Coexistence and Interaction of Spinons and Magnons in an Antiferromagnet with Alternating Antiferromagnetic and Ferromagnetic Quantum Spin Chains

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In conventional quasi-one-dimensional antiferromagnets with quantum spins, magnetic excitations are carried by either magnons or spinons, which is indicative of the quasi-two-dimensional nature with the neighboring Cu-Cu distance.

In conventional magnets with magnetic long range order (LRO), low-energy excitations are carried by spin waves, represented by massless bosons called magnons with $S = 1/2$ and spin structure of Cu$_2$(OH)$_3$Br, which consists of nearly decoupled, alternating antiferromagnetic and ferromagnetic spin-1/2 chains with weak interchain couplings. To the best of our knowledge, such an interaction between two different magnetic quasiparticles has not been investigated even in theory due to the unusual nature of the spin structure. Our study thus opens up a new research arena and calls for further experimental and theoretical studies.

Figures 1(a), 1(b) depict the crystal structure of Cu$_2$(OH)$_3$Br, which is indicative of the quasi-two-dimensional nature with the neighboring Cu-Cu distance.
occupied, they determine the nature of orbital ordering (partially discussed later, the differences in the local geometry (caused by the ordering of Br ions) of these two Cu sites are crucial: they determine the nature of orbital ordering (partially occupied d orbitals) of Cu1 and Cu2 and the sign of nearest-neighbor intrachain exchange interactions between Cu moments, Cu1-Cu1 and Cu2-Cu2.

Heat capacity and magnetic susceptibility measurements [inset of Fig. 1(c)] on a single crystal sample reveal a paramagnetic-antiferromagnetic phase transition at $T_N\approx 9.0$ K, in agreement with previous reports [22,23]. The main panel of Fig. 1(c) plots the temperature dependence of neutron diffraction intensity of ordering wave vector (0.5 0 0), affirming the antiferromagnetic nature of the magnetic long-range ordered state. The magnetic structure determined by Rietveld refinement (FullProf) [24] (Fig. S1 [25]) is presented in Fig. 1(d). Along the $b$ axis, Cu1 spins align ferromagnetically with spins oriented nearly along the diagonal direction in the $ac$ plane, while Cu2 spins align antiferromagnetically with spins oriented along the $a$ axis.

The nearest-neighbor spins of both Cu1 and Cu2 sites along the $a$ axis are antiparallel, as suggested by the ordering wave vector. The ordered moment for Cu1 and Cu2 sites are $\sim0.737(6) \mu_B$ and $\sim0.612(2) \mu_B$ respectively; both of these values are smaller than the full saturation value of $1 \mu_B$ for spin-1/2, resulting from strong quantum fluctuation.

To investigate the nature of the spin dynamics, we performed inelastic neutron scattering measurements on co-aligned single crystals in the (H K 0) scattering plane using the HYSPAC time-of-flight spectrometer at Spallation Neutron Source [37]. Intriguingly, we find that this system shows quasi-1D nature of the exchange interactions as seen in the momentum- and energy-resolved neutron scattering intensity maps presented in Figs. 2(a)–2(c). The nearly dispersionless behavior of the excitation spectrum along both $H$ [Fig. 2(a)] and $L$ [Fig. 2(b)] directions indicates weak coupling between Cu spins along both the $a$ and $c$ axes. In contrast, the $I(E, K)$ intensity map (integrated over all $H$ and $L$) presented in Fig. 2(c), shows unusual excitation features with well-defined magnon
dispersion and broad continuum above ~5 meV. These observations, combined with the refined spin structure shown in Fig. 1(d), demonstrate that this system consists of nearly decoupled, alternating ferromagnetic and antiferromagnetic chains. To the best of our knowledge, Cu₂(OH)₂Br is the only system discovered thus far to exhibit the coexistence of quasi-1D ferromagnetic and antiferromagnetic quantum spin chains.

As an initial attempt to understand the magnetic excitations of this system, we performed linear spin wave (LSW) calculations using SpinW [38]. The model magnetic Hamiltonian (H) [25] consists of nearest neighbor Heisenberg-Ising type exchange coupling with intrachain interactions (J₁ and J₂), interchain interaction (J₃, J₄), and the Dzyaloshinskii-Moriya (DM) interaction (D) [Fig. 1(d)]. The dominant interactions are J₁ (ferromagnetic) and J₂ (antiferromagnetic), whereas J₃ and J₄ are antiferromagnetic and small. The LSW fitting spectra are shown in Figs. 2(c) and 2(d) and the fitting parameters are J₁ = −2.6, J₂ = 9.9, J₃ = 1.2, J₄ = 0.3, and D = 1.0 meV. The anisotropy parameter of intrachain interactions are Δ₁ = 0.173 for J₁ and Δ₁AF = 0.045 for J₂, and the DM term is on the interchain bonds between Cu₁ and Cu₂ [25]. The good agreement between the experimental data and the LSW results reassures us that this system indeed is composed of quasi-1D ferromagnetic and antiferromagnetic alternating chains. The lower-energy branches associated with ferromagnetic chains have an energy gap of ~1.2 meV at the zone center (e.g., K = 0), while the higher-energy branches associated with antiferromagnetic chains have an energy gap of ~4.2 meV at the zone center (e.g., K = −1). These spin gaps arise from anisotropic exchange interactions and finite interchain coupling and the spectral gap in the ferromagnetic branch around 3.5 meV at K = −0.5 and −1.5 arises from the DM interaction.

As discussed in the introduction, the excitations of (quasi-1) 1D spin-1/2 antiferromagnets are spinons. As a result, one expects a broad continuum produced by pairs of spinons, which cannot be described within the framework of LSW theory [7]. Indeed, we do observe a broad continuum above 5 meV as shown in Fig. 2(c), similar to the spinon continuum feature observed in the prototypical quasi-1D antiferromagnet KCuF₃ [5,8]. This again affirms the quasi-1D nature of Cu²⁺ spins of Cu₂(OH)₂Br.

The measured magnetic excitations and their comparison with LSW simulations raise two important questions. First, what is the underlying mechanism that leads to ferromagnetic and antiferromagnetic alternating chains in this system? Second, how do the two different types of magnetic quasiparticles interact with each other?

In order to shed light on the magnetic interactions and the resultant unique spin structure of Cu₂(OH)₂Br, we performed first-principles density functional theory (DFT) based calculations. The total energy calculated with different long-range ordered magnetic states is listed in Fig. S4 of the Supplemental Material [25], with the lowest energy spin configuration agreeing with the experimental observation. Using only an isotropic Heisenberg model with nearest neighbor intra- and interchain couplings, the intrachain (J₁ and J₂) and the interchain chain (J₃ and J₄) couplings, illustrated in Fig. 1(d), were calculated. Their values are listed in Fig. S5 [25]. One can see that the intrachain interactions indeed dominate, with J₁ being ferromagnetic and J₂ antiferromagnetic. The weaker interchain couplings J₃ and J₄ are both antiferromagnetic. The theoretical results are in qualitative agreement with the exchange parameters obtained from LSW fitting. Note that spins of neighboring Cu₁ and Cu₂ with antiferromagnetic J₄ are not energetically favorable, while neighboring spins with antiferromagnetic J₃ are energetically favorable. The nonzero magnetic interaction J₄ leads to frustration, which facilitates the decoupling of Cu₁ and Cu₂ chains.

To understand the nature of these exchange interactions, in Fig. 3(a) we present the ground state spin density profile. The t₂g orbitals of Cu²⁺ ions are completely filled while there is a single hole in the e₉ manifold, which splits due to local crystal field. The spin density shows the half-filled e₉ orbital, which has (x²−y²)-like character in a local coordinate axis system. Interestingly, all the Cu e₉ orbital lobes extend toward the oxygen p orbitals but not toward the Br ions. This can be understood by the weaker crystal field associated with Br ions, which have −1 charge as opposed to −2 for the oxygen ions. The resulting crystal field pushes the Cu e₉ orbital with electron clouds extending towards oxygen ions to higher energies, a characteristic of the hole occupying this orbital and spin density associated with it. The crystal field, combined with the geometry and local coordinate of these two Cu sites, leads to antiferro-orbital
orientational order for Cu1 chains and ferro-orbital orientational order for Cu2 chains. Such an unusual orientational ordering of the active magnetic orbital, which can be considered as an improper orbital order imposed by the strongly asymmetric crystal field of the anions, gives rise to anion-mediated exchange interactions that are dominated by Cu-O-Cu exchange pathways, considering that only O orbitals σ-bond with the half-filled Cu eg orbitals. This is supported by nearly zero spin density on the Br ions as illustrated in Fig. 3(a), which indicates that Br does not hybridize with the spin-polarized Cu orbitals, and hence does not contribute to superexchange. The projected density of states (DOS) of Br, O, and the hole (i.e., the unoccupied states) of Cu2+ ions are shown in Fig. 3(b). Consequently, antiferro-orbital order along Cu1 chains leads to ferromagnetic spin coupling ($J_1 < 0$) whereas ferro-orbital order leads to antiferromagnetic spin coupling along the Cu2 chains ($J_2 > 0$) [39].

Next, we discuss magnon-spinon interaction via the weak interchain couplings ($J_3, J_4$) between neighboring AFM/FM chains. In the absence of interchain couplings, the system would host deconfined spinons propagating in the AFM chain and well-defined magnons propagating in the FM chain. With gradual increase of interchain couplings, the quasi-1D nature of the system is progressively destroyed and magnetic long-range order develops. It is known that in quasi-1D antiferromagnets composed of identical spin chains, such as KCuF_3 [12], there is an energy threshold which separates spinons and magnons. Above this threshold, spinons are deconfined; below this threshold, the spinon continuum turns into classical magnons because of the finite interchain couplings and resulting in long-range order [13,40]. Thus, in these systems, magnetic excitations are carried either by unbound spinons or classical magnons in different energy regimes, and they do not interact. In contrast, due to the coexistence of both ferromagnetic and antiferromagnetic chains in Cu$_2$(OH)$_3$Br, the corresponding magnon and spinon excitations can coexist in the same energy range and interact with each other through the finite interchain couplings.

To better understand the effects of interchain couplings, we have used the algorithms for lattice fermions implementation [41] of the finite temperature auxiliary field quantum Monte Carlo to carry out numerical simulations of the dynamical spin structure factor of a system consisting of alternating ferromagnetic and antiferromagnetic quantum spin chains with the inter-chain coupling $J_3 = 0$ (a), $J_3 = 0.1J_2$ (b), and $J_3 = 0.2J_2$ (c). (d) Constant energy cuts at $E = [8.79.7]$ meV showing the asymmetric spectral intensity about $K = 1$ induced by nonzero $J_3$. Note that the Bose factor but not magnetic form factor of Cu$^{2+}$ ions has been taken into account in the simulation.

FIG. 4. Magnetic excitation spectra via quantum Monte Carlo simulations. Simulated magnetic excitation spectra (with $H = 1$) of a system consisting of alternating ferromagnetic and antiferromagnetic quantum spin chains with the inter-chain coupling $J_3 = 0$ (a), $J_3 = 0.1J_2$ (b), and $J_3 = 0.2J_2$ (c). (d) Constant energy cuts at $E = [8.79.7]$ meV showing the asymmetric spectral intensity about $K = 1$ induced by nonzero $J_3$. Note that the Bose factor but not magnetic form factor of Cu$^{2+}$ ions has been taken into account in the simulation.

There are several important features to point out. First, both well-defined magnon dispersion and spinon continuum, which are associated with ferromagnetic chains and antiferromagnetic chains, respectively, are clearly seen, consistent with the experimental observation shown in Fig. 2(c). Second, by introducing nonzero $J_3$, the magnetic excitations associated with antiferromagnetic chains are pushed up to higher energy and a gap opens which increases with $J_3$. This gap opening is the result of molecular field arising from the neighboring ferromagnetic chains. Third, compared to the decoupled spin chains, nonzero $J_3$ introduces asymmetric spectral intensity centered about $K = 1$, as shown by the constant energy cut (at $E = [7.79.7]$ meV) presented in Fig. 4(d), which suggests that the interchain coupling induces redistribution of spectral weight.

To obtain further insights on the effects of interchain couplings and the resultant magnon-spinon interactions, we perform RPA calculations and compare the results with the INS excitation spectra. For this purpose, we adopt and generalize the RPA approach for coupled antiferromagnetic chains [44]. In the presence of interchain interaction, we obtain generalized susceptibilities $\chi_{\alpha \beta}^{\text{RPA}}(k, \omega)$ for the two types of chains.
and without (black) interchain couplings. One can see that RPA calculation with the inclusion of interchain couplings captures the redistribution of the spectral weight with the intensity at \( K = -0.5 \) larger than that at \( K = -1.5 \). This difference cannot be accounted for by magnetic form factor.

Note that \( J_{\perp}(\vec{k}) \) [Eq. (2)] is negative when \( K \) is in the range of \([-1, 0]\) and positive when \( K \) is in the range \([-2, -1]\). This difference in the sign leads to the asymmetry in the spectral weight about \( K = -1 \), which is consistent with the QMC simulation results shown in Figs. 4(b)–4(d). If we reduce the constant energy cut to \( E = 7.75 \) meV [Fig. 5(d)] and focus on the two peaks closest to \( K = -1 \), again the RPA spectrum with interchain couplings introduces asymmetry.

The agreement near \( K = -1.25 \) is very good but not so good for \( K = -0.75 \). Further comparison between experimental data and RPA calculation results is discussed in the Supplemental Material [25].

In summary, we have discovered that magnons and spinons coexist in Cu\(_2\)(OH)\(_4\)Br, which uniquely consists of quasi-1D ferromagnetic and antiferromagnetic quantum spin chains. Magnons and spinons interact with each other via weak but finite interchain couplings, which opens the gap of the spinon continuum and gives rise to a redistribution of the spectral weight. This study highlights a new toy model and research paradigm to study the interaction between two different types of magnetic quasiparticles.

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See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.037204 for details on experimental methods, Rietveld refinement, linear spin wave fitting, calculations of two-magnon continuum bounds, DFT calculations, quantum Monte Carlo simulations, and random phase approximation calculations, which include Refs. [26–36].

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