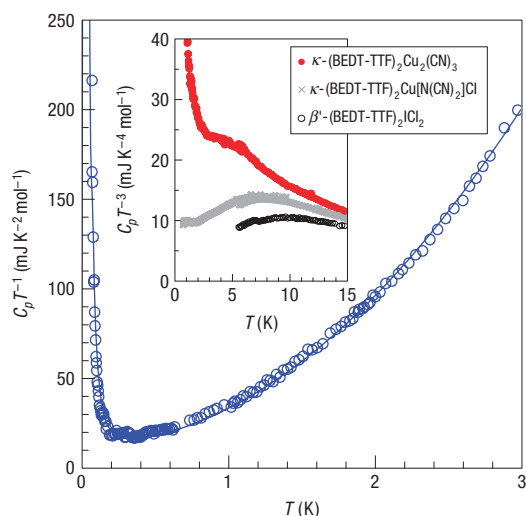
magnetic resonance (NMR) and static susceptibility measurements, they observed no static order down to 30 mK and concluded that the spins form a kind of liquid state. The likelihood that a spin-liquid model is appropriate is strengthened by the prediction of the resonating-valence-bond (RVB) model of large entropy at low temperatures and a possible temperature- ( $T$ -) linear term due to the spinon density of states in the heat capacity<sup>3,4</sup>. The heat capacity is considered as a very sensitive low-energy spectroscopic method for investigating the low-energy excitations from the ground state. We can explore a reliable discussion on what kind of ground state is realized through the entropy with absolute precision and without any external fields. In this respect, thermodynamic studies at temperatures as low as possible are necessary and required for demonstrating the quantum spin-liquid character for this material.

In Fig. 1, we show the temperature dependence of the heat capacity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> and other  $\kappa$ -type BEDT-TTF salts.  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> is a superconductor with a transition temperature ( $T_c$ ) of 9.4 K.  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is a Mott insulator with an antiferromagnetically ordered ground state below the Néel temperature  $T_N = 27$  K. Reflecting the same type of donor arrangement, the temperature dependencies of the lattice heat capacities of the samples are similar. The data for another Mott insulating compound,  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>, which gives the highest  $T_c$  of 14.2 K among organic superconductors under an applied pressure of 8.2 GPa (ref. 14), are also shown for comparison. A slight difference in the lattice contribution is observed, attributable to the difference of crystal packing, but the overall temperature dependence resembles that of the  $\kappa$ -type compounds. Although the overall tendency of the lattice heat capacity is similar, it should be emphasized that  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> shows large heat capacities at low temperatures as compared with typical Mott-insulating samples. This fact demonstrates that the spin system retains large entropy even at low temperatures and is free from ordering owing to the existence of the frustration.

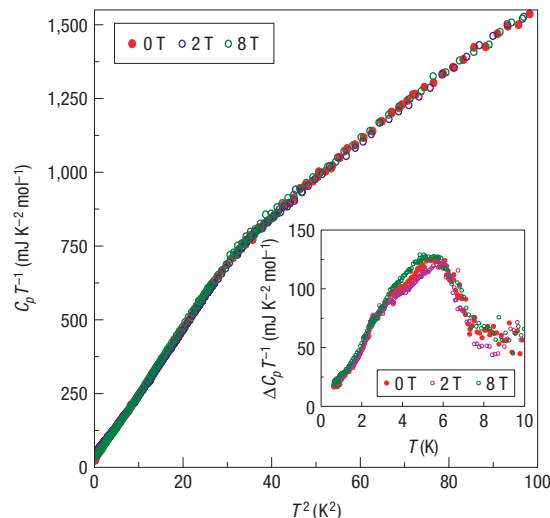
The temperature dependence of the heat capacity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is shown in a  $C_p T^{-1}$  versus  $T$  plot in the inset of Fig. 1. We also show data obtained under an

external magnetic field of 8 T applied perpendicular to the plane, demonstrating no drastic difference from the 0 T data over the whole temperature range in the figure. There is no sharp thermal anomaly indicative of long-range magnetic ordering. This is consistent with previous NMR experiments<sup>13</sup>. The data at low temperatures below 2.5 K, shown in Fig. 2, clearly verify the existence of a linearly temperature-dependent term (the  $\gamma$  term), even in the insulating state. The magnitude of  $\gamma$  is estimated at  $20 \pm 5 \text{ mJ K}^{-2} \text{ mol}^{-1}$  from the linear extrapolation of the  $C_p T^{-1}$  versus  $T^2$  plot down to  $T = 0$  K. However, the low-temperature data show an appreciable sample dependence. Figure 2a,b shows data for different samples, (a) and (b), respectively. In the low-temperature region, sample (a) shows a curious structure in addition to the finite  $\gamma$  term, which is somewhat field dependent. However, Fig. 2b does not show such behaviour. The magnetic field dependence seen in sample (a) is attributable to a possible paramagnetic impurity and seems to be extrinsic. In fact, the application of a magnetic field induces a kind of Schottky contribution, which is attributed to a magnetic impurity of less than 0.5%. The origin of this contribution is considered to be Cu<sup>2+</sup> contamination in the sample preparation, as reported by Komatsu *et al.*<sup>15</sup>. We measured several other samples and found that the data of the better-quality samples converge to those shown in Fig. 2b, with a small field-dependent contribution. It should be noted that these samples still possess a finite  $C_p T^{-1}$  value of about  $15 \text{ mJ K}^{-2} \text{ mol}^{-1}$ , as shown by the extrapolation of the data down to  $T = 0$  K. The existence of the  $\gamma$  term in the present insulating state is intrinsic.

The well known Mott insulators  $\kappa$ -(BEDT-TTF)<sub>2</sub>X (X = Cu[N(CN)<sub>2</sub>]Cl, deuterated Cu[N(CN)<sub>2</sub>]Br) and  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> with three-dimensional antiferromagnetic ordering show a vanishing  $\gamma$  value, as shown in Fig. 2b (ref. 16). It is evident that the low-temperature heat capacity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is extraordinarily large for an insulating system. A  $\gamma$  value of the present order ( $10^{1-1.5} \text{ mJ K}^{-2} \text{ mol}^{-1}$ ) is expected, for example, in spin-wave excitations in one-dimensional antiferromagnetic spin systems with intra-chain couplings of  $J/k_B = 100\text{--}200$  K or metallic systems with continuous excitations around the Fermi surface. However, these are obviously very different systems from the present two-dimensional insulating materials. Gapless excitations giving a  $T$ -linear contribution to the



**Figure 3**  $C_p T^{-1}$  versus  $T$  plot of the heat capacity for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. The solid curve shows the result of fitting to the formula  $C_p = A/T^2 + \gamma T + \beta T^3$ . The obtained  $\gamma$  is 12 mJ K<sup>-2</sup> mol<sup>-1</sup>, which demonstrates the existence of continuous excitations from the ground state. The inset shows  $C_p T^{-3}$  versus  $T$  for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and  $\beta'$ -(BEDT-TTF)<sub>2</sub>Cl<sub>2</sub>.



**Figure 4** Temperature dependence of the heat capacity around the anomalous temperature of 6 K.  $C_p T^{-1}$  versus  $T^2$  plots of the heat capacity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> under magnetic fields of 0 T (red), 2 T (purple) and 8 T (green). The inset shows the difference of the heat capacities of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, which highlights the hump structure around 6 K.

heat capacity are consistent with the RVB model. The coefficient  $\gamma$  is considered to be proportional to the spin density of states, as in the electron density of states at the Fermi surface of a metallic system. The Wilson ratio giving the relation between  $\gamma$  and finite susceptibility at low temperatures is of the order of unity<sup>17</sup>, which is analogous to the Fermi liquids of band electrons. To verify the low-temperature nature and determine the exact value of  $\gamma$ , the measurements were extended down to 75 mK. The results are shown in Fig. 3. The upturn appearing at the lowest temperatures may be attributed to a nuclear Schottky contribution of the copper cations in the counter-anion. Fitting the low-temperature heat-capacity data to the formula  $C_p = A/T^2 + \gamma T + \beta T^3$  gives the values  $A = 6.6 \times 10^{-2}$  mJ K mol<sup>-1</sup>,  $\gamma = 12$  mJ K<sup>-2</sup> mol<sup>-1</sup> and  $\beta = 21$  mJ K<sup>-4</sup> mol<sup>-1</sup>. An important point is that the  $\gamma$  term is not affected by the external magnetic field. This result also confirms that the  $T$ -linear term is related to the finite excitation density of states, as is the case for a metal system. This confirms the spin excitations postulated by Anderson for the spin-liquid state in two-dimensional materials. In organic systems, spin-orbit coupling is very small and the highest occupied molecular orbital is spread over the molecule. The large triangular unit cells and relatively strong quantum character prohibit long-range ordering, even though the triangle is deformed by 6%. A numerical study of the Hubbard model<sup>18</sup> predicts the existence of the spin-liquid state near the Mott transition, which is precisely the situation of the present salt<sup>19</sup>.

It is noted that a broad hump structure is observed, instead of a sharp peak signalling a kind of phase transition, around 6 K in the  $C_p T^{-1}$  versus  $T$  plot, as is shown in Fig. 4. The inset of Fig. 3 compares the data in a  $C_p T^{-3}$  versus  $T$  plot of the present system with other Mott insulating salts. Organic salts of this kind have large and complicated lattice heat capacities, even in this temperature range of several kelvin. Such heat capacities should yield a moderate temperature dependence below about 10 K, as seen in the data of the two antiferromagnetic insulators. However, a hump is visible around 6 K in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> as an extra contribution to the natural trend of the lattice heat

capacity. This hump is observed at the same temperature in all the crystals measured. If this is a manifestation of long-range magnetic order, it should be affected by external magnetic fields. However, the present hump does not show magnetic field dependence up to 8 T under external fields perpendicular to the layer. In fact, earlier NMR and muon spin spectroscopy experiments did not detect any internal magnetic fields in the limit of zero external field<sup>20,21</sup> and showed a temperature profile of relaxation rate quite different from the case of spin ordering or freezing. So far, no clear structural transition has been detected, and a search for possible sophisticated superstructure with relevance to the spinon physics mentioned below is underway (Y. S. Lee *et al.*, unpublished). Considering that the spin degrees of freedom are involved in this anomaly in a different manner from ordering, as shown by NMR, we speculate on a crossover of the spin state, namely a kind of condensation of the spin liquid from the Heisenberg state, where the nearest-neighbour interaction is dominant. The higher-order exchange interaction is thermally disturbed at high temperatures. However, in the low-temperature region under discussion, the system gradually obtains a quantum character, which cannot be explained by the Heisenberg model with the nearest-neighbour interaction alone. Such a crossover would not have a long-range nature like typical phase transitions. An alternative interpretation of the hump is given in terms of symmetry breaking of the pure two-dimensional system. An instability of the Fermi surface of spinons in the long-ranged RVB state has been proposed by Lee *et al.*<sup>17</sup>. Spin-chirality ordering is also a candidate for the possible symmetry breaking, although it is originally spin gapped or induced by a magnetic field<sup>22–24</sup>.

The slope of  $C_p T^{-1}$  versus  $T^2$  (the  $\beta$  term) of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> is twice as large as those of the other BEDT-TTF-based salts, reported as 10.8 mJ K<sup>-2</sup> mol<sup>-1</sup> for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, 12.0 mJ K<sup>-2</sup> mol<sup>-1</sup> for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br and 12.5 mJ K<sup>-4</sup> mol<sup>-1</sup> for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. Because the lattice heat capacity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> should not be so different from these  $\kappa$

salts, it is reasonable to assume that the excess  $\beta$  value contains a spin contribution with a  $T^3$  dependence below 2.5 K. This magnetic contribution is pertinent up to 6 K, where the hump appears. The qualitative discrepancy of  $C_p T^{-1}$  around 6 K between  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> is highlighted in the inset of Fig. 4, where the discrepancy is plotted as a function of temperature, assuming that the data of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> give a phonon background. Because the temperature dependence of quasi-particle excitations related to the superconducting state in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> shows a complicated behaviour in the low-temperature region even though its magnitude is small, the value of the  $\gamma$  term is not very accurate in this figure. However, the cusplike feature is clear in the temperature dependence of the magnetic contribution. The entropy around the hump is roughly estimated as 700–1,000 mJ K<sup>-1</sup> mol<sup>-1</sup>, which is about 10–20% of  $R \ln 2$ . This entropy release is unexpectedly large for an antiferromagnet with  $J/k_B = -250$  K (deduced from the susceptibility<sup>13</sup>), and provides additional evidence for the realization of a spin liquid with large degeneracy.

Finally, we discuss the experimental observations of the present material in comparison with the spin-liquid scenario. The distinct  $\gamma$  in a non-ordered non-spin-freezing state of a Mott insulator is a strong indication of fermionic liquid-like ground state predicated for example by RVB type theory. The  $\gamma$  term seems to appear as a consequence of gapless excitations around the spinon Fermi surface. The magnitude of  $\gamma$  is consistent with the susceptibility through the analogous idea of a Fermi-liquid framework. The insensitive feature of heat capacity to magnetic fields in a good-quality sample is consistent with the idea on the basis of this model. However the anomalous thermodynamic behaviour around 6 K is a new aspect, probably related to the spin-liquid formation relevant to a kind of crossover from thermally disordered to quantum-disordered states. The instability of the spinon Fermi surface is also a possible scenario in terms of the theoretical model on the basis of the spin liquid<sup>17</sup>.

## METHODS

We have made heat-capacity measurements by the thermal-relaxation technique using calorimeters developed for single-crystal measurements. The sample stage consists of a small ruthenium oxide thermometer (KOA) and a strain-gauge heater (1 k $\Omega$  at room temperature), onto which the crystals are attached by a small amount of Apiezon N grease. The sample stage is weakly linked to the heat sink through thin lead wires. A typical time constant of the temperature relaxation is 10–100 s, depending on the temperature range. The crystals of the present material were thin plates with typical dimensions of 0.5  $\times$  0.5  $\times$  0.02 mm<sup>3</sup>. To get sufficient resolution to examine the temperature dependence of the heat capacity, we adjusted the sample weight to be in the range 0.3–0.6 mg, which corresponds to two to four pieces of single crystal. In each measurement, the crystals were selected from the same batch and aligned on the sample stage. The measurements were made with two different calorimeters, equipped with a <sup>3</sup>He cryostat at Osaka University and a dilution refrigerator at IMR Tohoku University.

Received 1 March 2007; accepted 13 March 2008; published 27 April 2008.

## References

- Anderson, P. W. Resonating valence bonds: A new kind of insulator? *Mater. Res. Bull.* **8**, 153–160 (1973).
- Misguich, G., Bernu, B., Lhuillier, C. & Waldtmann, C. Spin liquid in the multiple-spin exchange model on the triangular lattice: <sup>3</sup>He on graphite. *Phys. Rev. Lett.* **81**, 1098–1101 (1998).
- Anderson, P. W. The resonating valence bond state in La<sub>2</sub>CuO<sub>4</sub> and superconductivity. *Science* **235**, 1196–1198 (1987).
- Anderson, P. W., Baskaran, G., Zou, Z. & Hsu, T. Resonating-valence-bond theory of phase transitions and superconductivity in La<sub>2</sub>CuO<sub>4</sub>-based compounds. *Phys. Rev. Lett.* **58**, 2790–2793 (1987).
- Kitaoka, Y. *et al.* Orbital frustration and resonating valence bond state in the spin-1/2 triangular lattice LiNiO<sub>2</sub>. *J. Phys. Soc. Jpn* **67**, 3703–3706 (1998).
- Vernay, F., Penc, K., Fazekas, P. & Mila, F. Orbital degeneracy as a source of frustration in LiNiO<sub>2</sub>. *Phys. Rev. B* **70**, 014428 (2004).
- Coldea, R., Tennant, D. A. & Tylczynski, Z. Extended scattering continua characteristic of spin fractionalization in the two-dimensional frustrated quantum magnet Cs<sub>2</sub>CuCl<sub>4</sub> observed by neutron scattering. *Phys. Rev. B* **68**, 134424 (2003).
- Siqueira, M., Nyéki, J., Cowan, B. & Saunders, J. Heat capacity study of the quantum antiferromagnetism of a <sup>3</sup>He monolayer. *Phys. Rev. Lett.* **76**, 1884–1887 (1996).
- Kanoda, K. Electron correlation, metal-insulator transition and superconductivity in quasi-2D organic systems, (ET)<sub>x</sub>. *Physica C* **282–287**, 299–302 (1997).
- Kanoda, K. Recent progress in NMR studies on organic conductors. *Hyperfine Interact.* **104**, 235–250 (1997).
- Kanoda, K. Metal-insulator transition in  $\kappa$ -(ET)<sub>x</sub>X and (DCNQI)<sub>2</sub>M: Two contrasting manifestations of electron correlation. *J. Phys. Soc. Jpn* **75**, 51007 (2006).
- Kagawa, F., Miyagawa, K. & Kanoda, K. Unconventional critical behaviour in a quasi-two-dimensional organic conductor. *Nature* **463**, 534–537 (2005).
- Shimizu, Y., Miyagawa, K., Kanoda, K., Maesato, M. & Saito, G. Spin liquid state in an organic Mott insulator with a triangular lattice. *Phys. Rev. Lett.* **91**, 1007001 (2003).
- Taniguchi, H. *et al.* Superconductivity at 14.2 K in layered organics under extreme pressure. *J. Phys. Soc. Jpn* **72**, 468–471 (2003).
- Komatsu, T., Matsukawa, N., Inoue, T. & Saito, G. Realization of superconductivity at ambient pressure by band-filling control in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *J. Phys. Soc. Jpn* **65**, 1340–1354 (1996).
- Nakazawa, Y. *et al.* Thermodynamic studies of electron correlation effects on organic salts based on BEDT-TTF and DCNQI molecules. *J. Phys. Chem. Solids* **62**, 385–388 (2001).
- Lee, S.-S., Lee, P. A. & Senthil, T. Amperean pairing instability in U(1) spin liquid state with Fermi surface and application to  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *Phys. Rev. Lett.* **98**, 067006 (2007).
- Morita, H., Watanabe, S. & Imada, M. Nonmagnetic insulating states near the Mott transitions on lattices with geometrical frustration and implications for  $\kappa$ -(ET)<sub>x</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *J. Phys. Soc. Jpn* **71**, 2109–2112 (2002).
- Kurosaki, Y., Shimizu, Y., Miyagawa, K., Kanoda, K. & Saito, G. Mott transition from a spin liquid to a Fermi liquid in the spin-frustrated organic conductor  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *Phys. Rev. Lett.* **95**, 177001 (2005).
- Shimizu, Y., Miyagawa, K., Kanoda, K., Maesato, M. & Saito, G. Emergence of inhomogeneous moments from spin liquid in the triangular-lattice Mott insulator  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *Phys. Rev. B* **73**, 140407 (2006).
- Ohira, S., Shimizu, Y., Kanoda, K. & Saito, G. Spin liquid state in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> studied by muon spin relaxation method. *J. Low. Temp. Phys.* **142**, 153–158 (2006).
- Kalmeyer, V. & Laughlin, R. Equivalence of the resonating-valence-bond and fractional quantum Hall states. *Phys. Rev. Lett.* **59**, 2095–2098 (1987).
- Baskaran, G. Novel local symmetries and chiral-symmetry-broken phases in  $S = 1/2$  triangular-lattice Heisenberg model. *Phys. Rev. Lett.* **63**, 2524–2527 (1989).
- Motrunich, O. I. Orbital magnetic field effects in spin liquid with spinon Fermi sea: Possible application to  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>. *Phys. Rev. B* **73**, 155115 (2006).

## Acknowledgements

We thank H. Fukuyama and P. A. Lee for valuable discussions and Y. S. Lee for informing us of structural data before publication. This work was carried out as a CREST project of JST and partially supported by a Grant-in-Aid on the Priority Area 'Novel functions of molecular conductors under extreme conditions' from the Ministry of Education, Science, Sports and Culture of Japan and a Grant-in-Aid for Scientific Research (No. 18340103) from JSPS.

## Author contributions

S.Y., Y.N. and M.O. carried out the thermodynamic measurements, data analysis and discussion. Y.O. and H.N. helped the instrumental construction and data collection in the extremely low-temperature region. Y.S., K.M. and K.K. prepared the samples and gave overall advice on susceptibility and NMR experiments.

## Author information

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to Y.N.