Highly Mobile Gapless Excitations in a Two-Dimensional Candidate Quantum Spin Liquid

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The nature of quantum spin liquids, a novel state of matter where strong quantum fluctuations destroy the long-range magnetic order even at zero temperature, is a long-standing issue in physics. We measured the low-temperature thermal conductivity of the recently discovered quantum spin liquid candidate, the organic insulator $EtMe_3Sb[Pd(dmit)_2]_2$. A sizable linear temperature dependence term is clearly resolved in the zero-temperature limit, indicating the presence of gapless excitations with an extremely long mean free path, analogous to excitations near the Fermi surface in pure metals. Its magnetic field dependence suggests a concomitant appearance of spin-gap–like excitations at low temperatures. These findings expose a highly unusual dichotomy that characterizes the low-energy physics of this quantum system.

Spin systems confined to low dimensions exhibit a rich variety of quantum phenomena. Particularly intriguing are quantum spin liquids (QSLs), antiferromagnets with quantum fluctuation–driven disordered ground states, which have been attracting tremendous attention for decades (*1*). The notion of QSLs is now firmly established in one-dimensional (1D) spin systems. In dimensions greater than one, it is widely believed that QSL ground states emerge when interactions among the magnetic degrees of freedom are incompatible with the underlying crystal geometry, leading to a strong enhancement of quantum fluctuations. In 2D, typical examples of systems where such geometrical frustrations are present are the triangular and kagomé lattices. Largely triggered by the proposal of the resonating-valence-bond theory on a 2D triangular lattice and its possible application to high-transition temperature cuprates (*2*), realizing QSLs in 2D systems has been a long-sought goal. However, QSL states are hard to achieve experimentally because the presence of small but finite 3D magnetic interactions usually results in some ordered (or frozen) state. Two recently discovered organic insulators, κ-[bis(ethylenedithio)-tetrathiafulvalene]$_2Cu_2(CN)_3$ [κ-(BEDT-TTF)$_2Cu_2(CN)_3$] (*3*) and $EtMe_3Sb[Pd(dmit)_2]_2$ (*4*, *5*), both featuring 2D spin-1/2 Heisenberg triangular lattices, are believed to be promising candidate materials that are likely to host QSLs. In both compounds, nuclear magnetic resonance (NMR) measurements have shown no long-range magnetic order down to a temperature corresponding to J/12,000, where J (~250 K for both compounds) is the nearest-neighbor spin interaction energy (exchange coupling) (*3*, *5*). In a triangular lattice antiferromagnet, the frustration brought on by the nearest-neighbor Heisenberg interaction is known to be insufficient to destroy the long-range ordered ground state (*6*). This has led to the proposals of numerous scenarios which might stabilize a QSL state: spinon Fermi surface (*7*, *8*), algebraic spin liquid (*9*), spin Bose metal (*10*), ring-exchange model (*11*), Z_2 spin liquid state (*12*), chiral spin liquid (*13*), Hubbard model with a moderate onsite repulsion (*14*, *15*), and one-dimensionalization (*16*, *17*). Nevertheless, the origin of the QSL in the organic compounds remains an open question.

To understand the nature of QSLs, knowledge of the detailed structure of the low-lying elementary excitations in the zero-temperature limit, particularly the presence or absence of an excitation gap, is of primary importance (*18*). Such information bears immediate implications on the spin correlations of the ground state, as well as the correlation length scale of the QSL. For example, in 1D spin-1/2 Heisenberg chains, the elementary excitations are gapless spinons (chargeless spin-1/2 quasiparticles) characterized by a linear energy dispersion and a power-law decay of the spin correlation (*19*), whereas in the integer spin case such excitations are gapped (*20*). In the organic compound κ-(BEDT-TTF)$_2Cu_2(CN)_3$, where the first putative QSL state was reported (*3*), the presence of the spin excitation gap is controversial (*18*, *21*). In this compound, the stretched, non-

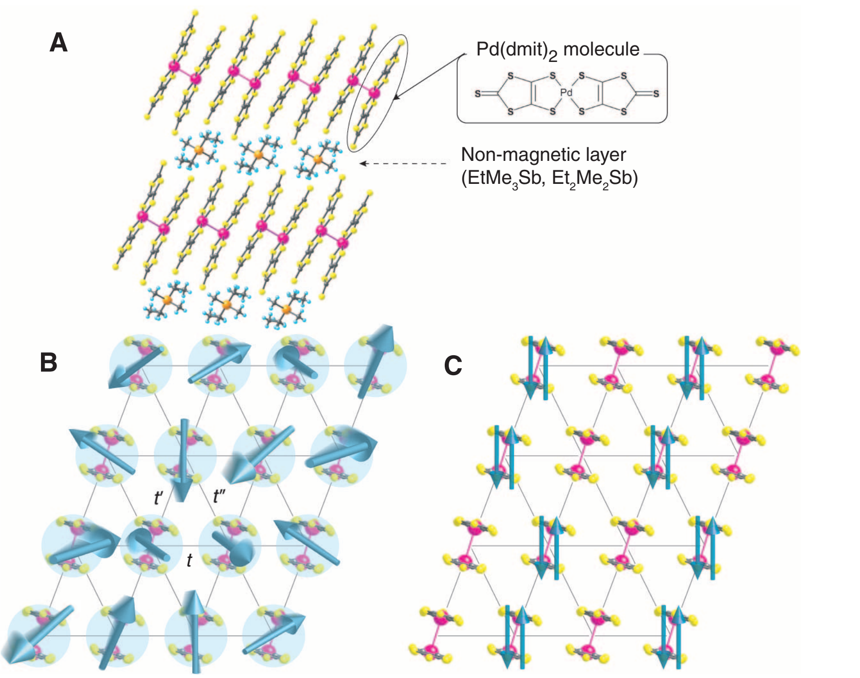

Fig. 1. The crystal structure of $EtMe_3Sb[Pd(dmit)_2]_2$ and $Et_2Me_2Sb[Pd(dmit)_2]_2$. (**A**) A view parallel to the 2D magnetic $Pd(dmit)_2$ layer, separated by layers of a nonmagnetic cation. (**B**) The spin structure of the 2D planes of $EtMe_3Sb[Pd(dmit)_2]_2$ (dmit-131), where Et = C_2H_5, Me = CH_3, and dmit = 1,3-dithiole-2-thione-4,5-dithiolate. $Pd(dmit)_2$ are strongly dimerized (table S1), forming spin-1/2 units $[Pd(dmit)_2]_2^-$ (blue arrows). The antiferromagnetic frustration gives rise to a state in which none of the spins are frozen down to 19.4 mK (*4*). (**C**) The spin structure of the 2D planes of $Et_2Me_2Sb[Pd(dmit)_2]_2$ (dmit-221). A charge order transition occurs at 70 K, and the units are separated as neutral $[Pd(dmit)_2]_2^0$ and divalent dimers $[Pd(dmit)_2]_2^{2-}$. The divalent dimers form intradimer valence bonds, showing a nonmagnetic spin singlet (blue arrows) ground state with a very large excitation gap (*24*).

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exponential decay of the NMR relaxation indicates inhomogeneous distributions of spin excitations (*22*), which may obscure the intrinsic properties of the QSL. A phase transition possibly associated with the charge degree of freedom at ~6 K further complicates the situation (*23*). Meanwhile, in $EtMe_3Sb[Pd(dmit)_2]_2$ (dmit-131) such a transition is likely to be absent, and a much more homogeneous QSL state is attained at low temperatures (*4*, *5*). As a further merit, dmit-131 (Fig. 1B) has a cousin material $Et_2Me_2Sb[Pd(dmit)_2]_2$ (dmit-221) with a similar crystal structure (Fig. 1C), which exhibits a nonmagnetic charge-ordered state with a large excitation gap below 70 K (*24*). A comparison between these two related materials will therefore offer us the opportunity to single out genuine features of the QSL state believed to be realized in dmit-131.

Measuring thermal transport is highly advantageous for probing the low-lying elementary excitations in QSLs, because it is free from the nuclear Schottky contribution that plagues the heat capacity measurements at low temperatures (*21*). Moreover, it is sensitive exclusively to itinerant spin excitations that carry entropy, which provides important information on the nature of the spin correlation and spin-mediated heat transport. Indeed, highly unusual transport properties including the ballistic energy propagation have been reported in a 1D spin-1/2 Heisenberg system (*25*).

The temperature dependence of the thermal conductivity κ_{xx} divided by T of a dmit-131 single crystal displays a steep increase followed by a rapid decrease after showing a pronounced maximum at $T_g \sim 1$ K (Fig. 2A). The heat is carried primarily by phonons (κ_{xx}^{ph}) and spin-mediated contributions (κ_{xx}^{spin}). The phonon contribution can be estimated from the data of the nonmagnetic state in a dmit-221 crystal with similar dimensions, which should have a negligibly small κ_{xx}^{spin}. In dmit-221, κ_{xx}^{ph}/T exhibits a broad peak at around 1 K, which appears when the phonon conduction grows rapidly and is limited by the sample boundaries. On the other hand, κ_{xx}/T of dmit-131, which well exceeds κ_{xx}^{ph}/T of dmit-221, indicates a substantial contribution of spin-mediated heat conduction below 10 K. This observation is reinforced by the large magnetic field dependence of κ_{xx} of dmit-131, as discussed below (Fig. 3A). Figure 2B shows a peak in the κ_{xx} versus T plot for dmit-131, which is absent in dmit-221. We therefore conclude that κ_{xx}^{spin} and κ_{xx}^{spin}/T in dmit-131 have a peak structure at $T_g \sim 1$ K, which characterizes the excitation spectrum.

The low-energy excitation spectrum can be inferred from the thermal conductivity in the low-temperature regime. In dmit-131, κ_{xx}/T at low temperatures is well fitted by $\kappa_{xx}/T = \kappa_{00}/T + bT^2$ (Fig. 2C), where b is a constant. The presence of a residual value in κ_{xx}/T at $T \rightarrow 0$ K, κ_{00}/T, is clearly resolved. The distinct presence of a nonzero κ_{00}/T term is also confirmed by plotting κ_{xx}/T versus T (Fig. 2D). In sharp contrast, in dmit-221, a corresponding residual κ_{00}/T is absent and only a phonon contribution is observed (*26*). The residual thermal conductivity in the zero-temperature limit immediately implies that the excitation from the ground state is gapless, and the associated correlation function has a long-range algebraic (power-law) dependence. We note that the temperature dependence of κ_{xx}/T in dmit-131 is markedly different from that in κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$, in which the exponential behavior of κ_{xx}/T associated with the formation of excitation gap is observed (*18*).

Key information on the nature of elementary excitations is further provided by the field dependence of κ_{xx}. Because it is expected that κ_{xx}^{ph} is hardly influenced by the magnetic field, particularly at very low temperatures, the field dependence is governed by $\kappa_{xx}^{spin}(H)$ (*26*). The obtained H-dependence, $\kappa_{xx}(H)$, at low temperatures is quite unusual (Fig. 3A). At the lowest temperature, $\kappa_{xx}(H)$ at low fields is insensitive to H but displays a steep increase above a characteristic magnetic field $H_g \sim 2$ T. At higher temperatures close to T_g, this behavior is less pronounced, and at 1 K $\kappa_{xx}(H)$ increases with H nearly linearly. The observed field dependence implies that some spin-gap–like excitations are also present at low temperatures, along with the gapless excitations inferred from the residual κ_{00}/T. The energy scale of the gap is characterized by $\mu_B H_g$, which is comparable to $k_B T_g$. Thus, it is natural to associate the observed zero-field peak in $\kappa_{xx}(T)/T$ at T_g with the excitation gap formation.

Next we examined a dynamical aspect of the spin-mediated heat transport. An important question is whether the observed energy transfer via elementary excitations is diffusive or ballistic. In the 1D spin-1/2 Heisenberg system, the ballistic energy propagation occurs as a result of the conservation of energy current (*25*). Assuming the kinetic approximation, the thermal conductivity is written as $\kappa_{xx}^{spin} = C_s v_s \ell_s /3$, where C_s is the specific heat, v_s is the velocity, and ℓ_s is the mean free path of the quasiparticles responsible for the elementary excitations. We tried to estimate ℓ_s simply by assuming that the linear term in the thermal conductivity arises from the fermionic excitations, in analogy with excitations near the Fermi surface in metals. The residual term is written as $\kappa_{00}/T \sim (k_B^2/da\hbar)\ell_s$, where d (~3 nm) and a (~1 nm) are interlayer and nearest-neighbor spin distance. We assumed the linear energy dispersion $\varepsilon(k) = \hbar v_s k$, a 2D density of states and a Fermi energy comparable to J (*26*). From the observed κ_{00}/T, we find that ℓ_s reaches as long as ~1 μm, indicating

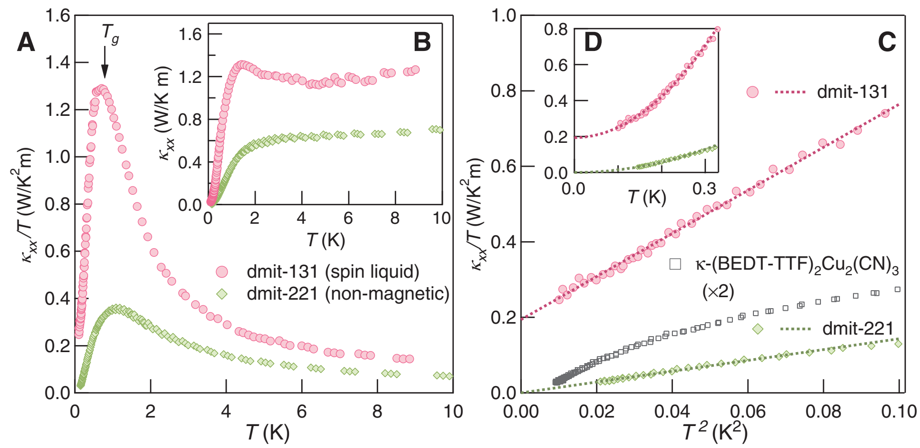

Fig. 2. The temperature dependence of $\kappa_{xx}(T)/T$ (**A**) and $\kappa_{xx}(T)$ (**B**) of dmit-131 (pink) and dmit-221 (green) below 10 K in zero field [$\kappa_{xx}(T)$ is the thermal conductivity]. A clear peak in κ_{xx}/T is observed in dmit-131 at $T_g \sim 1$ K, which is also seen as a hump in κ_{xx}. Lower temperature plot of $\kappa_{xx}(T)/T$ as a function of T^2 (**C**) and T (**D**) of dmit-131, dmit-221, and κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ (black) (*18*). A clear residual of $\kappa_{xx}(T)/T$ is resolved in dmit-131 in the zero-temperature limit.

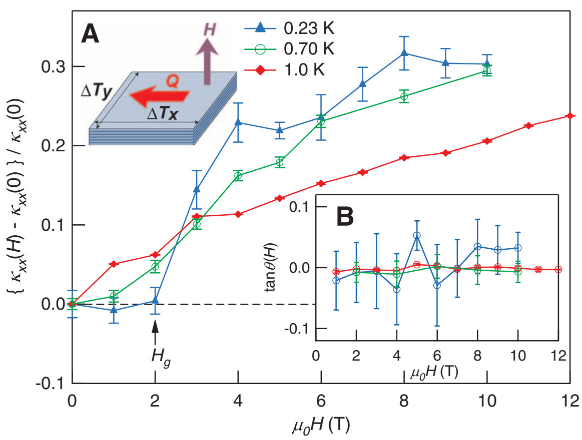

Fig. 3. (**A**) Field dependence of thermal conductivity normalized by the zero field value, $[\kappa_{xx}(H) - \kappa_{xx}(0)]/\kappa_{xx}(0)$ of dmit-131 at low temperatures. (Inset) The heat current ***Q*** was applied within the 2D plane, and the magnetic field ***H*** was perpendicular to the plane. κ_{xx} and κ_{xy} were determined by diagonal and off-diagonal temperature gradients, ΔT_x and ΔT_y, respectively. (**B**) Thermal-Hall angle $\tan\theta(H) = \kappa_{xy}/(\kappa_{xx} - \kappa_{xx}^{ph})$ as a function of H at 0.23 K (blue), 0.70 K (green), and 1.0 K (red).

that the excitations are mobile to a distance 1000 times as long as the interspin distance without being scattered. Remarkably, the observed ℓ_s is even longer than the mean impurity distance estimated from the susceptibility measurements (*5*). Although our simple estimation should be scrutinized, the nearly ballistic propagation seems to be realized in this QSL state, which bears a striking resemblance to the 1D Heisenberg system (*25*). Such a coherent motion of the excitation is only possible with an extremely long correlation length, consistent with the power-law correlation function with gapless excitations.

Our results indicate that there are two kinds of excitations in the low-temperature regime of dmit-131: One is a low-lying gapless excitation and another is a spin-gap–like excitation that couples to magnetic fields. The existence of the gapless mode imposes constraints on theories that can account for the QSL in this material. For instance, it contradicts the identification of the ground state of this system with a fully gapped short-range resonating-valence-bond state (*27*). It is intriguing that, although there has been no experimental observation, the coexistence of the gapless and gapped excitations has been theoretically predicted in highly frustrated kagomé lattice (*28*). In this case, the magnetic excitations are separated from the ground state by a spin-gap, which is filled with nonmagnetic excitations. It is a nontrivial problem, however, if such a state can be realized in a triangular lattice where less quantum degenerate states are expected.

Recently, the ground state of a QSL in the 2D triangular lattice has been discussed in terms of the spinon Fermi surface (*7*, *8*). The Fermi surface is suggested to have pairing instability at low temperatures, and a possible nodal gap structure appears that is analogous to *d*-wave superconductivity in high-transition temperature cuprates (*29*). In this scenario, the spin-gap–like behavior is attributed to the pairing gap formation, and the finite residual *T*-linear term stems from the zero-energy density of states similar to the disorder-induced normal fluid in *d*-wave superconductors. The low energy density of states is expected to be insensitive to Zeeman magnetic field as in a Fermi liquid. The nodal gap is expected to produce thermally excited quasiparticles, which may account for the observed T^2 dependence of κ/T with a much steeper slope than κ_{xx}^{ph}/T (Fig. 2C). This model also predicts a thermal-Hall effect of spinons that experience the Lorentz force, akin to the conduction electrons in metals (*30*). In an attempt to observe this effect, we measured the thermal-Hall conductivity κ_{xy}, and the tangent of the thermal-Hall angle, $\tan\theta(H) = \kappa_{xy}/(\kappa_{xx} - \kappa_{xx}^{ph})$ (Fig. 3B). The observed thermal-Hall angle is orders of magnitude smaller than the prediction (*26*), which calls for further studies. It is also an open question why continuous excitations are observed in the present compound whereas they are absent in κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ (*18*). Such excitations may be strongly suppressed by inhomogeneity.

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31. We thank M. P. A. Fisher, S. Fujimoto, T. Itou, H. Katsura, N. Kawakami, H. Kawamura, P. A. Lee, G. Misguich, Y. Nakazawa, and A. Tanaka for valuable discussion. This work was supported by Grants-in-Aid for Scientific Research (KAKENHI) from the Japan Society for the Promotion of Science and the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), a Grant-in-Aid for the Global Centers of Excellence Program "The Next Generation of Physics, Spun from Universality and Emergence," and a Grant-in-Aid for Scientific Research on Innovative Areas "Heavy Electrons" (No. 20102006) from MEXT, Japan.

Supporting Online Material

www.sciencemag.org/cgi/content/full/328/5983/1246/DC1
Materials and Methods
Figs. S1 and S2
Table S1
References

10 February 2010; accepted 29 April 2010
10.1126/science.1188200

Collective Lamb Shift in Single-Photon Superradiance

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Superradiance, the cooperative spontaneous emission of photons from an ensemble of identical atoms, provides valuable insights into the many-body physics of photons and atoms. We show that an ensemble of resonant atoms embedded in the center of a planar cavity can be collectively excited by synchrotron radiation into a purely superradiant state. The collective coupling of the atoms via the radiation field leads to a substantial radiative shift of the transition energy, the collective Lamb shift. We simultaneously measured the temporal evolution of the superradiant decay and the collective Lamb shift of resonant ^{57}Fe nuclei excited with 14.4–kilo–electron volt synchrotron radiation. Our experimental technique provides a simple method for spectroscopic analysis of the superradiant emission.

The development of quantum electrodynamics is very closely related to the discovery and explanation of the Lamb shift of atomic energy levels (*1*, *2*). The Lamb shift is a small energy shift of bound atomic states, mainly resulting from the emission and reabsorption of virtual photons within the same atom. An additional contribution emerges if many identical two-level atoms are interacting collectively with a resonant radiation field. In this case, a virtual photon that is emitted by one atom may be reabsorbed by another atom within the ensemble. The resulting collective Lamb shift scales with the optical density of the atoms and sensitively depends on their spatial arrangement (*3*–*9*). At high atomic densities, however, atom-atom interactions mask the collective Lamb shift, making it almost impossible to observe. Since the early theoretical studies (*3*), only one measurement of a collective line shift has been reported for a multiphoton excitation scheme in a noble gas (*10*, *11*). Experimental assessment of the collective Lamb

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