Potential antiferromagnetic Weyl nodal line state in LiTi₂O₄ material

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(Received 11 November 2020; revised 14 July 2021; accepted 14 July 2021; published 26 July 2021)

Magnetic topological semimetals have brought new insights into topological aspects because they nicely combine the band topology with intrinsic magnetic order. Comparing with ferromagnetic topological semimetals, antiferromagnetic (AFM) ones are even more special since they can break the time-reversal symmetry but show no net magnetic moment, and are highly expected for applications of topological AFM spintronics. Here, we report LiTi_2O_4 compound is an ideal AFM Weyl nodal line semimetal. It shows time-reversal breaking Weyl nodal lines in both the spin-up and spin-down channels. Each nodal line arises from the band in one single spin channel, thus is spin-polarized. The nodal lines locate quite near the Fermi level and do not coexist with other extraneous bands. The drumhead surface state of the nodal line can be clearly identified. The nodal lines are protected by the glide mirror symmetry and are robust against spin-orbit coupling. We also show that LiTi_2O_4 can transform into an AFM Weyl semimetal under an in-plane external magnetic field. Our results suggest LiTi_2O_4 can serve as an excellent platform to investigate AFM topological semimetals with attractive features.

DOI: 10.1103/PhysRevB.104.045143

I. INTRODUCTION

As a crucial participation of topological aspects of matter, topological semimetals have been hotly studied in recent years [1-5]. According to the degeneracy and dimensionality of the band crossings in the momentum space, topological semimetals can be divided into several categories. For the former, topological semimetals can be classified into Dirac semimetals [6–9], Weyl semimetals [10–14], triple-point semimetals [15–17], and so on. For the latter, topological semimetals can be classified into nodal point semimetals (such as Dirac/Weyl semimetals), nodal line semimetals [18-23], and nodal surface semimetals [24–26]. Each category of topological semimetals has been well studied in nonmagnetic (NM) system. Recently, an advanced encyclopedia, namely, Yu-Yang-Yao's encyclopedia [27] was built, providing concrete guidelines for studying emergent particles in three-dimensional crystals. Considering that magnetism can break the time-reversal symmetry (\mathcal{T}) , topological semimetals in magnetic system are believed to bring new insights into topological aspects. Unfortunately, magnetic topology semimetals have not been sufficiently studied currently because of the limit of candidate materials and experimental difficulties due to their complicated domain structures [28,29].

To the best of our knowledge, magnetic topological semimetal was initially proposed in pyrochlore iridates AIr_2O_7 (A = Y or rare-earth element), which were identified to show all-in/all-out magnetic order and intense spin-orbit

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coupling (SOC) [30]. Later, a ferromagnetic (FM) material namely HgCr₂Se₄ was theoretically proposed to be a novel Weyl semimetal with single pair of Weyl nodes with the chirality of ± 2 [31]. Soon after, Guan *et al.* experimentally evidenced the half-metal nature of HgCr₂Se₄ through the transport studies on its high quality single crystals [32]. Recently, it has seen several works on the magnetic topology characters (including Weyl nodes and nodal lines) in Co-based Heusler compounds including Co_2MnGa [33], Co_2TiX (X = Si, Ge, or Sn) [34], and Co₂XZ ($X = IV_B$ or V_B ; $Z = IV_A$ or III_A) families [35]. In 2018, Kim et al. convinced experimentally that the layered material Fe₃GeTe₂ is an excellent FM nodal line semimetal, which was stable when the orbital and spin angular momenta are perpendicular [36]. Recently, material Li₃(FeO₃)₂ and some materials with tetragonal structure including β -V₂PO₅ were proposed to be FM Weyl nodal line semimetals [37,38]. Besides, the FM LaX (X = Cl, Br) monolayers were also predicted to be nodal line semimetal in the absence of SOC [39,40]; monolayered MnN was proposed to be nodal line semimetal under SOC [41]. These examples provide good platforms to explore the novel properties of topological states in FM system.

So far, several works have reported reducing the stray magnetic field is good for enhance the properties in FM materials [42–45]. Fortunately, the AFM materials can over come the limitation of FM materials. The zero magnetic moment in AFM materials bring special advantages for the applications in spintronics, which include no stray magnetic field, reduced power requirement and higher frequency response during the device operating. Then, one may naturally wonder that, can topological semimetals exist in antiferromagnetic (AFM) materials? In AFM topological semimetals, the T

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symmetry is still broken but the system has no net magnetic moment. The zero magnetic moment in AFM materials bring special advantages for the applications in spintronics, which include no stray magnetic field, reduced power requirement and higher frequency response during the device operating. For the candidate materials of AFM topological semimetals, Yang et al. proposed that the noncollinear AFM materials Mn₃Sn and Mn₃Ge naturally host Weyl fermions, which can give rise large anomalous Hall effect [46]. Besides, compounds CuMnAs and CuMnP, which were theoretically predicted as Dirac semimetals [47], have already been confirmed as room-temperature antiferromagnets in experiments [48]. Compound EuCd₂As₂, which hosts an inter-layer AFM ordering, was identified as another AFM Dirac semimetal quite recently [49]. Unlike Dirac/Weyl counterparts, AFM nodal line semimetals are significantly rare. Compounds β -Fe₂PO₅ [50] and two-dimensional CrAs₂ are two such examples [51]. Remarkably, combing the topological characters with AFM magnetic ordering, quite recently Šmejkal et al. have made prospective study on the potential applications of topological AFM spintronics [52]. Considering these facts, exploring excellent AFM topological semimetals can be of great significance in the current stage.

Several FM spinel materials have been proposed to show excellent spin-polarized Weyl state and nodal line states [53–56]. Then, one may wonders that can AFM nodal lines be developed in spinel materials? In this work, we propose a spinel material, namely, LiTi2O4 is an excellent AFM topological semimetal. In LiTi₂O₄, the magnetic moments are found to be the most stable along the [001] direction with the AFM ordering. In the low-energy band structure, the spin degeneracy is removed because of the absence of the $\mathcal T$ symmetry. It respectively shows a pair of time-reversal breaking Weyl nodal lines in the spin-up and spin-down channels, protected by the glide mirror symmetry G₂. The nodal lines situate quite near the Fermi level and span a quite large region in the momentum space. Near the nodal lines there exist no other extraneous bands, thereby clear drumhead surface state can be identified. More importantly, the nodal line can be retained in the presence of SOC, unlike most nodal line materials proposed previously. An effective model has been constructed to describe the nodal lines. We further find LiTi₂O₄ can transform into an AFM Weyl semimetal under specific external magnetic field, which makes the topological properties of LiTi₂O₄ even more interesting.

II. COMPUTATIONAL DETAILS

The first-principles calculations were performed by using the Vienna ab initio Simulation Package in the framework of density functional theory (DFT) [57,58]. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof functional was adopted for the exchange-correlation potential [59]. The cutoff energy was set as 600 eV. The full Brillouin zone (BZ) was sampled by a Monkhorst-Pack *k* mesh [60] with size of $13 \times 13 \times 13$. The crystal structures was fully optimized with the energy and force convergence criteria set as 10^{-7} eV and 0.001 eV/Å, respectively. In addition, to describe the strongly correlated 3*d* electrons of the Ti atom, the GGA + *U* method was used [61,62]. The effective *U*



FIG. 1. (a) The crystal structure of LiTi_2O_4 compound. The green, blue and red spheres denote the Li, Ti, and O atoms, respectively. (b) The ground AFM ordering in the LiTi_2O_4 lattice. Here, only the Ti atoms are shown in the figure. The arrows in (b) denote the directions of spin in Ti atoms. (c) The primitive cell of LiTi_2O_4 . (d) Bulk and the (001) surface Brillouin zones of LiTi_2O_4 .

value of Ti atom was set as 4 eV. In this investigation, we have tested our results with U value changing in the range of 2–6 eV, and find that the conclusions are independent on the U value. The topological surface states were calculated based on the maximum-localized Wannier functions using the WANNIERTOOLS package [63,64].

III. CRYSTAL STRUCTURE AND MAGNETIC CONFIGURATION

The LiTi₂O₄ compound is an existing material which has been synthesized since 1997 [65]. LiTi₂O₄ is a famous functional material, which has been well studied as a superconductor [66-68] and battery electrodes [69,70]. It naturally crystallizes in the cubic spinel structure with the space group $Fd\overline{3}m$ (No. 227). As shown in Fig. 1(a), one Li atom bonds with four O atoms, forming the local structure of Li-O₄ tetrahedron. One Ti atom bonds with eight O atoms, constructing the Ti-O₈ octahedron. The Li-O₄ tetrahedron and Ti-O₈ octahedron stack with each other based upon the close-packed O atoms. In LiTi₂O₄, one unit cell of the face-centered-cubic (fcc) spinel structure consists 32 O atoms occupying the Wyckoff sites 32e (0.262, 0.262, 0.262), four Li atoms and eight Ti atoms occupying the positions of tetrahedral sites [8a (0.125, 0.125, 0.125)] and octahedral sites [16d (0.5, 0.5, 0.5)], respectively. These results are in good agreement with previous x-ray and neutron diffraction reports [65,68]. The optimized lattice constants are a = b = c = 8.465 Å, which are also well agreed with the experimental ones (a = b = c =8.421 Å) [68]. We use the optimized lattice structure in the following calculations. We have also checked our results with the experimental structure, and found the conclusions of our work will not change.

Because of the existence of transition-metal element Ti, before proceeding from the electronic band structure, we



FIG. 2. (a) The total density of states of LiTi_2O_4 under nonmagnetic and magnetic. (b) Fixed spin moment total energy as a function of constrained spin magnetization for LiTi_2O_4 per primitive cell. Note the instability of the nonspin polarized state compared to the ferromagnetic.

first determine the most stable magnetic configuration in $LiTi_2O_4$. The magnetism in $LiTi_2O_4$ has been hotly discussed since its discovery. Some works reported that LiTi₂O₄ is a resonating-valence bond (RVB) material, where one possible origin for the RVB state is the potential next-nearest-neighbor AFM interaction [71–74]. In addition, $LiTi_2O_4$ was proposed to a bipolar superconductor with the combination of AFM configuration [68,75]. Such AFM correlation was also evidenced by a ⁷Li NMR study one LiTi_{2-x} V_xO_4 samples, where Curie-Weiss behaviors were observed with x < 0.16 [76]. However, one recent work argued that long range AFM may be not present in $LiTi_2O_4$ from the transport experiments [77]. Even though, the interactions between superconductivity and magnetism in LiTi₂O₄ and related compounds are strongly believed to be present [78-82]. The theoretical work by Chevrier et al. found the Ti atoms in LiTi₂O₄ can carry magnetic moments during calculations [83]. The presence of long range magnetic ordering in LiTi2O4 and related compounds can be traced from the Stoner's mechanism [84]. Singh et al. proposed the existence of long range AFM in superconductive YFe2Ge2 based on the Stoner's mechanism by comparing the density of states (DOS) at different magnetic states [85]. They theoretical further found their prediction is consistent with the experimental results. Here we clarify the potential magmatism in LiTi₂O₄ by following a similar method. The total DOS at the nonmagnetic and magnetic states are shown in Fig. 2(a). For the nonmagnetic state, LiTi₂O₄ situates at a peak of the DOS at the Fermi level. However, under magnetic states, the DOS is sharped down at the Fermi level. In addition, we display the results of fixed spin moment calculations as shown in Fig. 2(b). We can clearly observe that there is a sizable ferromagnetic instability in LiTi₂O₄, which can be understood as a Stoner instability. Thus long range magnetism could be present in $LiTi_2O_4$, being similar to that of YFe_2Ge_2 [85].

Furthermore, here we have also compared the total energy in LiTi_2O_4 at different U values of Ti atoms. It is found that, LiTi_2O_4 shows no spin polarization when U = 0, while Ti will show magnetic moments under nonzero U values. In Ti-containing oxides, the correlation effect of Ti-3d electrons usually cannot be ignored in the DFT calculations. The well-known Mott insulator LaTiO₃ is a good example, where the DFT+U method describing the localization nature of d electrons could show an energy gap comparable to the experimental results [86–88]. The U values for Ti is usually taken in the range of 3–5 eV in Ti-containing oxides such as LaTiO₃, SrTiO₃, and GdTiO₃ [86–90]. For LiTi₂O₄, the nonmagnetic electronic structure was found to be nontrivial based on the catalog of topological electronic materials by Zhang *et al.* [91]. In this work, we will focus on the topological features of LiTi₂O₄ under magnetic configuration. For the magnetic state, our calculations show the ground AFM state will not change with U values in the range of 2–6 eV. In the following, our further calculations are performed by chosen the U value for Ti at 4 eV.

In LiTi₂O₄, one cubic crystal cell contains 16 Ti atoms. There exist many potential AFM configurations. We have considered several AFM configurations with high symmetry, where both interlayer and intralayer ones are included [92]. In every AFM configuration, different magnetization directions are considered, where the [001] magnetization has a bit lower energy than others. We display the ground magnetic configuration of LiTi₂O₄ in Fig. 1(b). We also compare the energy among different magnetic configurations containing the NM and FM states, the results are shown in Table I. We can find that, the FM state is lower than the NM state by 0.31 eV, indicating the presence of spin-polarization in Ti atoms. From the energy in Table I, the AFM ordering in different magnetization directions are almost degenerate, with the [001] magnetization a bit lower. This indicates LiTi₂O₄ has a "soft" magnetism, thereby the magnetic configurations can be easily tuned under external magnetic field. We have tested the magnetic anisotropy energy by changing the Uvalues in the range of 2-6 eV. We find the magnetic anisotropy energy keeps lower than 0.002 meV with U values within 2-5 eV and of about 0.250 meV at U = 6 eV. In addition, the magnetic anisotropy is also tested by using the full-potential WIEN2K method [93]. The results show that the magnetization at the [001] direction has a bit lower energy than typical [110] and [111] ones, suggesting the [001] as the most easy magnetization direction. Figures 1(c) and 1(d) show the primitive cell form of LiTi2O4 and the corresponding BZ. One primitive cell contains four Ti atoms, with the atomic magnetic moment calculated to be 0.469 μ_B for per Ti atom. To be noted, in the AFM LiTi₂O₄, the system possesses the glide mirror symmetry G_z : $(x, y, z) \rightarrow (x, y + 1/2, -z)$ [see Fig. 1(b)], which is import for the discussions below.

IV. ELECTRONIC BAND STRUCTURE

A. AFM Weyl nodal line without SOC

Here, we investigate the electronic band structure of LiTi_2O_4 under the AFM ground state. Figures 3(a) and 3(b) show the band structure of LiTi_2O_4 in the spin-up and spin-down channels, respectively. We find the bands near the Fermi level show distinct features at different spin channels. In the spin-down channel, the valence and conduction bands are separated with each other except for the touching point at the *X* point [see Fig. 3(b)]. In the spin-up channel, beside the touching point at the *X* point, the valence and conduction bands show two additional band crossings in the *k* paths *W*- Γ and *K*- Γ [P1 and P2, see Fig. 3(a)]. This suggests that the

TABLE I. Total en	ergy E _{tot} per primitive	cell (in meV, relativ	e to that of the NM	M state) and magnet	tic moment M (in	μ_B) per Ti atom for
the different magnetic	configurations. The va	lues are obtained by	the GGA+U+SO	C method with U_{Ti} :	= 4.0 eV.	

	NM	FM ₀₀₁	FM ₁₀₀	FM ₁₁₀	FM ₁₁₁	AFM ₀₀₁	AFM ₁₀₀	AFM ₁₁₀	AFM ₁₁₁
$E_{\rm tot}$	0	-312.684	-312.674	-312.672	-312.672	-343.939	-343.937	-343.914	-343.935
M_{Ti}	0	0.542	0.542	0.542	0.313	0.469	0.469	0.326	0.266

AFM LiTi₂O₄ possesses a spin-polarized electronic structure, being different with most AFM materials where the energy bands in different spin channels are fully coupled. To be noted, the electronic band structure, especially, the appearances of band crossings near the Fermi level are independent with the U values in the range of 2-6 eV [92]. As shown by the projected density of states (PDOS) in Figs. 3(a) and 3(b), we find the states in the vicinity of the Fermi level are mostly provided by the d orbitals of Ti atoms.

We pay our most attention on the band crossing points P1 and P2 in the spin-up channel. We notice that both k paths Γ -W and Γ -K situate in the $k_z = 0$ plane, which is a mirrorinvariant plane of the glide mirror symmetry G_z. Then, P1 and P2 may not be isolate nodal points, but are potential to reside on a nodal line protected by the G_z symmetry. Figure 4(a) shows the BZ of the $k_z = 0$ plane. Because of the reduction of symmetry induced by the AFM ordering, the high-symmetry point K (and W) becomes nonequivalent with K' (and W'). Therefore the band structure in additional k paths including Γ -W' and Γ -K' should be considered to show the whole signature in the $k_z = 0$ plane. The spin-resolved band structure in the high-symmetry paths in the $k_z = 0$ plane is shown in Fig. 4(c). Very interestingly, beside the crossing points P1 and P2 in the spin-up channel, the band structure in spin-down also shows two crossing points Q1 and Q2, situating at the Γ -W'



FIG. 3. Electronic band structure and the projected density of states of LiTi_2O_4 in (a) spin-up and (b) spin-down channels. In (a), the band crossing points in the *k* paths W- Γ and K- Γ are denoted as P1 and P2, respectively.

and Γ -*K'* path, respectively. After a careful scan of the band structure in the $k_z = 0$ plane, we find the system shows a pair of nodal lines in both spin channels, as shown in Figs. 4(d) and 4(e). We show the 3D dispersion of nodal lines in Fig. 4(b). We can clearly see the presence of a pair of nodal lines in the Brillouin zone. Moreover, along the nodal lines we also observe a slight fluctuation in energy. These results highly promise that LiTi₂O₄ can be characterized as an AFM nodal line semimetal.

To further clarify the topological nature of the nodal line in LiTi_2O_4 , we have calculated the Berry phase and the surface states by constructing a tight-binding model projecting onto the Wannier orbitals. Here, we only display the results for the spin-up channel, while the case for the spin down is essentially the same. We show the results in Fig. 5(a), where the Wanier band structure agrees well with the band structure from the



FIG. 4. (a) The BZ of the $k_z = 0$ plane with high-symmetry k points indicated. (b) Illustration of the nodal line in the $k_z = 0$ plane. (c) Spin resolved band structure in high-symmetry k paths in the $k_z = 0$ plane. The band crossing points are denoted as P1, P2, Q1, and Q2, respectively. The bands in the spin-up and spin-down channels are shown by the blue and red lines. (d) and (e) show the shapes of nodal line from DFT calculation in the spin-up and spin-down channels. The color map indicates the local gap between two crossing bands.



FIG. 5. (a) The comparison of the spin-up band structure from the Wannier model and DFT. (b) The Berry phase along the k paths $W-\Gamma-K$ in the $k_z = 0$ plane. (c) Calculated (001) surface band structure of LiTi₂O₄ in the spin-up channel. In (c), the arrows point the drumhead surface state.

DFT. The Berry phase is shown in Fig. 5(b), which confirms the nodal line is topologically nontrivial. The drumhead-like surface state is a distinguishing feature for nodal line materials, which can appear either outside or inside the projected nodal line [94–96]. From Fig. 5(c), we show the calculated surface band structure of LiTi₂O₄ for the (001) surface projection, where the nodal line can have finite projected areas. In Fig. 5(c), we can clearly observe the drumhead-like surface state originating from the nodal points along the Γ -W and Γ -K paths and at the X point. Such clear drumhead-like surface state can be readily observed in experiments.

We have following remarks on the nodal line state in $LiTi_2O_4$. The nodal lines in Figs. 4(d) and 4(e) are both formed by the crossing bands from a single spin channel (either spin-up or spin-down); hence, these nodal lines are in fact time-reversal breaking Weyl nodal lines and are spin-polarized. Correspondingly, their surface states are also spin-polarized. Similar spin-polarized Weyl nodal line was also proposed in some FM topological semimetals including Fe₃GeTe₂ [36], MnF₃ [97], half-metallic Li₃(FeO₃)₂ [37], and layered material GdSbTe [98]. Comparing with these FM examples, the AFM LiTi₂O₄ can show special advantages in potential spintronics applications because it has a zero net magnetic moment. The advantages include no stray magnetic field, reduced device power requirement and higher frequency response during the device operating. Indeed, Šmejkal et al. have already made prospective insights into potential applications of topological AFM spintronics quite recently [52]. In addition, we want to emphasize that, the nodal line structure in LiTi₂O₄ is very "clean" in the sense that, there exists no other extraneous bands near the nodal lines. Therefore the novel properties from the nodal line electrons are very promising to be detected in experiments.

B. Tunable topological states under SOC

In the following, we study the SOC impact on the topological band structure of LiTi_2O_4 . After examining the total energy of LiTi_2O_4 at different magnetization directions, we



FIG. 6. (a) Band structure of LiTi_2O_4 under SOC with magnetization along the [001] direction. (b) The enlarged band structures along the Γ -*K* and Γ -*W* paths under the [001] magnetization. The figure on the right panel shows the presence of nodal line (the blue ring) in this case. (c) The band structures along the Γ -*K* and Γ -*W* paths under the [110] magnetization. The figure on the right panel shows the presence of Weyl nodes (the red hollow/solid circles) in this case.

find the magnetization along the [001] axis is the most energetically stable. It is worth noticing that the energies among all potential magnetic configurations are very close. This suggests LiTi_2O_4 has a "soft" magnetism, thereby the magnetic configurations can be easily tuned under external magnetic field.

After taking into SOC, the band structure with the [001] magnetization direction is shown in Fig. 6(a). Under SOC, bands from different spins are coupled but the band details are nearly unaffected. Considering that magnetization along the [001] direction will not break the G_z symmetry, the nodal lines in LiTi₂O₄ are expected to be immune from opening gaps under SOC. We have carefully examined the band structures near P1 and P2, which indeed show no gap, as shown in Fig. 6(b). The band structures near Q1 and Q2 are also checked, where no gap is found either. Therefore LiTi₂O₄ can be well described as a nodal line semimetal even in the presence of SOC.

It is well known that, the magnetic symmetry is highly dependent on the magnetization direction, so the topological state may change when the magnetization direction shifts [99,100]. In LiTi₂O₄, the G_z symmetry will be broken under magnetization direction deviating from the [001] direction, thereby the nodal line will vanish correspondingly. To show this point, we use the [110] magnetization as an example.

Figure 6(c) shows the band structures of LiTi₂O₄ under the [110] magnetization. We indeed find the band crossing point P1 opens a tiny gap (~ 1.5 meV). However, the crossing point P2 is not gapped [see Fig. 6(c)]. We have also checked other parts of the nodal line, and find no other crossing points can be retained. Thereby, LiTi₂O₄ has transformed from the nodal line semimetal state into the Weyl semimetal state under the [110] magnetization, which shows one pair of Weyl nodes on the k_x - k_y axis in the $k_z = 0$ plane [see Fig. 6(c)]. The presence of Weyl nodes can be convinced by symmetry analyses. Under the [110] magnetization, all the group elements of the magnetic space group C_{2h} could be retained, which includes: I, C_2^{110} and TC_2^Z , $TC_2^{\overline{110}}$. Although the broken of G_z symmetry gaps the nodal line, the antiunitary symmetry TC_2^z can still allow the presence of Weyl nodes in the $k_z = 0$ plane. Similar symmetry analysis also apply for other in-plane magnetization cases. The Weyl semimetal state makes the topological properties of LiTi₂O₄ even more interesting.

V. SYMMETRY ANALYSIS AND TIGHT-BINDING MODEL

As we have discussed above, the nodal lines in the AFM LiTi_2O_4 appear in pairs. The symmetry argument for such occasion is direct and transparent. Since the antiferromagnet is spin neutral, it always shows one or more spin-flip operations $\hat{\mathcal{O}}$. As the result, when a nodal state (denoted as T_1) is spin-polarized (fully or partially), it inevitably leads to the appearance of another nodal state (denoted as T_2) with opposite spin polarization, guaranteed by the symmetry operations \mathcal{O} , namely, $\mathcal{O} : T_1 \rightleftharpoons T_2$. The operator \mathcal{O} can be either a certain spatial symmetry or a combination of \mathcal{T} and a spatial symmetry.

Further, in the spin polarized nodal states, the corresponding bands must not be spin degenerate, which requires the combined operation $\mathcal{P}T$ with \mathcal{P} the inversion symmetry must be broken. The nondegenerate bands for AFM materials without SOC (or with negligible SOC) always exhibit strong spin polarization, as the two spins are decoupled. For the materials with strong SOC, a mirror symmetry is needed, as only the bands residing on the mirror plane are fully spin polarized. However, a generic band crossing on a mirror plane would be a Weyl loop rather than a Weyl point. Thus the most generic doubling in antiferromagnets is the Weyl loop, which is the just case in current LiTi₂O₄.

We continue to consider a tight-binding (TB) model to demonstrate the appearance of the pairs of Weyl nodal loops. The unit cell of an antiferromagnet includes even number of lattice sites: up spins on the half of sites and down spins on the remaining half. In $LiTi_2O_4$, when the spin is taken into account, the system would show a tetragonal symmetry [see Fig. 1(b)]. Thus we here consider a model settled on a tetragonal lattice with four sites per unit cell, as shown in Fig. 7(a). Each site has an s-like orbital with two spin states. The lattice may have point group symmetry D_{4h} , which is generated by four-fold rotation C_{4z} , a twofold rotation $C_{2,110}$ and a horizontal mirror \mathcal{M}_z . Combining C_{4z} and M_z leads to inversion symmetry \mathcal{P} . Without antiferromagnetic ordering, the lattice also has time-reversal symmetry \mathcal{T} . Then in the absence of SOC, using the four sites as basis, the symmetry operators can be represented as $C_{4z} = \sigma_x \tau_0$, $C_{2,110} = \sigma_x \tau_x$, $\mathcal{M}_z = \sigma_0 \tau_x$,



FIG. 7. (a) The primitive unit cell of the lattice with four sites at positions $(\frac{1}{2}, 0, \pm \frac{1}{4})$ and $(0, \frac{1}{2}, \pm \frac{1}{4})$. The red and blue denote the spin alignment $\pm z$. (b) Shape of the two Weyl loops (the white curves). The color denotes the local band gap between conduction and valence bands at $k_z = 0$ plane. (c) Calculated electronic band structure for Ham. (3), with up-spin and down-spin bands denoted by red and blue curves. The inset of (c) shows the bulk BZ for the lattice.

and $\mathcal{T} = \sigma_0 \tau_0$, with $\sigma_0 (\tau_0)$ the identity matrix, $\boldsymbol{\sigma} (\boldsymbol{\tau})$ the Pauli matrices denoting the *A* or *B* (prime or nonprime) degree of freedom. The corresponding model Hamiltonian under these symmetry constraints may be written as

$$\mathcal{H}_{0} = t_{1} \cos \frac{k_{z}}{2} \tau_{x} + t_{2} \sin \frac{k_{z}}{2} \tau_{y} + t_{3} \cos \frac{k_{x}}{2} \cos \frac{k_{y}}{2} \sigma_{x} + t_{4} \cos \frac{k_{z}}{2} (\cos k_{x} + \cos k_{y}) \tau_{x} + t_{5} \cos \frac{k_{z}}{2} (\cos k_{x} - \cos k_{y}) \sigma_{z} \tau_{x}, \qquad (1)$$

with t_i the real parameters. One can check that the Hamiltonian (1) is invariant under the above symmetry operations.

Then, we turn on the AFM ordering. The magnetization is along z direction [see Fig. 7(a)], which is applied as the same direction for the LiTi_2O_4 compound. In this case, the model becomes

$$\mathcal{H} = \mathcal{H}_0 s_0 + J_z \sigma_z \tau_0 s_z, \tag{2}$$

with *s* the Pauli matrices acting on spin space and J_z denoting the strength of the AFM potential. The AFM ordering breaks \mathcal{T} and C_{4z} , while coexists with \mathcal{M}_z , $C_{2,110}$, \mathcal{P} , and the combined operation $C_{4z}\mathcal{T}$. Since the AFM model does not have $\mathcal{P}T$ symmetry, the electronic bands of system at a

generic momentum point will be nondegenerate and fully spin polarized.

When the AFM potential is much stronger than other hopping and energy terms, the eight bands are divided into two groups with each group including four bands. Since the two groups are separated in energy space by $2J_z$, the model (2) can be simplified as two effectively four-band model. The upper four-band model can be approximately expressed as

$$\mathcal{H}_{\rm u} = J_z + \mathcal{H}_{\rm eff}(k_x, k_y, k_z) \oplus \mathcal{H}_{\rm eff}(k_y, k_x, k_z), \qquad (3)$$

with $\mathcal{H}_{\text{eff}} = \cos \frac{k_z}{2} [t_1 + (t_+ \cos k_x + t_- \cos k_y)] \tau_x + t_2 \sin \frac{k_z}{2} \tau_y$ and $t_{\pm} = t_4 \pm t_5$. The basis of the upper subsystem is $(|A \uparrow \rangle,$ $|A'\uparrow\rangle, |B\downarrow\rangle, |B'\downarrow\rangle)^T$. For the lower subsystem, its basis is $(|A \downarrow\rangle, |A' \downarrow\rangle, |B \uparrow\rangle, |B' \uparrow\rangle)^T$. Interestingly, while the basis of the two subsystems are connected by \mathcal{T} -symmetry, their Hamiltonians are not connected by \mathcal{T} , as $\mathcal{H}_{d} = -J_{z} + J_{z}$ $\mathcal{H}_{\rm eff}(k_y, k_x, k_z) \oplus \mathcal{H}_{\rm eff}(k_x, k_y, k_z)$. In the following, we focus on the upper subsystem (3) and omit J_z from it, as it only shifts the bands. The calculated band structure base on the model is plotted in Fig. 7(c). To be noted, the band structure is not the exact the case of LiTi2O4 because of the different choice of bulk BZ. However, the model can reflect all the features for the pairs of nodal lines, because all the symmetries discussed above preserve in LiTi₂O₄ system. In Fig. 7(c), one observes that there exist two crossings around X point in the spin up channel. Since the crossings are in the mirror plane $(k_z = 0)$ plane), they generally are not isolated points. A more detailed calculation confirms this analysis, finding these points are residing on a nodal loop centered at X point. Moreover, due to $C_{2,110}$ (or $C_{4z}T$) symmetry, one more nodal loop in spin down channel can be found around Y point. The pairs of nodal loops are clearly shown in Fig. 7(b). Till now, this lattice model confirms the existence of the pairs of Weyl loops in spin polarized AFM materials, being consistent with our DFT calculations in LiTi₂O₄.

VI. SUMMARY

In summary, based on electronic structure calculations and symmetry analysis, we investigate the topological electronic structure of $LiTi_2O_4$ in the spinel crystal structure. $LiTi_2O_4$ naturally shows the AFM ground state with magnetic ordering in the [001] direction. Near the Fermi level, LiTi₂O₄ manifests a pair of nodal lines in both spin channels. The nodal lines situate in the $k_z = 0$ plane, under the protection of the glide mirror symmetry. Each nodal line is formed by the crossing of two bands from the same spin channel, showing the spin-polarized Weyl nodal line signature. The nodal lines do not coexist with other extraneous bands, and are characterized by clear drumhead surface state. The nodal line can also exist in the presence of SOC. Such SOC-robust nodal lines are still rare in realistic materials. These signatures suggest that LiTi₂O₄ is an excellent AFM Weyl nodal line semimetal, which is quite suitable for future experimental detections. In addition, LiTi2O4 will transform into an AFM Weyl semimetal under external magnetic field deviating from the [001] direction. The presence of the Weyl nodes in this occasion is also guaranteed by specific symmetry.

ACKNOWLEDGMENTS

The authors thanks Prof. Z.-M. Yu for helpful discussions. This work is supported by National Natural Science Foundation of China (Grants No. 11904074). The work is funded by Science and Technology Project of Hebei Education Department, the Nature Science Foundation of Hebei Province, S&T Program of Hebei (Grants No. A2019202222 and No. A2019202107), the Overseas Scientists Sponsorship Program by Hebei Province (Grant No. C20200319). The work is also supported the State Key Laboratory of Reliability and Intelligence of Electrical Equipment (Grant No. EERI_OY2020001), Hebei University of Technology. One of the authors (X.M.Z.) acknowledges the financial support from Young Elite Scientists Sponsorship Program by Tianjin.

- [1] C.-K. Chiu, J. C. Y. Teo, A. P. Schnyder, and S. Ryu, Rev. Mod. Phys. 88, 035005 (2016).
- [2] B. Yan and C. Felser, Annu. Rev. Condens. Matter Phys. 8, 337 (2017).
- [3] A. A. Burkov, Nat. Mater. 15, 1145 (2016).
- [4] X. Dai, Nat. Phys. 12, 727 (2016).
- [5] Y. Liu, Z.-M. Yu, C. Xiao, and S. A. Yang, Phys. Rev. Lett. 125, 076801 (2020).
- [6] Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, and Z. Fang, Phys. Rev. B 85, 195320 (2012).
- [7] Z. K. Liu, B. Zhou, Y. Zhang, Z. J. Wang, H. M. Weng, D. Prabhakaran, S.-K. Mo, Z. X. Shen, Z. Fang, X. Dai *et al.*, Science **343**, 864 (2014).
- [8] S. A. Yang, H. Pan, and F. Zhang, Phys. Rev. Lett. 113, 046401 (2014).
- [9] S. M. Young, S. Zaheer, J. C. Y. Teo, C. L. Kane, E. J. Mele, and A. M. Rappe, Phys. Rev. Lett. 108, 140405 (2012).
- [10] W. Meng, X. M. Zhang, T. He, L. Jin, X. Dai, Y. Liu, and G. Liu, J. Adv. Res. 24, 523 (2020).

- [11] A. A. Burkov and L. Balents, Phys. Rev. Lett. 107, 127205 (2011).
- [12] S. Murakami, New J. Phys. 9, 356 (2007).
- [13] Y. Xu, F. Zhang, and C. Zhang, Phys. Rev. Lett. 115, 265304 (2015).
- [14] A. A. Soluyanov, D. Gresch, Z. Wang, Q. Wu, and M. Troyer, Nature (London) 527, 495 (2015).
- [15] H. Yang, J. Yu, S. S. P. Parkin, C. Felser, C.-X. Liu, and B. Yan, Phys. Rev. Lett. **119**, 136401 (2017).
- [16] Z. Zhu, G. W. Winkler, Q. S. Wu, J. Li, and A. A. Soluyanov, Phys. Rev. X 6, 031003 (2016).
- [17] H. Weng, C. Fang, Z. Fang, and X. Dai, Phys. Rev. B 93, 241202(R) (2016).
- [18] L. Wang, L. Jin, G. D. Liu, Y. Liu, X. F. Dai, and X. M. Zhang, Appl. Mater. Today 23, 101057 (2021).
- [19] A. A. Burkov, M. D. Hook, and L. Balents, Phys. Rev. B 84, 235126 (2011).
- [20] L. Jin, X. M. Zhang, Y. Liu, X. F. Dai, X. Shen, L. Wang, and Guodong Liu, Phys. Rev. B 102, 125118 (2020).

- [21] T. L. He, X. M. Zhang, Y. Liu, X. F. Dai, Guodong Liu, Z.-M. Yu, and Yugui Yao, Phys. Rev. B 102, 075133 (2020).
- [22] K. Mullen, B. Uchoa, and D. T. Glatzhofer, Phys. Rev. Lett. 115, 026403 (2015).
- [23] T. He, X. Zhang, L. Wang, Y. Liu, X. Dai, L. Wang, and G. D. Liu, Mater. Today Phys. 17, 100360 (2021).
- [24] Q.-F. Liang, J. Zhou, R. Yu, Z. Wang, and H. Weng, Phys. Rev. B 93, 085427 (2016).
- [25] W. Wu, Y. Liu, S. Li, C. Zhong, Z.-M. Yu, X.-L. Sheng, Y. X. Zhao, and S. A. Yang, Phys. Rev. B 97, 115125 (2018).
- [26] X. M. Zhang, Z.-M. Yu, Z. M. Zhu, W. K. Wu, S.-S. Wang, X.-L. Sheng, and S. A. Yang, Phys. Rev. B 97, 235150 (2018).
- [27] Z.-M. Yu, Z. Zhang, G.-B. Liu, W. Wu, X.-P. Li, R.-W. Zhang, S. A. Yang, and Y. Yao, arXiv:2102.01517.
- [28] G. Chang, B. Singh, S.-Y. Xu, Guang Bian, S.-M. Huang, C.-H. Hsu, I. Belopolski, N. Alidoust, D. S. Sanchez, H. Zheng *et al.*, Phys. Rev. B **97**, 041104(R) (2018).
- [29] R. Ray, B. Sadhukhan, M. Richter, J. I. Facio, and J. Brink, arXiv:2006.10602.
- [30] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, Phys. Rev. B 83, 205101 (2011).
- [31] G. Xu, H. Weng, Z. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 107, 186806 (2011).
- [32] T. Guan, C. Lin, C. Yang, Y. Shi, C. Ren, Y. Li, H. Weng, X. Dai, Z. Fang, S. Yan, and P. Xiong, Phys. Rev. Lett. 115, 087002 (2015).
- [33] A. Sakai, Y. P. Mizuta, A. A. Nugroho, R. B Sihombing, T. Koretsune, M.-T. Suzuki, N. Takemori, R. Ishii, R. Arita *et al.*, Nat. Phys. 14, 1119 (2018).
- [34] G. Chang, S. Y. Xu, H. Zheng, B. Singh, C. H. Hsu, G. Bian, N. Alidoust, I. Belopolski, D. S. Sanchez, S. Zhang *et al.*, Sci. Rep. **6**, 38839 (2016).
- [35] K. Manna, Y. Sun, L. Muechler, J. Kübler, and C. Felser, Nat. Rev. Mater. 3, 244 (2018).
- [36] K. Kim, J. Seo, E. Lee, K. T. Ko, B. S. Kim, B. G. Jang, J. M. Ok, J. Lee, Y. J. W. Kang *et al.*, Nat. Mater. **17**, 794 (2018).
- [37] C. Chen, Z.-M. Yu, S. Li, Z. Chen, X.-L. Sheng, and S. A. Yang, Phys. Rev. B 99, 075131 (2019).
- [38] Y. J. Jin, R. Wang, Z. J. Chen, J. Z. Zhao, Y. J. Zhao, and H. Xu, Phys. Rev. B 96, 201102(R) (2017).
- [39] S. Nie, H. Weng, and F. B. Prinz, Phys. Rev. B 99, 035125 (2019).
- [40] Z. Liu, G. Zhao, B. Liu, Z.F. Wang, J. Yang, and F. Liu, Phys. Rev. Lett. 121, 246401 (2018).
- [41] S.-S. Wang, Z.-M. Yu, Y. Liu, Y. Jiao, S. Guan, X.-L. Sheng, and S. A. Yang, Phys. Rev. Materials 3, 084201 (2019).
- [42] Y. Wang, L. Wang, J. Xia, Z. Lai, G. Tian, X. Zhang, Z. Hou, X. Gao, W. Mi, C. Feng *et al.*, Nat. Commun. **11**, 3577 (2020).
- [43] Z. Hou, Q. Zhang, X. Zhang, G. Xu, J. Xia, B. Ding, H. Li, S. Zhang, N. M. Batra, P. M. F. J. Costa *et al.*, Adv. Mater. **32**, 1904815 (2020).
- [44] Z. Hou, L. Li, C. Liu, X. Gao, Z. Ma, G. Zhou, Y. Peng, M. Yan, X.-X. Zhang, and J. Liu, Mater. Today Phys. 17, 100341 (2021).
- [45] X. Wang, Z. Cheng, G. Zhang, H. Yuan, H. Chen, and X.-L. Wang, Phys. Rep. 888, 1 (2020).
- [46] H. Yang, Y. Sun, Y. Zhang, W.-J. Shi, S. S. P. Parkin, and B. Yan, New, J. Phys. 19, 015008 (2017).
- [47] P. Z. Tang, Q. Zhou, G. Xu, and S.-C. Zhang, Nat. Phys. 12, 1100 (2016).

- [48] F. Máca, J. Maśek, O. Stelmakhovych, X. Mart'1, H. Reichlová, K. Uhl'1 řová, P. Beran, P. Wadley, V. Novák, T. Jungwirth *et al.*, J. Magn. Magn. Mater. **324**, 1606 (2012).
- [49] G. Hua, S. Nie, Z. Song, R Yu, G. Xu, and K. Yao, Phys. Rev. B 98, 201116(R) (2018).
- [50] T. L. He, X. M. Zhang, W. Z. Meng, L. Jin, X. F. Dai, and G. D. Liu, J. Mater. Chem. C 7, 12657 (2019).
- [51] B. S. Wang, H. Gao, Q. Lu, W. H. Xie, Y. F. Ge, Y.-H. Zhao, K. C. Zhang, and Y. Liu, Phys. Rev. B 98, 115164 (2018).
- [52] L. Šmejkal, Y. Mokrousov, B. H. Yan, and A. H. MacDonald, Nat. Phys. 14, 242 (2018).
- [53] W. Jiang, H. Huang, F. Liu, J.-P. Wang, and T. Low, Phys. Rev. B 101, 121113(R) (2020).
- [54] N. C. Frey, M. K. Horton, J. M. Munro, S. M. Griffin, K. A. Persson, and V. B. Shenoy, Sci. Adv. 6, eabd1076 (2020).
- [55] H. P. Zhang, X. M. Zhang, Y. Liu, X. F. Dai, G. Chen, and G. D. Liu, Phys. Rev. B 102, 195124 (2020).
- [56] H. P. Zhang, X. M. Zhang, T. He, X. F. Dai, Y. Liu, G. D. Liu, L. Wang, and Y. Zhang, Phys. Rev. B 102, 155116 (2020).
- [57] G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
- [58] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [59] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [60] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- [61] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).
- [62] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- [63] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
- [64] Q. S. Wu, S. N. Zhang, H.-F. Song, M. Troyer, and A. A. Soluyanov, Comput. Phys. Commun. 224, 405 (2018).
- [65] M. A. Green, M. Dalton, K. Prassides, P. Day, and D. A. Neumann, J. Phys.: Condens. Matter 9, 10855 (1997).
- [66] A. Kumatani, T. Ohsawa, R. Shimizu, Y. Takagi, S. Shiraki, and T. Hitosugi, Appl. Phys. Lett. 101, 123103 (2012).
- [67] D. M. Packwood, S. Shiraki, and T. Hitosugi, Phys. Rev. Lett. 111, 036101 (2013).
- [68] E. G. Moshopoulou, J. Am. Ceram. Soc. 82, 3317 (1999).
- [69] T.-F. Yi, Y. Xie, Y.-R. Zhu, J. Shu, A.-N. Zhou, and H.-B. Qiao, J. Power Sources 198, 318 (2012).
- [70] N. Kumada, M. H. K. Rubel, A. Miura, and T. Takei, J. Ceram. Soc. Jpn. **122**, 307 (2014).
- [71] P. W. Anderson, Science 235, 1196 (1987).
- [72] P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. 58, 2790 (1987).
- [73] P. W. Anderson, Mater. Res. Bull. 81, 53 (1973).
- [74] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960).
- [75] A. Alexandrov and J. Ranninger, Phys. Rev. B 24, 1164 (1981).
- [76] Y. Itoh, N. Moritsu, and K. Yoshimura, J. Phys. Soc. Jpn. 77, 123713 (2008).
- [77] K. Jin, G. He, X. Zhang, S. Maruyama, S. Yasui, R. Suchoski, J. Shin, Y. Jiang, H. S. Yu, J. Yuan *et al.*, Nat. Commun. 6, 7183 (2015).
- [78] H. Pinto, M. Melamud, M. Kuznietz, and H. Shaked, Phys. Rev. B 31, 508 (1985).

- [79] T. Fujiwara, N. Aso, H. Yamamoto, M. Hedo, Y. Saiga, M. Nishi, Y. Uwatoko, and K. Hirota, J. Phys. Soc. Jpn. 76, SA60 (2007).
- [80] M. A. Avila, S. L. Budko, and P. C. Canfield, J. Magn. Magn. Mater. 270, 51 (2004).
- [81] J. Ferstl, H. Rosner, and C. Geibel, Physica B **744**, 378 (2006).
- [82] S. Ishida, S. Asano, and J. Ishida, J. Phys. Soc. Jpn. 55, 936 (1986).
- [83] V. L. Chevrier, S. P. Ong, R. Armiento, M. K. Y. Chan, and G. Ceder, Phys. Rev. B 82, 075122 (2010).
- [84] E. C. Stoner, Proc. R. Soc. London, Ser. A 165, 372 (1938).
- [85] David J. Singh, Phys. Rev. B 89, 024505 (2014).
- [86] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B 53, 7158 (1996).
- [87] E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, and O. K. Andersen, Phys. Rev. Lett. 92, 176403 (2004).
- [88] H. S. Ahn, D. D. Cuong, J. Lee, and S. Han, J. Korean Phys. Soc. 49, 1536 (2006).
- [89] D. D. Cuong, B. Lee, K. M. Choi, H.-S. Ahn, S. Han, and J. Lee, Phys. Rev. Lett. 98, 115503 (2007).
- [90] L. Bjaalie, A. Verma, B. Himmetoglu, A. Janotti, S. Raghavan, V. Protasenko, E. H. Steenbergen, D. Jena, S. Stemmer, and C. G. Van de Walle, Phys. Rev. B 92, 085111 (2015).

- [91] T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, and C. Fang, *Nature* (London) **566**, 475 (2019).
- [92] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.104.045143 for the considered magnetic configurations and band structure under different values.
- [93] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Technische Universität Wien, Austria, 2001).
- [94] H. Weng, Y. Liang, Q. Xu, R. Yu, Z. Fang, X. Dai, and Y. Kawazoe, Phys. Rev. B 92, 045108 (2015).
- [95] C. Fang, H. M. Weng, X. Dai, and Z. T. Fang, Chin. Phys. B 25, 117106 (2016).
- [96] Y. Chen, Y. Xie, S. A. Yang, H. Pan, F. Zhang, M. L. Cohen, and S. Zhang, Nano Lett. 15, 6974 (2015).
- [97] Y. Jiao, F. Ma, C. Zhang, J. Bell, S. Sanvito, and A. Du, Phys. Rev. Lett. **119**, 016403 (2017).
- [98] M. M. Hosen, G. Dhakal, K. Dimitri, P. Maldonado, A. Aperis, F. Kabir, C. Sims, P. Riseborough, P. M. Oppeneer, D. Kaczorowski et al., Sci. Rep. 8, 13283 (2018).
- [99] Z. Zhang, Q. Gao, C.-C. Liu, H. Zhang, and Y. Yao, Phys. Rev. B 98, 121103(R) (2018).
- [100] M. P. Ghimire, J. I. Facio, J.-S. You, L. Ye, J. G. Checkelsky, S. Fang, E. Kaxiras, M. Richter, and J. V. D. Brink, Phys. Rev. Research 1, 032044(R) (2019).