Dirac magnons in a honeycomb lattice quantum XY magnet CoTiO₃

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The discovery of massless Dirac electrons in graphene and topological Dirac-Weyl materials has prompted a broad search for bosonic analogues of such Dirac particles. Recent experiments have found evidence for Dirac magnons above an Ising-like ferromagnetic ground state in a two-dimensional (2D) kagome lattice magnet and in the van der Waals layered honeycomb crystal CrI₃, and in a 3D Heisenberg magnet Cu₃TeO₆. Here we report on our inelastic neutron scattering investigation on large single crystals of a stacked honeycomb lattice magnet CoTiO₃, which is part of a broad family of ilmenite materials. The magnetically ordered ground state of CoTiO₃ features ferromagnetic layers of Co²⁺, stacked antiferromagnetically along the c-axis. We discover that the magnon dispersion relation exhibits strong easy-plane exchange anisotropy and hosts a clear gapless Dirac cone along the edge of the 3D Brillouin zone. Our results establish CoTiO₃ as a model pseudospin-1/2 material to study interacting Dirac bosons in a 3D quantum XY magnet.

The discoveries of graphene and topological insulators have led to significant advances in our understanding of the properties of electron in solids described by a Dirac equation. In particular, the fruitful analogy between fundamental massless Weyl-Dirac fermions in Nature and electrons in graphene or topological semimetals has allowed physicists to simulate theories of particle physics using tabletop experiments. Remarkably, the concept of Dirac particles is not limited to electrons or other fermionic quasiparticles, prompting a search for analogues in photonic crystals, acoustic metamaterials, and quantum magnets. In particular, Dirac magnets, or more broadly defined topological magnons, have attracted much attention as platforms to investigate the effect of inter-particle interaction or external perturbations on Dirac bosons, and are proposed to be of potential interest in spintronic applications.

In contrast to light and sound, the symmetry broken states and emergent bosonic excitations of quantum magnets depend crucially on dimensionality and spin symmetry, which provides a fertile playground for examining the physics of topological bosons. To date, gapped topological magnons in Ising-like ferromagnets have been reported in a kagome lattice material Cu(1,3-bdc) and in a layered honeycomb magnet CrI₃. On the other hand, magnons exhibiting symmetry protected band crossings have been found only in a single material, a three-dimensional (3D) Heisenberg antiferromagnet Cu₃TeO₆. It is thus desirable to explore new test-beds with distinct spin symmetries to expand our understanding of the physics of Dirac magnons.

In this paper, we present a new model 3D quantum XY magnet realizing gapless Dirac magnons, CoTiO₃, which has a simple ilmenite crystal structure. The magnetic lattice of Co²⁺ ions in CoTiO₃ is a stacked honeycomb lattice, exactly the same as in ABC stacked graphene. Below Tₙ ≈ 38 K, this material exhibits magnetic order with ferromagnetic planes stacked antiferromagnetically along the c-axis. Our inelastic neutron scattering (INS) experiments reveal crystal field excitations and sharp low energy dispersive spin waves. Although Co²⁺ is a spin S = 3/2 ion, resulting in a large magnetic signal, our analysis of the observed low energy crystal field levels provides evidence for strong easy-plane single-ion anisotropy leading to a pseudospin S = 1/2 doublet ground state. The low energy spin-wave dispersion reveals clear crossings of magnon modes exhibiting Dirac cone dispersion in the 3D Brillouin zone (BZ). A simple model Hamiltonian with dominant nearest neighbor XY ferromagnetic (FM) exchange, and antiferromagnetic interlayer second-neighbor exchange, provides an excellent description of the magnon dispersion. In addition, the observed spin-wave intensities highlight the stark contrast between the two different transverse fluctuation modes, distinguishing this XY magnet from Ising-like or Heisenberg magnets.

Unlike the other materials mentioned above, large, pristine, single crystal samples of this material, suitable for neutron scattering and other experiments, can be grown using the conventional floating zone method. In addition, ilmenites can be grown as epitaxial thin films using conventional oxide film growth methods, permitting future explorations of epitaxial strain and incorporation in spintronic devices.

Crystal structure, crystal field levels: As shown in Fig. 1, CoTiO₃ crystallizes in an ilmenite structure (R3) that consists of alternating layers of edge-sharing
CoO₆ or TiO₆ octahedra [22]. Details of the synthesis and other experimental details are provided in the Supplemental Material. The magnetic properties of CoTiO₃ are determined by the Co²⁺ ions which reside in a slightly buckled honeycomb layer; see Fig. 1b. The layers are ABC stacked along the c direction, with neighboring honeycomb planes displaced diagonally by a third of the unit cell.

Atomically, each Co²⁺ in a high spin state is surrounded by a trigonally distorted oxygen environment depicted in the inset of Fig. 2b. Local electronic states in Co²⁺ are determined by a combination of trigonal distortion Δ_{trig} and spin-orbit coupling λ. To elucidate the magnetic ground state of each Co²⁺ ion, we measured the crystal field excitations using high energy inelastic neutron scattering (INS). The results shown in Fig. 2a and Fig. 2b clearly reveal three transitions at ~30 meV, ~60 meV, and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV. Their intensities decrease with increasing momentum transfers as shown in Fig. 2a, with no directional dependence of the crystal field excitations (see Supplemental Material for details), leading to transitions at ~60 meV and ~130 meV, together with a broad continuum between 60 meV-120 meV.
FIG. 3. (a)-(d) Momentum and energy resolved neutron scattering intensity map of magnons in CoTiO$_3$. The data was obtained with an incident neutron energy $E_i=50$ meV at SEQUOIA at the Spallation Neutron Source (SNS). An arbitrary intensity scale where red (blue) denotes large (small) scattering intensity is used to plot the data. (a)-(c) show magnon excitations along ($H$, -$H$) and ($H$, $H$) within the honeycomb plane at fixed $L=0.5$, while (d) shows excitations along $L$ for fixed in plane momentum (1,1). (e)-(h) Calculated magnon spectra using $J_{\parallel,1} = -4.41$ meV, $J_{\perp,1} = 0$ meV and $J_{\parallel,2',2''} = J_{\perp,2',2''} = 0.57$ meV after convolving with the energy experimental resolution of 1 meV. (i) Schematics of the 3D BZ and (j) 2D-projection of 3D reciprocal space onto the honeycomb plane. The $L=0.5$ plane has been shaded in blue in (i). Directions of momentum transfers within the $L=0.5$ plane in (a) to (c) are denoted with thick blue lines in (j). Intersection of the out-of-plane direction (1,1,1) in (d) with the 2D reciprocal space is shown as a filled blue circle. Red circles in (j) indicate positions of the Dirac point where magnon bands cross, which are denoted by red arrows in (b) and (c).

Acoustic magnon modes are found to emanate from these Bragg peaks. As shown in Fig. 1c, the magnetic unit cell is $\frac{2}{3}$ of the conventional structural unit cell along $c$; the magnon dispersion should therefore exhibit a periodicity of $1.5$ in $L$. This is inconsistent with the $L=3$ periodicity apparent in Fig. 2d. As we show below, this reflects the strong XY-nature of magnetic interactions in CoTiO$_3$.

Our data clearly show linear crossings of magnon bands at Dirac points whose positions in reciprocal space are denoted by $K$ and marked with red circles in Fig. 3. These crossings occur at $\hbar\omega^* \sim 8.5$ meV as highlighted by the red arrows in Fig. 3b and Fig. 3d. The linear dispersions of magnon modes away from these points along ($H$,$-H$) and ($H$, $H$) are well resolved in our data. These observations unambiguously demonstrate the existence of Dirac magnons in CoTiO$_3$. To visualize Dirac magnons in momentum space, we show slices of magnon dispersions in the (H,K) plane at the energy transfers of $\hbar\omega^*$

- Confined within the ab plane are ordered ferromagnetically within each honeycomb layer, and antiferromagnetically along the c direction, giving rise to the ordered structure shown in Fig. 1b. Energy and momentum resolved magnon spectra of CoTiO$_3$ were obtained by inelastic neutron scattering with an incident energy, $E_i=50$ meV. In Fig. 3, we show magnon spectra for momentum transfers along ($H$, -$H$) (Fig. 3a,b) and ($H$, $H$) (Fig. 3c) which lie within the honeycomb plane at fixed $L=0.5$ as well as along $L$ at (1, 1, L) (Fig. 3d). The directions of these momentum transfers have been denoted by thick blue lines in the 2D reciprocal space map in Fig. 3. Strongly dispersive magnon modes extending up to $\sim$12 meV are observed in all directions, which indicates the presence of significant intra-plane and inter-plane couplings in CoTiO$_3$. Magnetic Bragg peaks are located at (1,0,0.5) in Fig. 3a and (1,1,±1.5) in Fig. 3d consistent with earlier neutron diffraction results [22].
and $h\omega^* \pm 1$ meV in Fig. 4. The constant energy slice at $h\omega^*$ in Fig. 4 shows discrete points at K that come from crossings of magnon modes. Due to conical dispersions near the Dirac points, a slice of magnon dispersions at an energy below $h\omega^*$ should show closed loops in momentum space as illustrated in Fig. 3. This is not clear from our data due to finite energy resolution and the fact that the loop traverses three different BZs, each with a very different dynamical structure factor. However, this is clearly captured in our calculation as described below. Remarkably, the Dirac points at different L appear to merge into a nodal line in the 3D BZ (Fig. 5a), with very different dynamical structure factor. The weak magnon intensity due to crossings of magnon modes at the true periodicity. The weak magnon intensity due to the presence of four spins in a primitive unit cell. The scattering intensity in CoTiO$_3$ mostly comes from the two modes contributing to $S_{\parallel}$ because of the larger $g_{\parallel}$ as well as stronger in-plane spin fluctuations. This provides a natural explanation for the apparent $L = 3$ periodicity in Fig. 4. The prominent magnon mode emanating from $L = \pm 1.5$ is due to the $S_{\parallel}$ contribution, while the much weaker $S_{\perp}$ contribution is shifted by 1.5 along L with respect to $S_{\parallel}$. The overall periodicity in L is therefore 1.5, but the dominant intensity of $S_{\parallel}$ makes it difficult to see the true periodicity. The weak magnon intensity due to $S_{\perp}$ can be identified in the data in Fig. 5a and 5b, and in support of our effective spin model.

The calculated magnon spectra in Fig. 5 and Fig. 4 clearly show crossings of magnon modes at the K points, which is consistent with results shown in Fig. 3 and c. By taking into account finite energy resolution, constant energy slices in the vicinity of $h\omega^*$ determined from our model (Fig. 4b,d,f) are in good agreement with Fig. 4a,c,e. In particular, the triangular loops in the constant energy slice below $h\omega^*$ broaden into two lines.
Beyond the XXZ model: One important observation which is not captured by our XXZ model is the existence of a small magnetic anisotropy within the honeycomb plane. This is inferred from the highly non-linear magnetization at $T = 5\, \text{K}$ for in-plane fields $\sim 1-4\, \text{T}$, with a peak susceptibility at $\sim 2\, \text{T}$, which is likely a result of rotation of magnetic domains [29]. An in-plane anisotropy also implies the existence of a small gap at the magnetic zone center in the magnon dispersion. Although our experimental resolution does not allow us to determine the gap size directly, extrapolation of the magnon dispersion in Fig. 3a suggests a gap of order $\sim 1\, \text{meV}$ (See Supplemental Material). Such a gap to the Goldstone mode can arise from bond-anisotropic exchange couplings, like the Kitaev interaction, due to quantum order by disorder which pins the order parameter to the crystal axes. A phenomenological way to account for this is via a pinning field $(-1)^z g_\parallel \mu_B h \hat{S}_z$, staggered from layer to layer, deep in the ordered phase. We find that incorporating a pinning field $\sim 2\, \text{T}$, based on the magnetization data, leads to a $\sim 1\, \text{meV}$ zone center gap in the magnon dispersion consistent with the above INS estimate. The Hamiltonian including such a pinning field continues to support a DNL near the $\mathbf{K}$ points. A complete theoretical study of such weak bond-anisotropic exchanges will be discussed in a separate publication [30].

Conclusion: In conclusion, we show that the ilmenite antiferromagnet $\text{CoTiO}_3$ is a magnon analogue of ABC stacked graphene. Our identification of the Dirac magnon phase, and possibly a magnon analogue of a Dirac Nodal Line, in $\text{CoTiO}_3$ serves as a starting point to study transitions into other topological phases such as 3D Weyl magnons and magnon topological insulators. The ease of chemical substitution on both Co and Ti sites and high mechanical strength of $\text{CoTiO}_3$ make it an ideal material for future studies of the impact of doping, hydrostatic pressure, strain, and magnetic fields, on gapless Dirac magnons. The close resemblance between $\text{CoTiO}_3$ and graphene allows a direct comparison between bosonic and fermionic responses to external perturbations. For example, the Dirac magnons in $\text{CoTiO}_3$ are an ideal model system to study emergent gauge fields through strain engineering [51], or renormalization of the magnon bands resulting from the inter-particle interaction between Dirac bosons [12] [32]. Finally, unlike a simple Heisenberg ferromagnet, for which the electronic analogue is a simple tight-binding hopping Hamiltonian, the full model Hamiltonian for CoTiO$_3$ contains pairing terms analogous to the Bogoliubov de-Gennes Hamiltonian [6] of a superconductor. Such unconventional superconducting phases on the layered honeycomb lattice have begun to garner greater attention due to the recent discovery of superconductivity in ‘magic angle’ twisted bilayer graphene [33], providing further impetus to explore such remarkable analogies between electronic quasiparticles and bosonic magnons.
ACKNOWLEDGMENTS

Work at the University of Toronto was supported by the Natural Science and Engineering Research Council (NSERC) of Canada. GJS acknowledges the support provided by MOST-Taiwan under project number 105-2112-M-027-003-MY3. This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. Use of the MAD beamline at the McMaster Nuclear Reactor is supported by McMaster University and the Canada Foundation for Innovation.

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