Gapped magnetic ground state in the spin-liquid candidate κ-(BEDT-TTF)2Ag2(CN)3 suggested by magnetic spectroscopy [Letter]

Sudip Pal, Björn Miksch, Hans-Albrecht Krug von Nidda, Anastasia Bauernfeind, Marc Scheffler, Yukihoro Yoshida, Gunzi Saito, Atsushi Kawamoto, Cécile Mézière, Narcis Avarvari, John A. Schlueter, Andrej Pustogow, Martin Dressel

Angaben zur Veröffentlichung / Publication details:

Pal, Sudip, Björn Miksch, Hans-Albrecht Krug von Nidda, Anastasia Bauernfeind, Marc Scheffler, Yukihoro Yoshida, Gunzi Saito, et al. 2025. "Gapped magnetic ground state in the spin-liquid candidate κ-(BEDT-TTF)2Ag2(CN)3 suggested by magnetic spectroscopy [Letter]." *Physical Review B* 111 (22): L220404. https://doi.org/10.1103/physrevb.111.l220404.

Letter | Editors' Suggestion

Gapped magnetic ground state in the spin-liquid candidate κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$ suggested by magnetic spectroscopy

Sudip Pal,[1] Björn Miksch,[1] Hans-Albrecht Krug von Nidda,[2] Anastasia Bauernfeind,[1] Marc Scheffler,[1] Yukihoro Yoshida,[3,4] Gunzi Saito,[3,4] Atsushi Kawamoto,[5] Cécile Mézière,[6] Narcis Avarvari,[6] John A. Schlueter,[7,8] Andrej Pustogow,[9] and Martin Dressel[1]

[1]*Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany*
[2]*Experimental Physics V, Center for Electronic Correlations and Magnetism, Universität Augsburg, Universitätsstraße 1, 86159 Augsburg, Germany*
[3]*Faculty of Agriculture, Meijo University, Nagoya 468-8502, Japan*
[4]*Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[5]*Department of Science, Hokkaido University, Sapporo 060-0810, Japan*
[6]*Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, 49000 Angers, France*
[7]*Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439-4831, USA*
[8]*National Science Foundation, Alexandria, Virginia 22314, USA*
[9]*Institute of Solid State Physics, TU Wien, 1040 Vienna, Austria*

(Received 7 October 2024; revised 1 April 2025; accepted 7 May 2025; published 4 June 2025)

The nature of the magnetic ground state of highly frustrated systems remains puzzling to this day. Here, we have performed multifrequency electron spin resonance (ESR) measurements on a putative quantum spin liquid compound κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$, which is a rare example of $S = 1/2$ spins on a triangular lattice. At high temperatures, the spin susceptibility exhibits a weak temperature dependence which can be described by the Heisenberg model with an antiferromagnetic exchange interaction of strength $J/k_B \approx 175$ K. At low temperatures, however, the rapid drop of the static spin susceptibility, together with monotonic decrease of the ESR linewidth, indicates that strong singlet correlations develop below a pairing energy scale T^* accompanied by a spin gap. On the other hand, a weak Curie-like spin susceptibility and the angular dependence of the linewidth suggest additional contributions from impurity spins. We propose the gradual formation of spin singlets with an inhomogeneous spin gap at low temperatures.

DOI: 10.1103/PhysRevB.111.L220404

The so-called quantum spin liquid state (QSL) is an illusive magnetic phase [1,2] and its fundamental properties are extensively discussed in condensed matter physics at present. Initiated by the proposal of a resonating valence-bond state and its subsequent connection to high-temperature superconductivity [3,4], different classes of materials have been scrutinized in search of QSL states, starting from the organic Mott insulators to various inorganic materials such as Yb^{3+} based compounds [5], $Ba_3CoSb_2O_9$ [6,7], and Cu-based kagome-lattice systems such as Herbersmithite and related compounds [8]. In this context, the ground state of the organic compounds κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (abbreviated as κ-CuCN in the following) and β'-EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ were studied in depth over the past decade [9–14]. In the case of κ-CuCN, below a characteristic temperature $T^* \approx 6$ K, significant lattice and sound-velocity anomalies have been observed [15,16]. The spin susceptibility exhibits a rapid decay, which unambiguously indicates the opening of an energy gap in the spin excitation spectrum below T^* [17–19]. The low-entropy nature of the ground state has been further corroborated by the negative slope of the insulator-metal boundary in the T-p phase diagram and negative magnetoresistance around the Mott transition [20–22]. Despite these compelling experimental evidences that κ-CuCN forms a valence-bond solid ground state below T^*, the debate is not completely deceased [23–26].

The present study is devoted to κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$ (called κ-AgCN), a sibling compound to κ-CuCN. These quasi-two-dimensional organic charge-transfer salts possess a rather similar crystal structure displayed in Fig. 1. Layers of charge-donating organic BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] molecules alternate with inorganic anion layers. The (BEDT-TTF)$_2$ dimers form triangles with a high degree of geometrical frustration. For κ-CuCN the ratio of the transfer integrals in the bc plane $t'/t \approx 0.83$, whereas in κ-AgCN is even closer to unity, $t'/t \approx 0.97$ [13,27–29]. Since electron-electron interactions are more pronounced in κ-AgCN compared to the Cu analog [20], the title compound constitutes a rare model of a strongly correlated Mott insulator with $S = \frac{1}{2}$ spins arranged on an almost perfect triangular lattice. We have investigated the magnetic state of κ-AgCN by using broadband electron spin resonance spectroscopy down to $T = 0.56$ K. In addition, the electrochemical stability of silver ions prevents the oxidation of nonmagnetic Ag(I) to paramagnetic Ag(II) [30]; hence κ-AgCN contains one potential source of disorder less than the κ-CuCN, where Cu^{2+} impurity ions become a serious nuisance [17–19]. In the context of QSL, understanding the ground state of κ-AgCN provides a crucial piece of information.

Unfortunately, the experimental basis for κ-AgCN is not as broad as it is for κ-CuCN [14,19]. Thermal expansion

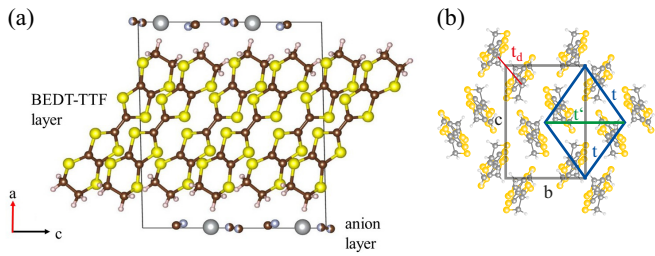

FIG. 1. Crystal structure of κ-(BEDT − TTF)$_2$Ag$_2$(CN)$_3$. (a) The organic (BEDT-TTF) layers and inorganic anion sheets alternate along the a axis with the BEDT-TTF molecules tilted in the c direction. (b) In the bc plane, the (BEDT-TTF)$_2$ dimers form an almost perfect triangular lattice with the nearest-neighbor and next-nearest-neighbor transfer integrals t and t', while t_d denotes the intradimer coupling.

measurements do not reveal any sharp lattice anomaly down to $T = 1.5$ K; albeit there is a broad extremum of the expansion coefficient around 12 K with anomalous contraction up to 18–20 K [29]. On the other hand, results of nuclear magnetic resonance (NMR) and specific heat were interpreted in terms of a gapless magnetic ground state [13]. Recently the emergence of a low-entropy state has been inferred below around 11 K based on ac-transport measurements [31]. Here, we present electron spin resonance (ESR) investigations of κ-AgCN single crystals. This method is known to be crucial for any deeper understanding of the magnetic ground state [18]. We show that at high temperatures the magnetic response of κ-AgCN can be approximated by the susceptibility expected from a two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet with an exchange interaction $J/k_B \approx 175$ K on a triangular lattice; most important, the rapid drop in spin susceptibility at low temperatures suggests a gapped magnetic ground state.

The single crystals of κ-AgCN were grown by electrochemical-oxidation method [13] in different laboratories. For sample characterization crystals were checked by resistivity and magnetic susceptibility measurements using standard methods. The crystals were oriented according to morphology supplemented by infrared optical reflectivity [18,20,32,33]. Our ESR spectra were collected in a Bruker X-band spectrometer ($\nu = 9.47$ GHz) equipped with a continuous flow He-cryostat working down to $T = 1.8$ K when pumped. In addition, we have also employed a Q-band spectrometer (Bruker Elexsys 500) at 34 GHz operating down to 4 K. As a complementary method, superconducting coplanar resonators were used to obtain the ESR spectra at $\nu = 11.5$ and 18.7 GHz (K band); for more details see the Supplemental Material [34] (see also Refs. [23–26] therein).

At room temperature, while for $H_{\rm dc} \parallel a^*$ the ESR absorption can be modeled by a single Lorentzian line shape, along the b and c directions the ESR line shape is Dysonian in nature (Fig. S2) [34]. The conductivity within the bc plane is considerable at room temperature, although κ-AgCN is a correlated insulator far away from the Mott metal-insulator boundary. This is in accord with dc, ac, and optical conductivity measurements [13,20,31,33]. For each temperature the ESR spectra are analyzed to obtain the center frequency

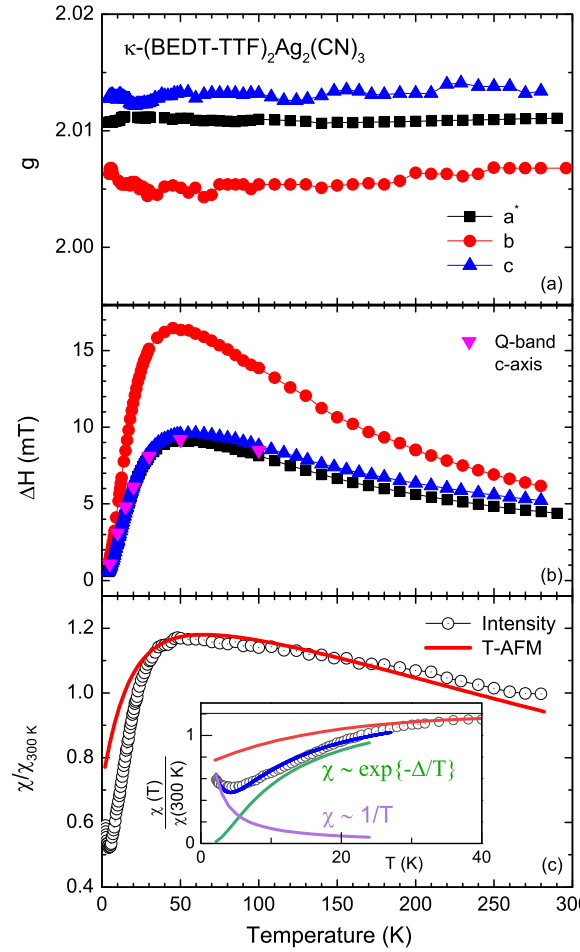

FIG. 2. Temperature dependence of (a) g factor and (b) linewidth for $H_{\rm dc}$ parallel to the a^*, b, and c axes, as indicated, recorded in the X band. The magenta down-pointing triangles in (b) correspond to data taken at 34 GHz (Q band) along the c axis. (c) ESR intensity of κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$ as a function of temperature. Upon cooling a maximum occurs around 50 K before susceptibility (χ) drops to less than half of its value. The red solid line corresponds to calculations of a two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnet on a triangular lattice with a coupling of $J/k_B = 175$ K. Below $T = 4$ K the spin susceptibility exhibits a small rise, as magnified in the inset. Besides the data (open circles) and the Heisenberg model (red line), we show a fit (blue line) of the low-T susceptibility by a Curie contribution (purple line) and resultant spin susceptibility of a gapped system (green line).

$h\nu = g\mu_B H_{\rm dc}$, the linewidth ΔH, and the intensity of the signal $I_{\rm ESR}$. In Fig. 2(a) $g(T)$ is plotted for each orientation a^*, b, and c; no considerable temperature dependence is observed. The linewidth ΔH, on the other hand, significantly varies with temperature, as presented in panel (b). As the temperature decreases, the lines become broader and $\Delta H(T)$ reaches a maximum around $T \approx 50$ K. Subsequently, $\Delta H(T)$ starts to decrease rapidly down to the lowest measured temperature of $T = 1.8$ K. We also show the linewidth obtained from Q-band data along the c axis, which matches the values derived from X-band data.

In Fig. 2(c) the temperature dependence of the spin susceptibility $\chi_s(T) \propto I_{\rm ESR}$ normalized to its room-temperature

value is plotted. As the temperature is reduced, the susceptibility increases slightly and exhibits a maximum around $T \approx 50\,\mathrm{K}$. At lower temperatures, it starts to decrease rapidly but does not vanish. Below approximately 4 K, the spin susceptibility rises slightly resembling a Curie tail. Overall, the temperature dependence of $\chi_s(T)$ does not reveal any signature of a phase transition to a long-range magnetically ordered state. The solid red line in panel (c) represents the theoretical curve for a two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnet on a triangular lattice (T-AFM) with nearest-neighbor exchange interaction $J/k_B = 175\,\mathrm{K}$ [35]. In this model, which is based on the high-temperature series expansion method, the magnetic susceptibility exhibits a maximum around $0.35J$ that matches well with the experiment. For $T < 30\,\mathrm{K}$, however, the spin susceptibility of κ-AgCN deviates from the model. In this context, comparison of the experimental susceptibility with other theoretical models such as the Lancoz method, the Monte Carlo method, etc., may also be useful.

Nonetheless, $\chi_s(T)$ shows an upturn below $T \approx 4\,\mathrm{K}$, which is quite dependent on the sample quality [34]. Such an enhancement is frequently observed in QSL systems at low temperatures [17,18]. Commonly this behavior is assigned to a Curie-type low-temperature T^{-1} response of paramagnetic impurity spins. However, there are other scenarios to be considered here, too [36]. In a system with random disorder, one possible ground state is the random singlet phase of a spin liquid, where the susceptibility shows a power law $\chi_s(T) \propto T^{-\gamma}$ ($\gamma < 1$). Such a phase is observed in systems with a considerable amount of disorder like doped Si, $YbMgGaO_4$, $1T$-TaS_2, etc. [37–40]. The emergence of an inhomogeneous energy gap was also shown as a possible scenario in materials, where spin singlets gradually appear with a spatially varying energy gap [41].

Therefore, to better understand the rapid drop of the spin susceptibility at low T, we model $\chi_s(T)$ with a combination of two contributions: a Curie term and an exponential decay with a fixed energy gap Δ. The fit is shown in the inset of Fig. 2(c), which matches the experimental only approximately assuming $\Delta \approx 10\,\mathrm{K}$. In addition, comparing I_{ESR} with the magnetic susceptibility obtained by standard SQUID magnetometry, we estimate an impurity concentration of $N \approx 0.002$ per unit cell, which matches quite well with the previous estimation [13,42]. We found considerable sample-to-sample variation of the Curie contribution (Fig. S6 in [34]). Interestingly, the first derivative of the susceptibility $d\chi_s(T)/dT$ indeed shows a broad feature around $T \approx 12\,\mathrm{K}$ (Fig. S4 in [34]), indicative of a distribution of the energy gap with an average of $\Delta \approx 10\,\mathrm{K}$. Interestingly, this temperature scale agrees with the temperature range where the ^{13}C NMR spectra starts broadening, stretched-exponential relaxation sets in, and T_1^{-1} steeply reduces towards a local minimum, below which a field-dependent maximum arises indicative of impurity spins [13,42].

Note that the linewidth also reduces rapidly at low temperatures. A similar tendency is often observed in one-dimensional spin-chain systems exhibiting a spin gap [43–45], where the decrease in $\Delta H(T)$ points towards the formation of spin singlets at lower temperatures. As a result, the relaxation time of the remaining orphan spins increases, yielding a reduction of the ESR linewidth. For a complete description we have first to consider the magnitude of the ΔH at elevated temperature, which provides additional information about the magnetic state of κ-AgCN. For this compound, the electrical conductivity strongly decreases on lowering the temperatures; thus we can neglect electron-phonon scattering and consider only sources of inhomogeneous broadening due to anisotropic interactions in the presence of strong isotropic exchange following the theory of exchange narrowing by Kubo and Tomita [46]. In the case of spin $S = 1/2$, dipole-dipole interaction, symmetric anisotropic exchange, and antisymmetric Dzyaloshinsky-Moriya (DM) interactions are the dominant sources of broadening [47]. In the present compound, only the DM interaction yields a significant linewidth with negligible contributions due to the other two types of interactions [34]. Indeed the existence of the DM interaction and its proper magnitude in κ salts has been discussed earlier [48,49]. Based on the identification of the DM interaction as a dominant source of line broadening at temperatures above the spin gap formation, the strong reduction of the linewidth at low temperatures clearly results from spin dimerization and corresponding singlet formation [50]. For the residual spins the DM interaction and symmetric anisotropic exchange practically vanish because of the lack of direct neighbors and the contribution of dipolar interactions reduces by $1/r^6$, where r denotes their mutual distance. Although the direct isotropic exchange does not connect the residual spins, fluctuations of the valence bonds work as a narrowing source and hence the line shape remains Lorentzian.

For more detailed discussion at low temperatures, Fig. 3 shows the low-temperature results obtained on κ-AgCN along the b axis at $\nu = 9.47$ and 18.7 GHz. In both cases the ESR intensity and absorption reveal a single Lorentzian line shape. The K-band linewidth (FWHM) increases by more than a factor of 2 when the temperature increases from 0.56 to 4 K. This is consistent with the behavior of $\Delta H(T)$ observed in the X band and Q band at high temperatures, as displayed in Fig. 2(b). The decrease in the linewidth discards the possibility of any long-range antiferromagnetic order down to $T = 0.56\,\mathrm{K}$ because this would lead to divergences of ΔH and FWHM. Also the g factor remains unchanged.

Although the low-temperature ESR absorption at X and K band can be modeled assuming a single Lorentzian line, the angular variation of the g factor and ΔH displayed in Figs. 3(e) and 3(f) provides a crucial information. The linewidth at $T = 2\,\mathrm{K}$ exhibits asymmetric angular variation along b and c axes and this asymmetry is highly sample dependent [34]. This gives a hint that there is indeed additional ESR absorption at low temperatures with similar anisotropy as indicated by the angular variation of the g factor. Here, we recall the broadened characteristic temperature of $T^* = 10-20\,\mathrm{K}$, which is quite different from the sister compound κ-CuCN where the exponential decay is relatively rapid. We believe that the ground state of κ-AgCN consists of finite-size domains of valence bond solids with inhomogeneous energy gaps. This explains the approximate match between experimental susceptibility and model curve assuming only a single energy gap in Fig. 2(c). In such a case, the additional ESR absorption and the Curie-like contribution may originate from the orphan spins lying as point or line defects across the

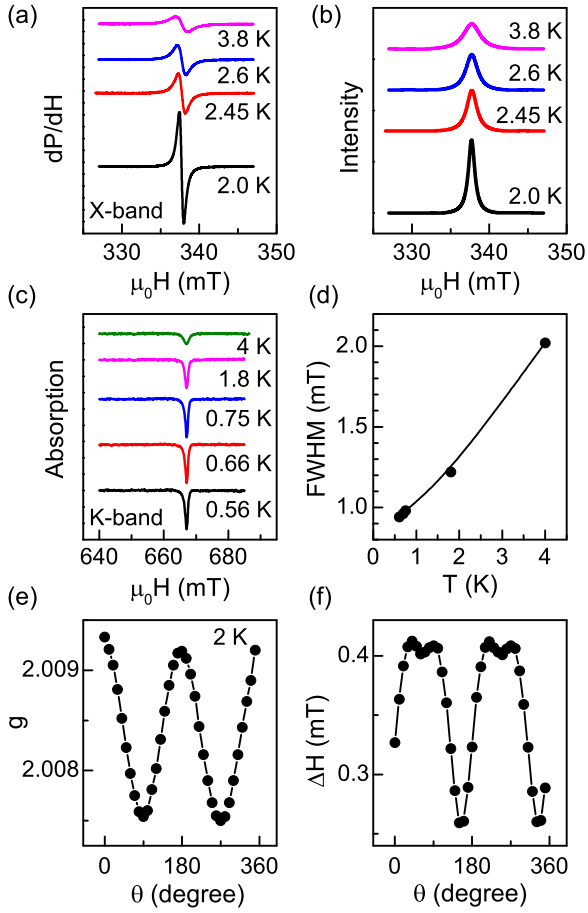

FIG. 3. Low-temperature ESR investigations on κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$. (a) X-band data and (b) integrated ESR spectra along the b axis below $T = 4\,\mathrm{K}$. (c) K-band absorption measured along b-axis by a parallel-plane resonator at $\nu = 18.7\,\mathrm{GHz}$ down to $T = 0.56\,\mathrm{K}$. (d) Temperature dependence of the corresponding full width at half maximum (FWHM). (e),(f) Angular variation of the g factor and linewidth ΔH recorded in the X band at $T = 2\,\mathrm{K}$.

domain wall. Defects may have strong influence on the ground state of the frustrated system, which is discussed theoretically. The random singlet state has been proposed to be the most possible ground state, however, only above a certain critical concentration of intrinsic or extrinsic disorder [51]. Also, the random singlet state is gapless and does not have any characteristic energy scale other than the exchange interaction J. In our case, the defect concentration is small. In the presence of weak randomness/disorder, the long-range valence bond solid phase (VBS) state spontaneously breaks up into finite size domains of different VBS patterns [38,52]. In such a case, orphan spins form in the form of point defects and near the domain walls.

At this point, we emphasize the angular dependence of the g-factor anisotropy in κ-CuCN and κ-AgCN around $T^\star$ shown in Fig. S10 [34]. We see that the g factor is reversed in κ-CuCN around T^*, as seen in Fig. S10(c) in [34], which is absent in κ-AgCN. A reversal of the g factor has also been observed for the spin liquid candidates Herbertsmithite [53] and α-$RuCl_3$ monolayers [54], which are proposed to be driven by lattice distortion. One possible explanation may be the less pronounced lattice effects in κ-AgCN compared to κ-CuCN [15,19,24]; albeit also for κ-AgCN there is a broad extremum in thermal expansion coefficient around 12 K [29] coincident with low-entropy signatures below this temperature in pressure-dependent dielectric measurements [31]. Overall, the different situation in κ-AgCN compared to κ-CuCN may be the result of distinct lattice properties.

On the theoretical side, although many models yield the presence of a quantum-spin-liquid state, the precise nature of the ground state, whether it is gapped or not, remains inconclusive so far [55–61]. Indeed, $S = \frac{1}{2}$ J_1-J_2 Heisenberg models on the triangular lattice predict gapped spin liquid states in the presence of weak next-nearest-neighbor exchange [62–64]. In this respect, unlike κ-CuCN the strongly correlated compound κ-AgCN without significant lattice anomaly can serve as a model system.

In conclusion, we have investigated the magnetic state of the spin liquid candidate κ-AgCN down to $T = 0.56\,\mathrm{K}$ using ESR spectroscopy at different frequencies. Although the system with $S = \frac{1}{2}$ on a triangular lattice behaves as a two-dimensional Heisenberg antiferromagnet at high temperatures, the rapid drop of magnetic susceptibility and a weak Curie tail at low T can be explained by assuming a gapped ground state with a small amount of impurity spins. An energy gap of $\Delta \approx 10\,\mathrm{K}$ in magnetic susceptibility along with broad features observed in complementary experiments is taken as an indication of a relevant characteristic temperature scale $T^* \approx 10-20\,\mathrm{K}$. The difference between the two prime spin-liquid candidates κ-CuCN and κ-AgCN might lie in the distinct involvement of the lattice degrees of freedom as well as other types and quantity of impurities.

We warmly thank M. Allain for checking the crystals produced in Angers; M. Girault is acknowledged for help with the preparation of the single crystals; G. Untereiner provided technical help with the ESR experiments in Stuttgart. We acknowledge the relevant discussions with K. Kanoda, R. K. Kremer, and M. Hemmida. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) via Grant No. DR228/68-1.

[1] Y. Zhou, K. Kanoda, and T.-K. Ng, Quantum spin liquid states, Rev. Mod. Phys. **89**, 025003 (2017).

[2] C. Broholm, R. J. Cava, S. A. Kivelson, D. G. Nocera, M. R. Norman, and T. Senthil, Quantum spin liquids, Science **367**, eaay0668 (2020).

[3] P. Anderson, Resonating valence bonds: A new kind of insulator? Mater. Res. Bull. **8**, 153 (1973); P. Fazekas and P. W. Anderson, On the ground state properties of the anisotropic triangular antiferromagnet, Philos. Mag. **30**, 423 (1974).

[4] P. W. Anderson, The resonating valence bond state in La_2CuO_4 and superconductivity, Science **235**, 1196 (1987).

[5] A. O. Scheie, E. A. Ghioldi, J. Xing, J. A. M. Paddison, N. E. Sherman, M. Dupont, L. D. Sanjeewa, S. Lee, A. J. Woods, D. Abernathy, D. M. Pajerowski, T. J. Williams, S.-S. Zhang, L. O.

Manuel, A. E. Trumper, C. D. Pemmaraju, A. S. Sefat, D. S. Parker, T. P. Devereaux, R. Movshovich *et al.*, Proximate spin liquid and fractionalization in the triangular antiferromagnet $KYbSe_2$, Nat. Phys. **20**, 74 (2024).

[6] Y. Shirata, H. Tanaka, A. Matsuo, and K. Kindo, Experimental realization of a spin-1/2 triangular-lattice heisenberg antiferromagnet, Phys. Rev. Lett. **108**, 057205 (2012).

[7] T. Susuki, N. Kurita, T. Tanaka, H. Nojiri, A. Matsuo, K. Kindo, and H. Tanaka, Magnetization process and collective excitations in the $s = 1/2$ triangular-lattice Heisenberg antiferromagnet $Ba_3CoSb_2O_9$, Phys. Rev. Lett. **110**, 267201 (2013).

[8] P. Khuntia, M. Velazquez, Q. Barthélemy, F. Bert, E. Kermarrec, A. Legros, B. Bernu, L. Messio, A. Zorko, and P. Mendels, Gapless ground state in the archetypal quantum kagome antiferromagnet $ZnCu_3(OH)_6Cl_2$, Nat. Phys. **16**, 469 (2020).

[9] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Spin liquid state in an organic Mott insulator with a triangular lattice, Phys. Rev. Lett. **91**, 107001 (2003).

[10] U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, H. A. Charlier Jr., J. E. Heindl, G. A. Yaconi, B. J. Love, M. W. Lathrop, J. E. Schirber, D. L. Overmyer, J. Ren, and M.-H. Whangbo, Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$: The first organic superconductor containing a polymeric copper cyanide anion, Inorg. Chem. **30**, 2586 (1991).

[11] M. Tamura, A. Nakao, and R. Kato, Frustration-induced valence-bond ordering in a new quantum triangular antiferromagnet based on [Pd(dmit)$_2$], J. Phys. Soc. Jpn. **75**, 093701 (2006).

[12] T. Itou, A. Oyamada, S. Maegawa, and R. Kato, Instability of a quantum spin liquid in an organic triangular-lattice antiferromagnet, Nat. Phys. **6**, 673 (2010).

[13] Y. Shimizu, T. Hiramatsu, M. Maesato, A. Otsuka, H. Yamochi, A. Ono, M. Itoh, M. Yoshida, M. Takigawa, Y. Yoshida, and G. Saito, Pressure-tuned exchange coupling of a quantum spin liquid in the molecular triangular lattice κ-(ET)$_2$Ag$_2$(CN)$_3$, Phys. Rev. Lett. **117**, 107203 (2016).

[14] M. Dressel and S. Tomić, Molecular quantum materials: Electronic phases and charge dynamics in two-dimensional organic solids, Adv. Phys. **69**, 1 (2020).

[15] R. S. Manna, M. de Souza, A. Brühl, J. A. Schlueter, and M. Lang, Lattice effects and entropy release at the low-temperature phase transition in the spin-liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. Lett. **104**, 016403 (2010).

[16] M. Poirier, M. de Lafontaine, K. Miyagawa, K. Kanoda, and Y. Shimizu, Ultrasonic investigation of the transition at 6 K in the spin-liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **89**, 045138 (2014).

[17] K. G. Padmalekha, M. Blankenhorn, T. Ivek, L. Bogani, J. A. Schlueter, and M. Dressel, ESR studies on the spin-liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$: Anomalous response below $T = 8$ K, Phys. B: Condens. Matter **460**, 211 (2015).

[18] B. Miksch, A. Pustogow, M. Javaheri Rahim, A. A. Bardin, K. Kanoda, J. A. Schlueter, R. Hübner, M. Scheffler, and M. Dressel, Gapped magnetic ground state in quantum spin liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Science **372**, 276 (2021).

[19] A. Pustogow, Thirty-year anniversary of κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$: Reconciling the spin gap in a spin-liquid candidate, Solids **3**, 93 (2022).

[20] A. Pustogow, M. Bories, A. Löhle, R. Rösslhuber, E. Zhukova, B. Gorshunov, S. Tomić, J. A. Schlueter, R. Hübner, T. Hiramatsu, Y. Yoshida, G. Saito, R. Kato, T.-H. Lee, V. Dobrosavljević, S. Fratini, and M. Dressel, Quantum spin liquids unveil the genuine Mott state, Nat. Mater. **17**, 773 (2018).

[21] A. Pustogow, Y. Kawasugi, H. Sakurakoji, and N. Tajima, Chasing the spin gap through the phase diagram of a frustrated Mott insulator, Nat. Commun. **14**, 1960 (2023).

[22] Y. Kawasugi, S. Yamazaki, A. Pustogow, and N. Tajima, Negative magnetoresistance near the Mott metal–insulator transition in the quantum spin liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, J. Phys. Soc. Jpn. **92**, 065001 (2023).

[23] K. Riedl, R. Valentí, and S. M. Winter, Critical spin liquid versus valence-bond glass in a triangular-lattice organic antiferromagnet, Nat. Commun. **10**, 2561 (2019).

[24] M. Matsuura, T. Sasaki, M. Naka, J. Müller, O. Stockert, A. Piovano, N. Yoneyama, and M. Lang, Phonon renormalization effects accompanying the 6 K anomaly in the quantum spin liquid candidate κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. Res. **4**, L042047 (2022).

[25] K. Riedl, E. Gati, and R. Valenti, Ingredients for generalized models of κ-phase organic charge-transfer salts: A review, Crystals **12**, 1689 (2022).

[26] J. Liebman, K. Miyagawa, K. Kanoda, and N. Drichko, Novel dipole-lattice coupling in the quantum-spin-liquid material κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **110**, 165105 (2024).

[27] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Revision of model parameters for κ-type charge transfer salts: An *ab initio* study, Phys. Rev. Lett. **103**, 067004 (2009).

[28] P. Foury-Leylekian, V. Ilakovac, P. Fertey, V. Baledent, O. Milat, K. Miyagawa, K. Kanoda, T. Hiramatsu, Y. Yoshida, G. Saito, P. Alemany, E. Canadell, S. Tomic, and J.-P. Pouget, New insights into the structural properties of κ-(BEDT − TTF)$_2$Ag$_2$(CN)$_3$ spin liquid, Acta Crystallogr. B **76**, 581 (2020).

[29] S. Hartmann, E. Gati, Y. Yoshida, G. Saito, and M. Lang, Thermal expansion studies on the spin-liquid-candidate system κ-(BEDT − TTF)$_2$Ag$_2$(CN)$_3$, Phys. Status Solidi B **256**, 1800640 (2019).

[30] T. Hiramatsu, Y. Yoshida, G. Saito, A. Otsuka, H. Yamochi, M. Maesato, Y. Shimizu, H. Ito, Y. Nakamura, H. Kishida, M. Watanabe, and R. Kumai, Design and preparation of a quantum spin liquid candidate κ-(ET)$_2$Ag$_2$(CN)$_3$ having a nearby superconductivity, Bull. Chem. Soc. Jpn. **90**, 1073 (2017).

[31] R. Rösslhuber, R. Hübner, M. Dressel, and A. Pustogow, Pressure-dependent dielectric response of the frustrated Mott insulator κ-(BEDT − TTF)$_2$Ag$_2$(CN)$_3$, Phys. Rev. B **107**, 075113 (2023).

[32] S. Elsässer, D. Wu, M. Dressel, and J. A. Schlueter, Power-law dependence of the optical conductivity observed in the quantum spin-liquid compound κ-(BEDT − TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **86**, 155150 (2012).

[33] M. Pinterić, P. Lazić, A. Pustogow, T. Ivek, M. Kuveždić, O. Milat, B. Gumhalter, M. Basletić, M. Čulo, B. Korin-Hamzić,

A. Löhle, R. Hübner, M. S. Alonso, T. Hiramatsu, Y. Yoshida, G. Saito, M. Dressel, and S. Tomić, Anion effects on electronic structure and electrodynamic properties of the Mott insulator κ-(BEDT − TTF)$_2$Ag$_2$(CN)$_3$, Phys. Rev. B **94**, 161105(R) (2016).

[34] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.111.L220404 for details on the measurement technique. In addition to the raw data, the sample to sample variation is discussed, as well as the angular dependence, which also includes Refs. [65–67].

[35] N. Elstner, R. R. P. Singh, and A. P. Young, Finite temperature properties of the spin-1/2 Heisenberg antiferromagnet on the triangular lattice, Phys. Rev. Lett. **71**, 1629 (1993).

[36] R. Pohle and L. D. C. Jaubert, Curie-law crossover in spin liquids, Phys. Rev. B **108**, 024411 (2023).

[37] T. Furukawa, K. Miyagawa, T. Itou, M. Ito, H. Taniguchi, M. Saito, S. Iguchi, T. Sasaki, and K. Kanoda, Quantum spin liquid emerging from antiferromagnetic order by introducing disorder, Phys. Rev. Lett. **115**, 077001 (2015).

[38] I. Kimchi, A. Nahum, and T. Senthil, Valence bonds in random quantum magnets: Theory and application to YbMgGaO$_4$, Phys. Rev. X **8**, 031028 (2018).

[39] S. Pal, K. Kumar, R. Sharma, A. Banerjee, S. B. Roy, J.-G. Park, A. K. Nigam, and S.-W. Cheong, Possible glass-like random singlet magnetic state in 1T-TaS$_2$, J. Phys.: Condens. Matter **32**, 035601 (2020).

[40] S. Pal and S. Roy, Understanding the magnetic response of the quantum spin liquid compound 1T-TaS$_2$, Phys. B: Condens. Matter **643**, 414121 (2022).

[41] J. Wang, W. Yuan, P. M. Singer, R. W. Smaha, W. He, J. Wen, Y. S. Lee, and T. Imai, Emergence of spin singlets with inhomogeneous gaps in the kagome lattice Heisenberg antiferromagnets Zn-barlowite and herbertsmithite, Nat. Phys. **17**, 1109 (2021).

[42] A. Pustogow, T. Le, H.-H. Wang, Y. Luo, E. Gati, H. Schubert, M. Lang, and S. E. Brown, Impurity moments conceal low-energy relaxation of quantum spin liquids, Phys. Rev. B **101**, 140401(R) (2020).

[43] F. Chabre, A. M. Ghorayeb, P. Millet, V. A. Pashchenko, and A. Stepanov, Low-temperature behavior of the ESR linewidth in a system with a spin gap: η-Na$_{1.286}$V$_2$O$_5$, Phys. Rev. B **72**, 012415 (2005).

[44] J. Deisenhofer, R. M. Eremina, A. Pimenov, T. Gavrilova, H. Berger, M. Johnsson, P. Lemmens, H.-A. K. von Nidda, A. Loidl, K.-S. Lee, and M.-H. Whangbo, Structural and magnetic dimers in the spin-gapped system CuTe$_2$O$_5$, Phys. Rev. B **74**, 174421 (2006).

[45] A. N. Vasiliev, O. S. Volkova, E. A. Zvereva, A. V. Koshelev, V. S. Urusov, D. A. Chareev, V. I. Petkov, M. V. Sukhanov, B. Rahaman, and T. Saha-Dasgupta, Valence-bond solid as the quantum ground state in honeycomb layered urusovite CuAl(AsO$_4$)O, Phys. Rev. B **91**, 144406 (2015).

[46] R. Kubo and K. Tomita, A general theory of magnetic resonance absorption, J. Phys. Soc. Jpn. **9**, 888 (1954).

[47] I. Yamada, M. Nishi, and J. Akimitsu, Electron paramagnetic resonance governed by the Dzyaloshinsky-Moriya antisymmetric exchange interaction in CuGeO$_3$, J. Phys.: Condens. Matter **8**, 2625 (1996).

[48] D. F. Smith, C. P. Slichter, J. A. Schlueter, A. M. Kini, and R. G. Daugherty, Precise determination of the orientation of the Dzialoshinskii-Moriya vector in κ-(BEDT − TTF)$_2$Cu[N(CN)$_2$]Cl, Phys. Rev. Lett. **93**, 167002 (2004).

[49] S. M. Winter, K. Riedl, and R. Valenti, Importance of spin-orbit coupling in layered organic salts, Phys. Rev. B **95**, 060404(R) (2017).

[50] M. A. Fayzullin, R. M. Eremina, M. V. Eremin, A. Dittl, N. van Well, F. Ritter, W. Assmus, J. Deisenhofer, H.-A. Krug von Nidda, and A. Loidl, Spin correlations and Dzyaloshinskii-Moriya interaction in Cs$_2$CuCl$_4$, Phys. Rev. B **88**, 174421 (2013).

[51] H. Kawamura and K. Uematsu, Nature of the randomness-induced quantum spin liquids in two dimensions, J. Phys.: Condens. Matter **31**, 504003 (2019).

[52] L. Liu, H. Shao, Y.-C. Lin, W. Guo, and A. W. Sandvik, Random-singlet phase in disordered two-dimensional quantum magnets, Phys. Rev X **8**, 041040 (2018).

[53] A. Zorko, M. Herak, M. Gomilšek, J. van Tol, M. Velázquez, P. Khuntia, F. Bert, and P. Mendels, Symmetry reduction in the quantum kagome antiferromagnet herbertsmithite, Phys. Rev. Lett. **118**, 017202 (2017).

[54] B. Yang, Y. M. Goh, S. H. Sung, G. Ye, S. Biswas, D. A. S. Kaib, R. Dhakal, S. Yan, C. Li, S. Jiang, F. Chen, H. Lei, R. He, R. Valentí, S. M. Winter, R. Hovden, and A. W. Tsen, Magnetic anisotropy reversal driven by structural symmetry-breaking in monolayer α-RuCl$_3$, Nat. Mater. **22**, 50 (2023).

[55] Y.-F. Jiang and H.-C. Jiang, Nature of quantum spin liquids of the $s = \frac{1}{2}$ Heisenberg antiferromagnet on the triangular lattice: A parallel DMRG study, Phys. Rev. B **107**, L140411 (2023).

[56] N. E. Sherman, M. Dupont, and J. E. Moore, Spectral function of the $J_1 - J_2$ Heisenberg model on the triangular lattice, Phys. Rev. B **107**, 165146 (2023).

[57] A. Szasz, J. Motruk, M. P. Zaletel, and J. E. Moore, Chiral spin liquid phase of the triangular lattice Hubbard model: A density matrix renormalization group study, Phys. Rev. X **10**, 021042 (2020).

[58] A. Szasz and J. Motruk, Phase diagram of the anisotropic triangular lattice Hubbard model, Phys. Rev. B **103**, 235132 (2021).

[59] Y. Iqbal, W.-J. Hu, R. Thomale, D. Poilblanc, and F. Becca, Spin liquid nature in the Heisenberg $J_1 - J_2$ triangular antiferromagnet, Phys. Rev. B **93**, 144411 (2016).

[60] T. Shirakawa, T. Tohyama, J. Kokalj, S. Sota, and S. Yunoki, Ground-state phase diagram of the triangular lattice Hubbard model by the density-matrix renormalization group method, Phys. Rev. B **96**, 205130 (2017).

[61] S. Hu, W. Zhu, S. Eggert, and Y.-C. He, Dirac spin liquid on the spin-1/2 triangular Heisenberg antiferromagnet, Phys. Rev. Lett. **123**, 207203 (2019).

[62] Z. Zhu and S. R. White, Spin liquid phase of the $s = \frac{1}{2}J_1 - J_2$ Heisenberg model on the triangular lattice, Phys. Rev. B **92**, 041105(R) (2015).

[63] W.-J. Hu, S.-S. Gong, W. Zhu, and D. N. Sheng, Competing spin-liquid states in the spin-$\frac{1}{2}$ Heisenberg model on the triangular lattice, Phys. Rev. B **92**, 140403(R) (2015).

[64] B.-B. Chen, Z. Chen, S.-S. Gong, D. N. Sheng, W. Li, and A. Weichselbaum, Quantum spin liquid with emergent chiral order in the triangular-lattice Hubbard model, Phys. Rev. B **106**, 094420 (2022).

[65] D. S. Rausch, M. Thiemann, M. Dressel, D. Bothner, D. Koelle, R. Kleiner, and M. Scheffler, Superconducting coplanar microwave resonators with operating frequencies up to 50 GHz, J. Phys. D: Appl. Phys. **51**, 465301 (2018).

[66] M. Scheffler, K. Schlegel, C. Clauss, D. Hafner, C. Fella, M. Dressel, M. Jourdan, J. Sichelschmidt, C. Krellner, C. Geibel, and F. Steglich, Microwave spectroscopy on heavy-fermion systems: Probing the dynamics of charges and magnetic moments, Phys. Status Solidi B **250**, 439 (2013).

[67] B. Miksch, M. Dressel, and M. Scheffler, Cryogenic frequency-domain electron spin resonance spectrometer based on coplanar waveguides and field modulation, Rev. Sci. Instrum. **91**, 025106 (2020).