Emergent spin-1 Haldane gap and ferroelectricity in a frustrated spin-1/2 ladder

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We report experimental and theoretical evidence that Rb$_2$Cu$_2$Mo$_3$O$_{12}$ has a nonmagnetic tetramer ground state of a two-leg ladder comprising antiferromagnetically coupled frustrated spin-1/2 chains and exhibits a Haldane spin gap of emergent spin-1 pairs. Three spin excitations split from the spin-1 triplet by a Dzyaloshinskii-Moriya interaction are identified in inelastic neutron-scattering and electron spin resonance spectra. A tiny magnetic field bears a ferroelectricity without closing the spin gap, indicating a novel class of ferroelectricity induced by a vector spin chirality order.

Quantum spin fluctuations offer a source of various nontrivial states including resonating valence bonds and quantum spin liquids [1]. They are manifested by the Berry phase term $S^B_1 = -iA$ in the Euclidean action, where $A = \int_0^\beta d\tau \int_0^1 du \, n \times (\partial n / \partial u)$ is the solid angle swept by a unit vector $n(\tau, u)$ of the spin direction during an evolution of the imaginary time $\tau$ and a fictitious parameter $u$ (Fig. 1(a)), with the inverse temperature $\beta = \hbar/k_B T$. In the one-dimensional (1D) antiferromagnet having only the first-neighbor exchange coupling $J_1$ (Fig. 1(b)), the spin quantum number $S$ critically determines the magnitude of quantum spin fluctuations of a long-wavelength mode $n(\tau, x)$ around a short-range Néel order. The sum of $S^B_1$ over the spin chain gives a contribution of $S^B_{1\text{DHAF}} = i2\pi SQ$ to a nonlinear-$\sigma$ model action for $n$ with a topological integer $Q = (1/2\pi) \int_0^\beta d\tau \int_0^1 dx \, n \times (\partial n / \partial x)$. Thus, $e^{-S^B_{1\text{DHAF}}}$ can take $-1$ for a half-integer $S$, allowing for gapless excitations from a disordered ground state. On the other hand, it is always unity for an integer $S$, leading to a so-called Haldane gap [2,3] in the $S = 1$ excitation spectrum from a nonmagnetic ground state [4,5], as experimentally evidenced in NENP [6,8].

In the presence of an antiferromagnetic second-neighbor exchange coupling $J_2$, however, the above simple arguments no longer hold. In particular, quasi-1D spin-1/2 multiferroic and/or magnetoelectric edge-sharing cuprates, such as LiCu$_2$O$_2$ [9,10], LiCuVO$_4$ [11], PbCuSO$_4$(OH)$_2$ [12], and Rb$_2$Cu$_2$Mo$_3$O$_{12}$ [15,17], involve a ferromagnetic $J_1$ because of nearly 90° Cu-O-Cu bond angles, in addition to an antiferromagnetic second-neighbor exchange coupling $J_2$. The $J_1$-$J_2$ frustrated spin-1/2 Heisenberg chain accommodates a dimerized spin-singlet short-range resonating valence bond ground state [18,19]. This state is formed by emergent spin-1 pairs (Fig. 1(c)) and has an extremely small Haldane gap and incommensurate short-range spin correlations. Weak but finite easy-plane exchange magnetic anisotropy then induces a quasi-long-range gapless incommensurate spin-spiral and long-range vector spin chirality [20], orders [19,21]. A coexisting phase of the vector spin chirality order and the Haldane gap also appears in between the two phases [22]. These states are, however, readily driven to a long-range spiral magnetic order by three-dimensional couplings. This scenario elucidates the ferroelectricity due to the cycloidal magnetism in LiCu$_2$O$_2$ [19], LiCuVO$_4$ [12], and PbCuSO$_4$(OH)$_2$ [13].

In fact, the ferroelectricity associated with the vector spin chirality order may appear robustly in the vector-chiral Haldane dimer phase without the long-range spiral magnetism, if the spin gap is enhanced [23] so that it dominates over the interchain interactions. Indeed, Rb$_2$Cu$_2$Mo$_3$O$_{12}$ provides a unique example of a field-induced ferroelectricity hosted by a nonmagnetic ground state with a spin gap [16,17]. In this Letter, we report...
combined experimental and theoretical evidence that in the quasi-1D cuprate $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$, a Haldane-gap ground state formed by emergent spin-1 pairs of $S = 1/2$ Cu spins (Fig. 1(d)) harbours a ferroelectricity stabilized by a tiny magnetic field.

Figures 2 shows a temperature dependence of thermodynamic properties of polycrystalline $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ samples. The dielectric constant $\varepsilon$ gradually increases on cooling. Then, as in most of magnetically induced ferroelectrics, it exhibits a kink for $B = 0.3$ and 0.5 T or a peak for $B = 1$ and 2 T at around 8 K (Fig. 2(a)), below which the electric polarization $P$ emerges at an even weaker magnetic field $B = 0.05$ T (Fig. 2(b)). Thus, the anomaly in $\varepsilon$ at $B \geq 0.05$ T should be ascribed to a ferroelectric transition at $T_{\text{FE}} \sim 8$ K. It is natural to expect that the ferroelectric polarization persists at $T < 2$ K because of no sign of a reentrant behavior in $\varepsilon$ and $P$ in the low temperature range. Remarkably, $\varepsilon$ does not show a significant decay on cooling down to 2 K for $B \leq 0.5$ T, while it does for $B \geq 1$ T. Furthermore, doping nonmagnetic Zn impurities into Cu sites by 2% [24] drastically suppresses $\varepsilon$ and removes the anomaly associated with the ferroelectric transition (Fig. 2(a)). Therefore, it is clear that the ferroelectricity is indeed triggered by a coherence in the spin degrees of freedom under the weak magnetic field.

The signals of both $\varepsilon$ and $P$ below $T_{\text{FE}}$ are larger for the configuration of $E, P \perp B$ than for $E, P \parallel B$ at least at 2 T (Figs. 2(a) and 2(b)), as in many edge-sharing multiferroic cuprates showing a cycloidal magnetic order [10,12,13]. This implies that the uniform vector spin chirality gives rise to a dominant contribution to the ferroelectric polarization among many mechanisms [25]. On the other hand, no anomaly is observed in the magnetic susceptibility $\chi$ and $d\chi/dT$ (Fig. 2(c)), in contrast to the multiferroic cuprates [10,12,13]. Moreover, a spin gap $\varepsilon_0 \sim 1.7$ K has been observed in both $\chi$ and the specific heat $C$ [15,17] (Figs. 2(c) and 2(d)).

The emergence of this spin gap is also confirmed by

FIG. 1. Structures of spin chains. (a) Spin Berry phase as a solid angle swept by $n$ while varying $\tau$ from 0 to $\beta$ and $\nu$ from 0 to 1. (b) Antiferromagnetic spin chain. (c) Frustrated spin-1/2 chain with emergent spin-1 pairs (blue clouds). Solid/broken lines represent antiferromagnetic/ferromagnetic interactions. (d) Short-range resonating valence bond state from 0 to 1. (b) Antiferromagnetic spin chain. (c) Frustrated spin-1 pairs. (e) Crystal structure of a pair of spin-1 involving tetramers (yellow plaquettes) connecting emergent interactions. (d) Short-range resonating valence bond state from 0 to 1. (f) An ideal centrosymmetric chain of edge-sharing distorted $\text{CuO}_6$ octahedra (black points), compared with the noncentrosymmetric one in $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$. Electric dipole moments due to ionic displacements are shown on the first-neighbor Cu spin pairs by green arrows. (g) A unit cell of $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$. Two-leg ladders are located in translucent orange tubes.

FIG. 2. Temperature dependence of thermodynamic properties of polycrystalline $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$. (a) Dielectric constant $\varepsilon/\varepsilon_0$. (b) Electric polarization $P$ at magnetic fields. (c) Magnetic susceptibility $\chi$ (open circles). The impurity contribution $\chi_{\text{imp}}$, responsible for the upturn of $\chi$ below 0.5 K, was fitted by the Curie-Weiss law with the spin vacancy concentration of 0.5 % and the Weiss temperature $-0.5$ K (blue dashed curve). Red points represent the data $\chi_{\text{imp}}$ subtracted by $\chi_{\text{imp}}$. Also shown is $d\chi/dT$ (green points). The inset shows a high-temperature fitting of $\chi$ (black curve) with a powder average of the exact diagonalization results (red curve). (d) Specific heat $C$ at $B = 0$. The solid curves in (c) and (d) are the fitting curves proportional to $\exp(-E_0/T)$ with the energy gap $E_0 = 1.7$ K.
the measurements of the magnetization $M$. Figures 3(a) and 3(b) present experimental results on $M$, and $dM/dB$ and $d^2M/dB^2$, respectively. A subtraction of a small impurity contribution as outlined in Fig. 2 caption reveals that $M$ at $T = 0.08$ K shows an activation by the threshold field $B_C$, $\sim 2.0$ T where $d^2M/dB^2$ exhibits a peak. On the other hand, at a much lower temperature $T = 2.0$ K than $T_{FE}$, $P(\perp B)$ steeply appears at a much lower field, at least 0.03 T, than $B_C$ (Fig. 3(c)). It exhibits a broad peak at around 0.2-0.3 T, and then gradually decays to a constant at higher fields up to 4 T. This observation confirms that the ferroelectricity is stabilized by a tiny magnetic gap and an onset of the magnetization at $B_C$.

All the above thermodynamic properties provide evidence of a spin-gapped ferroelectric behavior stabilized by the tiny applied magnetic field, most likely through the vector spin chirality. It should also be possible to confirm this from spectral properties. To probe $S = 1$ triplet excitations from the nonmagnetic ground state, low-energy inelastic neutron-scattering experiments have been performed on powder samples. Figure 4(a) represents the results at 1.5 K measured on the AMATERAS spectrometer. Discrete excited levels are clearly seen at 0.2, 0.38, and 0.6 meV around the wavenumber $Q = 0.2 \sim 0.4$ Å$^{-1}$, which roughly corresponds to a periodicity of eight spins along the chain. A natural interpretation will be that $S = 1$ triplet excitations are split into the three by Dzyaloshinskii-Moriya interactions.

The overall experimental results on the magnetic properties can be elucidated theoretically from the following two-leg ladder model of frustrated $J_1$-$J_2$ spin-1/2 chains (Fig.1(d)) [26]

$$H = \sum_{\ell} \sum_{\sigma = \pm} \left[ \sum_{j=1,2} J_j S_{\sigma,\ell} \cdot S_{\sigma,\ell+j} + J' S_{\sigma,\ell} \cdot S_{\sigma,\ell}, +\sigma (-1)^{\ell} D_u \cdot S_{\sigma,\ell} \times S_{\sigma,\ell+1} + D_u \cdot S_{\sigma,\ell} \times S_{\sigma,\ell+1} \right]$$

$$-g\mu_B B \cdot S_{\sigma,\ell}$$

(1)

with the $g$-factor $g = 2.16$ [26] and the applied magnetic field $B$, where $S_{\sigma,\ell}$ stands for an $S = 1/2$ spin at the site $\ell$ in the chain of edge-shared CuO$_6$ octahedra (Fig. 1(e)) labeled by the index $\sigma = \pm$. $D_u$ and $D_s$ represent the uniform and staggered components of intrachain Dzyaloshinskii-Moriya vectors caused by two inequivalent first-neighbor Cu-Cu bonds involving noncollinear electric dipole moments as shown by green arrows in Fig. 1(f). No crystal symmetry constrains the directions of the Dzyaloshinskii-Moriya vectors. However, since the numerical results shown below are insensitive to a nonzero value of $D_u \cdot D_s$, we take $D_u \perp D_s$. Henceforth, we adopt $J_1 = -114$ K, $J_2 = 35.1$ K, $J' = 20.5$ K, $D_s = 44.3$ K, and $D_u = 24.4$ K to explain
The scenario of a splitting of the $S = 1$ excited states due to Dzyaloshinskii-Moriya interactions is also supported by electron spin resonance (ESR) experiments on powder samples. Figure 5(a) presents the temperature dependence of the ESR transmission spectra at a frequency $f = 81$ GHz as a function of $B$. A paramagnetic resonance is found as a significantly broad peak at 2.7 T for a much lower temperature 8.7 K than $J_1$, $J_2$ and $J'$, as indicated by red arrows. It should appear as a much sharper peak in the absence of moderately large Dzyaloshinskii-Moriya interactions [28]. On cooling, the peak becomes even more broadened, and eventually bifurcates below 5 K. In the frequency dependence of the ESR spectra at 1.6 K (Fig. 5(b)), this new low-energy mode (green arrows) has been identified, as well as another lower-energy mode (blue arrows). These two modes are plotted with $\Delta$ and $\nu$ in the $B$-$f$ diagram of Fig. 5(c), in favorable comparison with a density plot of the theoretical results [26] on the optical absorption power [29] at the same temperature. The dominant contributions to the two series originate from thermally activated transitions. Theoretically, the second-lowest-energy mode ($\nu$) is ascribed to transitions from the first excited state to the second at the wavevector $Q_b = 1/4$ r.l.u. (the right panel of Fig. 5(d)) and from the first excited state to the second at $Q_b = 0$ (the left panel of Fig. 5(d)), as shown by solid and dashed curves in Fig. 5(c), respectively. The lowest-energy mode ($\Delta$) is ascribed to transitions from the first excited state to the second and from the second to the third at $Q_b = 1/4$ r.l.u. (the right panel of Fig. 5(d)), as shown by two solid curves in Fig. 5(c). A significantly large dependence of the excitation energies on the field direction in the theoretical calculations shown in Fig. 5(d) also elucidates the unusually broad spectral features identified in the powder ESR experiments.

The current frustrated spin-1/2 ladder model, which has reproduced overall experimental results on Rb$_2$Cu$_2$Mo$_3$O$_{12}$, actually has a tetramer-singlet ground state formed by emergent $S = 1$ spins with a Haldane gap. (See Fig. 1(d).) This ground state is adiabatically connected to the limit of the two decoupled chains with $J' = 0$, each of which has a singlet Haldane dimer ground state [22], and then to the two decoupled spin-1 Haldane chains, as in an antiferromagnetic spin-1 ladder [30]. At present, it remains open to explain the ferroelectricity stabilized by a tiny magnetic field. Nevertheless, it is clear from the symmetry that it is accompanied by a genuine long-range vector spin chirality order, which is not parasitic to a (quasi-)long-range spiral magnetic order. This is the state that has long been sought since the proposal by Villain [20]. This uncovers a novel class of magnetically induced ferroelectricity in the absence of a long-range magnetic order, in contrast to many multiferroic magnets due to a cycloidal magnetism. A quest to more microscopic properties of this novel ferroelectric (vector-spin-chirality ordered) emergent Haldane-gap state will demand experiments on the single crystals and the associated microscopic theoretical analyses in the future.

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**FIG. 5.** Electron spin resonance spectra of polycrystalline Rb$_2$Cu$_2$Mo$_3$O$_{12}$. (a) Temperature dependence of the experimental transmission spectra at 81 GHz. Arrows represent the resonance fields. (b) Experimental transmission spectra at 1.6 K for designated frequencies. Green and blue arrows denote two sequences of resonance fields. (c) Theoretical optical absorption power at 1.6 K. Experimentally observed resonance fields indicated by blue and green arrows in (a) are plotted by $\Delta$ and $\nu$, respectively, for comparison. (d) Energy levels at $Q_b = 0$ (left) and $Q_b = 1/4$ r.l.u. (right) computed under $B$ applied along the $x$, $y$, and $z$ directions, where $D_u \parallel z$ and $D_v \parallel x$. Transitions denoted by the arrows in the left/right panel produce resonance spectra shown by dashed/solid curves in (b).
triple-axis spectrometer LTAS installed at JRR-3 reactor, Japan. Numerical calculations were partially performed by using the RIKEN Integrated Cluster of Clusters and the RIKEN HOKUSAI supercomputers. The time-of-flight neutron-scattering experiments were performed using the chopper spectrometers AMATERAS and 4SEASONS at J-PARC (Proposal Nos. 2012P0202 and 2009A0093). The work was partially supported by Grants-in-Aid for Scientific Research (Grant 24244059, 24740253, 25220803, 25246006, 25800221, 16K05426, 17001001, 17H06137 and 17K14359) from Japan Society for the promotion of Science and by the RIKEN iTHES project and by the FRIS Program for the creation of interdisciplinary research at Tohoku University. H.U. is grateful to S. Yunoki for his support.

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FIG. S1. Crystal structure of the spin-1/2 ladder in Rb$_2$Cu$_2$Mo$_3$O$_{12}$. We take the following representations of three primitive lattice vectors: $a = (26.3844, 0, -8.1956)$ Å, $b = (0, 5.1018, 0)$ Å, and $c = (0, 0.19, 290)$ Å. (a) Crystal structure of Rb$_2$Cu$_2$Mo$_3$O$_{12}$. (b) Gif animation of the structure displayed in Fig. 1(e) of the main text. (c) Gif animation of the structure displayed in Fig. 1(f) of the main text. In (b) and (c), thin lines represent the bonds connected from Cu to the apical oxygens.

SUPPLEMENTAL MATERIAL FOR “EMERGENT SPIN-1 HALDANE LADDER FROM THE ONE-DIMENSIONAL FRUSTRATED SPIN-1/2 MAGNET RB$_2$Cu$_2$Mo$_3$O$_{12}”

CRYSTAL STRUCTURE OF RB$_2$Cu$_2$Mo$_3$O$_{12}$

The quasi-one-dimensional spin-1/2 frustrated chain compound Rb$_2$Cu$_2$Mo$_3$O$_{12}$ belongs to the space group C$2/c$ above $T_{FE} \sim 8$ K (ref. [31]). The unit cell comprises four symmetry-related two-leg spin ladders (Fig. 1(g)). Two spin chains in each ladder are related by an inversion operation. Each spin chain contains two Cu$^{2+}$ sites in the unit cell with a slight alternation of the first-neighbor Cu-Cu distances along the chain direction, namely, the crystallographic $b$ axis [31] (Fig. S1(a)). The first-neighbor Cu-O-Cu bond angles approximate to 90°, leading to ferromagnetic first-neighbor exchange couplings. A large buckling of CuO$_2$ chains yields the Cu-Cu-Cu bond angle $\theta = 111.75$° along each chain and the direction from the Cu$^{2+}$ ion to the apical oxygen alternates in each chain. These distortions should produce a moderately large magnetic anisotropy in the exchange coupling. The structures shown in Figs. 1(e) and 1(f) of the main text can be viewed from various directions by a rotation about the $b$ axis in Figs. S1(b) and S1(c).

DETERMINATION OF THE EXCHANGE COUPLING CONSTANTS

Model.

Here we construct a plausible model for Rb$_2$Cu$_2$Mo$_3$O$_{12}$. The material contains two inequivalent edge-shared CuO$_6$ octahedra that are aligned alternately in a zigzag manner along the crystallographic $b$ axis, as shown in Fig. S1. Each spin chain couples to its partner transformed by a spatial inversion and separated from each other by 4.91 Å (Fig. 1(e)), which is comparable to the second-neighbor intrachain Cu-Cu distance. This suggests a nonnegligible antiferromagnetic interchain coupling $J'$ of the order of $J_2$. Both of the two inequivalent CuO$_6$ octahedra are largely distorted from regular octahedra (Fig. 1(f)). In effect, the directions of apical oxygens from Cu sites and thus the $d$-orbital shapes of unpaired electrons alternate, in sharp contrast to a simple edge-sharing CuO$_6$ octahedral network in many other compounds. This should yield a relatively large Dzyaloshinskii-Moriya interaction, as it is expected to elucidate the experimentally observed splitting of the triplet excitations. Thus, as a minimal effective Hamiltonian for describing low-energy magnetic properties of Rb$_2$Cu$_2$Mo$_3$O$_{12}$, we propose a frustrated $J_1$-$J_2$ spin-1/2 two-leg ladder model with noncollinear uniform and staggered Dzyaloshinskii-Moriya (DM) interactions, namely,

$$H = H_{SU(2)} + H_{DM} + H_Z.$$  \[(S1)\]
Here,

\[
H_{SU(2)} = \sum_\ell \left[ \sum_{\sigma = \pm} \sum_{j=1,2} J_j \mathbf{S}_{\sigma,\ell} \cdot \mathbf{S}_{\sigma,\ell+j} + J' \mathbf{S}_{+,\ell} \cdot \mathbf{S}_{-,\ell} \right],
\]

is the SU(2)-symmetric exchange interaction part with the ferromagnetic first-neighbor coupling \( J_1 < 0 \), the antiferromagnetic second-neighbor coupling \( J_2 > 0 \), and the antiferromagnetic interchain rung coupling \( J' > 0 \), while

\[
H_{DM} = \sum_\ell \sum_{\sigma = \pm} \left[ (-1)^\ell \mathbf{D}_u \cdot (\mathbf{S}_{\sigma,\ell} \times \mathbf{S}_{\sigma,\ell+1}) + \mathbf{D}_u \cdot (\mathbf{S}_{\sigma,\ell} \times \mathbf{S}_{\sigma,\ell+1}) \right],
\]

is the DM interaction part with the DM vectors \( \mathbf{D}_u \) and \( \mathbf{D}_s \) for the uniform and staggered components, respectively. A magnetic field \( \mathbf{B} \) is introduced through the Zeeman term

\[
H_Z = -g \mu_B \mathbf{B} \cdot \sum_\sigma \sum_\ell \mathbf{S}_{\sigma,\ell},
\]

with the \( g \) factor \( g = 2.16 \) (Fig. S8). The relation between the spin coordinate and crystallographic coordinate frames will be fixed later.

Now, before explaining how the model parameters are determined, we give some comments on an issue of a single chain versus a two-leg ladder. In the previous papers [23, 22], a single spin-1/2 \( J_1-J_2 \) XXZ chain has been studied by taking into account a small bond alternation in the amplitude of \( J_1 \), which is crystallographically present in the material. Then, it has been found that an infinitesimally small bond alternation drastically changes the phase diagram: a vector-spin-chirality ordered phase showing quasi-long-range gapless incommensurate spin correlations in the case with a moderately large easy-plane exchange anisotropy [19] is split into two vector-spin-chirality ordered phases showing only short-range gapped spin correlations [32]. Actually, the two phases are topologically distinct in the presence of the time-reversal symmetry and separated by a single critical line [23]. A possibility of explaining the experimental results for Rb\(_2\)Cu\(_2\)Mo\(_3\)O\(_{12}\) in terms of an either phase has then been examined, before proceeding to detailed analyses of the two-leg ladder model given by Eq. (S1). However, we have found that neither is the case: the vector-spin-chirality ordered phase with less easy-plane XXZ anisotropy has a too small spin gap. If we enhance the spin gap by increasing the bond alternation to an unphysically large value, then the incommensurate wavevector of spin correlations approaches a periodicity of four spins, in contrast to eight spins in experiments. The other phase with more easy-plane anisotropy may have a large spin gap compared to the experiment, but then the initial slope of the magnetization curve, namely, the magnetic susceptibility, within the easy-plane directions becomes an order of magnitude larger than in the experimental results. Furthermore, replacing the XXZ exchange anisotropy with DM interactions does not improve the case. Thus, we conclude that a different interaction should dominantly enhance the spin gap. The most natural candidate is the antiferromagnetic interchain rung interaction \( J' \), as we have already explained. In fact, when \( J' \) and \( D_s \) are both finite, the small bond alternation in \( J_1 \) is found to have negligibly small effects and has been left out.

**SU(2)-symmetric exchange coupling constants.**

First, we consider the predominant SU(2)-symmetric part \( H_{SU(2)} \), to adjust \( J_1/J_2 \) and \( J'/J_2 \). We numerically compute the spin gap between the ground state in the \( S = 0 \) sector and the sixfold degenerate first excited states in the \( S = 1 \) sector as well as equal-time spin-spin correlation functions in the ground state by means of the infinite-size density matrix renormalization group (iDMRG) technique [33, 34]. In particular, a four-spin unit is adopted for the matrix-product state whose matrix dimension is taken up to 800 to ensure the convergence.

The spin gap and the maximum peak position \( q_0 \) in the Fourier transform

\[
S^\sigma,\ell(q) = \sum_{\ell=1}^N \langle S^\sigma_+ S^\sigma_- \rangle \exp \left( -\frac{q\ell b}{2N} \right)
\]

with \( N = 256 \) and half the lattice constant \( b/2 = 2.55 \) Å are plotted as functions of \( J_1/J_2 \) and \( J'/J_2 \) in Figs. S2(a) and S2(b), respectively. In the experimental data of the inelastic neutron scattering spectrum shown in Fig. 4(a) of the main text, the intensities of three dispersionless spin excitation levels that are located at \( \omega = 0.20 \), 0.38, and 0.60 meV rise at around \( Q_b \sim 0.3 \) Å\(^{-1}\). This value of the incommensurate wavevector gives a constraint that
FIG. S2. Spin gap and incommensurability in the SU(2)-symmetric model. (a) Spin gap between the ground state with $S = 0$ and the first excited states with $S = 1$. (b) Maximum peak position $q_0$ in the Fourier component $S^x(q)$ of Eq. (S5) as a function of $J_1/J_2$ and $J'/J_2$ for the SU(2)-symmetric Hamiltonian $H_{SU(2)}$.

FIG. S3. (a) Curie-Weiss fitting of $\chi = (g\mu_B/2)^2/(T - \Theta) + \chi_0$ for the magnetic susceptibility $\chi$ of $B = 0$ in the scale of $1/\chi$ with $g = 2.16$ and the Bohr magneton $\mu_B$, where the best fit has been obtained in a temperature range $T = [200, 350]$ K for $\Theta = -2.3$ K and the sum $\chi_0 = -6.1 \times 10^{-5}$ (emu/Cu mol) of the van Vleck and diamagnetic susceptibilities. (b) Temperature dependence of $\chi$. It has been calculated by the numerical diagonalization of the 16-site cluster. The blue and black curves represent the numerical results for $H_{SU(2)}$ with $J_2 = 34.4$ K and for $H_{SU(2)} + H_{DM}$ with $J_2 = 35.1$ K, $D_u/|J_1| = 0.215$, and $D_s/|J_1| = 0.39$. In the both cases, $J_1/J_2 = -3.24$ and $J'/J_2 = 0.583$ are commonly taken.

$J_1/J_2$ and $J'/J_2$ should lie around a boundary between blue area and green region in the numerical results shown in Fig. S2(b). Note that the first excited $S = 1$ states in the SU(2)-symmetric case are split and largely affected by the DM interaction, as we will show below. On the contrary, the high-temperature magnetic susceptibility is insensitive to the DM interactions. Indeed, under the above constraint $q_0 \sim 0.3$ Å$^{-1}$ $\sim 0.25$ r.l.u., we have succeeded in fitting the experimental results in the inset of Fig. 2(c) reasonably well by the numerical exact-diagonalization results on a 16-site cluster for a choice of $J_1/J_2 = -3.24$ and $J'/J_2 = 0.583$, and $J_2 = 34.4$ K if we take into account the sum $\chi_0$ of the van Vleck and diamagnetic susceptibilities (Fig. S3(a)), as shown in Fig. S3(b).

**DM coupling constants.**

Next, we fix the ratios of $J_1/J_2 = -3.24$ and $J'/J_2 = 0.583$, as have been determined above. Then, we adjust the DM coupling constants as well as $J_2$ so that the first excited $S = 1$ levels at $Q_b = q_0$ in the SU(2)-symmetric
case are split into three located at 0.2, 0.38, and 0.6 meV, as in experimental observations. Note that the magnetic susceptibility and the incommensurability examined above are almost intact. We have found that two types of DM interactions dominantly control the level splitting: a uniform DM interaction $D_u$ and a staggered DM interaction $D_s$ with their DM vectors $D_u$ and $D_s$ being perpendicular to each other. To be explicit, we henceforth take $D_u \parallel x$ and $D_s \parallel z$.

In Fig. S6 we present several lowest-energy eigenvalues of $H_{SU(2)} + H_{DM}$ computed as a function of $D_u$ for several choices of $D_s$ by means of the numerical diagonalization. When $D_u = 0$, there is a U(1) symmetry in the spin space. Then, the three-fold degenerate $S = 1$ excited levels are split by finite $D_u$ into a first excited level and doubly degenerate second excited levels. The second excitation energy monotonically decreases with increasing $D_u$. Therefore, it is clear that $D_u$ is not the only DM interaction in the material. Next, we turn on $D_s$. The doubly degenerate levels are then split into two. We have also checked that relaxing a condition of $D_u \perp D_s$ does not drastically change the excitation spectra. Then, adjusting three parameters $J_2$, $D_s/|J_1|$, and $D_u/|J_1|$, we have successfully found a reasonable parameter set of $J_2 = 35.1$ K, $D_s/|J_1| = 0.39$ and $D_u/|J_1| = 0.182$, for which the three levels are within the different orange bands $0.20 \pm 0.01$, $0.38 \pm 0.01$, and $0.60 \pm 0.01$ meV, as shown in Fig. S5. Comparing $J_2$, $D_s/|J_1|$, and $D_u/|J_1|$ from the numerical diagonalization with those from the iDMRG, we find there is relative errors of $\sim 10\%$ in $J_2$ and $D_u/|J_1|$ and $\sim 30\%$ in $D_u/|J_1|$.

Now, we reexamine the magnetic susceptibility and the incommensurate wavevector, since we have modified $J_2$ and introduced finite $D_s$ and $D_u$. We first calculate a powder average of the magnetic susceptibility,

$$\chi(T) = \lim_{B \to 0} \frac{1}{4\pi B} \int_0^\pi \! \! \sin \theta d\theta \int_0^{2\pi} \! d\phi M(B,\theta,\phi, T)$$  \hspace{1cm} (S6)

for $H_{SU(2)} + H_{DM}$ with the above choice of exchange parameters, where $M(B, T)$ is a magnetization parallel to the applied magnetic field $B$, which is expressed in spherical coordinates $(B, \theta, \phi)$. Since the angle integrations are numerically too costly, we approximate it by the average of those for $B$ applied only along the $x$, $y$, and $z$ axes,

$$\chi(T) \approx \lim_{B \to 0} \frac{1}{3B} \left[ M(B, \pi/2, 0, T) + M(B, \pi/2, \pi/2, T) + M(B, 0, 0, T) \right] .$$  \hspace{1cm} (S7)

The theoretical results are shown in Fig. S3(b) in comparison with those obtained in the SU(2)-symmetric case as well as the experimental results. We have also checked that the incommensurate wavevector is not affected by the DM interactions, as is expected since the DM interactions in the two chains of the ladder have a destructive interference.

The exchange parameters for the total Hamiltonian $H_{SU(2)} + H_{DM}$ are summarized as

$$J_1 = -114 \text{ K}, \ J_2 = 35.1 \text{ K}, \ J' = 20.5 \text{ K}, \ D_s = 44.3 \text{ K}, \ D_u = 24.4 \text{ K}.$$  \hspace{1cm} (S8)

In the main text and the rest of Supplementary Information, we adopt these values.

**NUMERICAL CALCULATIONS OF THE CRITICAL MAGNETIC FIELD**

Here, we compute a critical magnetic field. We perform iDMRG calculations to reveal an evolution of several low-energy excited levels $E$ from the ground state energy $E_0$ under the magnetic field applied along the $x$, $y$, and $z$ axes. Figure S6 shows the results for $B$ and $D_s$ being parallel to $x$, in which the magnetic field lowers the first excited level most rapidly, leading to a closing of the spin gap. Then, the critical magnetic field $B_c = 2.15 \text{ T}$ has been obtained from an extrapolation to $E - E_0 \to 0$, as shown by the dotted line in Fig. S6. This value of $B_c$ is comparable with the reported critical field 2.3 T in the experiment [17] and 2.0 T of the peak position in $d^2M/dB^2$ as shown in Fig. 3(b) of the main text.
FIG. S4. Three lowest-energy levels with $q_0 = 1/4$ r.l.u. calculated by numerical diagonalization for a 16-site cluster at zero magnetic field. We have taken the Hamiltonian $H_{3U(2)} + H_{DM}$ with $J_1/J_2 = -3.24, J'/J_2 = 0.583, J_2 = 35.1$ K for (a) $D_0/J_1 = 0.2$, (b) $D_0/J_1 = 0.21$, (c) $D_0/J_1 = 0.215$, and (d) $D_0/J_1 = 0.22$. The horizontal orange bands point to the three low-energy spin excitation levels observed in neutron scattering experiments shown in Fig. 4(a) of the main text.

NUMERICAL CALCULATIONS OF INELASTIC NEUTRON-SCATTERING SPECTRA

Formulation.

Here, we compute inelastic neutron-scattering cross-sections at $T = 0$ through

$$I(Q, \omega) = \sum_{\alpha=x,y,z} \sum_{\beta=x,y,z} (\delta_{\alpha\beta} - Q_{\alpha}Q_{\beta}/Q^2) \left[ \sum_{\alpha'} \sum_{\beta'} R_{\alpha\alpha'} R_{\beta\beta'} S_{\alpha'\beta'}^{\alpha\beta}(Q, \omega) \right] F(Q)^2,$$

(S9)

where $R$ stands for a globally defined rotation matrix $R$, which connects the spin coordinate system with the crystallographic. We have also introduced the dynamical spin structure factor,

$$S^{\alpha\beta}(Q, \omega) = -\frac{1}{\pi} \text{Im}[\langle 0 | S^\alpha_{-Q}(\omega + i\eta + E_0 - H)^{-1} S^\beta_{Q} | 0 \rangle],$$

(S10)

with the magnetic form factor $F(Q)$ of Cu and the ground-state wavefunction $|0\rangle$ and energy $E_0$. Here, the Fourier transform $S^\alpha_Q$ of spin operators in a single two-leg ladder with the number $2L$ of spins is defined by

$$S^\alpha_Q = \frac{1}{\sqrt{2L}} \sum_{\sigma = \pm} \sum_{\ell = 0}^{L-1} e^{iQd_{\sigma,\ell}} S^\alpha_{\sigma,\ell},$$

(S11)

where the vectors $d_{\sigma,\ell}$ indicates the positions of Cu atoms in the ladder and are given by

$$d_{\sigma,\ell} = \begin{cases} \ell b/2 & (\sigma = +, \ell = \text{even}) \\ \ell b + d_1/2 & (\sigma = +, \ell = \text{odd}) \\ \ell b/2 + d_2 & (\sigma = -, \ell = \text{even}) \\ \ell b/2 + d_1 + d_2/2 & (\sigma = -, \ell = \text{odd}) \end{cases}$$

(S12)
FIG. S5. Several lowest-energy levels calculated by iDMRG at zero magnetic field. We have taken the Hamiltonian $H_{SU(2)} + H_{DM}$ with $J_1/J_2 = -3.24$, $J'/J_2 = 0.583$, $J_2 = 39$ K for (a) $D_u/|J_1| = 0.175$, (b) $D_u/|J_1| = 0.180$, (c) $D_u/|J_1| = 0.182$, and (d) $D_u/|J_1| = 0.185$. The horizontal orange bands point to the three low-energy spin excitation levels observed in neutron scattering experiments shown in Fig. 4(a) of the main text. Three dashed black curves in each figure are guides to the eyes for trajectories of twofold degenerate levels.

with $d_1 = (-4.669, 0.1337, 1.473)$ Å and $d_2 = (0.5849, 2.545, 1.627)$ Å [31]. An inversion operation and a $2_1$ screw operation about the $b$ axis on the ladder generate the other three ladders in the unit cell. Therefore, as far as interladder correlations are ignored, $S^{x\beta}(Q, \omega)$ per ladder both for $Q = (0, Q_b, 0)$ and after the powder averaging is independent of the ladder index.

For numerical calculations of $S^{x\beta}(Q, \omega)$, we perform a block continued-fraction expansion based on block Lanczos method [36] and the Schur complement, which are straightforward extensions of a continued fraction expansion based on the Lanczos algorithm [37,38]. We adopt $\eta = 0.016J_2$ for Figs. 4(b) and 4(c) and $\eta = 0.043J_2$ for Fig. 4(e) in the main text.

**Powder averaging.**

The powder average of neutron scattering spectra is given by the angle average,

$$I_{\text{p.a.}}(Q, \omega) = \frac{1}{4\pi} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi I(Q(Q, \theta, \phi), \omega). \quad (S13)$$

with the spherical coordinates $(Q, \theta, \phi)$ of $Q$. In the current case of the finite ladder, by taking the $b$ axis in the direction to the north pole $\theta = 0$, we can write the above Eq. as

$$I_{\text{p.a.}}(Q, \omega) = \frac{1}{2k_0 + 1} \sum_{k=-k_0}^{k_0} \frac{1}{2\pi} \int_0^{2\pi} d\phi I \left( Q \left( \sqrt{Q^2 - |Q_b^{(k)}|^2}, \pi/2, \phi \right) + Q_b^{(k)}, \omega \right), \quad (S14)$$

with $Q_b^{(k)} = (4\pi k/L)(b/b)$, where $k_0$ is an integer determined by $|Q_b^{(k_0)}| \leq Q < |Q_b^{(k_0+1)}|$ in the range $0 \leq k_0 \leq L/2-1$. 
FIG. S6. Magnetic field dependence of low-energy excitation levels. The exchange parameters given in Eq. (S8) are $J_1/J_2 = -3.24, J'/J_2 = 0.583, J_2 = 39\text{ K}, D_u/|J_1| = 0.182$ and $D_s/|J_1| = 0.285$. The dotted curve indicates the polynomial-fitted line for the lowest excitation gap. The gap collapses at a critical magnetic field $B_c \sim 2.15\text{ T}$.

Connecting the spin coordinate frame to the crystallographic.

In this subsection, we fix $L = 8$ unless otherwise noted. The neutron-scattering cross-sections actually depend on how the spin and crystallographic coordinate frames are related to each other, as is clear from Eq. (S9). Now we make the following observation by a close look at Fig. 4(a): The intensity at $Q = |Q_b^{(3)}| \sim 0.9\text{ Å}^{-1}$ is much smaller than that at $Q = |Q_b^{(1)}| \sim 0.3\text{ Å}^{-1}$, although the former can be as large as the latter since $Q_b^{(3)}$ is related to $-Q_b^{(1)}$ by the reciprocal lattice vector $(2\pi/b)(b/b)$. Therefore, we adjust the rotation matrix $R$ in Eq. (S9) so that the ratio,

$$\frac{\int_0^{1\text{ meV}} d\omega I(Q_b^{(3)},\omega)}{\int_0^{1\text{ meV}} d\omega I(Q_b^{(1)},\omega)}$$

is minimized. The solution has been obtained by the simplex method [40] as the Euler angles

$$\phi = 0.542\pi, \quad \theta = 0.724\pi, \quad \psi : \text{arbitrary},$$

for b-c-b (z-x-z) type rotations.

Interpolation of the results at discrete wavevectors.

The continuous spectra shown in Fig. 4(c) have been obtained by polynomial interpolations of three lowest eigen-energy spectra on a 28-site cluster with the parameter set $J_1/J_2 = -3.24, J_2 = 39\text{ K}, J'/J_2 = 0.583, D_u/|J_1| = 0.285$ and $D_s/|J_1| = 0.182$ estimated by iDMRG shown in Fig. S7. We assume the polynomial functions take minima at $Q_b = 0.25 (0.75)$ r.l.u. to ensure the consistency with the iDMRG result on the incommensurate wavevector in this particular parameter set. We have also performed linear interpolations of the intensities at discrete $Q_b$’s.

CALCULATIONS OF ELECTRON SPIN RESONANCE SPECTRA

Here, we deal with the absorbed microwave power [29] in electron spin resonance experiments. The absorption is given by

$$I(\omega, B, T) \propto \mu_0^{-1} B^2 \omega \sum_\alpha S_{B,T}^{\alpha}(\omega, Q = 0),$$

where $S_{B,T}^{\alpha}(\omega, Q = 0)$ is the density of states at zero wavevector and temperature. The symbol $\sum_\alpha$ denotes the summation over all spins. The term $\mu_0^{-1}$ is the magnetic permeability of free space.
FIG. S7. Inelastic neutron-scattering cross-section along the specific cut $Q = (0, Q_b, 0)$. The raw data are depicted by + symbols at the discrete energy levels with the associated magenta circles whose radii represent the relative intensities. The results obtained by polynomial interpolations are shown in the color map for comparison and in Fig. 4(c).

with the permeability $\mu_0$ of the vacuum, where we have introduced the diagonal part of the same dynamical spin structure factor as in the previous section but for $Q = 0$ under a magnetic field $B$ at a finite temperature $T$,

$$S^{\alpha \alpha}_{B,T}(\omega, 0) = -\frac{1}{\pi} \text{Im} \sum_{k=0}^{L/2-1} \sum_{n} e^{-\frac{E_{B,k,n}}{i\omega}} \langle B, k, n | S^{\alpha}_{0} (\omega + i\eta + E_{B,k,n} - H)^{-1} S^{\alpha}_{0} | B, k, n \rangle,$$

(S18)

where $|B, k, n\rangle$ and $E_{B,k,n}$ are the $n$th excited state and the associated eigenenergy of the total Hamiltonian $H$ given by Eq. (S1) with the wavenumber $k$ along the chain under the magnetic field $B$. At $T = 1.6$ K, which is comparable to the spin gap at $B = 0$, transitions among a few low-energy excited states at the incommensurate wavevector and at zero wavevector largely contribute to the spectra. We take the same 16-site cluster and perform the numerical exact diagonalization with $\eta = 0.007 J_2$. The results on the spectra are displayed in Fig. 5(c).

**EXPERIMENTS**

Set up of neutron scattering experiments

In the low-energy neutron scattering experiments using AMATERAS [41], the speed of the monochromating disk chopper was fixed at 300 Hz and the other disk choppers were fixed at appropriate conditions to achieve necessary incident energies and resolutions. In the high-energy neutron scattering experiments using 4SEASONS [42], the speed of the Fermi chopper was fixed at 150 Hz. The data were analyzed using the software UTSUSEMI [43]. Lastly, we comment that in a recent $\mu$SR study, the internal magnetic field and the muon spin relaxation rate indicate a formation of the singlet state below $\sim 7$ K and a saturation at around 1-2 K with decreasing the temperature [44]. This is consistent with the scenario of the nonmagnetic singlet ground state.

$g$ factor of polycrystalline $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$

We revisit the estimation of the $g$ factor of polycrystalline $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ by use of the electron spin resonance spectra with high magnetic field $B > 2$ T. Broad but clear resonances appear in the experimental transmission spectra at 76 K (Fig. S8(a)), and the resonance frequency monotonically increases with increasing magnetic field (Fig. S8(b)). By use of the linear fitting of the data in the frequency range $f = [59.3 : 291.4]$ GHz, the $g$ factor is estimated to be $g = 2.16 \pm 0.01$, which is larger than the reported value 2.03 [15].
FIG. S8. Electron spin resonance spectra of polycrystalline Rb$_2$Cu$_2$Mo$_3$O$_{12}$. (a) Experimental transmission spectra at 76 K for designated frequencies. (b) Magnetic field dependence of the resonance frequency.