Topological semimetal phases manifested in transition metal dichalcogenides intercalated with 3d metals

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In the search for stable topological semimetals with clean band profiles, we have screened all the 3d metal-intercalated transition metal dichalcogenides (3dII-TMDCs) by performing hybrid-functional-based ab initio calculations. Two classes of topological materials featuring 12 Weyl points (WPs) in the k, = 0 plane (without spin-orbit interactions) are identified: (a) ferromagnetic Weyl semimetals VT3X6 and (b) spinless Weyl semimetals MnT3X6 (nonmagnetic), where T=Nb, Tn; X=S, Se. VNb3Se8, prototypical of class (a), is half-metallic with only two bands crossing at the Fermi level to form WPs. If spin-orbit interactions are included, VNb3Se8 is a Weyl semimetal with only two WPs for magnetization m in the basal plane, whereas it is a ferromagnetic topological insulator for m normal to the plane. MnNb3Se6 in the nonmagnetic phase is essentially a spinless version of VNb3Se8 featuring an equally clean band profile. Interestingly, both materials exhibit a quasinodal line connecting the WPs, which we explain in terms of the quasimirror symmetry and the orbital nature of the bands. 3dII-TMDCs are chemically and thermally stable stoichiometric compounds containing no toxic elements and are a viable platform for the study of topological condensed-matter physics.

Introduction: The topological view of condensed matter, shaped gradually in the latter half of the 20th century, came to the forefront of condensed-matter research with the discovery of topological insulators.12 The field has since been evolving rapidly with target materials expanding from insulators to semimetals3–9. Topological semimetals can be broadly classified into Dirac semimetals (DSMs), Weyl semimetals (WSMs), and nodal-line semimetals (NLSMs).

DSMs are characterized by having two energy bands, each spin-degenerate, crossing linearly near the Fermi level EF at isolated points in the Brillouin zone (BZ). The crossing point (Dirac point) is therefore fourfold degenerate, which is possible only if the system respects both time-reversal and spatial-inversion symmetries. If one or both of these symmetries is broken, a Dirac point splits into two doubly degenerate points, turning the material into a WSM. The degeneracy points (Weyl points or WPs) have chirality C = ±1 depending on whether the node is a sink or source of Berry curvature. The total chirality of the BZ must vanish; therefore, WPs come in pairs with opposite signs of C. The degeneracy is lifted only when WPs of opposite chiralities approach each other and annihilate in pairs. Therefore, WPs are robust against weak perturbations. In contrast to DSMs and WSMs having degeneracies at discrete k points, NLSMs have degeneracy along a one-dimensional path in the BZ. Such a line degeneracy arises, for example, if the crystal has a mirror plane on which the bands have different mirror eigenvalues.

A salient feature of topological materials is the emergence of surface states associated with their bulk topology.6 DSMs and WSMs have topologically protected surface states called Fermi arcs, which give rise to quantum oscillations in magnetotransport or quantum interference in tunnel conductance. NLSMs tend to have rather flat surface bands in the shape of drumheads inside or outside the nodal loop projected onto the surface BZ. High-temperature superconductivity and special collective modes involving drumhead surface states have been predicted.10,11

The material realization of topological semimetals has been spearheaded by ab initio calculations. Density functional theory calculations have successfully identified inversion-breaking WSMs, such as transition metal monopnictides12,13 and trigonal Te and Se14, and time-reversal-breaking WSMs such as Co2TiX (X=Si, Ge, Sn)15 and Co2ZrSn16. As regards DSMs, NaX317 and Cd3As218 were discovered by calculations. The NLSMs identified include Co2As2 (and related compounds)19 fcc alkaline earth metals20 and Y2C21,22. (Extensive lists of predicted materials are given in recent reviews.23–25) Such materials, however, are often unstable under ambient conditions or may require the tuning of EF to the band-crossing points by pressure or alloying. In time-reversal-breaking materials, magnetic domain formation can be a hindrance. Also, materials with only two bands crossing at EF are preferable since the presence of intervening non-topological bands would mask topological effects. Further effort is needed to discover topological materials with more desirable electronic structures.

In this Rapid Communication, we revisit 3d metal-
intercalated transition metal dichalcogenides (3dI-TMDCs), studied intensively from the 1970’s to the 1980’s, and show that V/Mn intercalation compounds are topological semimetals with fascinating features. 3dI-TMDCs are interesting in that (i) they form stoichiometric compounds that are chemically and thermally stable, (ii) their structures are well understood, (iii) most of them show a nonmagnetic-magnetic transition at temperatures below ~100 K, which allows the realization of both time-reversal-symmetric and -asymmetric states, (iv) the carrier density and magnetism can be tuned readily by alloying or the selection of intercalants, and (v) a narrow carrier density and magnetism can be tuned readily by alloying or the selection of intercalants, and (v) a narrow energy gap of the host. Two of the Mn electrons transfer to the host unit cell. As the band structures of the hosts are similar, the electronic structures and properties of 3dI-TMDCs are determined mainly by the intercalant species. These properties, particularly the magnetic properties, attracted considerable attention from the 1970’s to the 1980’s. Table I summarizes the key experimental results for the NbS$_2$-derived compounds.

Figure 1(c) shows the density of states of MnNb$_3$S$_6$ in the nonmagnetic phase ($T > T_N$). Whereas the host 4d bands are largely unaffected by intercalation, the Mn 3d orbitals form rather narrow bands near $E_F$, spanning the energy gap of the host. Two of the Mn electrons transfer to the host 4d$_z$ band and stabilize the system. This rigid band picture generally holds true for all members of the 3dI-TMDC family. The number of 3d electrons increases from Ti to Ni (Table I), giving rise to material-specific magnetic order. The compounds undergo a nonmagnetic-magnetic transition at temperatures between 25 and 115 K. Similar magnetic trends have also been observed in 3dI-TMDCs derived from other hosts.

Calculation method: We calculated the electronic structures of all the 3dI-TMDCs with known structures using the hybrid-functional (HSE06) method in the projector augmented wave (PAW) framework, as implemented in the Vienna $ab$ initio simulation package (VASP) [33–34]. [See SM for calculational details and a comparison between the hybrid-functional and generalized gradient approximation (GGA)+U results.] The experimental crystal structures were assumed.

Results and discussion: Figure 2(a) shows the band
structure of VNb$_3$S$_6$ in the ferromagnetic phase without SOI. (Since spin and spatial freedoms are completely decoupled in the absence of SOI, the rotational and screw symmetries are preserved irrespective of the direction of the magnetization.) Electrons transferred from the intercalated V fill up a minority-spin 4d band of the host (black curve with a peak slightly below $E_F$ at $\Gamma$) and bring $E_F$ to the points (WPs) where two majority-spin bands (red curves) cross. Among the two crossing bands, the steep band with a peak at $\Gamma$ mainly has the character of Nb 4d$_{z^2}$, whereas the narrower band with a minimum at $\Gamma$ consists predominantly of V 3d$_{z^2}$; we call them “Nb-like band” and “V-like band”, respectively. Note the extremely simple and clean half-metallic band structure with only two minority-spin bands at $E_F$. There are 12 WPs arranged circularly on the $k_z = 0$ plane [Fig. 2(b)], six with $C = +1$ on $\Gamma$-M and six with $C = -1$ on $\Gamma$-K. The crossing on $\Gamma$-M ($\Gamma$-K) arises because the little group on the line comprises an in-plane twofold rotation $C'_2$ ($C''_2$) whose eigenvalues are different ($+1$ vs $-1$) for the two bands. [The eigenvalues are indicated in Fig. 3(a).] The two types of WPs differ in energy by only 0.6 meV with $E_F$ located between them. The band degeneracy is lifted off the symmetry lines, but the gap remains remarkably small ($\ll 1$ meV) along a circular loop passing through the WPs [Fig. 2(c)].

The orbital weights of the two bands at $\Gamma$ and at a WP on $\Gamma$-M are shown in Figs. 2(f) and (g), respectively. The plots reconfirm that on either $k$ point, the V-like band consists overwhelmingly of V $d_{z^2}$, whereas the Nb-like band is made of Nb $d_{z^2}$ and S $p_z$ orbitals. If one ignores S and considers a hypothetical crystal made of V and Nb, it has a horizontal mirror plane passing through a V site [Fig. 1(a)]. This situation is reminiscent of mirror-protected NLSMs whose line degeneracy results from the crossing of bands with different mirror eigenvalues on the mirror plane. The points in question are on the $z$ axis, and $S$ is a mirror plane. This quasimirror symmetry explains the quasinodal-line degeneracy observed in VNb$_3$S$_6$ (and similar 3d-TMDCs). In SM, it is shown that the quasimirror symmetry stems from the in-plane twofold rotation axes combined with the orbital nature of the bands.\[23\]

When SOI is taken into account, the band structure depends on the direction of the magnetization $\mathbf{m}$. Figure 2(d) shows the result in box (A) in Fig. 2(a) obtained for $\mathbf{m} \parallel \Gamma$-M$_0$ [see Fig. 2(b)]. Since the system is still $C_2$-symmetric around this line, the WPs on $\Gamma$-M$_0$ [the crossing between the red solid curves in (d)] and $\Gamma$-M$_1$ (the crossing between the blue dashed-dotted curves) remain, but the WPs on the other $\Gamma$-M lines have disappeared. As regards the WPs on $\Gamma$-K, they are all removed by SOI owing to the loss of $C_2$ symmetry therearound. Therefore, VNb$_3$S$_6$ in this configuration is a minimal WSM hosting only two WPs with $C = +1$ and $-1$. A similar situation arises when $\mathbf{m}$ is aligned with $\Gamma$-K, as can be seen in Fig. 2(d) for $\mathbf{m} \parallel \Gamma$-K$_0$. Only two WPs remain: one on $\Gamma$-K$_0$ ($C = 1$) and the other on $\Gamma$-K$_1$ ($C = -1$). When $\mathbf{m}$ is rotated in the basal plane, the WPs are found to persist and rotate around $\Gamma$ following the rotation of $\mathbf{m}$. If, on the other hand, $\mathbf{m}$ is tilted out of the basal plane, the two WPs are annihilated, transforming the system into a ferromagnetic topological insulator with a small gap of 1 meV. (For more results including anomalous Hall conductivity, see SM\[23\].)

MnNb$_3$S$_6$ in the nonmagnetic phase is essentially a spinless version of VNb$_3$S$_6$ [Fig. 3(a)]. Time-reversal symmetry together with the neglect of SOI cause each of the two bands to be spin-degenerate, and there are spinless WPs at the crossing points. The WPs on $\Gamma$-M and $\Gamma$-K are only 1 meV apart, and $E_F$ is located between them. The bands are rather isotropic in the $k_z = 0$ plane and nearly degenerate along a loop, making MnNb$_3$S$_6$ a quasinodal-line semimetal similar to VNb$_3$S$_6$ [Fig. 3(c)]. With the inclusion of SOI, the spin degeneracy is lifted and the WPs disappear, but there is no global band gap [Figs. 3(d) and 3(e)].

Figures 4(a) and 4(b) show the V-terminated and S-terminated (001) surface spectral functions, respectively, for VNb$_3$S$_6$ in the absence of SOI. Only the minority spin channel is plotted. In performing this calculation, we constructed tight-binding Hamiltonians \[H\] from the hybrid-functional results using the WANNIER90 code\[41,42\] and from \[H\] obtained the Green’s functions for semi-infinite space\[43\] using the WannierTools package.\[43\] On the V-terminated surface [Fig. 4(a)], there is a flat surface state around $E_F$ that connects the projections of the bulk WPs onto the surface BZ. It has the shape of a drumhead, characteristic of NLSMs, rather than a Fermi arc usually seen in WSMs. This is consistent with the quasi-NLSM character of the bulk. For the S-terminated surface [Fig. 4(b)], there is no clearly

| magnetic order (easy axis) | Ti | V | Cr | Mn | Fe | Co | Ni |
|---------------------------|---|---|---|---|---|---|---|
| $T_c$ (K)                 | NM | FM (ab) | FM (ab) | FM (ab) | AFM (c) | AFM (-) | AFM (-) |
| $N_d$ (valence)          | 1 (+3) | 2 (+3) | 3 (+3) | 5 (+2) | 6 (+2) | 7 (+2) | 8 (+2) |
FIG. 2. (a) Band structure of VNb$_3$S$_6$ in the ferromagnetic phase without SOI. The majority-spin (minority-spin) bands are shown in red (black). (b) Position of the WPs in the absence of SOI in the BZ ($k_z=0$ plane). The small red (large blue) spheres denote WPs with $C=+1$ ($-1$). (c) Two-dimensional band plot in the $k_z=0$ plane in the absence of SOI. Note that the two bands are highly isotropic and appear to touch each other along a circular loop. (d) Band structure including SOI corresponding to box (A) in (a) for nonequivalent $\Gamma$-M paths [$\Gamma$-M$_1$, $\cdots$, $\Gamma$-M$_3$ in (b)] for magnetization $m$ parallel to $y$ ($M_1$-$\Gamma$-$M_0$). Of the 12 WPs in the absence of SOI, one on $\Gamma$-M$_0$ ($C=+1$, red sphere) and another on $\Gamma$-M$_1$ ($C=-1$, blue sphere) remain. ($k$ is in units of $\pi/a$ where $a$ is the in-plane lattice constant.) (e) Band structure including SOI corresponding to box (B) in (a) for $m$ parallel to $x$ ($K_1$-$\Gamma$-$K_0$). Two WPs remain, one on $\Gamma$-K$_0$ ($C=+1$, red sphere) and the other on $\Gamma$-K$_1$ ($C=-1$, blue sphere). In (d) and (e), the positions and chiralities of the Weyl points are indicated in the boxes corresponding to the box in (b). (f)-(g) Atomic orbital weights (modulus squared of the coefficients per atom) in the wave functions at $\Gamma$ and at a WP on $\Gamma$-$M$, respectively.

discernible surface state connecting the bulk WPs. Similar results were obtained for MnNb$_3$S$_6$ [Figs. 4(c) and 4(d)]. A topological surface band is seen only in the Mn-terminated surface.

Concluding Remarks: We have screened all the 3dI-TMDCs from the topological perspective and identified (a) time-reversal-breaking WSMs VT$_3$X$_6$ ($T < T_C$) and (b) spinless WSMs MnT$_3$X$_6$ ($T > T_C$), where $T=$Nb, Ta and X=S, Se. VNb$_3$S$_6$, representative of class (a), is half-metallic, where only two bands are present at $E_F$ and cross each other. When SOI is taken into account, VNb$_3$S$_6$ is a minimal WSM with two WPs or a ferromagnetic topological insulator, depending on whether the magnetization is in the basal plane or perpendicular to it. This finding, combined with the soft magnetism reported in the literature,$^{25}$ suggests the interesting possibility of tuning the topological signature of the material with a small external magnetic field. MnNb$_3$S$_6$ in the nonmagnetic phase, belonging to class (b), is essentially a spinless version of VNb$_3$S$_6$, a WSM with an equally clean and simple band profile. The WPs in these materials are located at or within a few meV of $E_F$, implying that there is no need for Fermi level tuning.

Magnetic 3dI-TMDCs, except Fe compounds, are soft magnetic materials$^{25}$ with the magnetization direction and domain size readily controllable by the application of a weak magnetic field. This makes ferromagnetic 3dI-TMDCs enticing, because magnetic domains tend to suppress topological properties.

On a final note, clean topological band structures similar to those of VNb$_3$S$_6$ and MnNb$_3$S$_6$ are also found in compounds derived from other hosts$^{23}$ making 3dI-TMDCs an attractive platform for the study of topological condensed-matter physics.

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FIG. 4. (001) surface spectral function in the absence of SOI for the (a) V-terminated and (b) S-terminated VNb$_3$S$_6$ and the (c) Mn-terminated and (d) S-terminated MnNb$_3$S$_6$. For VNb$_3$S$_6$ only the majority spin channel is plotted because there is no minority spin surface state near $E_F$. For V/Mn termination, surface states originating from the bulk WPs are clearly seen around $E_F$. No such surface band is visible near $E_F$ for S-terminated surfaces.

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