High energy spin excitations in the quantum spin liquid candidate Zn-barlowite probed by resonant inelastic x-ray scattering

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A quantum spin liquid is a novel ground state that can support long-range entanglement between magnetic moments, resulting in exotic spin excitations involving fractionalized $S = \frac{1}{2}$ spinons. Here, we measure the excitations in single crystals of the spin liquid candidate Zn-barlowite using resonant inelastic X-ray scattering. By analyzing the incident polarization and temperature dependences, we deduce a clear magnetic scattering contribution forming a broad continuum that surprisingly extends up to $\sim 200$ meV ($\sim 14J$, where $J$ is the magnetic exchange). The excitation spectrum reveals that significant contributions arise from multiple pairs of spinons and/or antispinons at high energies.

A fascinating phenomenon in quantum magnets is the possibility of having magnetic excitations with fractional quantum numbers. In particular, this may occur in a quantum spin liquid (QSL), which is characterized by long-range quantum entanglement of the spins in the absence of long-range magnetic order.18 Here, the fundamental $\Delta S = 1$ excitations may fractionalize into pairs of $S = \frac{1}{2}$ spinons. A promising host of a QSL is the kagome material, Zn-substituted barlowite ($\text{Cu}_x\text{Zn}_{1-x}(\text{OH})_6\text{Cl}_2$); however, a small percentage of excess Cu$^{2+}$ impurities are found on the nonmagnetic Zn$^{2+}$ sites between the kagome layers.14–17 To better understand how disorder and their coupling to the kagome moments affect the spin excitations, measurements on new materials are needed.

A related spin-$\frac{1}{2}$ kagome material, Zn-substituted barlowite ($\text{Cu}_x\text{Zn}_{1-x}(\text{OH})_6\text{FBr}$), was recently identified as a QSL candidate that has a different impurity environment and layer stacking arrangement compared to herbertsmithite.18–21 We had synthesized the first single crystals of Zn-barlowite with a Zn substitution of $x = 0.56$, referred to as Zn$_{0.56}$-barlowite.20 Its hexagonal structure is shown in Fig. 1A: the kagome layers are fully occupied by Cu$^{2+}$, while the interlayers have a majority of nonmagnetic Zn$^{2+}$ ions interspersed with Cu$^{2+}$ impurities.21 Zn$_{0.56}$-barlowite has no long-range magnetic order down to $T = 0.1$ K, making it a good QSL candidate.20 However, the lack of large single crystals has impeded measurements of the spinon physics with neutron scattering, a technique which provides high energy resolution and a well-defined cross-section for scattering from $\Delta S = 1$ excitations.

Resonant inelastic X-ray scattering (RIXS) offers a unique opportunity to study this kagome QSL candidate. RIXS is a powerful probe of elementary electronic excitations, including magnetic excitations, and has the capability of measuring small single crystals (< 1 mm in length).22–25 Furthermore, RIXS naturally probes significantly higher energy transfers than neutrons and has a different cross-section for the inelastic scattering. For magnetic scattering, the RIXS cross section may detect $\Delta S = 0$ as well as $\Delta S = 1$ excitations, and therefore can probe excitations that evade the sensitivity of neutrons.23, 26 While the application of RIXS to materials with low-energy or overlapping excitations has been limited by the resolution, significant advances have recently improved the achievable resolution to 15–30 meV for soft X-rays. Recent experimental and computational advances in soft X-ray RIXS have focused on compounds with 1D chains or 2D square lattices of Cu$^{2+}$,23–27, 30 however, even though the kagome quantum magnets with Cu$^{2+}$ cations display much interesting physics, no experimental RIXS investigation has yet been published.

We present RIXS measurements on small single crystals of the kagome QSL candidate Zn-barlowite Zn$_{0.56}$.20 RIXS data were collected on beamline 2-ID at the NSLS II at Brookhaven National Laboratory at the Cu $L_3$-edge ($\approx 930$ eV) (Fig. 1A).31, 32 The energy resolution, shown as the black bar in Fig. 1D (inset), was approximately 29 meV. X-ray absorption spectroscopy confirms the presence of Cu$^{2+}$ (Fig. S1 in the Supplemental Material). We collected RIXS data at a scattering angle of $2\theta = 90^\circ$ in both $\pi$ and $\sigma$ incoming photon polarizations. At $2\theta = 90^\circ$ with $\pi$ polarization, the elastic charge scattering and phonon scattering should be suppressed relative to the magnetic scattering. However, precise quantification may be complicated by the lower point group symmetry of the kagome Cu$^{2+}$ $d$-orbitals compared to square lattice cuprates.33 Figure 1D shows a wide energy loss ($\omega$) range of the data, where scatter-
FIG. 1. A) Crystal structure of Zn-barlowite with \( x = 0.56 \) (Zn_{0.56}) in the kagome \((ab)\) plane; H atoms are not shown, and the structure is from Ref. [20]. B) Schematic of the sample orientation on the beamline showing the \((H0L)\) scattering plane and the \(\pi\)- or \(\sigma\)-polarization directions. C) Calculated static spin structure factor \(S(q, S_z)\) with total spin \(S_z = 0\). The Brillouin zone is depicted with dashed lines, and the measured \(q\)-locations are shown as purple triangles and black squares for scattering angles \(\theta = 90^\circ\) and \(150^\circ\), respectively. D) RIXS signal of Zn-barlowite Zn_{0.56} at \((q||, q\perp) = (0, 1.0)\) collected in both \(\pi\) and \(\sigma\) polarizations. The band of \(dd\) excitations is visible between \(~1\,–\,2.5\) eV, and charge transfer scattering is visible as a broad hump between \(~3\,–\,6\) eV. The inset magnifies the region near \(\omega = 0\) meV showing the elastic component and inelastic scattering. The black bar represents the instrumental resolution (29 meV). The elastic components were fit with Pseudo-Voigt lineshapes denoted by the shaded area (see Supplemental Material, Section IC). The data were collected at \(T = 30\) K and \(2\theta = 90^\circ\).

For this quasi-2D material, \(\vec{q}\) can be decomposed into in-plane and out-of-plane components \((q||, q\perp)\). Here, \(q||\) is along \((H,0,0)\), and \(q\perp\) is along \((0,0,L)\) (see Fig. S2). For weakly coupled layers, the scattering at high energies should depend primarily on \(q||\) within the kagome layer and be weakly dependent on (or independent of) \(q\perp\). Subtracting the elastic component reveals the inelastic scattering as a broad continuum (Fig. 2A–B). The lack of any sharp components suggests that scattering from individual phonon modes is weak under these experimental conditions, although there may be some contribution within the energy range of the continuum (Fig. S6). We fit the inelastic scattering with a damped harmonic oscillator (DHO) cross section (see Supplemental Material, Section ID), which provides a qualitatively good description of the data. The fitted width (\(\Gamma\)) and integrated intensity are weakly dependent on \(q||\) and are plotted in Fig. 2C–F, respectively. The \(\pi\)-polarized data, which should be less affected by the charge scattering, has a consistently higher integrated intensity than the \(\sigma\)-polarized data, indicating that the continuum likely has a substantial magnetic component.

To measure larger wavevectors, we also collected data at \(2\theta = 150^\circ\) (Fig. 2C–D). The inelastic scattering at \(T = 30\) K has a broad tail that extends up to \(~200\) meV, consistent with that at \(2\theta = 90^\circ\). At \(T = 300\) K, the high energy scattering is somewhat reduced, revealing a more well-defined peak near 60 meV that is likely due to phonons, as this energy is consistent with previously calculated phonon modes [34]. We therefore fit the \(2\theta = 150^\circ\) data at both temperatures with a model consisting of a DHO and a phonon mode (see Supplemental Material, Sections IE and II). As seen in the individual fit components drawn in Fig. 2G, when the phonon mode is taken into account, a DHO with similar parameters as previously determined describes the remaining continuum. The integrated intensities (Fig. 2F) of the \(T = 30\) K data have a weak maximum at small \(q||\) values. In contrast, the room temperature intensities are relatively suppressed and are flat across \(q||\). Thus, if the broad continuum is magnetic in origin, then the spin correlations grow upon cooling as would generally be expected.

To further investigate the magnetic origin of the sig-
FIG. 2. A) and B) The $q$-dependence of the inelastic scattering of Zn-barlowite $\text{Zn}_{0.56}$ collected at $T = 30$ K and scattering angle $2\theta = 90^\circ$ in both A) $\pi$ and B) $\sigma$ polarizations. C) and D) The $q$-dependence of the inelastic scattering of $\text{Zn}_{0.56}$ collected at C) $T = 30$ K and D) $T = 300$ K at $2\theta = 150^\circ$. Both $\sigma$ (open symbols) and $\pi$ (closed symbols) polarization are shown. In A)–B), the data were fit with a damped harmonic oscillator (DHO) curve from $-100$–$500$ meV with the DHO center fixed at $65$ meV. In C)–D), the data were fit with a DHO and a phonon mode (see Supplemental Material, Section IE) from $-100$–$500$ meV, masking out $-35$–$35$ meV. The best fits are shown as black lines. The shading denotes in A)–B) a region of high uncertainty due to the elastic subtraction and in C)–D) these region were masked out during fitting. Vertical offsets were applied to separate the spectra. E)–F) The fitted DHO width $\Gamma$ and integrated intensity as a function of $q||$. Horizontal dashed lines denote average values, while curves are guides to the eye. G) An example of the “DHO + phonon” model showing the fit components (red and blue lines, respectively) and the overall fit (black line).

Now, because $\text{Zn}_{0.56}$ does not have long-range magnetic order at any measured temperature, the broad continuum does not originate from scattering from conventional magnons. This leads to an interpretation in terms of scattering from pairs of spinons or spinon-antispinon pairs.[23, 35] The fact that the signal extends to a high energy of \( \sim 14J \) suggests that the entirety of the scattering does not arise from a single pair of spinon excitations. The high-energy tail of the RIXS scattering can be empirically fit to a power law \( \sim 1/\omega^\alpha \) with \( \alpha \approx 2 \), as shown in Fig. 3C. In the context of scattering from a single spinon pair, we fit the magnetic signal in Fig. 3C with the functional form \( S(q,\omega) = A/\omega^{2-\eta} \) used to describe
possible QSL states. The fitted $\eta$ would have to be quite small ($<0.25$) to describe the continuum within these scenarios.

Therefore, the high energy RIXS scattering in Zn-barlowite $\text{Zn}_{0.56}$ likely includes significant contributions from multiple spinon pairs. Since RIXS can measure spin excitations with $\Delta S = 0$, scattering from spinon-antispinon pairs may also be present. Calculations for the Raman cross section of the Dirac spin liquid and a broad spectrum of scattering extending up to $q \sim a$ for barlowite indicate that spinon-antispinon pairs (as discussed above regarding the Raman predictions) may have a substantial contribution from scattering from spinon-antispinon pairs (as discussed above regarding the Raman predictions). However, the RIXS cross section for these processes has not yet been calculated.

We additionally collected RIXS data on small crystals of the magnetically ordered parent compound $\text{Cu}_4(\text{OH})_6\text{FBr}$, barlowite 2, which does not have disorder related to cation substitution. The parent compound has $T_N \sim 10$ K and maintains hexagonal symmetry at low temperatures, which is distinct from the variant that becomes orthorhombic. Both $\text{Zn}_{0.56}$ and barlowite 2 exhibit qualitatively similar RIXS spectra at low temperatures. Data collected at $T = 300$ K (Fig. 4B and inset) likewise appear similar to Zn-barlowite, exhibiting a broad continuum.

The similarity of the inelastic spectrum in barlowite 2 and Zn-barlowite indicates that spinon-based scattering can dominate at high energies even if magnetic order occurs at low temperatures. Furthermore, this shows that the high energy dynamics are not sensitive to interlayer disorder or interactions at much smaller energy scales, which eventually play a role in the ground state physics. In other systems, RIXS measurements on a $S = \frac{1}{2}$ chain compound that orders at low temperatures revealed the presence of 4-spinon scattering. Even in two dimensions, the ordered $S = \frac{1}{2}$ square lattice antiferromagnet shows evidence for spinon continuum excitations at high energies probed with neutrons. Future studies of Zn-barlowite and barlowite at the oxygen $K$-edge will be useful to better understand the multi-spinon excitations.

Our data reveal that the magnetic excitations in the QSL candidate Zn-substituted barlowite forms a broad
continuum extending up to ~14J. The results indicate scattering from multiple spinon-antispinon and/or spinon-spinon pairs—a remarkable first sighting for the RIXS technique. Further work on understanding the multi-spinon excitations for the kagome QSL’s (and their competing states) and calculating the appropriate RIXS cross-sections would be most illuminating.

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FIG. 4. A) Comparing the inelastic scattering of Zn-barlowite Zn$_{1.56}$ and barlowite 2 collected at $q_{||} = 0$, $T = 30$ K, and $2\theta = 90^\circ$. The shading denotes a region of high uncertainty due to the elastic subtraction. B) The $\vartheta$-dependence of the inelastic scattering of barlowite 2 collected at $T = 300$ K and $2\theta = 150^\circ$. The data were fit with the “DHO + phonon” model (Supplemental Material, Section VI); the best fits are shown as black lines. The shaded region was masked out during fitting. Vertical offsets were applied to separate the spectra. Inset: fitted integrated intensity as a function of $q_{||}$. The horizontal dashed line is the average value.

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