Spin Liquid in a Spin-Frustrated Organic Mott Insulator

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Magnetism of interacting localized spins on triangular lattice has been of keen interest. We found a quantum spin liquid state in an organic Mott insulator with nearly triangular lattice by means of nuclear-magnetic-resonance experiments. The absence of long-range magnetic ordering was evidenced at low temperatures down to 30 mK in spite of an antiferromagnetic exchange interaction of 250 K between the neighboring spins. Realization of the spin liquid is attributable to the proximity of the present system to the Mott transition, consistent with the theoretical study of the triangular-lattice Hubbard model. Field-induced inhomogeneous spin state is argued in terms of the effect of disorder on the spin liquid.

§1. Introduction

Quantum fluctuations destroy ordering of the interacting many bodies, which would be stabilized in the classical regime. The resultant quantum liquid is seen in various systems such as liquid He free from solidification and metals free from the Wigner crystallization. The electron spin is of course a quantum object and should exhibit quantum fluctuations in the orientational degrees of freedom. However, most of the real spin systems show ordering although the fluctuations manifest itself in the spin contraction for example. The exotic liquid state can be sought in sophisticated spin systems on particular lattices where the spins feel strong frustration against ordering. The triangular lattice (TL) is one of them. However, elaborate theoretical investigations are leading to a consensus that the ground state of the TL Heisenberg model is an ordered state with a 120-degree orientation between the neighboring spins,[1)–5)] as seen in several real materials,[6)] although the one-dimensional anisotropy is expected to give rise to a spin liquid phase.[7)–11)] On the other hand, the recent study on the TL Hubbard model with a half-filled band predicts a spin liquid phase in the Mott insulator near a transition to the metal.[12)–16)] The spin liquid state was also

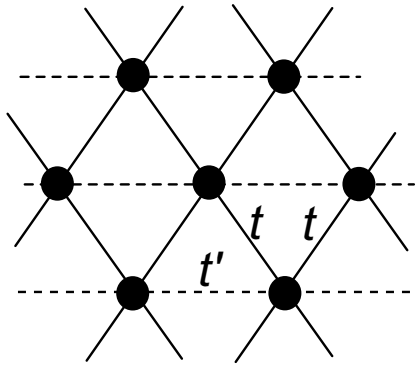

Fig. 1. Schematic representation of the conducting layer of κ-$(ET)_2X$, where the dots represent the ET dimer units.

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predicted by the ring-exchange model which takes into account the higher order exchange interactions.[17),18)]

The layered organics, κ-$(ET)_2X$, are model systems for the TL Hubbard physics, where ET denotes an electron donating molecule and X stands for various kinds of anions with closed shells.[19),20)] In the two-dimensional ET layer, where ET's are arranged in a pattern specified as the κ type, strongly dimerized ET_2 form anisotropic TL with two kinds of transfer integrals, t and t', as depicted in Fig. 1, where each lattice point stands for the dimer. The carrier is a hole per dimer on average, which makes the dimer band half filled. As the bandwidth and the Coulomb repulsion energy are comparable in the κ-$(ET)_2X$ family, they are situated around Mott transition, as is seen in Table I, which lists the observed ground states and the ratios t'/t for various anions X. In the present work, we have studied the spin state of the two Mott insulators, κ-$(ET)_2X$ [X = $Cu[N(CN)_2]Cl$ and $Cu_2(CN)_3$], which have anisotropic ($t'/t = 0.75$) and nearly isotropic ($t'/t = 1.06$) TLA's, respectively, through NMR experiments and susceptibility measurements. It is shown that a spin liquid phase competes with an antiferromagnetically ordered phase, depending on the TL anisotropy. Moreover, it is found that the spin liquid has inhomogeneous moment organization of a small amplitude under a magnetic field and/or in the presence of crystal imperfections.

Table I. The observed ground state and the ratio of transfer integrals between dimers, estimated from the extended Hückel calculation, in κ-$(ET)_2X$.

X	ground state	t'/t
$Cu_2(CN)_3$	Mott insulator	1.06
$Cu[N(CN)_2]Cl$	Mott insulator	0.75
$Cu[N(CN)_2]Br$	superconductor	0.68
$Cu(NCS)_2$	superconductor	0.84
$Cu(CN)[N(CN)_2]$	superconductor	0.68
$Ag(CN)_2{\cdot}H_2O$	superconductor	0.60
I_3	superconductor	0.58

§2. Magnetic susceptibility

Figure 2 shows the temperature dependence of the magnetic susceptibility χ_0 of the two Mott insulators, κ-$(ET)_2Cu_2(CN)_3$[21)] and κ-$(ET)_2Cu[N(CN)_2]Cl$.[22)] The latter is known to exhibit an antiferromagnetic transition with a weak ferromagnetism due to a spin canting at 27 K, resulting in a rapid increase in χ_0. In κ-$(ET)_2Cu_2(CN)_3$, χ_0 has a broad peak around 70 K and decreases gradually below 50 K without an indication of magnetic transition. The temperature-insensitive behavior at high temperatures manifests an effect of spin frustration which suppresses the development of the antiferromagnetic spin fluctuations and ordering. Indeed, the experimental data is well fitted to the triangular-lattice Heisenberg model[23)] with an exchange interaction $J \sim 250$ K down to $T \sim J/4$, the lower limit for applying a high-temperature series expansion, as shown in Fig. 2. The extended analysis based on the anisotropic triangular lattice model recently showed that κ-$(ET)_2Cu_2(CN)_3$ is close to the isotropic triangular lattice,[24)] which is consistent with the result of the quantum chemistry calculations in Table I. In contrast, the monotonous decrease in χ_0 of κ-$(ET)_2Cu[N(CN)_2]Cl$ is unlikely to be fitted to the Heisenberg model which would show a broad peak below J, even when we assume the anisotropic triangular

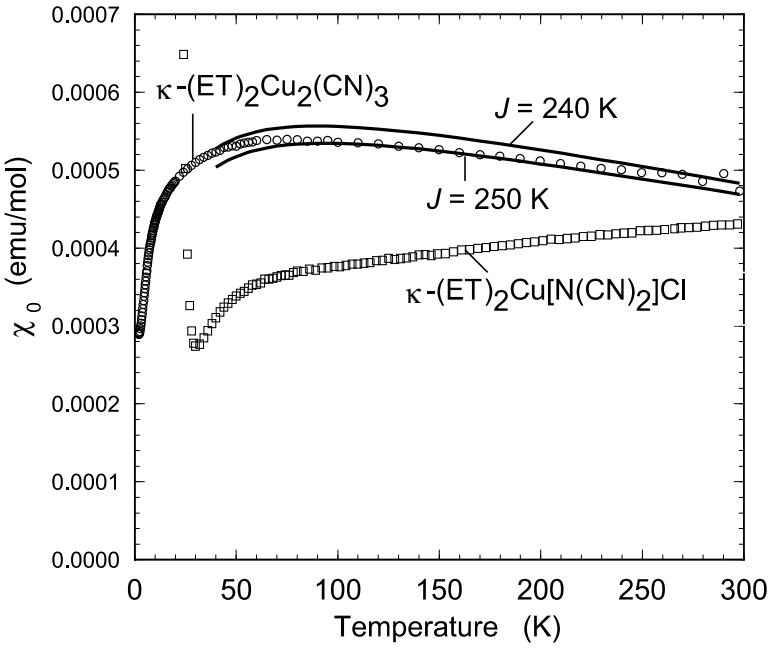

Fig. 2. Temperature dependence of the magnetic susceptibility of κ-$(ET)_2Cu_2(CN)_3$ and κ-$(ET)_2Cu[N(CN)_2]Cl$. The solid lines represent the results of the series expansion of the triangular-lattice Heisenberg model using [7,7] Padé approximation with $J = 240$ K and 250 K.

lattice.[24] The possible reason is that κ-$(ET)_2Cu[N(CN)_2]Cl$ is situated much closer to the Mott transition than κ-$(ET)_2Cu_2(CN)_3$; the critical pressure to the Mott transition is 20–30 MPa for the former[25)–27)] and 200–400 MPa for the latter.[36),37)] Therefore, the charge fluctuations and the long-range interaction would be crucial in κ-$(ET)_2Cu[N(CN)_2]Cl$, so that the Heisenberg model considering only the nearest neighbor interaction may not be applicable. Numerical studies of χ_0 using Hubbard model on the anisotropic triangular lattice will be needed.

The steep decrease in χ_0 below 20 K implies an opening of the spin gap. However, a finite value of χ_0 still remains even at 2 K. Therefore the spin gap, if any, is much less than $J/20$ or disturbed by a small and inhomogeneous magnetization as shown later.

§3. NMR spectra

Nuclear magnetic resonance (NMR) technique using ^{1}H nuclei at the edges of the ET molecule can detect long-range magnetic order with a precision of $0.01\mu_B$/dimer through the line splitting or broadening. We show in Fig. 3 the ^{1}H NMR spectra for the single crystal of the two Mott insulators, κ-$(ET)_2Cu[N(CN)_2]Cl$ and κ-$(ET)_2Cu_2(CN)_3$, under the magnetic field applied perpendicular to the conducting plane. The high-temperature line shape, which comes from the nuclear dipole interaction, is different between the two materials. This is attributable to the different orientation of the ET molecules with respect to the field axis applied normal

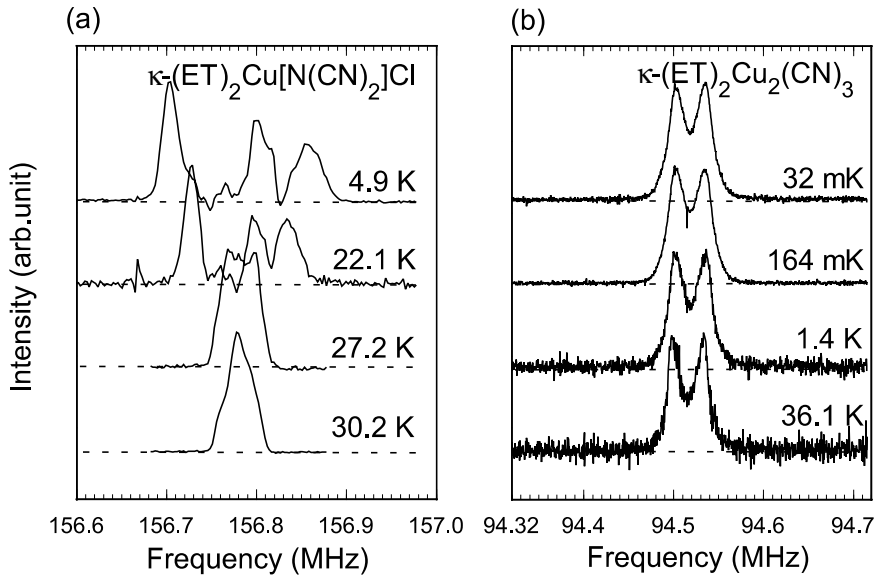

Fig. 3. Temperature variation of ^{1}H NMR absorption spectra for single crystals of (a) κ-$(ET)_2Cu[N(CN)_2]Cl$ and (b) κ-$(ET)_2Cu_2(CN)_3$ under a magnetic field perpendicular to the conducting plane.

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to the conducting layers and a slight misalignment of the sample, since the nuclear dipole interaction is sensitive to the direction of magnetic field. If the commensurate antiferromagnetic transition occurs, the ^{1}H NMR spectrum shows a clear splitting below the Néel temperature, reflecting the large internal field due to the staggered moment of $0.4\mu_B$/dimer, as demonstrated in Fig. 3(a). In contrast, there is no significant change observed in the spectra of κ-$(ET)_2Cu_2(CN)_3$ down to 32 mK as shown in Fig. 3(b). The result indicates that the long-range magnetic order is absent down to the temperature far below the energy scale of J ($\sim 10^{-4}J$). Therefore, the spin liquid state is considered to be realized in this Mott insulator with triangular lattice due to the strong spin frustration. Strictly speaking, the ^{1}H NMR spectra show a slight broadening ($\sim \pm 2$ kHz) below 4 K. If the broadening were due to the magnetic order, the magnetic moment is no more than $0.01\mu_B$/dimer under the magnetic field of 2 T. It is also noted that the μSR measurements at zero magnetic field did not detect any internal fields down 20 mK.[28)]

To see the electron spin state more closely, we have measured ^{13}C NMR spectra which can resolve the local spin susceptibility, owing to the much larger hyperfine coupling at the ^{13}C site than at the ^{1}H site. Figure 4 shows ^{13}C NMR spectra of a single crystal of κ-$(ET)_2Cu_2(CN)_3$ measured at 8 T. The three lines at 50 K come from four ^{13}C sites in two inequivalent ET molecules with two inequivalent ^{13}C sites. Two of the four ^{13}C sites are overlapped on the left line, leading to the double

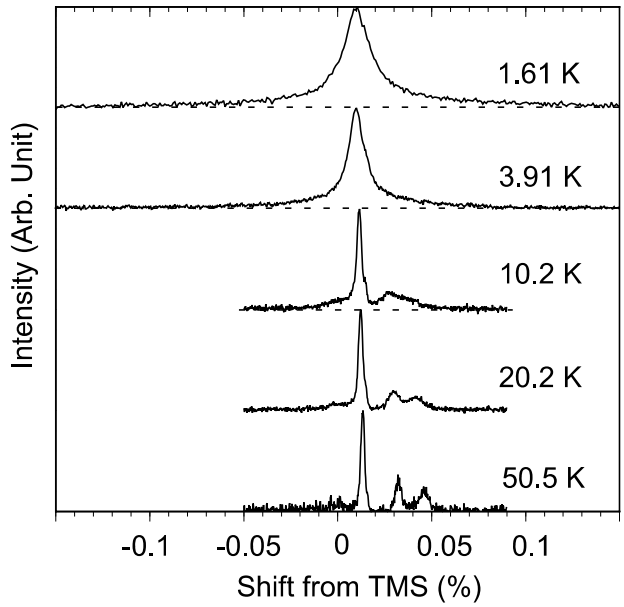

Fig. 4. ^{13}C NMR spectra of κ-$(ET)_2Cu_2(CN)_3$ under an external field of 8T applied at the magic angle.

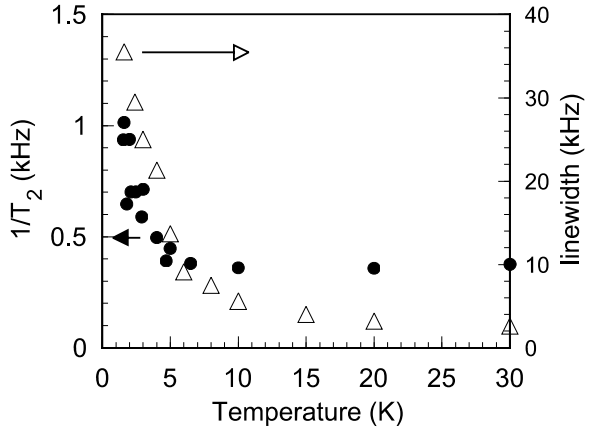

Fig. 5. Temperature dependence of the nuclear spin-spin relaxation rate (spin-echo decay rate) $1/T_2$ (closed circle) and linewidth (open triangle) at the magic angle.

intensity in the spectrum. These lines broaden and Knight shifts are diminished on cooling. Since the spin susceptibility decreases below 50 K, the hyperfine coupling constant of these ^{13}C site are all positive. The spectral broadening is developed below 4 K, which is consistent with the slight broadening of ^{1}H NMR spectra, considering the several-tens-times difference in the hyperfine coupling constants between the two nuclei. There are two possible origins of the spectral broadening of NMR; (i) slow spin fluctuations arising from a strong antiferromagnetic interaction and (ii) inhomogeneous spin state caused by disorder such as crystal defects or a charge inhomogeneity.

In order to investigate the origin of the anomalous broadening of ^{13}C NMR spectra, we have measured the nuclear spin-spin relaxation rate $1/T_2$ called the spin-echo decay rate. The $1/T_2$ extracts a dynamical (homogeneous) part out of the spectral width. The result is displayed in Fig. 5 together with the linewidth of spectra. It is noted that the scale of the vertical axis is different more than one order of magnitude from each other, although they vary similarly with temperature. It indicates that the main origin of the broadening is the inhomogeneous one rather than the homogeneous one. In addition, the nearly symmetrical line shape at 1.61 K with a large positive and negative shift distribution despite the positive hyperfine coupling constant suggests that the inhomogeneity stems from some locally organized moments with the spiral or staggered alignment. However, it is unlikely that the broadening is a manifestation of long-range magnetic order, considering the temperature dependence of the linewidth, $1/T_1$ and $1/T_2$ as described later. We consider that the inhomogeneous moment is induced by disorder such as impurities, since such a highly degenerate spin liquid state is usually perturbed by a small amount of impurities as known in the one-dimensional quantum antiferromagnets.[30)–35)] In fact, the linewidth increases with magnetic field, suggesting that the inhomogeneous magnetization is induced by magnetic field. It is again consistent with the μSR experiments which detected no internal field at a zero field. Since the largest hyperfine coupling constant among the three lines in this magnetic field orientation is about 0.2 T/μ_B, the maximum moment estimated at the edge of the spectra is $0.04\mu_B$/dimer at 1.61 K under a magnetic field of 8 T. The Lorentzian like shape suggests that the inhomogeneous moments appear in a small faction of the volume and the spatial decay is faster than the power law, possibly reflecting the spin correlation function.

§4. Low-lying spin excitation

The low-lying spin excitation in the highly-degenerated triangular-lattice antiferromagnet is never trivial. The spin-lattice relaxation rate $1/T_1$ measures a wave vector $\boldsymbol{q}$-summation of dynamic spin susceptibility $\mathrm{Im}\chi(q)$ at the resonance frequency of ω_0 ($\sim$ 86 MHz), and therefore probes the low-lying spin excitations over the $\boldsymbol{q}$ space. Figure 6 shows the temperature dependence of $1/T_1$ of the two Mott insulators. The enhancement of $1/T_1$ above 200 K stems from the local-field fluctuations by the thermally activated molecular vibration of ethylene groups, which decays on cooling and becomes negligible around 150 K. Therefore, the dominant contribution to $1/T_1$ at low temperature is the spin fluctuations of electrons. When the antiferromagnetic transition occurs, $1/T_1$ shows a sharp peak at the Néel temperature, associated with the critical slowing down of the spin fluctuations, as seen around 27 K in κ-$(ET)_2Cu[N(CN)_2]Cl$. On the other hand, the $1/T_1$ values of κ-$(ET)_2Cu_2(CN)_3$ are enhanced about twice compared with κ-$(ET)_2Cu[N(CN)_2]Cl$ above 50 K. A remarkable difference between the two materials appears below 50 K. Namely, while $1/T_1$ of κ-$(ET)_2Cu[N(CN)_2]Cl$ increases due to the critical slowing down, that of κ-$(ET)_2Cu_2(CN)_3$ continuously decreases with temperature rather steeply below 10 K, as if the spin gap opens. However, it does not go to zero straightforwardly but turns to increase around 4 K, and then shows a very broad maximum around 1 K.

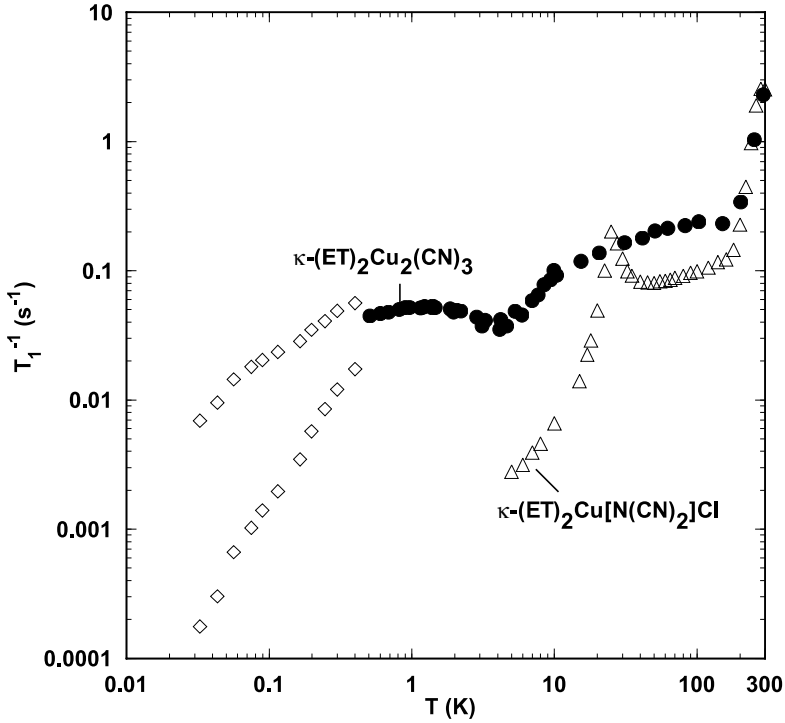

Fig. 6. ^{1}H nuclear spin-lattice relaxation rate $1/T_1$ of κ-$(ET)_2Cu_2(CN)_3$ (closed circles) and κ-$(ET)_2Cu[N(CN)_2]Cl$ (open triangles). $1/T_1$ at low temperature part in κ-$(ET)_2Cu_2(CN)_3$ (open diamonds) is obtained from a double-exponential fit of recovery curves.

This anomaly is too moderate to be attributed to a magnetic transition. In fact, the linewidth does not increase any more below 1 K.[29] Moreover, $1/T_2$ does not show a peak around 1 K but behaves constant below 1 K,[29] which indicates that slow spin fluctuations persist toward $T = 0$ without freezing.

At further low temperatures below 0.5 K, the nuclear spin-lattice relaxation becomes non-exponential. If we assume two relaxation components to fit the nuclear magnetization recovery, each $1/T_1$ shows a power law decay with temperature: $1/T_1^{\rm fast} \sim T$ and $1/T_1^{\rm slow} \sim T^2$. The recent ^{13}C NMR measurements also observed the inhomogeneous relaxation below 4 K and the power law decay in the low-temperature limit.[29] Therefore, the low-lying spin excitation from the ground state is likely gapless. Combined with the spectral broadening below 4 K, the inhomogeneous and gapless relaxation is considered to originate in the distribution from the inhomogneneous moments and mask the intrinsic spin excitation of the genuine spin liquid state. The spin-lattice relaxation should come from a spinon excitation of the spin liquid, but probably perturbed by impurity, and the spin-wave like excitation of the staggered or spiral part. They are somewhat averaged out by the spin-spin relaxation (T_2) process during such a long T_1 ($\sim 10^4$ s in ^{1}H NMR and $\sim 10^3$ s in ^{13}C NMR) at low temperatures.

The nature of the spin excitation in the genuine spin liquid phase (fully gapped, nodally gapped, or fully gapless) is an important problem but is still open in the

present study due to the emergence of inhomogeneity at low temperatures. As shown in Fig. 2, the static spin susceptibility decreases steeply below 20 K, which supports the opening of spin gap (full gap or nodal gap). We have expected to determine the spin susceptibility at further low temperatures by measuring the Knight shift of ^{13}C NMR, but the large line broadening prevented resolving the absolute value of the spin susceptibility. Although the present experimental data on the spin excitation and susceptibility do not allow us to make a straightforward interpretation on the ground state of the spin liquid, our tentative picture is that the inhomogeneous moment is induced as an extrinsic effect in the nonmagnetic spin liquid with nodal or full spin excitation gap. Assuming that the moment generation arises from the external perturbation of the magnetic field and/or crystal imperfection, the rapid spatial decay of the moments inferred from the ^{13}C NMR spectra seems to support the gapped spin excitation picture.

§5. Conclusion

The magnetism of the two organic Mott insulators, κ-$(ET)_2Cu[N(CN)_2]Cl$ and κ-$(ET)_2Cu_2(CN)_3$, with anisotropic and nearly isotropic triangular lattices, respectively, was investigated by NMR and susceptibility measurements. The anisotropic system exhibits a clear antiferromagnetic ordering at 27 K. However, the isotropic system shows no long-range magnetic ordering down to 30 mK, which is four orders of magnitude smaller than the exchange interaction J of 250 K. This indicates that the spin liquid state is realized in κ-$(ET)_2Cu_2(CN)_3$. However, quite small and inhomogeneous moments of a tiny fraction were identified in the ^{13}C NMR spectra highly-sensitive to the electron spins. This is anomalous since the moments are developed with the applied field and has no feature of magnetic transition in $1/T_1$ and $1/T_2$. All these results are explained in terms of the nucleation of inhomogeneous staggered or spiral moments induced by the symmetry-breaking crystal imperfection and impurities in the highly degenerate spin-liquid ground state. The spin state near the defect or impurity on the triangular-lattice antiferromagnet is an interesting future study of theory and experiment.

Under pressure, this material shows a Mott transition to the Fermi liquid, which undergoes a superconducting transition at a low temperature.[36),37)] The intriguing problem of the superconductivity emerging from the spin liquid is now attracting much interest.[38)–40)]

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