Concurrence of topological electrons and magnons in the Kagome ferromagnet CoCu$_3$(OH)$_6$Cl$_2$

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Spin and charge are two interrelated properties of electrons. However, most of previous works on topological matter study the electronic and magnonic excitations separately. In this paper, by combining density functional theory calculations with the Schwinger boson method, we determine the topological electronic band structures and topological magnon spectrum simultaneously in the ferromagnetic ground state of the narrow-band-gap CoCu$_3$(OH)$_6$Cl$_2$, which is an ABC stacking Kagome lattice material with fractional occupancy on Cu sites. This material provides an ideal platform to study the interplay of different types of topological excitations. Our work also proposes a useful method to deal with correlated topological magnetic systems with narrow band gaps.

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Introduction — The topological phases of matter have attracted intensive interest in the last decades. While the studies of topological states originally focus on electronic systems [1–8], a route has been inspired towards the generalization of topological states to bosonic quasiparticles. For instance, topologically nontrivial bands have been characterized in photonic [9], phononic [10], and magnonic [11] systems. The topological magnon excitations are particularly interesting, which can be viewed as the magnetic counterpart of electronic systems in the vector space of spin waves. In the presence of strongly correlated electrons, the topological properties of the magnon bands and electron bands become intrinsically connected. Yet, their relationships and mutual influences are comparatively less studied and require more research efforts.

The Kagome lattice provides an ideal platform to study the interplay of topological states and correlated electrons. The system has been known to yield flat bands and Dirac points [12], which could further give rise to topological and Chern insulating phases by considering the spin-orbit coupling (SOC) and ferromagnetism [13–15]. Furthermore, a class of Herberstsmithite-type Kagome materials exhibits spin liquids [16], viscous electron fluids [17], and $f$-wave superconductivity [18]. In Kagome magnets, the bosonic magnon quasiparticles may have a Dirac-like spectrum or form topologically nontrivial insulating phases [11,19,20]. Inelastic neutron scattering experiments have observed anomalous thermal Hall effects and protected chiral edge modes from the topological magnon band structures in insulating Kagome ferromagnets [21,22]. Nonetheless, previous works on topological magnons mostly focus on the Heisenberg model [20,22], in which electron charges are frozen and the whole system becomes a bosonic system composed of localized spins. However, this supposition does not apply to materials with narrow band gaps, where electron hoppings cannot be neglected, and the charge and spin degrees of freedom are both significant.

In this work, starting from density functional theory (DFT) calculations, we build a $t-J$ model to study the Kagome ferromagnet CoCu$_3$(OH)$_6$Cl$_2$. By using the Schwinger boson mean-field theory (SBMFT) [23,24], we take into account both the charge and the spin degrees of freedom and obtain topologically nontrivial fermionic and bosonic excitation spectra simultaneously.

FIG. 1. (a) Rhombohedral primitive cell of CoCu$_3$(OH)$_6$Cl$_2$ with space group R-3m (No. 166). (b) Top view along the hexagonal c-axis to show the Cu Kagome layer. H and Cl ions are omitted. (c) Brillouin zone and high-symmetry path. (d) The hybridized Wannier orbital centered on a Cu site.
approximation + Hubbard Burke-Ernzerhof (PBE) type of the generalized gradient ab initio simulation package (VASP) [25, 26]. Perdew-the ABC-stacking Kagome layers formed by the Cu ions. The topological properties using WannierTools [30].

The maximally localized Wannier functions of the Cu

determine fillings of the Cu-ions exhibit diverse valences, which give rise to different fillings of the Cu-(d_{x^2−y^2}&d_{xy}) states and various topological properties [15–18]. We emphasize that the third ionization energy of Co is very close to that of Ga, and the octahedral environments in CoCu_3(OH)_6Cl_2 and GaCu_3(OH)_6Cl_2 are very similar. As a result, the Co ions tend to be trivalent, as opposed to the divalent Zn ions in ZnCu_3(OH)_6Cl_2. The Co^{3+} ions will lead to the fractional valence of Cu^{2+}, which means that the filling number of (d_{x^2−y^2}&d_{xy})^* is 4/3 per Cu ion (n = 4/3). Such filling makes the Dirac points cross the Fermi level exactly in the NM phase without the SOC, as shown by the black bands in Fig. 2b. When the SOC is considered, a topologically nontrivial gap of about 20 meV is opened, which gives rise to a weak topological insulator (TI) with the index Z_2 = 1.

We first calculate the nonmagnetic (NM) phase by GGA, and plot the density of states (DOS) with SOC and electronic band structures with/without SOC in Figs. 2b & 2c, respectively. By analyzing the projected DOS, it is clear that the states of the O, H and Cl ions are far from the Fermi level (0 eV), while all states between −1.25 ~ 1.5 eV are dominated by the 3d-orbitals of Co and Cu ions. Since the Co ions are in an octahedral environment, the crystal-field effect will split the 3d-orbitals into two manifolds – the lower-energy t_{2g} states between −1.25 ~ −0.5 eV and the higher-energy e_g states between 1.0 ~ 1.5 eV, which suggests that the crystal field splitting is about 2.2 eV. The energy window of −0.5 ~ 0.5 eV is dominated by the Cu 3d-orbitals – specifically the (d_{x^2−y^2}&d_{xy}) states.

Our NM calculations suggest that the Co ion is trivalent. In the Herbertsmithite family MCo_3(OH)_6Cl_2 (M = Li^{+}, Na^{+}, Zn^{2+}, Mg^{2+}, Ga^{3+}, Sc^{3+}, etc.), the M ions exhibit diverse valences, which give rise to different fillings of the Cu-(d_{x^2−y^2}&d_{xy})^* states and various topological properties [15–18]. We emphasize that the third ionization energy of Co is very close to that of Ga, and the octahedral environments in CoCu_3(OH)_6Cl_2 and GaCu_3(OH)_6Cl_2 are very similar. As a result, the Co ions tend to be trivalent, as opposed to the divalent Zn ions in ZnCu_3(OH)_6Cl_2. The Co^{3+} ions will lead to the fractional valence of Cu^{2+}, which means that the filling number of (d_{x^2−y^2}&d_{xy})^* is 4/3 per Cu ion (n = 4/3). Such filling makes the Dirac points cross the Fermi level exactly in the NM phase without the SOC, as shown by the black bands in Fig. 2b. When the SOC is considered, a topologically nontrivial gap of about 20 meV is opened, which gives rise to a weak topological insulator (TI) with the index Z_2 = 1.

To demonstrate the bulk-boundary correspondence, we construct the Wannier functions of the Cu-(d_{x^2−y^2}&d_{xy})^* states to build a single-orbital tight-binding model in the Herbertsmithite Kagome materials. In Fig. 1, we plot our Wannier function in real space and find that the first interlayer hopping is much weaker than the second
interlayer hopping, and many qualitative features are correctly captured when only the latter is retained. This is the reason why we use the second interlayer hopping in our \( t-J \) model for later discussions. By using the Green’s function method, we investigate the surface states of the (001) plane as shown in Fig. 2. It is clear that there are two Dirac cones on the (001) plane, which is consistent with the conclusion that only an even number of surface Dirac cones can appear on crystal planes with Miller index \( \vec{h} = \sum_i h_i b_i \) satisfying \( h_i \neq \nu_i \) mod 2 [31]. Moreover, \( (\nu_1 \nu_2 \nu_3) = (111) \) demonstrates that this weak TI can be taken as 2D TI (QSH system) layers stacked along the (111) direction, i.e., \( c \)-axis of the hexagonal unit cell. Therefore, there will be oscillatory transitions between 2D QSH insulators and trivial insulators if one cleaves the weak TI into slabs along the \( c \)-axis. In Fig. 2, we plot the Wilson loop evolution for the slab with three layers, which confirms it fall into the 2D TI phase. In contrast, the Wilson loop of the slab with two layers shown in Fig. 2 identifies it as a trivial insulator. Further calculations illustrate that the slabs with odd numbers of layers are 2D TIs, while the slabs with even numbers of layers are trivial, as depicted in Fig. 2. Such results agree well with our expectations and are consistent with a similar crystal structure studied in Ref. [32].

Considering that Co and Cu usually exhibit magnetism and correlation effects, we further calculate multiple magnetic structures by using the DFT + \( U + \) SOC method. Interestingly, our calculations show that no magnetic moments were stabilized on Co\(^{3+} \). This is because the crystal field splitting (2.2 eV) is much larger than the typical Hund’s coupling (0.5 eV) and the Zeeman splitting on Co\(^{3+} \) (0.1 eV). As a result, the six Co-3d electrons fully occupy the \( t_{2g} \) bands, and no magnetic moment could be left on Co\(^{3+} \). Similar properties also exist in other compounds with Co\(^{3+} \) centered octahedra [33]. Based on the above analysis, we hereafter focus on the magnetism of Cu with ferromagnetic (FM) and frustrated antiferromagnetic (AFM) orders (as shown in Fig. 1). We should note that both magnetic phases are much lower in energy than the NM phase in our calculations. Thus, once one electron will totally occupy the \( C \) = 1 band, and the system becomes a 3D layered Chern insulator [13], which provides the possibility to realize a quantum anomalous Hall (QAH) insulator by cleaving off a few layers [35].

\[ H_{\text{Hubbard}} = \sum_{i \neq j} \sum_{\alpha \beta} t_{ij}^\alpha \tilde{c}_{i\alpha}^\dagger c_{j\beta} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \]  

(1)

where \( c_{i\alpha}^\dagger, c_{j\beta} \) creates/destroys an electron on sites \( i,j \) with spin \( \alpha, \beta = \uparrow, \downarrow, \) \( n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha} \), \( U \) is an on-site Coulomb repulsion and the hopping parameters \( t_{ij}^\alpha = t_{ij} \delta_{\alpha\beta} - i \vec{\omega}_{ij} \cdot \vec{\sigma}_{\alpha\beta} \) take into account the SOC, with \( \vec{\sigma} \) being the Pauli vector and \( \vec{\omega}_{ij} = -\vec{\omega}_{ji} \). According to previous studies [36], \( U \approx 4 \) eV is much greater than \( t \approx 0.2 \) eV in Herbertsmithites. Thus, Eq. (1) can be reduced to a \( t-J \) model \( H_{t-J} = H_t + H_J \) given by

\[ H_t = \sum_{i \neq j} \sum_{\alpha \beta} t_{ij}^\alpha P_{\alpha \beta} c_{i\alpha}^\dagger c_{j\beta} P, \]

(2a)
are plotted in Fig. 4, which shows that our fermionic model Hamiltonian nicely reproduces both the energy dispersion and the topological properties of the electronic bands calculated by DFT.

Based on the filling $n = 4/3$, the self-consistently determined doublon occupancy is $(f_1 f_1) = 1/3$ in our $t - J$ model. Then according to Eq. (3) and that the total magnetic moment is $2\mu_B/p.c.$, we have $(b_1^\dagger b_1) = 2/3$ and $(b_2^\dagger b_2) = 0$, confirming that the FM phase is realized in Co-Herbertsmithite. As a result, only the spin-up spinons exist in the bosonic ground state, in which all spinons condense at the $\Gamma$ point, and the magnonic excitation is given by the spin-down spinon bands, as discussed in Ref. [40]. This is because creating a magnon in the FM phase is equivalent to destructing a spin-up spinon in the Bose condensate and recreating a spin-down spinon that carries the momentum of the magnon. Our calculations show that $\Delta E_F$ is independent of the Heisenberg couplings $J_{ij}$, which is consistent with Ref. [41]. Another important feature in Fig. 4b is that the three magnon bands are well-separated by the SOC-induced k-dependent Dzyaloshinskii-Moriya interactions [42]. We calculate the magnon Chern numbers in a fixed $k_z$ plane and obtain $C_{1-3}^{\text{magn}} = -1, 0, 1$ from bottom to top, which agree with previous studies on topological magnon insulators in Kagome ferromagnets [43, 44].

For any fixed $k_z$, the fermionic and bosonic Hamiltonians in Eqs. (5)–(6) become 2D systems with nontrivial Chern numbers. We then use the Green’s function method to calculate the edge states for $k_z = 0$ and plot them in Figs. 4 & 5. Fig. 5 shows the fermionic local density of states in the X direction. There is a chiral edge mode across the Fermi level propagating along +X, which agrees with the Chern number $C = 1$ of the occupied band from DFT calculations. In Fig. 4, we illustrate the magnonic excitation spectrum of a semi-infinite quasi-1D sample along the X direction, which clearly shows two chiral edge modes in the bulk gaps of 90 $\sim$ 115 meV and 165 $\sim$ 190 meV. The edge modes in Fig. 4 have the same chirality and both propagate in the $-X$ direction, which is a natural consequence of the Chern numbers $C_{1-3}^{\text{magn}} = -1, 0, 1$. Since magnons can carry heat currents, the magnon Chern numbers are closely related to the thermal Hall conductivity in topological magnon systems [43, 44]. We expect that the magnon thermal Hall effect can be realized in FM Co-Herbertsmithite, which has been observed in other Kagome ferromagnets [21, 22].

**Conclusion** — We have formulated a Schwinger boson method for the spin-orbital coupled $t - J$ model constructed based on first-principles calculations, which gives the electronic and magnonic excitation spectra and their topological properties self-consistently. Our approach is advantageous for narrow-band-gap magnetic systems, where electrons do not freeze into fully local-
ized spins as assumed in the Heisenberg model. We apply our method to the Co-Herbertsmithite and obtain 3D topological Chern bands of electrons and magnons simultaneously. The present work demonstrates that the Schwinger boson method is suitable for narrow-band-gap correlated topological materials, where both the charge and spin contribute to the low-energy physics.

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