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Citation	PHYSICAL REVIEW LETTERS (2003), 91(10)
Issue Date	2003-09-05
URL	http://hdl.handle.net/2433/49940
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Type	Journal Article
Textversion	publisher

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Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice

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^{1}H NMR and static susceptibility measurements have been performed in an organic Mott insulator with a nearly isotropic triangular lattice, κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, which is a model system of frustrated quantum spins. The static susceptibility is described by the spin $S = 1/2$ antiferromagnetic triangular-lattice Heisenberg model with the exchange constant $J \sim 250$ K. Regardless of the large magnetic interactions, the ^{1}H NMR spectra show no indication of long-range magnetic ordering down to 32 mK, which is 4 orders of magnitude smaller than J. These results suggest that a quantum spin liquid state is realized in the close proximity of the superconducting state appearing under pressure.

The magnetism of the Mott insulator, which is the mother phase giving the unconventional superconductivity in the high-T_C cuprates and κ-(BEDT-TTF)$_2X$ organics, has been attracting much attention, because it holds the key to understanding the mechanism of the superconductivity, where BEDT-TTF (ET) denotes bis(ethylenedithio)-tetrathiafulvalene and X denotes inorganic monovalent anion [1,2]. The ground states of the Mott insulators studied so far in these materials are antiferromagnets. The stage of the interacting spins are quasi-two-dimensional square lattice or anisotropic triangular lattice with the nearest neighbor transfer t and the second-nearest neighbor transfer t'. If the lattice is close to isotropic triangle ($t'/t \sim 1$), however, the geometrical frustration gets to work significantly against the long-range magnetic ordering (LRMO), and a spin liquid state without symmetry breaking, which attracts great interest as an exotic state, can emerge [3].

In the case of κ-(ET)$_2X$, dimerization of a face-to-face ET pair is strong enough to treat the dimer as a unit [Fig. 1(a)], and the system can be effectively described by the Hubbard model on an anisotropic triangular lattice [Fig. 1(b)] with a half-filled conduction band [6,7]. The effective transfer integrals between the dimers are given as $t = (|t_p| + |t_q|)/2$ and $t' = t_{b2}/2$, respectively, where t_p, t_q, and t_{b2} are transfer integrals shown in Fig. 1(a) and evaluated with the extended Hückel method and the tight-binding approximation. Among the κ-(ET)$_2X$ family, a Mott insulator κ-(ET)$_2$Cu$_2$(CN)$_3$ [4,5] is unique in that the ratio of transfer integrals is almost unity ($t'/t = 1.06$) [7], suggesting that the $S = 1/2$ nearly isotropic triangular lattice is realized and it can be a promising candidate of the spin liquid insulator. Actually, the EPR measurement has shown no signature of the antiferromagnetic (AF) transition down to 1.7 K [5], although the nature of the spin state is still unknown. It is in sharp contrast to another Mott insulator κ-(ET)$_2$Cu[N(CN)$_2$]Cl with $t'/t \sim$

0.75, which exhibits the AF transition at $T_N = 27$ K at ambient pressure [8,9] and the superconducting transition at $T_C = 12.8$ K under pressure [10]. It is also noted that moderate hydrostatic pressure induces superconductivity in κ-(ET)$_2$Cu$_2$(CN)$_3$ with T_C of 3.9 K [5].

In this Letter, we report the magnetic properties of κ-(ET)$_2$Cu$_2$(CN)$_3$ revealed by the ^{1}H NMR and the static susceptibility measurements. We have observed no LRMO down to 32 mK well below the exchange constant $J = 250$ K estimated from the magnetic susceptibility at ambient pressure and T_C under soft pressure. These results strongly suggest that a quantum spin liquid state is likely realized in the neighborhood of the superconducting phase.
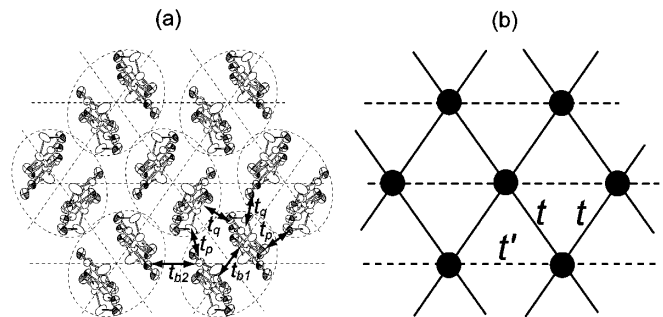

FIG. 1. (a) Crystal structure of an ET layer of κ-(ET)$_2$Cu$_2$(CN)$_3$ viewed along the long axes of ET molecules [4]. The transfer integrals between ET molecules, t_{b1}, t_{b2}, t_p, and t_q, are calculated as 224, 115, 80, and -29 meV, respectively [5]. For the large t_{b1} compared with other transfer integrals, the face-to-face pair of ET molecules connected with t_{b1} can be regarded as a dimer unit consisting of the triangular lattice. (b) Schematic representation of the electronic structure of κ-(ET)$_2X$, where the dots represent the ET dimer units. They form the anisotropic triangular lattice with $t = (|t_p| + |t_q|)/2$ and $t' = t_{b2}/2$.

The single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$ were prepared by the standard electrochemical method [4,5]. The magnetic susceptibility was measured for a polycrystalline sample in a temperature range from 1.9 to 298 K at 0.32 T. The ^{1}H NMR experiments were performed for a polycrystalline sample in a temperature range of 1.4–200 K at a field of 3.9 T and for a single crystal weighing 76 μg in a range of 32 mK–36 K at 2.2 T applied normal to the conducting plane. The latter measurements were performed using the dilution refrigerator of the top-loading type with the crystal soaked to the ^{3}He-^{4}He mixture. The absence of Cu^{2+} impurity ($< 0.01\%$) was confirmed by EPR before the ^{1}H NMR measurement. The NMR spectra were obtained by the fast Fourier transformation of the quadrature-detected echo signals. The relaxation curves of nuclear magnetization were obtained from the recovery of the echo intensity following saturation comb pulses and the solid-echo pulse sequence, $(\pi/2)_x - (\pi/2)_y$.

Temperature dependence of the static susceptibility, χ, of κ-(ET)$_2$Cu$_2$(CN)$_3$ is shown in Fig. 2, where the core diamagnetic contribution of -4.37×10^{-4} emu/mol is already subtracted. With decreasing temperature, χ increases slightly and shows a very broad maximum around

70 K (5.4×10^{-4} emu/mol). Below 50 K, χ starts to decrease rapidly, but remains to be paramagnetic even at 1.9 K (2.9×10^{-4} emu/mol). The behavior is quite different from that of κ-(ET)$_2$Cu[N(CN)$_2$]Cl which shows a monotonous decrease with temperature and the weak ferromagnetism below 27 K due to canting of the AF ordered spins [9]. The temperature dependence of χ for κ-(ET)$_2$Cu$_2$(CN)$_3$ is fitted to the high-temperature series expansion of spin $S = 1/2$ triangular-lattice Heisenberg model [11] as shown in Fig. 2, where the [6/6] and [7/7] Padé approximants are adopted with $J = 250$ K. This model was successful in explaining χ of another organic triangular-lattice system [12]. The peak temperature is much lower than the J value, suggesting that the strong spin frustration suppresses the development of the short-range spin correlations. The difference between the experimental result and the Heisenberg model may be partially attributed to the weak spin localization in the present system situated in the vicinity of the Mott transition.

Figure 3 shows the temperature dependence of the ^{1}H NMR spectra of a single crystal of κ-(ET)$_2$Cu$_2$(CN)$_3$ along with the previous result of κ-(ET)$_2$Cu[N(CN)$_2$]Cl for comparison [9]. The width and the shape of the spectra of both salts above 30 K represent typical nuclear dipole interactions between the protons in the ethylene groups of ET molecules. Since the shape of the spectra is sensitive to the direction of the external static magnetic field, the difference of the spectra between the two salts at high temperatures is explained by the difference in the orientation of ET molecules against the applied field and does not matter. A remarkable difference in the shape of the
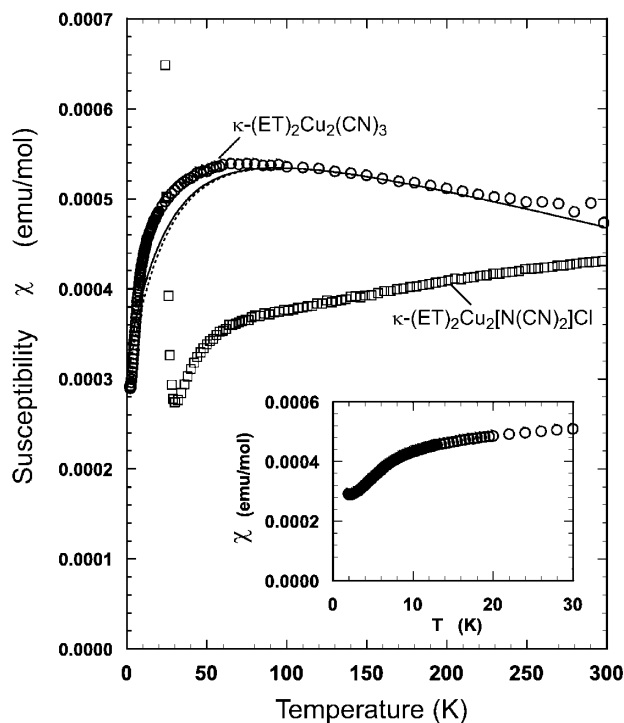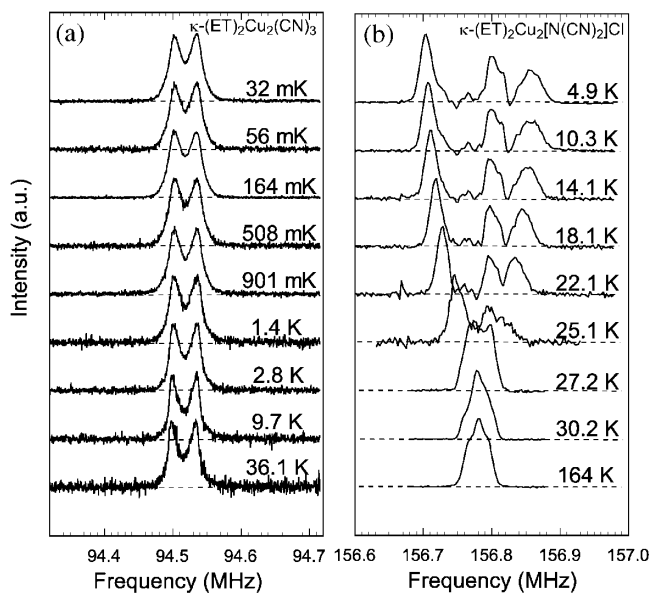
FIG. 2. Temperature dependence of the magnetic susceptibility of the randomly orientated polycrystalline samples of κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu[N(CN)$_2$]Cl [9]. The core diamagnetic susceptibility is already subtracted. The solid and dotted lines represent the result of the series expansion of the triangular-lattice Heisenberg model using [6/6] and [7/7] Padé approximants, respectively, with $J = 250$ K. The low-temperature data of κ-(ET)$_2$Cu$_2$(CN)$_3$ below 30 K are expanded in the inset.

FIG. 3. (a) ^{1}H NMR absorption spectra for single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu[N(CN)$_2$]Cl [9] under the magnetic field perpendicular to the conducting planes.

spectra between the two salts was observed at low temperatures. The spectra of κ-(ET)$_2$Cu[N(CN)$_2$]Cl clearly split below 27 K and the splitting width reaches ± 80 kHz, reflecting the commensurate AF ordering [9] with a magnetic moment of $0.45\mu_B$ per an ET dimer [13]. On the other hand, the spectra of κ-(ET)$_2$Cu$_2$(CN)$_3$ show neither distinct broadening nor split down to 32 mK. The result indicates that no LRMO exists in κ-(ET)$_2$Cu$_2$(CN)$_3$ at least down to 32 mK, which is 4 orders of magnitude below the J value of 250 K. The fact strongly suggests the realization of the quantum-disordered spin liquid state in κ-(ET)$_2$Cu$_2$(CN)$_3$ due to the strong spin frustration of the nearly isotropic triangular lattice. Taking a closer look at the data, the full width of the spectra at the half-maximum intensity shows a slight broadening of ± 2 kHz with decreasing temperature from 4 to 1 K. It may originate from the random dipole field of a small amount of magnetic impurity or the intrinsic T_2 broadening as was observed in the triangular-lattice compound, LiNiO$_2$ [14], where T_2 is the spin-spin relaxation time. The magnetic moment, if any below 4 K, is estimated as less than $0.01\mu_B$ per an ET dimer with reference to the moment/shift ratio observed in κ-(ET)$_2$Cu[N(CN)$_2$]Cl.

The nuclear spin-lattice relaxation rate, T_1^{-1}, of κ-(ET)$_2$Cu$_2$(CN)$_3$ is shown in Fig. 4 as a function of temperature together with that of κ-(ET)$_2$Cu[N(CN)$_2$]Cl [9]. An enhancement of T_1^{-1} above 150 K is a motional contribution due to the thermally activated vibration of the ethylene groups. The motional contribution almost dies away around 150 K, below which the relaxation is electronic in origin. From 150 to 50 K, T_1^{-1} behaves nearly temperature independently. The values of T_1^{-1} in this region are more than twice as large as those of κ-(ET)$_2$Cu[N(CN)$_2$]Cl.

Below 50 K, T_1^{-1} of κ-(ET)$_2$Cu$_2$(CN)$_3$ decreases with temperature down to 4 K in a manner similar to χ. It is seen that there is no difference between the polycrystalline and single crystal data in the overlapping temperature range of 1.4–36 K. This temperature dependence markedly contrasts with that of κ-(ET)$_2$Cu[N(CN)$_2$]Cl having a sharp peak at 27 K, which is characteristic of the magnetic transition. Since χ and T_1^{-1} measure the $\mathbf{k} = \mathbf{0}$ uniform component and the summation of the spin fluctuations in the $\mathbf{k}$ space, respectively, the results of χ and T_1^{-1} suggest that the spin excitations are suppressed below 50 K over the $\mathbf{k}$ space. Below 4 K, however, T_1^{-1} of κ-(ET)$_2$Cu$_2$(CN)$_3$ turns to increase and shows a broad peak around 1 K as shown in the inset of Fig. 4. It is noted that χ has no appreciable anomaly around 4 K, where T_1^{-1} shows an upturn. The broad peak is considered to reflect the characteristic structure in the spin excitation spectrum of quantum liquid with slow spin dynamics.

Below about 0.4 K the relaxation curve starts to bend gradually and fits to a sum of two exponential functions with comparable fractions. The temperature dependences
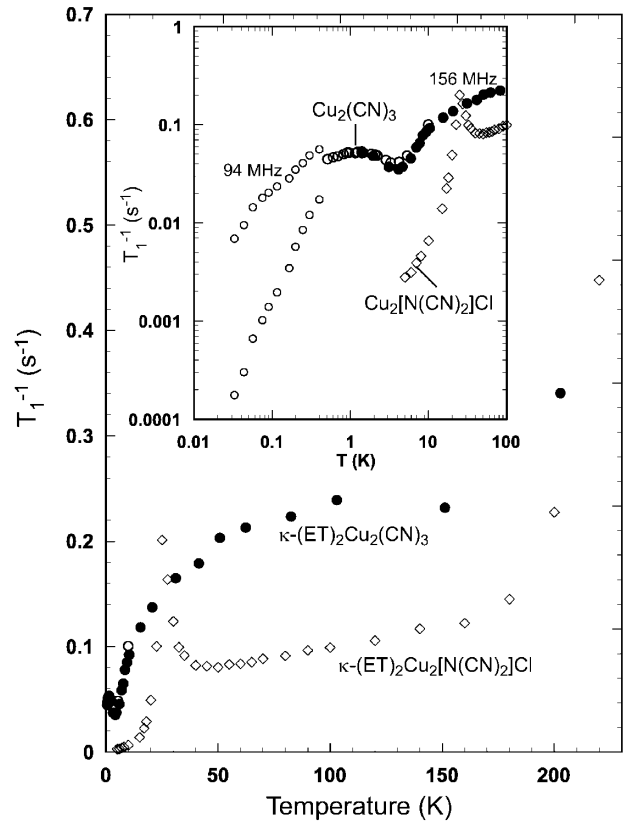

FIG. 4. ^{1}H nuclear spin-lattice relaxation rate T_1^{-1} above 1 K for a single crystal (open circles) and a polycrystalline sample (closed circles) of κ-(ET)$_2$Cu$_2$(CN)$_3$ and a single crystal of κ-(ET)$_2$Cu[N(CN)$_2$]Cl (open diamonds) [9]. The inset shows the data down to 32 mK in logarithm scales.

of the two components of T_1^{-1} are proportional to $\sim T^2$ and $\sim T$. It means that the two kinds of proton sites with different T_1 are separated in a macroscopic scale but not in a molecular scale, because the T_1 distribution in the molecular scale would be averaged by the T_2 process during such a slow spin-lattice relaxation as in the present case ($T_1 \sim 10^2$ and 10^4 sec at the lowest temperature). It is unlikely that LRMO or spin glass transition occurs below 0.4 K, since T_1^{-1} has no critical behavior above 0.4 K and the NMR spectra show no broadening below 1 K. Actually, the recent μSR experiment also shows no internal magnetic field down to 20 mK [15]. Taking into account that the highly degenerate quantum state on the triangular lattice is likely sensitive to randomness [16], crystal imperfections or dilute impurity moments may induce some secondary phase with different spin dynamics from the primary phase. It is noted that the inhomogeneous NMR relaxation like the present observation is also encountered in an inorganic frustrated spin system with kagomé lattice [17]. In general, the spin liquid state is discussed to have a finite spin excitation gap [3]. In such a case, T_1^{-1} should fall exponentially with lowering temperature. In the present case, however, T_1^{-1}'s follow

power laws at low temperatures, indicating that the ground state has low-lying spin excitations of a gapless nature.

The ground state of the $S = 1/2$ triangular-lattice Heisenberg model has been intensively studied [18] since Anderson proposed the spin liquid state [3]. Now, there is an accepted consensus that the ground state of the isotropic triangular lattice is the 120° spiral ordered state. The quantum-disordered state is suggested to appear when the triangular lattice becomes anisotropic [19], which is, in fact, realized in Cs_2CuCl_4 ($J'/J \sim 3$) under high magnetic fields [20]. On the other hand, the path integral renormalization group analysis of the Hubbard model has predicted that a nonmagnetic insulating state appears in a restricted region of the U/t vs t'/t plane with moderate values of U/t exceeding the critical value of the Mott transition and the region is widened as t'/t approaches unity [21]. Here U represents the effective on-site Coulomb repulsive energy. The band structure calculation suggests that κ-$(ET)_2Cu_2(CN)_3$ ($U/t = 8.2$, $t'/t = 1.06$ [5]) is just located in the predicted nonmagnetic region. It is interesting that the frustrated Hubbard ladder model predicts a similar phase diagram in the U/t vs t'/t plane [22]. These theoretical works imply the reason the promising candidates of the spin liquid phase are realized on the nearly isotropic triangular lattice in organics, where U/t is usually not so large. Actually, the fact that κ-$(ET)_2Cu_2(CN)_3$ undergoes the Mott transition under soft hydrostatic pressure [5] indicates the marginal U/t at ambient pressure.

Finally, it should be noted that the superconducting phase appears in κ-$(ET)_2Cu_2(CN)_3$ with the maximum T_C of 3.9 K under moderate hydrostatic pressure. To our knowledge, this is the first example of a Mott insulator which shows no LRMO well below the superconducting transition appearing under pressure or carrier doping. The superconducting and metallic phases emerging from the spin liquid insulator can have novel aspects unseen in the high-T_C oxides and the other organic analogues [1,23] where the d-wave superconductors and the pseudogapped metals emerge from the AF insulators. It is noted that recently discovered superconductor $Na_xCoO_2 \cdot yH_2O$ with triangular lattice is another candidate that resides near the spin liquid [24].

In conclusion, through the ^1H NMR study on the Mott insulator κ-$(ET)_2Cu_2(CN)_3$ with nearly isotropic triangular lattice, we found the evidence for the absence of LRMO down to 32 mK, despite the large AF interaction of hundreds Kelvin. The result is quite different from the other Mott insulators such as κ-$(ET)_2Cu[N(CN)_2]Cl$ and

indicates that the spin liquid state is realized in the proximity of the superconducting phase under pressure.

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