Emergence of Topological Nodal Lines and Type II Weyl Nodes in Strong Spin–Orbit Coupling System InNbX$_2$(X=S,Se)

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Using first–principles density functional calculations, we systematically investigate electronic structures and topological properties of InNbX$_2$ (X=S, Se). In the absence of spin–orbit coupling (SOC), both compounds show nodal lines protected by mirror symmetry. Including SOC, the Dirac rings in InNbS$_2$ split into two Weyl rings. This unique property is distinguished from other discovered nodal line materials which normally requires the absence of SOC. On the other hand, SOC breaks the nodal lines in InNbSe$_2$ and the compound becomes a type II Weyl semimetal with 12 Weyl points in the Brillouin Zone. Using a supercell slab calculation we study the dispersion of Fermi arcs surface states in InNbSe$_2$, we also utilize a coherent potential approximation to probe their tolerance to the surface disorder effects. The quasi two–dimensionality and the absence of toxic elements makes these two compounds an ideal experimental platform for investigating novel properties of topological semimetals.

I. I. INTRODUCTION

In the past few years, topological semimetals, such as Weyl semimetals (WSM) [1, 2], Dirac semimetals (DSM) [3–9] and Nodal Line semimetals (NLS) [10–13], have received tremendous research interest. In a Weyl semimetal, the electrons around Weyl points, which are the crossing points of two non–degenerate linearly dispersing energy bands, behave exactly like Weyl fermions [1, 2]. With definite chirality, each Weyl point can be considered as a topologically protected charge, thus extending classification of topological phases of matter beyond insulators [1, 2]. Weyl points are extremely robust against weak perturbations and can only be annihilated when pairs of Weyl points with opposite topological charge meet with each other. Then the system opens a gap evolving into either a normal insulator or an Axion insulator [1, 14].

One of the most remarkable properties of WSMs is the existence of topological surface states in a form of Fermi arcs [1]. This serves as an unambiguous evidence to identify this state of matter. A great number of other exotic phenomena has also been proposed for WSMs: a highly anisotropic negative magnetoresistance related to chiral anomaly effect [15, 16], a topological response [17], unusual non–local transport properties [18], novel quantum oscillations from Fermi arcs [19], etc. A further classification here has been given to distinguish WSMs whose bulk Fermi surfaces shrink to Weyl points (called type I), or to exotic hyperboloid surfaces (called type II), where the cones are titled and induce a finite density of states at the nodal point [20, 21]. Due to the tilted nature of the nodes, the low energy excitations break Lorentz invariance, cause absence of the chiral anomaly at certain magnetic–field angles, magnetic breakdown and novel Klein tunneling [20, 21].

There has been a great progress in searching for signatures of WSMs in real materials. Starting from the original proposal on pyrochlore iridates [1], several systems, such, e.g., as HgCr$_2$Se$_4$ [22], TaAs [23, 24], WTe$_2$ [20], NbP [25], TaP [26, NbAs [27], MoTe$_2$ [28], MoP$_2$, WP$_2$ [29], LaAlGe [30], etc. have been predicted to exhibit WSM behavior. A large amount of recent experimental work has been devoted to study properties of TaAs family [25, 27, 31–34]. In many of the proposed materials, however, the Weyl points do not exactly cross but only close to the Fermi level, and, in addition, there also are trivial Fermi states. The contribution from these trivial states significantly complicates the analysis of topological surface states and their novel transport behavior.

In addition to WSMs, a three–dimensional (3D) DSM [3–9] has also been proposed. The Dirac points in DSM are four–fold degenerate, and can be viewed as a merge of two Weyl fermions with opposite chirality in the Brillouin zone (BZ). The Dirac points usually require a protection by time reversal, inversion and additional crystal symmetry [4, 7].

Different from WSMs and DSMs which have finite numbers of band touching points in the BZ, a third topo-
logical semimetal, NLS has a whole crossing line in momentum space \[10–13\]. Same as 3D DSM, NLS also needs crystal symmetry to stabilize its band crossing line \[5, 35\]. The most exotic property of NLS is its two dimensional (2D) drumhead–like surface state \[10–13, 36–44\]. It has been speculated that this special state may realize high–temperature superconductivity \[45, 46\].

Several materials have been predicted to be topological NLSs \[10–13, 36–44\]. However, most of these predictions are based on calculations without spin–orbit coupling (SOC) \[11–13, 36–42\], inclusion of which leads normally to gapping out the nodal line \[11–13, 36–42\]. Only in a few systems, this was found to be not the case, where TlTaSe\(_2\) and PbTaSe\(_2\) are predicted to remain NLS behavior in calculations with SOC \[43, 44\].

Formally, topological semimetals exist only for 3D systems. However, quasi–2D layered materials that are easier to cleave and study their surface electronic structures are more favorable from the experimental perspective. Also, toxic elements like As, P, Tl and Hg found in many of the discovered materials create additional complications. Thus, searching for new topological systems and finding ways to remove the effects of trivial states meanwhile preserving contributions from topological Fermi arcs, are important problems of this emergent field of condensed matter physics.

In this work, we use first–principles calculations based on density functional theory (DFT) in its generalized gradient approximation (GGA) \[47\] to predict that InNbS\(_2\) and InNbSe\(_2\) show nodal lines and Weyl semimetal behavior, respectively. Without considering SOC, both of them are NLSs, and the band crossing lines are formed by four–fold degenerate Dirac points. The nodal lines, which are located around H point in the \(k_z = \pi\) plane (i.e. L-H-A plane) in the BZ, are protected by the mirror symmetry. Including SOC, the four–fold degenerate nodal line in InNbS\(_2\) splits into two Weyl type nodal lines which are again protected by the mirror symmetry. On the other hand, the SOC changes InNbSe\(_2\) to a type II WSM for which we predict the Fermi arc surface states to appear on a easily cleavable (001) Indium terminated surface. Using a combination of DFT with Coherent Potential Approximation (CPA) we also simulate the effects of surface disorder to study the robustness of the Fermi arcs in this system. Our theoretical work shows that the InNbS\(_2\) and InNbSe\(_2\) are very promising materials for studying NLSs and WSMs, respectively.

II. CRYSTAL STRUCTURE

The crystal structures of InNbX\(_2\) (X=S, Se) belong to space group \(P\overline{6}m2\) (NO. 187) which is non–centrosymmetric \[48–50\]. The In layer is intercalated between two niobium dichalcogenides layers. As shown in Fig. 1(a) and Fig. 1(b), the mirror plane is located at In layer or Nb layer. As discussed later in our work, this mirror plane plays a key role in protecting the nodal line.

As shown in Fig.1, the In atoms in InNbS\(_2\) are aligned with Nb atoms in the vertical direction, while in InNbSe\(_2\), they are aligned with Se atoms. This difference in the lattice structure results in different topological features for these two compounds.

III. RESULTS FOR INNBS\(_2\)

Here we discuss our band structure results for InNbS\(_2\). We perform its density functional GGA calculation by using a full potential linear muffin tin orbital (FP–LMTO) method \[51\] and also cross check the results with linearized augmented plane wave method as implemented in WIEN2K package \[52\]. Both methods provide identical electronic structures. The orbital character analysis shows that 3\(s\) and 3\(p\) bands of S atoms are mainly located at -14 to -12 eV and -7 to -1 eV, respectively. This
indicates that the S–3s and S–3p orbitals are almost completely filled. Nd–5d states, which are mainly located between -1 and 4 eV, have also a spectral weight between -7 and -1 eV, indicating a considerable hybridization between Nb and S. On the other hand, In–5p bands are distributed mainly above -1 eV. As shown in Fig.2(a), the bands around the Fermi level are mainly contributed by Nb–5d_{z^2−y^2}/5d_{xy} and In–6p_x/6p_y states. The Nb–5d_{z^2−y^2}/5d_{xy} bands are higher in energy than the In–6p_x/6p_y states, however, there is a band inversion around H point as shown in Fig. 2(c). This band inversion has also been confirmed by the modified Becke-Johnson (mBJ) exchange potential calculations [53]. Since L–H–A plane possess mirror symmetry, the In–6p_x/6p_y (Nb–5d_{z^2−y^2}/5d_{xy}) states around H point can be classified in terms of the mirror eigenvalues -1 (+1), as shown in Fig. 2(c). Combining with the time reversal symmetry, this band inversion guarantees a nodal line in the L–H–
A plane \[\text{[53 54]}\]. The schematics of the nodal lines in InNbS\(_2\) is shown in Fig. 1(c).

To clarify the origin of the band inversion at H point, we calculate the electronic structure of InNbS\(_2\) by applying an in-plane tensile strain. We denote the magnitude of the in-plane strain by \((a - a_0)/a_0\), where \(a\) and \(a_0\) denote lattice parameters of the strained and unstrained systems, respectively. Our calculation reveals that the energy difference between In–6p\(_x\)/6p\(_y\) state and Nb–5d\(_{x^2−y^2}/5d_{xy}\) states decreases as the in-plane tensile strain increases, and when the in-plane strain becomes larger than 7%, the band inversion at H point disappears. Therefore, the band inversion originates from the crystal field effect instead of SOC.

To explore the role of the mirror symmetry, we break it by shifting a Nb atom by 0.01 Å along z direction. Without mirror symmetry, the In–6p\(_x\)/6p\(_y\) and Nb–5d\(_{x^2−y^2}/5d_{xy}\) states belong to the same irreducible representation and can hybridize with each other. Thus, the band crossing around the H point becomes gapped as shown in Fig. 2(c). This clearly demonstrates that the nodal line in InNbS\(_2\) is indeed protected by the mirror symmetry.

As a relativistic effect, SOC always exists. Thus we also perform the calculation to check the effect of SOC. Without inversion, SOC splits each band into two branches as shown in Fig. 2(b). As a result, there are spinfull bands near the Fermi level as shown in Fig. 2(d). Due to the mirror symmetry at L–H–A plane, we can classify these four bands by mirror eigenvalues \(\pm i\). Two red bands have mirror eigenvalues \(-i\), while blue ones have mirror eigenvalues \(i\). Since SOC does not eliminate the band inversion, there are two separate Weyl rings around the H point. This unique two separate nodal lines can have unique surface state as discussed in Refs. \[\text{[52 53]}\]. When mirror symmetry is broken, four bands around H point are found to belong to the same irreducible representation. Consequently the Weyl rings are gapped out as shown in Fig. 2(f). This again shows that the mirror symmetry play a key role in protecting the nodal lines in InNbS\(_2\).

\[\gamma_n^{P_l,s} = \text{Im} \log((n(k_l,s)|n(k_l+u_1,s))\langle n(k_l+u_1+u_2,s)|n(k_l+u_2,s)\rangle \langle n(k_l+u_2,s)|n(k_l,s)\rangle)\]

where \(k_l\) is a vector at \(l\)th mesh point, \(s=1–6\) denotes each of six faces of the cube, \(u_1\) and \(u_2\) are vectors between nearest mesh points for the two directions of the \(k\) vector on the surface of the cube, \(P_l\) is \(l\)th smallest closed path passing by the points \(k_l\) and its nearest mesh point. In this formula, the Chern number is given by the sum over coarse mesh of phases \(\gamma_n^{P_l,s}; C_n = \sum_{P_l,s} \gamma_n^{P_l,s}\).

The Bloch wave functions \(|n(k_l,s)\rangle\) are obtained from our first-principles calculations. We employ the 15×15 \(k\)-mesh on each of the six faces of the cube, which we found to be sufficient for numerical convergence. We calculate the Chern number of the Weyl point located at \((0.298, 0.298, 0.444)\) using this method and obtain the numerical result equal to +1. The location of this and other Weyl points is schematically shown in Fig. 3(f).

We notice that the Weyl points here exist at the boundaries between electron and hole pockets, therefore the
FIG. 3: (color online). (a) Bulk band structure of InNbSe$_2$ without SOC. The weights of In-6p$_x$/6p$_y$ (Nb-5d$_{x^2-y^2}$/5d$_{xy}$) states are proportional to the width of red (blue) curves. (b) Bulk band structure of InNbSe$_2$ including SOC. (c) Closeup of band structure around H point as marked in panel (a). The red denote mirror eigenvalue +1, while the blue denote mirror eigenvalue -1. (d) Closeup of band structure around H point as marked in panel (b). The red denote mirror eigenvalue +i, and the blue denote mirror eigenvalue -i. (e) Band structure around Weyl point. The insert is the value of $|T(k)|/|U(k)|$, the magnetic field within the blue area (i.e. $|T(k)|/|U(k)| > 1$) can induce negative magnetoresistance, while the red one ($|T(k)|/|U(k)| < 1$) cannot have negative magnetoresistance. (f) The schematic of the Weyl points in the first Brillouin Zone. Blue (red) color denote the Chern number +1(-1).

compound can be classified as a type II WSM. Our Fig. 3(e) showing a detailed band dispersion in the vicinity of one Weyl point is very similar to the case of WTe$_2$ where this new type of Weyl points has been recently introduced. They appear due to the tilting term in the linear Weyl Hamiltonian which has led to a finer classification of topological semimetals. Around the Weyl points, the energy spectrum can be written as: $\varepsilon_{\pm}(k) = T(k) \pm U(k)$. As a result, we expect that InNbSe$_2$ will display negative magnetoresistance related to chiral anomaly only when the direction of the magnetic field falls within the cone where $|T(k)|/|U(k)| > 1$ (i.e. the blue area in Fig. 3(e)). We monitor the contact between electron and hole pockets in InNbSe$_2$ by computing the constant energy surface with a slightly shifted position (by 0.2 eV up) of the Fermi level for stoichiometric compound. The result is shown in Fig. 4(a) where the green–magenta surface is the hole pocket while the red–blue one is the electron pocket. We can see that the hole pocket almost touches the electron pocket near the position of the Weyl point. Fig. 4(b) shows the same in the immediate vicinity of the Weyl point together with the spin distribution of electronic states shown by arrows. For an ideal Weyl Hamiltonian, the spins are either parallel or antiparallel to the velocities corresponding to the positive/negative chiralities. In real compounds such as InNbSe$_2$, considered here, this becomes only approximate, and as seen in Fig. 4(b), spins show a rather high degree of anisotropy.
FIG. 4: (color online). Calculated constant energy surface with a slightly shifted position (by 0.2 eV up) of the Fermi level for stoichiometric InNbSe$_2$ showing type II character of the predicted Weyl semimetal: (a) the green–magenta surface is the hole pocket while the red–blue one is the electron pocket. (b) The same but in the immediate vicinity of the Weyl point. Arrows show spin directions of the one–electron states.

V. FERMI ARCS AND EFFECT OF SURFACE DISORDER

In order to examine the Fermi arc surface states of InNbSe$_2$ we determine the one–electron energy bands of 6 unit–cell (24 atomic layers) slab structure using the full potential linear muffin–tin orbital (FP–LMTO) method[51]. The slab is extended along (001) direction and terminated by Se atomic layer at the top and by In atomic layer at the bottom. The spacing between the slabs is set to 12 Å. The distance between In and Se atoms is largest in the original unit cell which together with the quasi–two–dimensionality of the crystal structure prompts that this should be most easily cleavable surface in an experimental setup.

In order to compute the surface Fermi states, we compute surface projected imaginary Green functions

$$\text{Im} G(k, E) = \text{Im} \sum_j \frac{\langle k| P_s |k_j \rangle}{E - E_{k,j} - i\delta}$$

where we set $\delta = 0.001Ry$, and where the surface projector operator $P_s$ is chosen as a sum over 4 top/bottom atomic layers $\tau$

$$P_s = \sum_{lm\tau} |\phi_{lm\tau}\rangle\langle\phi_{lm\tau}|.$$

Here $\phi_{lm\tau}$ are the solutions of the radial Schroedinger equation inside a muffin–tin sphere of atom $\tau$ taken with the spherically symmetric part of the potential[50].

Fig. 5 shows the result of our calculation, where we visualize $\text{Im} G(k, E)$ as a function of $k$ by a color (white is 0 and black is $1/\delta = 1000$) within a part of the planar Brillouin Zone corresponding to the (001) surface unit cell. We distinguish cases for Se terminated (plots a,b) and In terminated (plots c,d) surfaces. Since the Weyl points are located not exactly at the Fermi level, we plot $\text{Im} G(k, E)$ for the energy $E = E_F$ (plots a, c) as well as for the energy $E = E_F + 0.2eV$ (plots b, d) which corresponds to the location of the Weyl points. We note that although (001) surface should be easy to cleave, the chosen atomic configuration assumes that the Weyl points of opposite chiralities project onto the same $k$–point in the surface BZ. It means that the Fermi arcs extending between opposite chiral charges can potentially start and end at the same projected Weyl point. We found this to be the case for the Se terminated surface where small arcs are clearly visible especially on Fig.5(b) corresponding to the position of the Fermi level tuned to the Weyl point. The situation is more complicated for the In terminated surface where there are essentially two lines that are resolved as connecting the Weyl points on Fig.5(d). We interpret one line to be potentially the Fermi arc and another one to be either a regular surface state or a bulk Fermi state projected to the surface BZ.

In a recent work[57] we argued, based on a simulation of a tight–binding model, that the Fermi arcs should be more surface disorder tolerant than the regular surface states especially in the vicinity of the Weyl points where
the arcs electronic wave functions are extended well into the bulk and become less sensitive to the surface disorder. We also found that the particular sensitivity to the surface disorder depends on the shape of the Fermi arc with the straight arc geometry showing its most disorder tolerance. Surface disorder is inevitable in a real experimental setting with vacancies being its primary source. It is therefore interesting to examine this effect in our proposed InNbSe$_2$ WSM.

In order to perform simulation of vacancies on the surface of InNbSe$_2$, we use a combination of DFT with a coherent potential approximation (CPA)\cite{58}, a self–consistent method that allows to extract disorder induced self–energies $\hat{\Sigma}_{CPA}(E)$ from the FP–LMTO calculation. Our recent implementation within FP LMTO method is described in Ref.\cite{57}. Figure 6(a,b) shows evolution of the one–electron Fermi states of the InNbSe$_2$ slab structure that are projected onto the Se terminated surface for two concentrations, $x=0.05$ and $x=0.1$, respectively, of substitutional vacancies that we impose at its topmost Se layer. For both concentrations, the Fermi arcs are still visible and increasing the disorder results in broadening the arcs especially in the regions always from the Weyl points. Since the arcs electrons are continuously connected to the bulk Weyl points, the area in the vicinity of the Weyl points is less affected by disorder. We can contrast this behavior with the regular surface states which we expect to be more susceptible to surface disorder. We do not impose any bulk disorder in this calculation, therefore the bulk states projected onto the surface BZ are unaffected by the surface vacancies.

The situation is more complicated for the Fermi arcs appeared at the In terminated (001) surface. Figure 6(c,d) shows their behavior for $x=0.05$ and $x=0.1$, respectively. We notice that the arcs that connect the Weyl points in Fig 5(d) slightly change their shape with disorder which possibly connected to the effect induced by the real part of the disorder self–energy $\text{Re} \Sigma_{CPA}(E=E_F)$. One state is seen in this simulation to get closer to the $\bar{K}$ point of the surface BZ while another state has its shape

FIG. 5: (color online). Surface Fermi states of the InNbSe$_2$ slab for the Se terminated (a,b) and In terminated (c,d) (001) surfaces. The position of the Fermi level in (a) and (c) corresponds to the stoichiometric compound. Plots (b) and (d) show Fermi surfaces corresponding to the Fermi level shifted by 0.2 eV when it is tuned to the Weyl points to better visualize the appearance of the Fermi arcs.
FIG. 6: (color online). Effect of surface vacancies on the surface Fermi states of the InNbSe₂ slab for the Se terminated (a,b) and In terminated (c,d) (001) surfaces. Plots (a) and (c) correspond to 5% of vacancies imposed at the top Se and bottom In layer, respectively. Plots (b) and (d) correspond to 10% of the vacancies. The Fermi level is tuned to the position of the Weyl points to better illustrate the degradation of the Fermi arc states.

resembling a regular bulk Fermi state projected onto the surface BZ. Both states acquire much less broadening if we compare them with other surface states that broaden a lot and almost disappear when x=0.1. As these arcs show a lot less curvature than the arcs resolved at Se terminated surface, we therefore speculate that this is likely the effect of the disorder tolerance for the straight Fermi arcs that we proposed in our recent work [57].

VI. SUMMARY

In summary, by using first-principles calculations, we investigated topological properties of InNbS₂ and InNbSe₂. Our theoretical analysis showed that InNbS₂ is a nodal line semimetal even with the included spin orbit coupling as long as the mirror symmetry preserved. This significant feature is different from previously proposed materials which normally neglects SOC. InNbSe₂ is proposed to be a Type II WSM with 12 Weyl nodes at the same energy level. We also studied the Fermi arcs surface states and their tolerance to the surface disorder effects. These two compounds are quasi-2D and easy to cleave, therefore can potentially serve as an interesting platform for further experimental studies of their topological electronic states.

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