Disorder and slowing magnetic dynamics in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br

T. Le,[1] A. Pustogow,[1] J. Wang,[2] A. Henderson,[3,4] T. Siegrist,[4,5] J. A. Schlueter,[6] and S. E. Brown[1]
[1]Department of Physics and Astronomy, UCLA, Los Angeles, California 90095, USA
[2]Kuang Yaming Honors School, Nanjing University, Nanjing 210023, China
[3]Department of Physics, Florida State University, Tallahassee, Florida 32310, USA
[4]National High Magnetic Field Laboratory, 1800 E Paul Dirac Drive, Tallahassee, Florida 32310, USA
[5]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida 32310, USA
[6]Division of Materials Research, National Science Foundation, Alexandria, Virginia 22314, USA

(Received 22 May 2020; revised 27 August 2020; accepted 29 September 2020; published 16 November 2020)

The magnetic properties of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br are examined using ^{13}C NMR methods. Measurements of the spin lattice relaxation rate indicate a first-order metal-insulator transition at $T_{MI} = 90$ K and a pronounced maximum at 5 K, ascribed to dynamical slowing of magnetic fluctuations. T_{MI} is also associated with the onset of weak line broadening, indicative of a disordered form of charge disproportionation. The line width increases strongly for $T < 40$ K, exceeding 4000 ppm at 2 K and applied magnetic field $B = 9.50$ T. The lack of long-range magnetic order is attributed to the disordered charge disproportionation onsetting at higher temperature.

DOI: 10.1103/PhysRevB.102.184417

I. INTRODUCTION

Since Anderson proposed a new phase of matter on the $S = 1/2$ insulating triangular lattice, dubbed the resonating valence bond state [1], it is widely accepted that the search for quantum spin liquid (QSL) ground states in dimensions $D > 1$ is appropriately guided toward geometrically frustrated lattices. Indeed, over the past two decades, the majority of quasi-two-dimensional QSL candidates were identified in triangular, kagome, or honeycomb hosts [2–6]. First among many now considered as candidates for QSL states was the charge-transfer salt, κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [κ-CuCN; BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene] [7], where organic donor molecules are separated by polymeric anion sheets, as shown in Fig. 1(a). It is commonly described as a 1/2-filled Mott insulator on a slightly anisotropic triangular lattice, with the ratio of intralayer transfer integrals close to unity, $t'/t \approx 0.83$ [8]. The empirical observations identifying this compound as a QSL candidate include the lack of magnetic order to temperatures about two orders of magnitude less than the inferred nearest-neighbor exchange energies [7,9], and an interpolated value for $\gamma = C_p/T > 0$ (C_p is the specific heat), indicative of a gapless excitation spectrum [10]. Much more recently, experiments on the isomorphic κ-(BEDT-TTF)$_2$Ag$_2$(CN)$_3$ (κ-AgCN) [11] revealed a similar lack of magnetic order [12]. Nevertheless, concerns on the interpretation as a gapless QSL in the magnetically disordered κ phases have not been set aside. For example, thermal transport [13] experiments indicate that the continuum of excitations leading to $\gamma \neq 0$ are localized and therefore possibly associated with quenched disorder. Moreover, the so-called 6 K anomaly in the thermodynamic properties of κ-CuCN awaits further clarification [10,14,15].

The isomorph κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (κ-CuCl), orders antiferromagnetically at $T_N = 26$ K [16]. For long, the operational hypothesis for the different behaviors was the reduced frustration in κ-CuCl compared to κ-CuCN [7]. However, after 500 hours of x-ray irradiation, signatures for long-range order are no longer observed in κ-CuCl [17], and the results were taken to highlight the possible role of quenched disorder in suppressing magnetic order. For at least the above-mentioned reasons, a clear understanding of the ground state remains elusive, and related to that the absence of magnetic order in the κ-CuCN and κ-AgCN compounds.

A complementary pathway towards understanding of the low-temperature properties of the κ-phase systems may come by way of investigating κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl (κ-HgCl) and κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br (κ-HgBr). These materials differ with respect to the strength of structural dimerization, and its relationship to the intradimer transfer integral t_d as defined in Fig. 1(b), left side. Namely, they involve significantly smaller ratio t_d/t than κ-CuCN, κ-AgCN and κ-CuCl indicated above [18]. As such, the Hg-based compounds are considered more susceptible to charge order [see Fig. 1(b) right] because the intersite Coulomb interaction V is more relevant as t_d is reduced [19]. This is important here since charge order generally reduces frustration, as discussed in Ref. [20], for instance. The important question arises, whether the magnetic ground state of the κ-phase materials could be controlled or affected by stabilizing/destabilizing charge order [21].

An empirical signature for charge order (CO) in the BEDT-TTF-based charge-transfer salts is a distinct metal-insulator transition (MIT) also coincident with the symmetry-breaking onset of CO. Both compounds, κ-HgCl and κ-HgBr, undergo a discontinuous MIT, at 30 K and 90 K, respectively. Here,

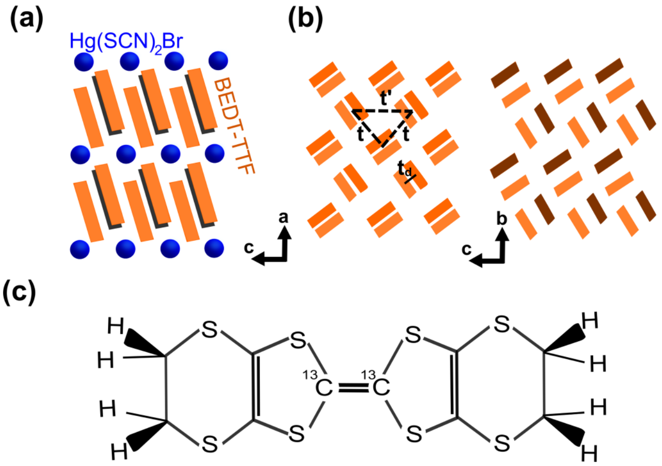

FIG. 1. (a) Structure of κ-HgBr, which consists of alternating layers of anions (blue) and (BEDT-TTF)$_2$ cations (orange) along the *a* axis. (b) Intralayer arrangement of cations in the *bc* plane with the respective transfer integrals, as indicated. While the left side depicts a strongly dimerized structure ($t_d \gg t, t'$), giving rise to Mott-insulating behavior, weakly bound dimers (right) pronounce intersite Coulomb interaction, with a tendency to charge order. Charge-rich and -poor molecules are distinguished by light and dark colors, respectively. (c) The two central carbon atoms of BEDT-TTF have been spin labeled by ^{13}C for NMR investigations.

we report on ^{13}C NMR spectroscopy and relaxation measurements of κ-HgBr focusing on the nature of the MIT, and the emergent low-temperature magnetic properties.

In spite of the MIT and the expectation for reduced frustration, a proposed ground state for κ-HgBr is a gapless QSL [22], similar to that discussed for κ-CuCN and κ-AgCN. As described, a key element for stabilization of a QSL in κ-HgBr is that it emerges from a highly frustrated intermediate phase, the quantum dipole liquid (QDL) [23]. The QDL is described as an insulating phase exhibiting short-range, fluctuating charge order for $T \to 0$. In this picture, the magnetic frustration is maintained if the temporal charge correlations are sufficiently short so as to suppress an associated reduced frustration.

Our experimental results challenge this interpretation of κ-HgBr. We find evidence for charge disproportionation (CD) in the ^{13}C NMR spectra at $T < T_{MI}$. Without well-defined, resolved spectral features, there is a case for associating the CD with considerable quenched disorder and a resulting widely distributed disproportionation in the insulating state. On cooling to $T < 40$ K, there is enormous line broadening, that is an increase in full width half maximum (FWHM), that we associate with short-range magnetic correlations. Thus, the ^{13}C NMR results indicate that κ-HgBr is not a QDL, and whether the magnetic ground state is quantum disordered or not remains an open question. However, our findings include inhomogeneous line widths one order of magnitude greater than for κ-CuCN [9], and spin-lattice relaxation rates two orders of magnitude greater. We propose that both are linked to substantial exchange disorder in κ-HgBr, which results from the strongly inhomogeneous short-range CD. Since the freezing of ethylene end groups (EEG) in related κ-phase compounds occurs around $T^* \approx 60$ K [24], which is below $T_{\rm MI}$, we suggest that charge order is strongly affected by the associated quenched disorder.

II. EXPERIMENTAL DETAILS

Single crystals of κ-HgBr used in this study were synthesized by the standard electrochemical method, as previously reported [25]. BEDT-TTF with the ^{13}C central atoms labeled was obtained from Aldrich. The electrolyte consisted of a mixture of Hg(SCN)$_2$ and [P(C$_6$H$_5$)$_4$]Br in a 90/10 1,1,2-trichloroethane/ethanol solvent. As is usual, the relevant hyperfine fields are associated with 100% ^{13}C spin labeling of the two bridging central carbon sites of the BEDT-TTF molecules, see Fig. 1(c). A full crystal structure determination was performed (for crystals with a natural isotopic abundance) with a more complete x-ray diffraction data set and refinement than previously reported [26,27]. See Supplemental Material [28] for details on how to obtain the crystallographic data. NMR measurements on a crystal with approximate dimensions $1.5 \times 1.5 \times 0.10$ mm^3 were performed using a home-built homodyne spectrometer at magnetic field strengths of $B = 9.50$ T and 6.54 T, orientated parallel to the a^* axis, to an uncertainty of 10°. The relaxation rates, T_1^{-1} and T_2^{-1}, approach extrema when $B \parallel a^*$, thus are not expected to change significantly within the stated range of variation. A variable-temperature helium gas flow cryostat provided the necessary cooling for measurements covering the range $2\text{ K} < T < 115$ K.

III. RESULTS AND ANALYSIS

As shown in Fig. 2(c), metallic behavior with temperature-independent $(T_1T)^{-1}$ occurs for $T > T_{MI}$. The discontinuous

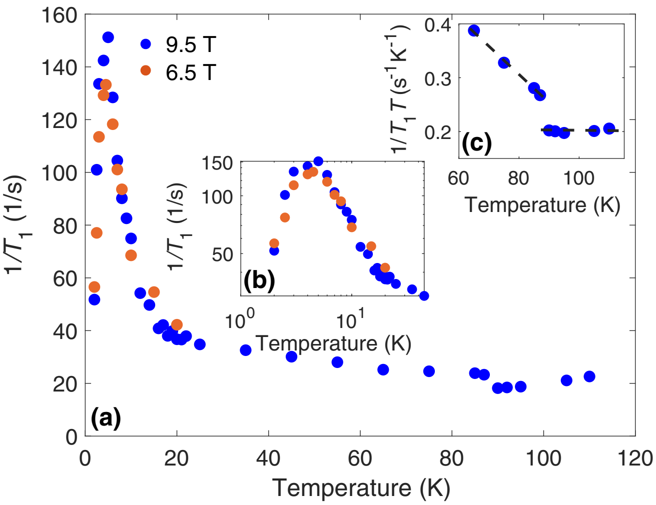

FIG. 2. (a) The spin lattice relaxation rate, acquired at 6.5 T and 9.5 T, as a function of temperature. At higher temperatures, the pulse excitations are nonselective. However, as a result of large inhomogeneous line widths and a fixed spectrometer bandwidth, the results below 40 K correspond only to the center of the spectrum. (b) The maximum in T_1^{-1} is highlighted on a logarithmic scale. (c) $(T_1T)^{-1}$ emphasizes the metal-insulator transition at $T_{\rm MI} = 90$ K.

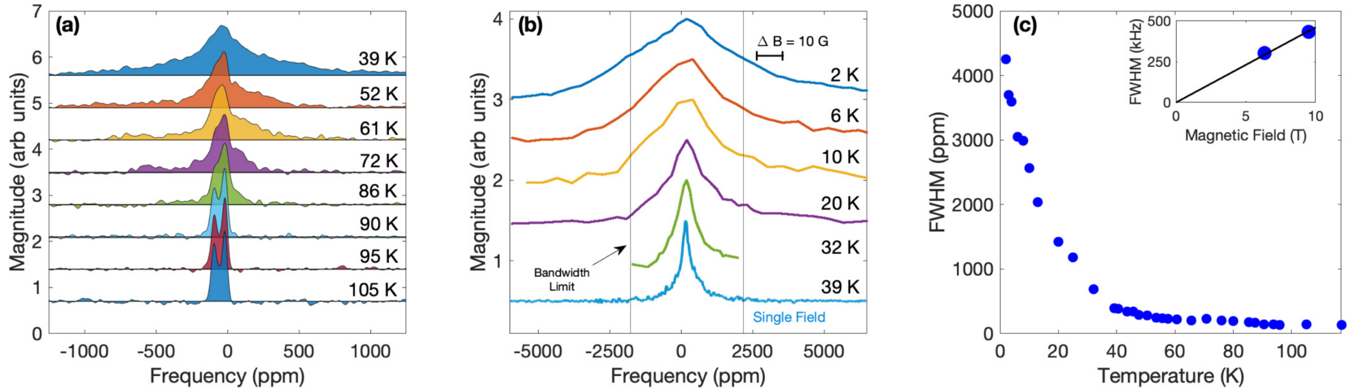

FIG. 3. (a) Temperature-dependent evolution of ^{13}C NMR spectra at 9.5 T (101.660 MHz). (b) Due to excessive line broadening, the spectra below 39 K were acquired via magnetic field sweeps. The 39 K spectrum from single field acquisition is included for comparison. (c) Full width half maximum (FWHM) of the 9.5 T spectra as a function of temperature. FWHM were obtained from the entire, broad spectrum. Inset: Field dependence at 2 K of FWHM.

increase at $T_{\mathrm{MI}} = 90$ K is consistent with the previously reported first-order MIT [29,30], very similar to the abrupt jump of T_1^{-1} seen in κ-HgCl when charge order sets in Ref. [31]. Upon cooling to $T < T_{\mathrm{MI}}$, a weak temperature dependence is observed, characteristic of paramagnetic behavior. A notable increase in T_1^{-1} occurs at $T \lesssim 20$ K, forming a maximum at $T \simeq 5$ K. We find only weak variations between the two field strengths, 6.54 and 9.50 T, although some care should be taken as the pulse excitations are selective as a consequence of the increasingly large and field-dependent line widths.

While the spectra in Fig. 3(a) exhibit no appreciable temperature dependence in the metallic state, a small but distinct increase of the line width sets in below T_{MI} and the spectral features are seen to broaden. A much stronger inhomogeneous broadening develops below $T = 40$ K [Fig. 3(b)], in the same temperature range as the strong increase in T_1^{-1} as shown in Fig. 3(c). At the lowest temperature measured here ($T = 2$ K, $B = 9.5$ T), the field-swept line width is 4320 ppm.

T_2^{-1} decreases down to $T \simeq 60$ K, as shown in Fig. 4(b), and remains roughly constant down to 20 K, settling at ${T_2^{-1}}_{\mathrm{min}} \simeq 0.3\ \mathrm{ms}^{-1}$. The temperature-independent T_2^{-1}, combined with the considerably larger, steadily changing line widths in the insulating state, suggests the spectra are inhomogeneously broadened from a distribution of hyperfine fields, which we will interpret below as a signature of CD for $T < T_{\mathrm{MI}}$. An increase in T_2^{-1} accompanies the steep rise of T_1^{-1} below 20 K.

The behavior of the homogeneous and inhomogeneous line width, as well as T_1^{-1} in the metallic regime $T > T_{\mathrm{MI}}$, is typical of conducting (BEDT-TTF)$_2X$ compounds. That is, $(T_1T)^{-1}$ changes only weakly with temperature, and the decreasing T_2^{-1} upon cooling is tentatively attributed to fluctuating hyperfine fields, which are modulated by an electronic coupling to thermally activated conformational fluctuations of the EEGs [32]. In the range 20–60 K, T_2^{-1} acquires a temperature-independent value, which is similar to that from internuclear dipolar coupling [9], indicating that EEGs are frozen below $T \simeq 60$ K similar to related compounds [24]. An important consequence of this thermally activated process is quenched disorder in the molecular conformations (eclipsed and staggered) [33,34], a phenomenon well known to influence the electronic properties (see Ref. [35] and references therein).

Thus, quenched conformational disorder reasonably influences the details of a CO transition that could be underlying

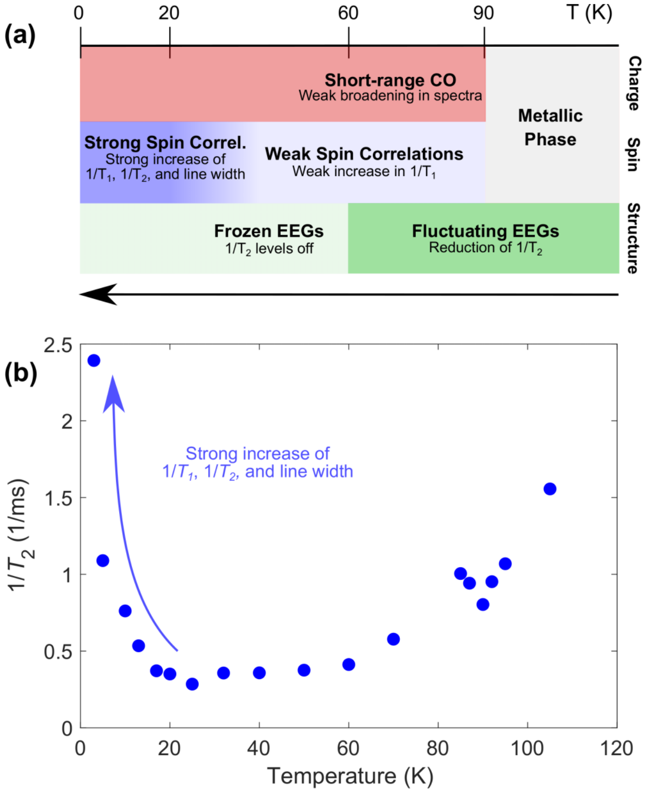

FIG. 4. (a) Chart of the proposed charge, spin, and structural degrees of freedom for κ-HgBr versus temperature upon cooling. (b) T_2^{-1} between 2.5 K and 110 K. T_2^{-1} was determined by a measure of the echo decay on varying the pulse separation. At higher temperatures, the pulse excitations are nonselective. However, a result of large inhomogeneous line widths and a fixed spectrometer bandwidth, the results below 40 K correspond only to the center of the spectrum.

broken symmetry associated with the MIT. The coexistence of sharp and broad peaks in the spectra persists to $T \simeq 40$ K, which could be taken as evidence for a macroscopic and temperature-dependent phase segregation below a discontinuous phase transition. We note that the temperature range of metal-insulator coexistence at the first-order CO transition of α-(BEDT-TTF)$_2$I$_3$ is considerably extended by internal strain [36]. Disorder may have an even stronger effect on locally modulating the electronic correlation strength, thus generating a random variation of transition temperatures on the nanoscale. Some caution is warranted, however, since apart from the spectra shown in Fig. 3(a) we know of no independent evidence for metallic regions persisting down to $T \simeq 40$ K in κ-HgBr.

The spectral features of the inhomogeneously broadened NMR lines, due to short-range charge order on a strongly disordered lattice, are consistent with all results: We propose that a broad distribution of spatial and temporal magnetic correlations is indirectly linked to the quenched structural conformations of the BEDT-TTF molecules, since the conformations first suppress long-range order in the charge disproportionation, which onsets at T_{MI}. Furthermore, we note that the inhomogeneous and homogeneous line broadening at low temperatures, as well as the increase in spin-lattice relaxation rate below $T = 20$ K, are all naturally associated with slowing of magnetic correlations, an observation consistent with the anomalous magnetic response reported in Ref. [29]. A possible explanation for why the effects are seen first in the spectra lie within the fact that T_1^{-1} and T_2^{-1} below 40 K measure only the spins at the center of the spectra, a consequence of large inhomogeneous line widths. The spectra at low temperature were measured via field sweeps, thus the entire spectra are accounted for in the FWHM measurements. We map the proposed charge, spin, and structural degrees of freedom of κ-HgBr upon cooling in Fig. 4(a).

The pronounced maximum in relaxation rate at $T \simeq 5$ K is consistent with a dynamical slowing of magnetic fluctuations, which can be modeled as producing a nuclear relaxation rate given by

$$\frac{1}{T_1} \sim \gamma^2 h^2 \frac{\tau}{1 + (\omega\tau)^2},$$

where h^2 is the mean square fluctuating transverse hyperfine field, τ a temperature-dependent characteristic correlation time, and ω the nuclear Larmor frequency. Such a slowing process, when coupled with the substantial increase in line widths, is naturally attributed to an increase in antiferromagnetic correlations.

The increase in T_2^{-1} below 20 K can also be associated with the slowing of magnetic correlations. The magnitude of T_2 reveals that the ^{13}C NMR spectra remain dominated by inhomogeneous broadening. The observed FWHM at low temperatures is two orders of magnitude larger than the homogeneous line width expected from $1/(\pi T_2)$. Indeed, the data presented here exhibit no sharply defined peaks, consistent with a broad onset of short-range magnetic correlations. At the lowest temperature measured, the field-swept line width (432 kHz at 9 T) corresponds to an on-site field-induced moment of order several tenths of a Bohr magneton. In other words, there is strong evidence that spectral broadening below 40 K is the result of nuclear spin coupling to field-induced and slowly fluctuating magnetic moments, possibly approaching a glassy state [30].

TABLE I. Comparison of ^{13}C NMR quantities for κ-HgBr, κ-CuCN, and κ-AgCN [9,12]. T_2^{-1} and FWHM are the $T \to 0$ saturated values for $B \simeq 8$ T for κ-CuCN and κ-AgCN.

	κ-HgBr	κ-CuCN	κ-AgCN
$T_1^{-1}{}_{\text{max}}$	150 s^{-1}	3 s^{-1}	1.5 s^{-1}
T_2^{-1}	2.5 ms^{-1}	1 ms^{-1}	
FWHM	500 kHz	50 kHz	40 kHz

IV. DISCUSSION

In relation to expectations for the QDL scenario, the manifestation of broad, featureless spectra in ^{13}C NMR suggests the presence of a nonzero CD that is static relative to the time scale of the intrinsic homogeneous line broadening associated with internuclear spin coupling, $\simeq 1$ ms, or longer. If electric dipoles associated with CD were fluctuating faster than this, the spectral impact of CD would be motionally narrowed, such that extensive broadening of the NMR lines would not occur. In this respect, it is not clear how to reconcile these results with the QDL state proposed for κ-HgBr in Ref. [22].

Thus, there is an apparently unresolved experimental discrepancy. The prior advocation for the QDL state was based on a Raman study of the ν_2 intramolecular vibrational mode [22], whereby the resonance frequency is sensitive to the molecular charge of BEDT-TTF sites [37], and therefore a probe of CD. The crucial finding was the lack of evidence for distinct molecular environments over a temperature range spanning widely on either side of T_{MI}. While it is unclear how to account for the difference, for the moment we simply note that the optical spectra reported in Ref. [29] do provide evidence for at least two molecular environments. That is, the resolved splitting of the optically active ν_{27} vibrational mode is consistent with a finite CD of 0.13 e [37].

For the sake of completeness, it is worthwhile to compare and contrast the observations reported here to comparable measurements of ^{13}C line broadening (FWHM), T_2^{-1}, T_1^{-1}on κ-CuCN and κ-AgCN [9,12], see Table I. For each of these quantities, the values are far greater for κ-HgBr. The significance is that while the relatively small line broadening observed for κ-CuCN and κ-AgCN was reasonably attributed to a small number of magnetic impurities [9,12], the results for κ-HgBr indicate a far greater magnetic response. When converted to an effective scale, the magnetic moment of κ-HgBr is of order 0.4 μ_B and keeps increasing at the lowest temperatures.

From the very large quantitative differences in relaxation rates, as well as the line widths at comparable fields, we infer that a physical description of the low-temperature properties of κ-HgBr is likely also qualitatively different than for the QSL candidates κ-CuCN and κ-AgCN. In the present case, disorder effects are likely much more pronounced, likely related to the MIT and the resulting short-range charge order, leveraging the occurrence of microscopic inhomogeneities of the exchange interaction. While in the two related compounds, as well as in κ-HgCl, dilute impurities dominate the low-temperature relaxation consistent with a spin-gapped scenario [31], the NMR properties in κ-HgBr rule out a gap in the temperature range measured and strongly suggest fluctuations of the intrinsic spin degrees of freedom. A remaining question is whether the present system exhibits a glasslike state, with substantial static moments in the absence of an applied magnetic field in the limit $T \rightarrow 0$.

V. CONCLUSION

In summary, we scrutinized the ^{13}C NMR spectra, spin-lattice relaxation, and spin-spin relaxation of κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br for $T = 2$ K–115 K. The sharp increase in $1/T_1$ and $1/T_2$ for $T \lesssim 20$ K as well as large line broadening of the spectra around the same temperature range suggests slowing magnetic fluctuations. The symmetric nature of the broadening and field-dependent line widths indicate that the slowing is driven by dominantly antiferromagnetic correlations. At the lowest temperature measured, the field dependence of the line width indicates that the system is still in a fluctuating disordered phase and, otherwise, the evidence for slowing dynamics could be a precursor for the onset of glassy behavior at lower temperatures. Altogether, the low-temperature spin degrees of freedom in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br are best described by short-range antiferromagnetism. It is also highly frustrated, and additionally quenched disorder results in short-range static charge disproportionation and consequently also strongly varying nearest-neighbor exchange interaction. Strong quenched disorder in the electronic structure of this insulating material is evidently associated with disordered and gapless magnetic degrees of freedom. It remains to be explored whether a glassy state is stabilized at lower temperatures. In any case, the system is unlikely a host of propagating spinons.

ACKNOWLEDGMENTS

We thank M. Dressel for fruitful discussions. This material is based upon work supported by the National Science Foundation (DMR-709304 and DMR-2004553). A.P. acknowledges support by the Alexander von Humboldt Foundation through the Feodor Lynen Fellowship. A.H. and T.S. acknowledge that work carried out at the NHMFL was supported by the NSF under Grant No. DMR-1644779 and the State of Florida. J.A.S. acknowledges support from the Independent Research/Development program while serving at the National Science Foundation.

---

[1] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
[2] L. Balents, Nature (London) **464**, 199 (2010).
[3] M. R. Norman, Rev. Mod. Phys. **88**, 041002 (2016).
[4] Y. Zhou, K. Kanoda, and T.-K. Ng, Rev. Mod. Phys. **89**, 025003 (2017).
[5] L. Savary and L. Balents, Rep. Prog. Phys. **80**, 016502 (2017).
[6] C. Broholm, R. J. Cava, S. A. Kivelson, D. G. Nocera, M. R. Norman, and T. Senthil, Science **367**, eaay0668 (2020).
[7] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. **91**, 107001 (2003).
[8] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **103**, 067004 (2009).
[9] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. B **73**, 140407(R) (2006).
[10] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Nature Phys. **4**, 459 (2008).
[11] 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, Bull. Chem. Soc. Jpn. **90**, 1073 (2017).
[12] Y. Shimizu, T. Hiramatsu, M. Maesato, A. Otsuka, H. Yamochi, A. Ono, M. Itoh, M. Yoshida, M. Takigawa, Y. Yoshida, and G. Saito, Phys. Rev. Lett. **117**, 107203 (2016).
[13] M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, Nature Phys. **5**, 44 (2009).
[14] R. S. Manna, M. de Souza, A. Brühl, J. A. Schlueter, and M. Lang, Phys. Rev. Lett. **104**, 016403 (2010).
[15] S.-S. Lee, P. A. Lee, and T. Senthil, Phys. Rev. Lett. **98**, 067006 (2007).
[16] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).
[17] T. Furukawa, K. Miyagawa, T. Itou, M. Ito, H. Taniguchi, M. Saito, S. Iguchi, T. Sasaki, and K. Kanoda, Phys. Rev. Lett. **115**, 077001 (2015).
[18] A. C. Jacko, E. P. Kenny, and B. J. Powell, Phys. Rev. B **101**, 125110 (2020).
[19] H. Seo, J. Phys. Soc. Jpn. **69**, 805 (2000).
[20] E. Gati, J. K. H. Fischer, P. Lunkenheimer, D. Zielke, S. Köhler, F. Kolb, H.-A. K. von Nidda, S. M. Winter, H. Schubert, J. A. Schlueter, H. O. Jeschke, R. Valentí, and M. Lang, Phys. Rev. Lett. **120**, 247601 (2018).
[21] K. Yoshimi, H. Seo, S. Ishibashi, and S. E. Brown, Phys. Rev. Lett. **108**, 096402 (2012).
[22] N. Hassan, S. Cunningham, M. Mourigal, E. I. Zhilyaeva, S. A. Torunova, R. N. Lyubovskaya, J. A. Schlueter, and N. Drichko, Science **360**, 1101 (2018).
[23] C. Hotta, Phys. Rev. B **82**, 241104(R) (2010).
[24] E. Gati, S. M. Winter, J. A. Schlueter, H. Schubert, J. Müller, and M. Lang, Phys. Rev. B **97**, 075115 (2018).
[25] P. Batail, K. Boubekeur, M. Fourmigué, and J. C. P. Gabriel, Chem. Mater. **10**, 3005 (1998).
[26] S. V. Konovalikhin, G. V. Shilov, O. A. D'yachenko, M. Z. Aldoshina, R. N. Lyubovskaya, and R. B. Lyubovskii, Bull. Russian Acad. Sci. Div. Chem. Sci. **41**, 1819 (1992).
[27] Crystallographic data for κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br : $C_{22}H_{16}BrHgN_2S_{18}$, $M = 1165.95$, monoclinic, space group $C2/c$, $a = 37.0923(6)$, $b = 8.32780(10)$, $c = 11.7296(1)$ Å, $V = 3623.18(10)$ Å^3. $T = 300K$, $Z = 4$, $\mu(\mathrm{MoK}_\alpha) = 6.412$ mm^{-1}, 34713 reflections measured, 50000 unique ($R_{\mathrm{int}} = 0.0296$), which were used in all calculations. The final

agreement factors were $R_1 = 0.0390$, $wR_2 = 0.0774$, GoF = 1.025. CCDC number 2000969.

[28] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.102.184417 for details on how to obtain the crystallographic data.

[29] T. Ivek, R. Beyer, S. Badalov, M. Čulo, S. Tomić, J. A. Schlueter, E. I. Zhilyaeva, R. N. Lyubovskaya, and M. Dressel, Phys. Rev. B **96**, 085116 (2017).

[30] M. Hemmida, H.-A. Krug von Nidda, B. Miksch, L. L. Samoilenko, A. Pustogow, S. Widmann, A. Henderson, T. Siegrist, J. A. Schlueter, A. Loidl, and M. Dressel, Phys. Rev. B **98**, 241202(R) (2018).

[31] A. Pustogow, T. Le, H.-H. Wang, Y. Luo, E. Gati, H. Schubert, M. Lang, and S. E. Brown, Phys. Rev. B **101**, 140401(R) (2020).

[32] M. Sawada, S. Fukuoka, and A. Kawamoto, Phys. Rev. B **97**, 045136 (2018).

[33] P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, J. M. Williams, V. Petricek, and P. Coppens, J. Am. Chem. Soc. **106**, 7644 (1984).

[34] A. J. Schultz, H. H. Wang, J. M. Williams, and A. Filhol, J. Am. Chem. Soc. **108**, 7853 (1986).

[35] D. Guterding, R. Valentí, and H. O. Jeschke, Phys. Rev. B **92**, 081109(R) (2015).

[36] A. Pustogow, A. S. McLeod, Y. Saito, D. N. Basov, and M. Dressel, Sci. Adv. **4**, eaau9123 (2018).

[37] T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, and H. Taniguchi, J. Phys. Chem. B **109**, 15226 (2005).