Gapped magnetic ground state in quantum spin liquid candidate $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

Björn Miksch$^1$, Andrej Pustogow$^{1,2}$, Mojtaba Javaheri Rahim$^1$, Andrey A. Bardin$^3$, Kazushi Kanoda$^4$, John A. Schultheis$^{5,6}$, Ralph Hübner$^1$, Marc Scheffler$^1$, Martin Dressel$^{1,*}$

Geometrical frustration, quantum entanglement, and disorder may prevent long-range ordering of localized spins with strong exchange interactions, resulting in an exotic state of matter. $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is considered the prime candidate for this elusive quantum spin liquid state, but its ground-state properties remain puzzling. We present a multifrequency electron spin resonance (ESR) study down to millikelvin temperatures, revealing a rapid drop of the spin susceptibility at 6 kelvin. This opening of a spin gap, accompanied by structural modifications, is consistent with the formation of a valence bond solid ground state. We identify an impurity contribution to the ESR response that becomes dominant when the intrinsic spins form singlets. Probing the electrons directly manifests the pivotal role of defects for the low-energy properties of quantum spin systems without magnetic order.

The exotic properties of quantum spin liquids (QSL) have continuously drawn interest since Anderson's seminal study half a century ago (1), where he considered spin models that possess an extensive degeneracy of states. At low temperatures, classical spins in magnetically interacting systems usually achieve a long-range periodic arrangement. However, it is widely believed that geometrical frustration may suppress conventional magnetic ordering down to $T = 0$ K, giving rise to a distinctive, fluctuating, quantum-disordered state (2–4). Organic charge-transfer salts were the first and most versatile QSL candidates because their microscopic parameters can be easily tuned by chemical means. These salts crystallize in a near-isotropic triangular arrangement of $S = \frac{1}{2}$ spins on molecular dimers (5) (Fig. 1), in contrast to most inorganic QSL candidates, such as pyrochlore compounds or herbertsmithite, which form tetrahedral or kagome lattices (6, 7), respectively.

For two decades, QSLs have been intensely explored by various magnetic probes, but for most materials, crucial questions remain unanswered: How is magnetic order prevented? What is the ground state? And what is the spin excitation spectrum? For the two-dimensional charge-transfer salts, the importance of disorder became evident only recently (8–12). On the fundamental issue of the existence of a spin gap in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ however, conflicting conclusions can be drawn from magnetic torque (13), muon spin rotation ($\mu$SR) (14), thermal transport (15), specific heat (16), and nuclear magnetic resonance (NMR) measurements (17). The necessity of studying the range $T \rightarrow 0$ favors experimental methods that are not susceptible to, among other things, impurity spins. Measurements of the bulk susceptibility do not distinguish between its intrinsic and extrinsic components. $\mu$SR and NMR spectroscopies are indirect probes, because they record the influence of local magnetism on the spectral and relaxation properties of muons and atomic nuclei, respectively. In contrast, electron spin resonance (ESR) directly probes the magnetic excitation spectrum of the conduction electrons, which allows us to unambiguously identify the intrinsic response and separate it from other contributions. Commonly used commercial instruments do have a very high sensitivity, but they are restricted in frequency and temperature. For that reason, we developed a broadband ultra-low-temperature ESR technique based on coplanar waveguide resonators. The technique can be operated in a dilution refrigerator, increasing the temperature range to the millikelvin regime, and allows measurements not only at a single microwave frequency but also at multiple harmonics of the fundamental frequency of the one-dimensional resonators (18).

In Fig. 2A, we plot the temperature dependence of the spin susceptibility $\chi_S(T)$, as derived from the X-band ESR spectra on $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ single crystals shown in Fig. 2B. At temperatures above 10 K, the overall behavior can be described by a Heisenberg model on a triangular lattice with strong antiferromagnetic exchange interaction $J = 250$ K. In agreement with previous estimates (17). However, at $T^* = 6$ K, a rapid drop in $\chi_S(T)$ is observed; this is at the very same temperature where an anomaly was consistently identified by various methods (15–17, 19–21). Fitting the decay by an activated behavior with functional form $\chi_S(T) \propto T^{1/2} \exp\{-(\Delta/T)\}$ yields a spin gap of $\Delta = 12.1$ K, as shown by the green line; details are given in (18). Because the $g$ value of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ remains unchanged at low temperatures (fig. S2), long-range magnetic order or any well-defined local moments can be ruled out, in accord with previous NMR results that show no splitting in the spectra (17). Thus, our ESR investigations unambiguously identify the anomaly at $T^*$ as a phase transition to a gapped magnetic ground state.

Because our findings clearly rule out the widely assumed gapless QSL state with itinerant spins (16, 17), we consider possible...
scenarios for a spin-gapped ground state on a slightly distorted triangular lattice (Fig. 1B), such as a valence bond solid (VBS), an Amperean pairing instability, $Z_2$ QSL, or other resonating valence bond phases (2–4, 22, 23).

First, we notice that $\chi_b(T)$ resembles that of other well-known spin-Peierls transitions in organic linear-chain compounds (24), or inorganic CuGeO$_3$ and $\alpha'$-NaV$_2$O$_5$ (25, 26), as elaborated in (18). Similar to these quasi-1D systems, $\kappa$(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ exhibits a structural anomaly with anisotropic thermal expansion at the transition (19), corroborating the idea of a broken-symmetry ground state that couples to the lattice. Such a transition occurs when the energy gain by the formation of spin singlets exceeds the energy required for the lattice distortion. Here, the shrinkage of the $c$ axis below $T^*$ that is accompanied by pronounced lattice softening (20) suggests that the ($b+c$) directions are the preferable orientations of the valence bonds (Fig. 1C). Taken together, these experimental signatures are fully consistent with a VBS, a non-magnetic ground state in which neighboring spins of opposite direction form valence bond singlets arranged in a regular fashion—a scenario also discussed for kagome (27) and higher-dimensional QSL candidates (28).

Besides the VBS scenario, a gapped QSL phase could be the result of a topological $Z_2$ spin liquid found in perfect triangular-lattice dimer models with some analogy to a phase-disordered Bardeen-Cooper-Schrieffer (BCS) superconductor (3, 4, 29). However, the present in-plane anisotropy and potential symmetry breaking at $T^*$ put tight constraints on a conceivable $Z_2$ state. Alternatively, it was suggested that an Amperean pairing instability can impose a gap to mobile spinons, with an incommensurate modulation of the amplitude (30), in order to explain the phase transition at $T^*$ and other low-temperature properties of the title compound. Yet this scenario is rather difficult to reconcile with the vanishing thermal transport (15) and the presence of unscreened orphan spins, discussed below. Precise structural studies through $T^*$, by reducing the valence bond arrangement, may prove decisive in distinguishing between the above scenarios.

Having clarified the ground state as a nonmagnetic spin-singlet phase, we next ask: Why did its nature remain unresolved for decades despite much experimental effort? To address this, carefully consider the ESR raw data in Fig. 2B. Below room temperature, the Dysonian absorption at the resonance field $B_{\text{main}} \approx 337$ mT acquires a Lorentzian shape as the conductivity decreases in accordance with dc transport measurements (31). The line initially broadens when cooled to 40 K, followed by a moderate reduction of the line width $\Delta B$ at lower temperatures (figs. S2 and S3). Near $T^*$, the signal narrows extremely, and the doubly integrated area (corresponding to $\chi_b(T)$) is strongly reduced. Most importantly, a second component with an even smaller $\Delta B$ appears at $T^*$, as illustrated in Fig. 2C. Although just below $T^*$ the resonance field of the two features is indistinguishable, Fig. 2D shows that the newly emerging component splits off as an additional peak that shifts away from $B_{\text{main}}$ for $T < 2.5$ K. We attribute this contribution, whose intensity increases upon cooling (orange symbols in Fig. 2A), to defects, in accord with previous considerations (10–12, 21). The feature actually consists of two or three individual lines with slightly different angle dependence and field variation, consistently observed in all crystals from four different laboratories (figs. S9 and S10); whereas the type of defect is always the same, the density varies from sample to sample. As the defect signals emerge from the main ESR.

![Fig. 2. X-band ESR results of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. All datasets but one show sample #1; the exception is stated. (A) Temperature dependence of the normalized spin susceptibility $\chi_b$ measured on two samples along different directions. The data shown for $B_{\parallel}c$ are for sample #2. At elevated temperatures, $\chi_b(T)$ is described by an antiferromagnetic Heisenberg model on a triangular lattice with $J = 250$ K (black line). Below the anomaly at $T^* = 6$ K, an exponential decay of the main signal evidences the opening of a spin gap $\Delta = 12$ K (green line). The orange diamonds correspond to the signal from defect spins, which becomes obvious for $T < T^*$. Inset: Susceptibility data up to $T = 300$ K for $B_{\parallel}a$. (B) Temperature evolution of the X-band spectra with the magnetic field $B_{\parallel}c$. The signal at $T = 10$ K and below is divided by the factors indicated in the figure to account for the increasing peak in $dP/db$ as the line sharpens. (C) Below $T^*$, an additional narrow component appears, requiring a second Lorentzian function to fit the spectra satisfactorily. As an example, the 4 K data are shown with the respective decomposition. (D) Upon cooling below 2.5 K, this new signal separates and shifts to lower resonance fields; we attribute the signal to defect spins not involved in the singlet formation. (E) Anisotropy of the ESR resonances of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The main signal (solid blue line) is identified by the zero-crossing of $dP/db$ from positive (green) to negative (violet) and shows a small angular variation of 0.3 mT when measured within the bc plane at $T = 2$ K. In contrast, the signal of the defect spins (dashed orange line) has a huge anisotropy of 10 mT offset from the crystallographic c direction by an angle of 22° and caused by dipolar interaction to local moments, possibly Cu$^{2+}$ (see text).](https://science.sciencemag.org/content/372/6542/276/suppl/DC1/fig2.pdf)
The magnetic field is rotated within the angled dependence of the ESR line while the signal at $B_{\text{main}}$ corresponds to the constant field-independent offset of the defect signal. The solid blue line on one of the neighboring dimers (sketched in Fig. 3C) thus, Cu$^{2+}$ impurities may be responsible for the observed defect spins with a $(3\cos^2 \theta - 1)$ ESR signal. Full clarification of the nature and origin of the local magnetic moments remains a desideratum for experiment as well as theory.

The emergent local fields for $B|a^*$ are of comparable strength to the low-temperature $^{13}$C NMR line width (4.8 mT) (20) and signatures in the µSR data (14). The distinct anisotropy also explains the angular shift and diverging susceptibility in the magnetic torque observed for low $T$ and $B$ (10, 13). To elucidate the relation to the weak-moment antiferromagnetic phase suggested in (14), we performed broadband ESR experiments at different fields down to millikelvin temperatures using superconducting coplanar waveguide resonators as illustrated in Fig. 3A. Figure 3B displays a representative temperature evolution of the ESR absorption of the crystal measured with the fundamental mode at 11 GHz upon cooling from 4 K to 25 mK. The defect signal, affected by local moments, separates from $B_{\text{main}} = 40$ mT at a temperature $T_{\text{loc}} \approx 1$ K and saturates at lower fields upon cooling; the field dependence of $T_{\text{loc}}$ is in accord with the suggested phase boundaries (14). Figure 3C illustrates the approximately field-independent offset of the defect signal with respect to $B_{\text{main}}$ at the base temperature $T_{\text{base}} = 25$ mK.

What is the origin of the second line in Fig. 3B at $B_{\text{main}}$? Although thermal excitations across the spin gap exceed the defect contributions close to $T^*$ (Fig. 2), they should not contribute at $T_{\text{base}} = \Delta/500$. As sketched in Fig. 1C, there is a possibility of intrinsic valence bond imperfections, for instance through domain walls or other types of broken singlets (10, 11, 23). In the absence of a nearby magnetic moment, the corresponding ESR line remains at $B_{\text{main}}$.

There is an obvious advantage of using electron spins to directly probe the magnetic properties of quantum spin liquids. Because the NMR spin-lattice relaxation rate is susceptible to any kind of unpaired spins in the sample, it will be dominated by impurities in the event that a spin gap opens. Indeed, a recent field-dependent NMR study on several $\kappa$-type organic QSL compounds suggests that the contribution of the defect spins can dominate over the intrinsic relaxation but is suppressed by fields of order $B = 10$ T or higher (12). Of course, impurities such as Cu$^{2+}$ do not disappear when warming above $T^*$, but they are overwhelmed by the large number of intrinsic paramagnetic moments. Whereas high densities of Cu$^{2+}$ will dope the system into a metallic state (32), tiny amounts of charged defects embedded in a
Mott-insulating matrix are a potential source of electrical polarization, possibly accounting for the controversially discussed relaxor-like dielectric response (37, 34).

The scenario of localized unpaired spins, possibly pinned to Cu$^{2+}$, dispersed in a VBS dielectric response (41), whereas much larger disorder effects are expected for the inorganic QSL candidate herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ owing to Cu-Zn antisite exchange on the order of 10% (36, 37). Nevertheless, defect spins may prove crucial for the low-temperature magnetic properties of all quantum spin systems that lack magnetic order. There are now few QSL candidates remaining where the opening of a spin gap has not been proven beyond any doubt. The broadband low-T ESR spectroscopy developed here provides a versatile tool to tackle these and related issues.

**REFERENCES AND NOTES**

18. See supplementary materials.

**ACKNOWLEDGMENTS**

We thank S. E. Brown, K. Holzer, R. K. Kremer, G. Gorgon Lesseux, A. Tsirlin, and S. M. Winter for fruitful discussions. Funding: The work at the University of Stuttgart was supported by the Deutsche Forschungsgemeinschaft (DFG226/35-3). A.P. acknowledges support from the Alexander von Humboldt Foundation through the Fedor Lynen Fellowship. K.K. was supported by the Japan Society for the Promotion of Science (grant 18H05225). J.A.S. acknowledges support from the Independent Research and Development program from the NSF while working at the foundation and from the National High Magnetic Field Laboratory (NHMFL) User Collaboration Grants Program (UCGP). Author contributions: M.D. conceived of the project. M.S. designed the low-temperature ESR facilities. B.M. and M.J.R. performed the experiments. B.M. and A.P. analyzed and interpreted the results. In perpetual exchange with M.D. A.A.B., K.K., J.A.S., and R.H. were responsible for the crystal growth. B.M., A.P., and M.D. wrote the manuscript, with contributions from the other authors. Competing interests: The authors declare that they have no competing financial interests. Data and materials availability: All data shown are publicly available on Zenodo (39).

**SUPPLEMENTARY MATERIALS**

science.sciencemag.org/content/372/6539/276/suppl/DC1 Materials and Methods

Figs. S1 to S14

References (40–65)

5 May 2020; accepted 9 March 2021

10.1126/science.abc6363
Gapped magnetic ground state in quantum spin liquid candidate \(\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3\)

Björn Miksch, Andrei Pustogow, Mojtaba Javaheri Rahim, Andrey A. Bardin, Kazushi Kanoda, John A. Schlueter, Ralph Hübner, Marc Scheffler and Martin Dressel

Science 372 (6539), 276-279.
DOI: 10.1126/science.abc6363

A gapped spin liquid
Quantum spin liquids avoid conventional magnetic ordering down to the lowest temperatures. Among the candidates for this state of matter, organic salts such as \(\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3\) have been prominent. Miksch et al. studied this material using electron spin resonance to elucidate the nature of its ground state. Instead of the expected gapless state, the temperature dependence of spin susceptibility suggests the formation of a spin gap.

Science, this issue p. 276