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Proximate Quantum Spin Liquid on Designer Lattice

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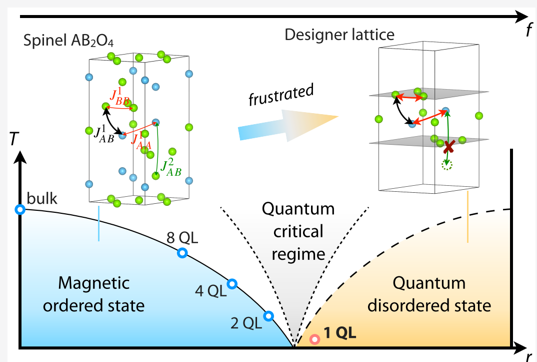
ABSTRACT: Complementary to bulk synthesis, here we propose a designer lattice with extremely high magnetic frustration and demonstrate the possible realization of a quantum spin liquid state from both experiments and theoretical calculations. In an ultrathin (111) $CoCr_2O_4$ slice composed of three triangular and one kagome cation planes, the absence of a spin ordering or freezing transition is demonstrated down to 0.03 K, in the presence of strong antiferromagnetic correlations in the energy scale of 30 K between Co and Cr sublattices, leading to the frustration factor of ∼1000. Persisting spin fluctuations are observed at low temperatures via low-energy muon spin relaxation. Our calculations further demonstrate the emergence of highly degenerate magnetic ground states at the 0 K limit, due to the competition among multiply altered exchange interactions. These results collectively indicate the realization of a proximate quantum spin liquid state on the synthetic lattice.



KEYWORDS: *ultrathin films, frustration, spin liquids, emergent magnetism*

In a magnetic crystal, the basic notion of minimizing free energy necessitates that after cooling down to sufficiently low temperature all spins should lock into a long-range ordered pattern. However, on a lattice where the exchange interactions between localized spins cannot be simultaneously satisfied, the system becomes magnetically frustrated with the tendency of forming unusual disordered phases significantly different from a simple paramagnet.[1−5] Furthermore, in recent years from a theory standpoint the combination of electronic correlations, quantum fluctuations, spin−orbit couplings, and lattices supporting frustrated magnetic interactions has been a remarkably fertile ground for predicting unconventional entangled states of quantum matter including magnetic monopoles in spin ice, topological superconductor, axion insulator, Weyl semimetal, magnetic fragmentation, and a variety of liquid-like spin states.[6−23] A quantum spin liquid (QSL) belongs to one of these exotic states; generally, it possesses no long-range magnetic order, lacks any spontaneously broken symmetry, and carries a spectrum of fractional excitations.[24−27]

As for the experimental realization of a QSL, the currently existing "recipes" are illuminating but limited.[28−34] On one hand, a general guiding principle is that in order to reach a QSL, significant frustration resulting either from the lattice geometry, multiple exchange terms, or bond conflict is an essential prerequisite.[31] After tremendous decades-long efforts, promising candidate materials have been proposed and synthesized, including the prototypical examples of the widely studied organic salts $EtMe_3Sb[Pd(dmit)_2]_2$ and κ-(ET_2)-$Cu_2(CN)_3$,[19] the herbertsmithite $ZnCu_3(OH)_6Cl_2$ and barlowite $Cu_3Zn(OH)_6FBr$,[29] and the Kitaev QSLs α-$RuCl_3$ and A_2IrO_3 (A = Na, Li).[32] On the other hand, however, the underlying lattices of almost all known QSLs are bound to five types of geometries, namely, triangular, pyrochlore, kagome, hyperkagome, and honeycomb lattices.[24,30,33] This in turn limits the pursuit of novel QSL candidates and brings to the focus open questions of whether any additional lattice motifs can host a QSL and how can it be achieved experimentally.

In recent years, complementary to bulk synthesis, heteroepitaxial engineering of ultrathin films, multilayers, and superlattices by means of advanced deposition techniques have been developed into a powerful platform for materials design and innovation.[35−41] In particular, geometrical lattice engineering principally aiming at the design and fabrication of lattices with artificial geometry by stacking on demand a specific number of atomic planes along unconventional crystallographic directions has been recognized as a promising path to emergent phenomena.[42−48] This framework once

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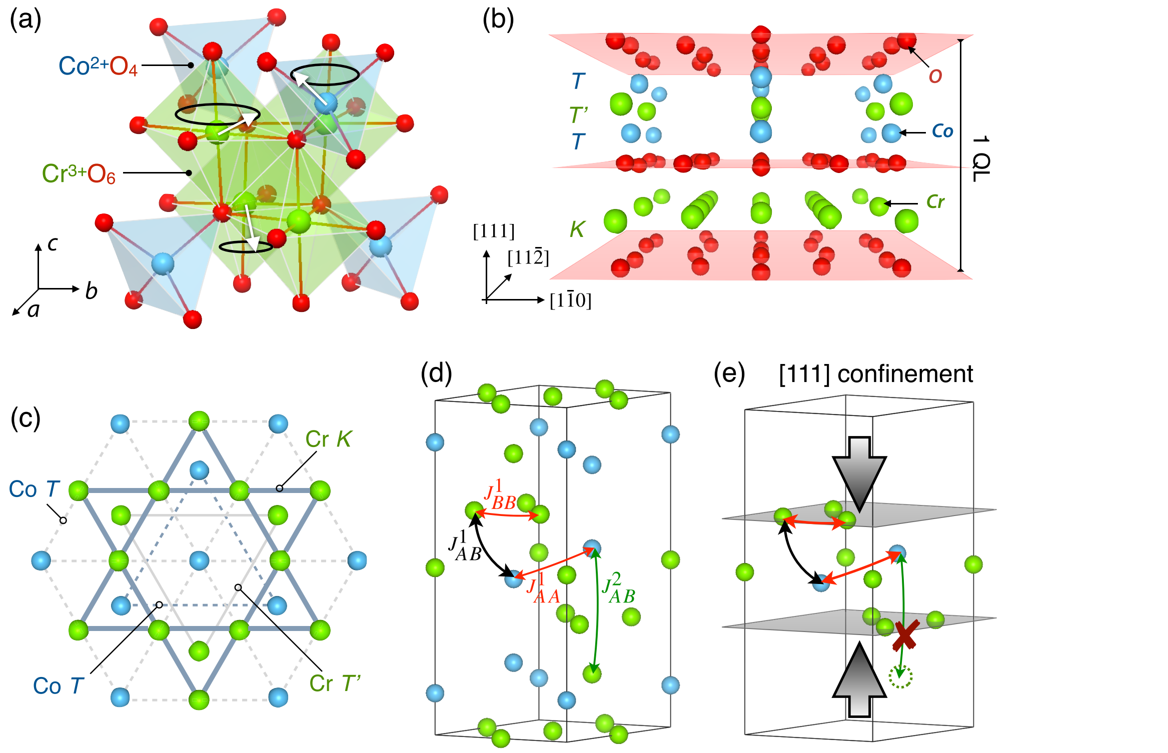

Figure 1. (a) Schematic representation of bulk $CoCr_2O_4$ composed of networks of $Co^{2+}O_4$ tetrahedra and $Cr^{3+}O_6$ octahedra. The arrows depict the conical spin configuration of the ground state. (b) Definition of one quadruplet layer (1 QL) of $CoCr_2O_4$ along the [111] direction, including four alternative cation planes: kagome Cr plane (K), triangle Co plane (T), triangle Cr plane (T′), and triangle Co plane (T). Note that such a quasi-2D lattice motif does not naturally exist, nor it can be realized via exfoliation of bulk crystals. (c) [111] top view of the alternative cation planes in 1 QL. (d) Magnetic exchange pathways in (111)-oriented $CoCr_2O_4$. (e) Effects of confinement on the exchange couplings in 1 QL $CoCr_2O_4$.

experimentally validated can offer an alternative approach for creating new classes of synthetic lattices, potentially hosting QSL and other intriguing states of quantum matter.

In this Letter, we address these challenges and propose a generic design of a novel quasi-two-dimensional (quasi-2D) lattice derived from the spinel structure and demonstrate its feasibility for supporting a QSL phase from both comprehensive sets of experiments and theoretical calculations. We note that although our system is an $S > 1/2$ system, its spin-fluctuation dynamics is still far from the large S limit, and the spins, in principle, can exhibit quantum features.[49−51] Concretely, using $CoCr_2O_4$ as a prototype, we fabricated a series of (111)-oriented ultrathin films, confined by non-magnetic Al_2O_3 layers into a quantum well geometry. Compared to its bulk counterpart, the onset of the ferrimagnetic transition decreases monotonically with reduced thickness and eventually shuts off in a single-unit slab of (111) $CoCr_2O_4$. In this quasi-2D limit, the degree of magnetic frustration becomes enhanced by almost 3 orders of magnitude with persisting spin fluctuations down to 30 mK. Our first-principles density functional theory (DFT) calculations and classical Monte Carlo (MC) simulations on this designer lattice reveal the presence of strongly frustrated magnetic configurations with a tremendous degree of degeneracy, which prevents the system from achieving a definite long-range ordering at 0 K limit. These combined results imply the realization of a proximate QSL in the single-unit (111) $CoCr_2O_4$ slice.

$CoCr_2O_4$ belongs to the normal spinel (AB_2O_4) chromite family, MCr_2O_4 (M = Mn, Fe, Co, and Ni)[52] where the magnetically active M^{2+} ions occupy the tetrahedral A sites of diamond sublattice and the Cr^{3+} ions occupy the octahedral B sites of pyrochlore sublattice, possessing complex spin configuration of the ground state.[53] Specifically, in bulk $CoCr_2O_4$ [Figure 1a], a collinear ferrimagnetic state first forms with the Curie temperature of ∼93 K, which transforms into an incommensurate spiral ferrimagnetic state at ∼26 K. An incommensurate to commensurate lock-in transition further takes place at ∼14 K.[54,55] When viewed along the [111] direction, the structure is an intrinsic stacking of triangle (T) and kagome (K) cation planes from Co and Cr ions embedded in the oxygen cubic close-packed frame. This leads to a sequence of "−O−Cr(K)−O−Co(T)−Cr(T′)−Co(T)−" in a single unit with four cation layers, which we denote as one quadruplet layer (1 QL) [Figure 1b,c].

Bulk $CoCr_2O_4$ is weakly frustrated due to the interplay of multiple exchange couplings [Figure 1d]. The most dominant first-neighbor J^1_{AB} interatomic coupling is antiferromagnetic (AFM), which alone would favor a Néel-type collinear ferrimagnetic ordering. The weak magnetic frustration originates from the competition between J^1_{AB} and the intra-atomic AFM couplings J^1_{BB} and J^1_{AA} and is partially relieved by the second-neighbor ferromagnetic coupling J^2_{AB}. Because of the entwined nature of those couplings, one can conjure that if the lattice is made [111] confined [Figure 1e], the magnetic frustration could be markedly elevated as a result of enhanced geometric frustration from J^1_{BB} and J^1_{AA} on kagome and triangle planes plus termination of the out-of-plane J^2_{AB}, which may collectively trigger the formation of QSL.

On the basis of this design idea, [n QL $CoCr_2O_4$/1.3 nm Al_2O_3]$_4$ (n = 1, 2, 4; 1 QL ≈ 4.8 Å) superlattices were fabricated by pulsed laser deposition on (0001)-oriented single

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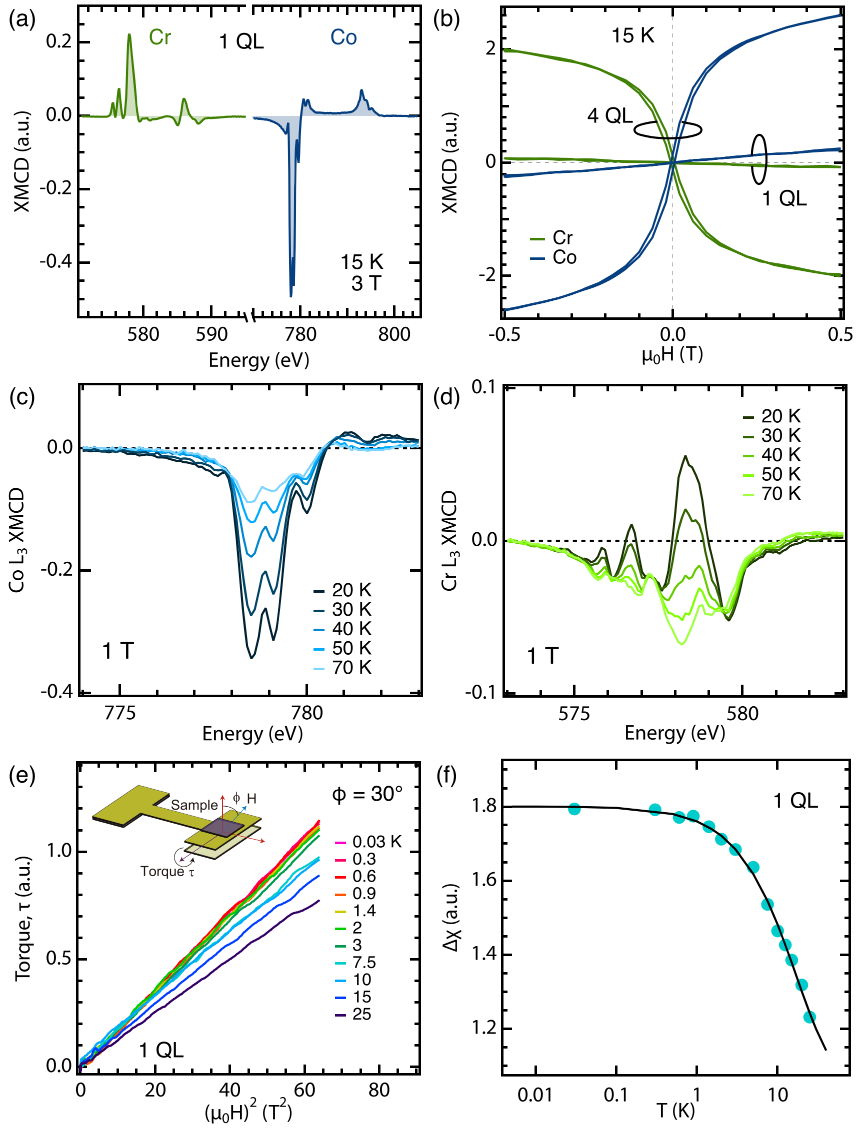

Figure 2. (a) XMCD spectra at $L_{2,3}$ edges of both Co and Cr in 1 QL $CoCr_2O_4$. (b) Field dependence of the XMCD L_3 intensity of Co (∼778 eV) and Cr (∼577 eV). Results of both 4 and 1 QL $CoCr_2O_4$ are shown for comparison. (c,d) Co and Cr L_3 XMCD spectra at various temperatures. (e) Torque magnetometry curves of 1 QL $CoCr_2O_4$ at the temperatures between 25−0.03 K. (f) Temperature dependence of $\Delta\chi$ extracted from linear fit of the τ versus H^2 curves [$\tau = \Delta\chi(\mu_0 H)^2$] from (e). The solid line is a guide for the eye.

crystal Al_2O_3 substrates. Details of the synthesis and characterization were reported elsewhere.[56,57] It is noteworthy that, recently, an emergent Yafet-Kittel type ferrimagnetic state due to the enhanced frustration in 4 and 2 QLs of $CoCr_2O_4$ was reported in ref 48. In this Letter, we primarily focus on the 1 QL case.

First, we start with the investigation of the magnetic behavior of each sublattice by recording the resonant X-ray absorption spectroscopy (XAS) taken with left- and right-circularly polarized beams. The difference between those two spectra, called X-ray magnetic circular dichroism (XMCD), reflects the net magnetization of a specifically probed element.[58] As shown in Figure 2a, XMCD of both Cr and Co are clearly observed at 15 K with opposite sign, as indicated by the distinct features at the L_3 edges (Cr ∼ 577 eV and Co ∼ 778 eV). These results confirm that at low temperatures due to the AFM J^1_{AB} term, the overall orientation of spins on the Co sublattice is along the field, whereas that on the Cr sublattice is against the field. Then at high temperatures where the thermal energy overcomes the exchange interaction, a paramagnetic state is expected with the orientation of all spins aligned parallel to the external field. This is in fact demonstrated by temperature-dependent XMCD spectra at L_3 edges, where the sign of Cr flips at temperatures above ∼30 K [see Figure 2c,d].

With the knowledge about the scale of J^1_{AB}, we can explore whether a long-range magnetic ordering is present in 1 QL $CoCr_2O_4$. The J^1_{AB} term favors a ferrimagnetic state with a ferromagnetic spin arrangement on each sublattice.[59] As a result, hysteretic behavior is anticipated from field-dependent XMCD scans. As seen in Figure 2b, this is indeed observed in the thicker 4 QL $CoCr_2O_4$ that exhibits clear hysteresis loops at both Co and Cr L_3 edges, consistent with the previous study that the ground state of 4 QL $CoCr_2O_4$ hosts an emergent Yafet-Kittel type ferrimagnetic ordering.[48] However, in sharp contrast no hysteresis loop but a linear XMCD versus H relationship is found on both Co and Cr in 1 QL $CoCr_2O_4$, typical of a paramagnetic behavior.

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In order to further examine if any long-range spin ordering emerges at extremely low temperatures, we performed the torque magnetometry measurements on 1 QL $CoCr_2O_4$ from 30 K down to 0.03 K. This technique quantifies the magnetic torque response of a sample with respect to the applied magnetic field ($\tau \propto \mathbf{M} \times \mathbf{H}$) and is an exquisitely sensitive utility to probe vanishingly small magnetic signals from ultrathin samples and interfaces.[60,61] The result shown in Figure 2e confirms that within the resolution of measurement and entire temperature range, no hysteresis but a reversible parabolic $\tau \propto (\mu_0 H)^2$ relationship is observed for 1 QL, which implies a quantum paramagnetic behavior persisting down to 0.03 K. To make a thorough comparison and eliminate questions about sensitivity of the measurement, we also collected the torque signal on 4 QL $CoCr_2O_4$ using the same geometry. The data clearly exhibit distinct hysteretic loops (a hallmark of ferro-/ferri-magnetism) appearing below the Curie temperature of 58 K [see SI, Figure S3]. These observations agree well with the field-dependent XMCD results, providing strong evidence for the absence of long-range magnetic ordering in 1 QL $CoCr_2O_4$ down to 0.03 K. In addition, formation of a spin glass is likely ruled out, as its torque signal usually exhibits a nonparabolic relationship to H.[62] A combination of these data results in the extremely large frustration factor $f = \Theta_{CW}/T_C \sim 1000$ in 1 QL, which is almost 3 orders of magnitude larger than that of bulk $CoCr_2O_4$ ($f \sim 6$).[63] Furthermore, it is notable that the extracted anisotropic susceptibility $\Delta\chi$ gradually increases as the temperature decreases and becomes finite and temperature-independent below ~1 K, as guided by the solid line in Figure 2f. These results lend strong support for the existence of low-lying magnetic excitations, implying the appearance of nearly degenerate ground states in 1 QL.[64]

Next, we turn to investigate the spin dynamics of 1 QL $CoCr_2O_4$ by low-energy muon spin relaxation (μSR) spectroscopy from 70 to 4 K in both zero-field (ZF) and 30 G transverse-field (TF) setup. Thanks to its high sensitivity to local fields and capability to characterize the time scale of spin fluctuations, μSR can reliably distinguish between the presence of static moments due to conventional spin ordering or freezing, and dynamical spin moments due to frustration and degeneracy.[65−72] In ZF-μSR, a simple exponential decay with no oscillatory signal is observed, whereas a slowly relaxing signal precessing at the muon Larmor frequency is clearly observed in all of the TF-μSR spectra (see SI Figure S5 for detailed data). As a result, no coherent precession of the incident μ^+ is found, ruling out the formation of a static uniform local field, characteristic of magnetic phases without long-range ordering (i.e., ferro-/ferri-magnet and commensurate antiferromagnet).[66]

The spin asymmetry and the relaxation rate λ are extracted by fitting the spectra of the time evolution of polarization [see SI for more details], and their temperature dependencies are shown in Figure 3. While below 30 K, the asymmetry decreases with the lowered temperatures, both relaxation rates (in ZF and TF) first increase, reaching a broad "hump" at around 10 K, followed by a reduction again at the base temperatures. These results deem a spin glass transition to be absent because (1) the simple exponential relaxation observed at all temperatures is not the expected form for any type of spin glass;[73,74] (2) in addition, the ZF-μSR time spectra lack the characteristic "tail" of polarization recovery to one-third, which is expected in spin glasses with static random local fields;[66] (3) the ZF λ only

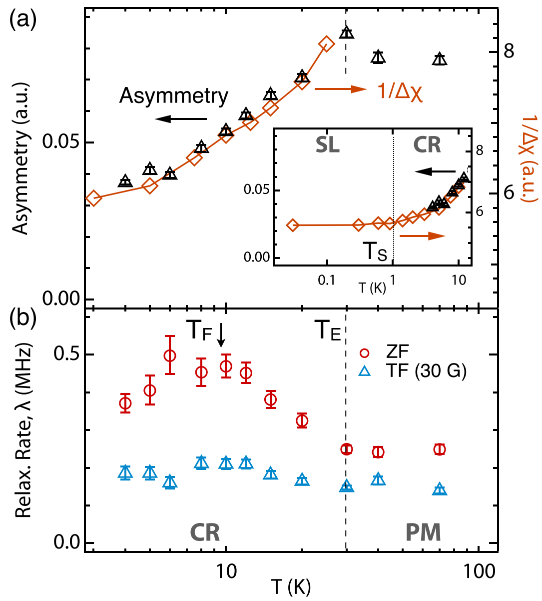

Figure 3. (a) Temperature dependence of the spin asymmetry (left axis) from μ^+ decay and $1/\Delta\chi$ (right axis) from torque measurements on 1 QL $CoCr_2O_4$. Inset shows the data at 0.03−10 K with T_S indicating the temperature-independent behavior of $1/\Delta\chi$ below ~1 K. (b) Temperature dependence of the μ^+ spin relaxation rate λ from both zero field (red) and 30 G transverse field (blue) measurements. Both asymmetry and λ show a temperature-independent behavior above $T_E \sim 30$ K; below 30 K, λ gradually increases to a broad peak at $T_F \sim 10$ K. PM, CR, and SL represent "paramagnet", "crossover region", and "spin liquid", respectively.

slightly increases from ~0.25 MHz at 70 K to 0.35 MHz at 4 K, while below the freezing point of a spin glass, λ typically increases by an order of magnitude ($\lambda \sim 1$−20 MHz).[69]

From the spin dynamics viewpoint, three characteristic temperatures, T_E, T_F, and T_S appear in 1 QL $CoCr_2O_4$ [Figure 3]. Specifically, above $T_E \sim 30$ K, the muon spins are mainly depolarized by the rapid fluctuations of local fields due to thermal excitations, leading to both asymmetry and λ as nearly constant, which are conventional paramagnetic features. This observation is also consistent with the XMCD results, indicating the thermal energy overcomes the most dominant J^1_{AB} at 30 K. Next, asymmetry starts to decrease accompanied by the increase in λ suggesting the slowing down of spin fluctuations due to the onset of J^1_{AB}, triggering short-range spin−spin correlations between Co and Cr ions. We recap that the local moments of both Co^{2+} ($S = 3/2$) and Cr^{3+} ($S = 3/2$) are ~3.7 μ_B, which should correspond to a local distribution ~4500 G for a fully static spin.[75] In contrast, we observed a field of only ~500 G, which corresponds to a static moment ~0.4 μ_B only. This indicates that majority of the Co and Cr moments do not freeze and remain fluctuating at finite frequency down to 4 K.

At this point, it is interesting to compare $\Delta\chi$ deduced from the torque data with the local spin susceptibility sensed by muons. As shown in Figure 3a, the trend in spin asymmetry very closely resembles that of the inverse $\Delta\chi$. Namely, it monotonically drops to about 50% at 4 K and becomes practically temperature-independent below $T_S \sim 1$ K. Thus, we can conjecture that below 1 K the spins are entangled all over the sample with persisting dynamics of spin fluctuations. On the other hand, the relaxation rates also have a tendency to level off at very low temperatures. This behavior in λ is similar

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to that of several well-characterized gapless QSL candidates including both $S = 1/2$ and $S > 1/2$ systems.[76−81]

To obtain a microscopic insight into how the designer lattice topology and quantum confinement alter the exchange interactions and consequently the magnetic ground state, we performed DFT calculations and MC simulations on bulk, 2 and 1 QL $CoCr_2O_4$. We calculate the normalized strength of each exchange term J^N_{ij}/J^1_{AB}. As shown in Figure 4, toward the

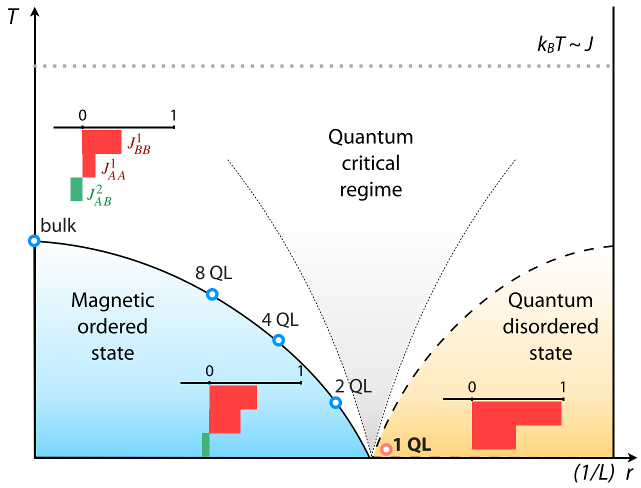

Figure 4. Evolution of the magnetic states of n QL $CoCr_2O_4$ mapped onto a generic diagram of quantum phase transition. r refers to a nonthermal control parameter (in this case, $1/L$, inverse of the out-of-plane dimension) . For bulk, $n = 2$ and $n = 1$, the normalized strength of each exchange coupling (J^N_{ij}/ J^1_{AB}) is exhibited by the bar chart; red (green) color indicates AFM (FM) coupling.

2D limit ($1/L \to \infty$), it is striking that the relative strengths of J^1_{BB} and J^1_{AA}, which act to enhance frustration, increase, whereas the contribution of J^2_{AB}, which tends to relieve frustration, rapidly decreases. The computational data reveal this key effect is a consequence of the markedly smaller number of second-neighbor interactions along (111) in the ultrathin films compared to bulk. In fact, for 1 QL $CoCr_2O_4$ with J^2_{AB} completely suppressed, J^1_{BB} and J^1_{AA} reach almost the same scale as J^1_{AB}, in contrast to the behavior in the bulk. This trend agrees very well with the experiments which evidently indicates the presence of extremely large magnetic frustration in 1 QL. Additionally, our classical MC simulations lend further support to this claim, affirming the presence of a paramagnetic phase with a plethora of competing magnetic ground states in 1 QL $CoCr_2O_4$ [see SI Figures S9−S11].

Finally, we can map the ground state of the n QL $CoCr_2O_4$ system onto a generic quantum phase transition diagram.[19,82] In the bulk ($n \to \infty$), the ground state is a well-defined long-range magnetically ordered state. As n is reduced, it becomes more and more difficult to stabilize a conventional ordered state due to the enhancement of magnetic frustration. Eventually the ground state becomes highly degenerate in 1 QL $CoCr_2O_4$, unleashing dynamical spin fluctuations. We note this is the regime where quantum effects play a pivotal role in bringing the system into a proximate QSL state without a spin gap.

To summarize, we proposed a general design protocol for novel nonbipartite lattices supporting QSL and demonstrated its realization in 1 QL $CoCr_2O_4$ where the magnetic frustration is profound and the ground state is highly degenerate with robust spin fluctuations. Our findings call for further investigation on the excitation spectrum and open a window to a versatile class of new synthetic QSL candidates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04498.

Additional information regarding sample fabrication, synchrotron XAS and XMCD, torque magnetometry measurements, μSR experiments, DFT calculations, and Monte Carlo Simulations (PDF)

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Notes

The authors declare no competing financial interest.

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