Impurity-induced topological phase transitions in \( Cd_3As_2 \) and \( Na_3Bi \) Dirac semimetals

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Topological Dirac materials are a class of advanced materials characterized by electronic excitations with a linear dispersion about some nodal points close to the Fermi level\(^1\). Since the theoretical prediction\(^2\) and the subsequent experimental discovery\(^3\), the existence of such gapless nodes in 3D bulk systems was predicted by Murakami as a transition point between the quantum spin Hall and the insulator phases\(^4\). In systems possessing both inversion symmetry (IS) and time-reversal symmetry (TRS), this transition results in four-fold degenerate 3D Dirac nodes. For systems in which IS is broken, the gapless nodes are two-fold degenerate nodes known as Weyl points (WPs). Since the WP appears at the Fermi level, the materials that host these nodes are termed as Dirac semimetals (DSMs) and Weyl semimetals (WSMs), respectively. The materials that host Dirac or Weyl fermions as elementary excitations in condensed matter systems have the potential to revolutionize low-energy high-performance electronics. The robust topological quantum states of these materials may be utilized for different spintronics applications.

The WPs in WSMs are characterized by a topological charge of a definite (positive or negative) chirality, which acts as a source or sink of Berry curvature in momentum space. The topological charge is in fact a bulk Chern number that provides topological protection to the unique properties of the WSM. The DPs in DSMs, on the other hand, may be viewed as a superposition of two Weyl nodes with opposite chirality, giving a total Chern number equal to zero. Since DPs do not carry any Chern number, the degeneracy of the nodes may be lifted by external perturbations, making the Dirac nodes unstable. Therefore, the stability of the Dirac nodes in a DSM requires additional crystalline symmetries other than the IS and TRS\(^10,11\). A detailed review of the properties topological semimetals, can be found in Ref.\(^12\).

The search for stable 3D DSMs in realistic systems experienced a breakthrough with the studies of \( Na_3Bi \) and \( Cd_3As_2 \) compounds. Using density functional theory (DFT) methods, it was shown theoretically that a pair of stable 3D DPs, protected by the rotational symmetry of the space groups of these crystals, exists on the \( k_z \) axis\(^13,14\). Eventually, by employing angle-resolved photoemission spectroscopy, these Dirac nodes were observed in \( Na_3Bi \)\(^15,16\) and \( Cd_3As_2 \)\(^17,18\) semimetals. Since the realization of WSM requires breaking of IS or TRS or both, it was predicted theoretically that pyrochlore iridates\(^19\), topological multilayer structures\(^19\) or \( TaAs \) class of systems\(^20,22\) can host Weyl nodes. Shortly after these predictions, the existence of WSMs was verified in experiments with \( TaAs \)\(^23\) and \( TaP \)\(^24\).

As mentioned above, the degeneracy associated with a WP does not rely on any particular symmetry other than the translation symmetry of the crystal lattice. This makes the properties of bulk electronic bandstructure topologically robust against external perturbations. Moreover, as a result of the bulk-edge correspondence,
the robust non-trivial topology of the bulk WSM crystal gives rise to unique Fermi arc surface states [19, 24–26]. Similar to WSMs, double Fermi arc surface states are also observed in DSMs [27] but they may not have any topological protection in general [28, 29]. Weyl fermions of both bulk and Fermi arc states on the surface of a WSM are predicted to possess unusual transport phenomena [30]. For example, Weyl fermions in the bulk can give rise to negative magnetoresistance, the anomalous Hall effect, non-local transport and local non-conservation of ordinary current [31–34]. Fermi arc states on the surface are predicted to show novel quantum oscillations in magnetotransport and quantum interference effects in tunnelling spectroscopy [32, 37].

Apart from naturally occurring WSM materials such as the ones belonging to the TaAs class, it is interesting and important to investigate materials that can become WSMs as a result of topological phase transitions induced by external perturbations. For example, phase transitions from DSM to other topological phases, included WSMs, were discussed by Yang et al., using theoretical models [38]. The simplest way to turn a DSM into a WSM is to apply an external magnetic field, which breaks TRS. In fact, a negative longitudinal magnetoresistivity was observed in Bi$_{1-x}$Sb$_x$ (x ≈ 0.03) alloy [39] in a magnetic field, which is a signature of a Weyl phase [40]. However, a negative magnetoresistance alone may not be sufficient to distinguish between DSM and WSM [40]. In Cd$_3$As$_2$, a magnetic field–driven splitting of Landau levels and a nontrivial Berry phase were detected [41], which are consistent with the Weyl phase.

On the other hand, considerably less investigated are the topological phase transitions induced by doping DSMs. Different types of impurities and different ways in which they are incorporated in pristine DSM materials can selectively break the symmetries that are required for the stability of the Dirac nodes in a DSM, leading to a variety of phase transitions to both topologically trivial or non-trivial phases. First principles studies of Na$_3$Bi and Cd$_3$As$_2$ DSMs alloyed respectively with Sb and P, carried out within coherent potential approximation (CPA) where the crystal symmetries are preserved, find that these materials remain at the DSM phase up to 50% concentration before making transition to trivial insulators [12]. More recently, the effect of magnetic impurities in DSMs has been studied theoretically within a model Hamiltonian approach, showing that the breaking of TRS by magnetic impurity potential splits a Dirac node into two Weyl nodes [13].

In this work, using DFT methods, we have systematically investigated the effect of nonmagnetic impurities (Zn) and magnetic manganese (Mn) impurities in the prototypical Cd$_3$As$_2$, and antimony (Sb) and Mn in Na$_3$Bi DSMs. In particular, we have carefully introduced impurities to break selectively different symmetries, and have analyzed the consequences of terms that break individual or multiple symmetries on the topological properties. We have also investigated the combined effect of doping and strain on the topological properties. Our work shows that a DSM makes transitions to a WSM, a topological insulator or an ordinary insulator phase, depending on which symmetry is broken. When both IS and TRS are broken, the system makes a transition to a magnetic Weyl phase. Importantly, we find that in doped Cd$_3$As$_2$ where IS is broken by nonmagnetic impurities while TRS and rotational symmetry are preserved, modified DSM and WSM phases can even coexist at special points of the parameter space that can be reached by applying an external strain. This occurrence bears some similarities to the mixed phase recently found theoretically in polar hexagonal $ABC$ Crystal SrHgPb [44]. The paper is organized as follows. In Sec. II we describe the details of the computational approach, which include the DFT methods and the topological analysis based on the calculations of different topological invariants carried in atomistic tight-binding models extracted form DFT. In Sec. III we first present the results for pure Cd$_3$As$_2$ and the consequences of different symmetry breaking. We then discuss the case of doped Na$_3$Bi DSM. Finally, in Sec. IV we present the conclusions and outlook.

II. COMPUTATIONAL DETAILS

We have used three different computational tools to study the electronic and the topological properties of Cd$_3$As$_2$ and Na$_3$Bi DSMs.

DFT – To perform electronic structure calculations, we have first relaxed the crystal structure for both the cell parameters and the atomic positions using the Quantum Espresso ab-initio code [45]. Relaxation is continued until the stress on the cell and the forces on the atoms are very small (see below). The final relaxed structure is then used to study electronic properties in the presence of spin-orbit coupling, by employing the full-potential all-electron linearized augmented plane-waves method as implemented in WIEN2K ab-initio code [46]. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) is used for the exchange correlation functional [47].

We first discuss the details of the computational study of Cd$_3$As$_2$. The crystal structure of Cd$_3$As$_2$ at ambient conditions has the tetragonal symmetry D$_{4h}^{15}$ (P4/nmc), with a 40-atom unit cell [43]. The important symmetries that play a crucial role in the electronic properties of the crystal are TRS, IS, two mirror planes (M$_{xz}$ and M$_{yz}$), and a non-symmorphic 4$_z$ screw symmetry S$_{4z}$ (consisting of a 4-fold rotation about the z-axis followed by a half lattice translation along the z-axis). We will see later that this screw axis is essential for the stability of the DPs. Note that apart from these symmetries, the point group of the crystal also contains dihedral mirror planes and C$_2$ rotation axes.

We have constructed the cell using the experimental lattice constants and have relaxed both the cell param-
eters and the atomic positions until the forces are ≤ 1 mRy/au. This calculation is performed using Quantum Espresso with the cutoff energies $E_{\text{cutoff}} = 80$ Ry for the wave function and $E_p = 600$ Ry for the charge density and potential; a uniform Monkhorst-Pack mesh of 7x7x5 k-points has been used. The relaxation increases the cell parameters from $(a=b=16.887347, c=23.962859$ bohr) to $(a=b=17.273283, c=24.272846$ bohr). The atomic positions also change after relaxation, but not very significantly. The relaxed positions are shown in Table I.

| Atom | W.P. | X     | Y    | Z     |
|------|------|-------|------|-------|
| Cd1  | 8g   | 0.250000 | 0.531213 | 0.165053 |
| Cd2  | 8g   | 0.250000 | 0.034167 | 0.132560 |
| Cd3  | 8g   | 0.250000 | 0.994409 | 0.396994 |
| As1  | 4c   | 0.750000 | 0.250000 | 0.005427 |
| As2  | 4d   | 0.250000 | 0.250000 | 0.992112 |
| As3  | 8f   | 0.494033 | 0.505967 | 0.250000 |

This relaxed structure is the basis of the remaining calculations performed in this work. The topological phase transitions are studied by introducing different realizations of substitutional Zn or Mn impurities at Cd sites in order to break different symmetries of the system. The different types of chemical dopings and the different impurity concentrations that we have considered are the following:

1. 4 Zn atoms in the 40-atoms unit cell, with 24 Cd atoms (~17% of dopants), placed in order to maintain inversion symmetry (IS) while breaking the $S_{4z}$.
2. 1 Zn atom (~4% of dopants), in order to break both IS and $S_{4z}$.
3. 12 Zn atoms (50% of dopants), which simulates $\delta$ dopings (dopants placed on planes perpendicular to the rotation axis), in order to break IS while preserving $S_{4z}$ (see Fig. 1).
4. 1 Mn atom (~4% doping in the cell, in order to break all the three symmetries, including the time reversal symmetry (TRS). We also have studied single Mn doped case with 80 atom supercell.

After relaxing the system for each of these impurity cases, we have investigated their bandstructure and the density of states using the Wien2k code. The Kohn-Sham orbitals obtained from the Wien2k calculations are then used to construct Maximally Localized Wannier functions (MLWFs) as described below.

Wannier90 – For the topological studies of this system, we have constructed a real-space tight-binding (TB) Hamiltonian in the basis of the Wannier states. The Wannier90 code is used to construct MLWFs from the Kohn-Sham orbitals obtained from the Wien2k calculations. Since the DFT calculations show that the states near the Fermi level are predominantly the 5s of Cd, the 4s and 4p of As, and the 4s of Zn atoms (more detailed discussion is in section III), we chose to initially project the Bloch states on the s orbital of Cd and Zn atoms and on the s, p orbitals of As atoms. Furthermore, taking into account the spin-orbit coupling, we have considered the Wannier functions as spinors, namely two component states, and therefore a total of 176 Wannier functions have been chosen. In the case of Mn magnetic impurities, we have taken into account also their 3d orbitals, which increased the total Wannier functions up to 186. The accuracy of the calculation of the topological properties relies on the accuracy of MLWFs. We have used two criteria for acceptable accuracy: (i) the spread of the Wannier functions should be smaller than the smallest lattice constant; (ii) the bands calculated from the Wannier Hamiltonian should be a good match with the DFT bands. Furthermore, to reduce the numerical error during the Wannierization, we have also implemented disentanglement, a procedure to project out the contribution of the relevant from unwanted bands.

FIG. 1. Relaxed structure of Cd$_3$As$_2$ doped with 12 Zn atoms to break IS but while preserving $S_{4z}$. This type of doping is known as $\delta$ doping and is easily realizable experimentally.
say \( k_z \). The WCC of band \( n \) is then the expectation value of \( r_n(k_z, k_y) \) in this hybrid Wannier function. The evolution of the WCCs along a \( k \)-path in a given plane, say the \( k_z - k_y \) plane, of the BZ can be used to calculate the topological properties of the plane. For details see Ref. 52.

A similar strategy has been also employed to study the electronic and topological properties of \( Na_3Bi \). The unit cell of hexagonal \( Na_3Bi \) crystal contains eight atoms (two Bi and six Na atoms). It turns out that the crystal structure is such that in order to break one specific symmetry without breaking the remaining ones (for example, breaking the screw symmetry while maintaining the IS) requires considerably large supercells. A large supercell requires many Wannier functions for achieving an acceptable Wannierization procedure, and it also introduces many bands in the first BZ due to band folding, which makes it difficult to study the topological properties reliably. For this reason, we will discuss only two impurity cases: (i) breaking of IR; (ii) breaking of both IR and TRS. To break IS without breaking TRS we have substituted a Bi by an antimony (Sb) in the unit cell, which corresponds to 50\% impurity concentration, whereas to break both IS and TRS we have substituted Bi by a Mn.

### III. RESULTS

#### A. Pure \( Cd_3As_2 \)

The presence of both IS and TRS in pure \( Cd_3As_2 \) leads to the double degeneracy of each band. When the band inversion between the conduction band (primarily consisting of Cd and As \( s \) states with a small admixture of As \( p \) states) and the valence band (primarily consisting of As \( p \) states) occurs along the \( Z-\Gamma \) path and around the \( \Gamma \)-point, two Dirac nodes, symmetrically placed about the \( \Gamma \)-point at \((0, 0, \pm 0.165)\), are formed, as shown in Fig. 3(a). This result is in agreement with previous work [15, 53, 55] and serves as a benchmark for the calculations of the doped cases. The two DPs lie at -0.008 eV, slightly below the Fermi energy.

The system has six time reversal invariant planes (TRIPs), namely \( k_z = 0, \pi; k_y = 0, \pi; k_z = 0, \pi \). The presence of nodes on the \( k_z \)-axis implies that the bands are not gapped on the \( k_z = 0 \) and \( k_y = 0 \) planes. Therefore, to study the topological properties we have calculated \( Z_2 \) topological invariant for \( k_z = 0, \pi, k_z = \pi, k_y = \pi \) TRIPs. Our calculation shows that \( Z_2 = 1 \) only for \( k_z = 0 \) TRIP. As shown in Fig. 3(b), the evolution of WCC on this plane clearly shows that the degenerate bands at \( k_y = 0 \) do not recombine at \( k_y = \pi \) and a generic horizontal line cuts the branches at a single point which reveals their non-trivial topological character [52]. To further confirm the topological nature, we have calculated the chirality of each Dirac point by calculating the flux of the Berry curvature through small spheres surrounding these points and, as expected, the result is trivial for both nodes.

One of the characterizing features of DSMs is the existence of double Fermi arcs surface states [28]. Since the two DPs in \( Cd_3As_2 \) lie on the \( k_z \) axis, we expect to see two Fermi arcs on all the surfaces perpendicular to the \( k_z = 0 \) plane. In Fig. 3(c) we have plotted the projection of the DPs on the (100) plane, which clearly shows the presence of Fermi arcs, albeit slightly blurred at the contact points due to the presence of bulk states.

![FIG. 2. Comparison of the Zn-doped \( Cd_3As_2 \) DFT bandstructure and the bandstructure of the same system calculated from the real-space tight-binding Hamiltonian in the maximally localized Wannier basis. The very good agreement between the two demonstrates that the Wannierization procedure is satisfactory.](image)

![FIG. 3. (a) The bandstructure of pure \( Cd_3As_2 \) in the presence of spin-orbit coupling. The band inversion between \( s \) and \( p \) states around the \( \Gamma \)-point leads to Dirac node on the \( Z-\Gamma \) path. The inset shows the BZ of \( Cd_3As_2 \). (b) Evolution of the Wannier Charge Centers (WCC) on the \( k_z = 0 \) plane demonstrating the nontrivial nature of the bands in this plane. (c) The Fermi arc surface states projected on to (100) surface. The scale for the density of states is logarithmic.](image)
B. Non-magnetic impurity in $Cd_3As_2$

As mentioned in section II in this work we have studied different possible topological phases induced by breaking different symmetries by introducing impurities in the system. The crystal structure of $Cd_3As_2$ is characterized by three important symmetries, namely IS, TRS and $S_{12}$ screw symmetry. Each of these symmetries plays a crucial role in determining the topological properties of this system. In this work we have broken different crystal symmetries by introducing substitutional non-magnetic Zn impurity at Cd sites. Here we discuss three different impurity realizations and their consequences on the topological properties.

1. Transition to $Z_2$ semimetal phase

In order to break $S_{12}$ screw symmetry while preserving IS (and TRS), we have substituted four Cd atoms by 4 Zn atoms. Since both TRS and IS are still present, all bands are two-fold degenerate. However, by breaking the screw symmetry we also break other symmetries such as mirror planes and, consequently, the space group reduces to P-1, which contains only the IS. The conduction and valence band states belong to the same irreducible representation in this space group and, therefore, they are allowed to mix when they approach each other. Consequently, $Z$-$\Gamma$ path becomes gapped, as shown in Fig 4(a). Our DFT calculations show that the smallest gap is of the order of 12 meV at around $(0, 0, \pm 0.197)$, which is slightly away from the DPs of the pure $Cd_3As_2$.

The DOS plot in Fig 4(b) shows that the valence band is predominantly of As $p$ character whereas the conduction band is predominantly of Cd $s$ and Zn $s$ character. It is also evident that there is a considerable presence of $s$ states just below the Fermi level and $p$ states above the Fermi level, indicating the occurrence of a band inversion at the $\Gamma$-point, which gives rise to the non-trivial topology.

We note from the bandstructure that this system is not a proper insulator, but rather a semimetal, since the Fermi level crosses both the conduction and valence bands, creating an electron pocket on Z-$\Gamma$ path and a hole pocket on $\Gamma$-$X$ path, respectively. However, since the valence band has a finite direct bandgap everywhere in the BZ, it can be topologically classified in the same way as it is done for bismuth and antimony semimetals. Therefore, we have calculated the $Z_2$ indices for all the six TRIPs. Our calculation show that $Z_2=1$ for the $k_x, k_y, k_z = 0$ planes and zero for all other planes. The topological index of the system is then $\nu=(1;1,1,1)$, which is the same index of a strong 3D topological insulator. Although this system is considered as a semimetal due to the presence of a few states at the Fermi level, the non-trivial $Z_2$ topology suggests the existence of non-trivial surface states for this system.

This calculation clearly shows the importance of the rotational screw symmetry for the stability of the DPs in the $Cd_3As_2$. It also demonstrates how breaking this symmetry can cause a transition to a topologically distinct phase.

2. Transition to a Weyl phase

In this section we discuss the effect of breaking both the IS and the $S_{12}$ screw symmetry. This can be achieved simply by replacing one Cd atom by one Zn atom in the unit cell. As a result of this impurity configuration, the space group of the crystal changes to Pm space, which contains only a reflection plane. Since the IS is absent in this space group, the bands are no longer doubly degenerate, except at the TRIMs. Therefore, in this system there cannot be any Dirac nodes at any high symmetry line, for instance the Z-$\Gamma$ path. However, this opens up the possibility that each Dirac node may split into two Weyl nodes. To investigate this case in more detail, we have first calculated the bandstructure shown in Fig 4. The lack of the IS lifts the two-fold degeneracy of the bands, and it is evident from the figure that along this high symmetry path there are no nodes in the bands.

To search for the Weyl nodes, we have constructed the real-space TB Hamiltonian in the WF basis as described in section II. We have then searched for the nodes between the highest occupied and the lowest unoccupied bands in the entire BZ using WannierTools. Our calculations show that there are four nodes in the BZ. To characterize the topological nature of these nodes, we have calculated their chirality. We find that two of the nodes have chirality +1 and the other two have chirality -1.

![Fig. 4](image-url)
FIG. 5. (a) The bandstructure of \( \text{Cd}_3\text{As}_2 \) with broken IS and \( S_{4z} \) screw symmetry. Each Dirac node splits into two Weyl nodes as listed in Table II. (b) The DOS showing the distribution of As \( p \) and Cd and Zn \( s \) characters.

which we tentatively interpret as 4 Weyl nodes originating from the two original Dirac nodes. The occurrence of four Weyl nodes is consistent with a non-magnetic WSM that lacks IS but preserves TRS. The positions of the Weyl nodes in the BZ, along with their energies and chiralities, are listed in Table II. Note that the nodes are closer to the \( \Gamma \) point compared to the location of the Dirac nodes in the pure \( \text{Cd}_3\text{As}_2 \).

TABLE II. Positions the 4 Weyl points (WPs) in the BZ in units of the reciprocal lattice vector, their energies and chiralities.

| WPs | \( k_x \) | \( k_y \) | \( k_z \) | \( E \) (eV) | Chir. |
|-----|--------|--------|--------|-----------|------|
| WP1 | +0.097 | +0.036 | -0.087 | -0.0025 | +1   |
| WP2 | +0.097 | -0.036 | -0.087 | -0.0025 | -1   |
| WP3 | -0.097 | +0.036 | +0.087 | -0.0025 | -1   |
| WP4 | -0.097 | -0.036 | +0.087 | -0.0025 | +1   |

To further confirm that these nodes are indeed Weyl points, we have calculated the Berry curvature since a Weyl point acts as a source or a drain of Berry curvature in the momentum space. In Fig. 6(a) we have plotted the curvature in the \( k_x - k_z \) plane, at fixed \( k_y = 0.0362\pi/b \). Two WPs with opposite chiralities are shown (blue for negative, red for positive), at which the Berry curvature diverges. (b) and (c) Enlarged view of the curvature at the two WPS. (d) Fermi arc surface states projected onto (010) surface. Two Fermi arcs are from the projection of 4 different Weyl points on the same surface.

Similarly to the case of pure \( \text{Cd}_3\text{As}_2 \), the bands are fully gapped on the \( k_z = 0 \) TRIP and our calculations confirm that \( Z_2 = 1 \) on this plane, suggesting a nontrivial gap. This opens up the possibility of observing the quantum spin Hall effect in this plane, similar to that predicted for the TaAs WSM family. Our calculations clearly demonstrate that the insertion of a single Zn IS-breaking impurity in the \( \text{Cd}_3\text{As}_2 \) unit cell causes a topological phase transition to a Weyl phase, which is more robust than the DSM phase.

3. Coexisting of Dirac and Weyl phases

Here we discuss the last example of nonmagnetic doping in \( \text{Cd}_3\text{As}_2 \), consisting in a \( \delta \)-type doping of Zn impurities (see Fig. I) such that IS is broken while the \( S_{4z} \) screw symmetry is preserved. The dopants substitute twelve Cd atoms in two different parallel planes perpendicular to the tetragonal axis (along the \( z \) direction), resulting in a different space group, namely the \( P42mc \). This space group contains the \( M_{xz} \) and \( M_{yz} \) mirror planes along with the \( S_{4z} \) screw axis.

This is a particularly interesting case. Since \( M_{yz} \) and \( S_{4z} \) are symmetries of this space group, they commute with the Hamiltonian: \([M_{yz}, H] = 0 , [S_{4z}, H] = 0 \). However, the two symmetries do not commute with each other, but rather they anticommute. The anticommutation of these two crystal symmetries \( \{M_{yz}, S_{4z}\} = 0 \) ensures that all bands are two-fold degenerate along the tetragonal axis, \( k_z \) (\( \Gamma-Z-Z \) path). For a review of the role of mirror symmetry on topological properties see...
Ref. [57]. Away from this axis, the double degeneracy is lifted due to the broken IS. In pure $Cd_3As_2$ band inversion occurs precisely along $Z$-$\Gamma$-$Z$ path. Because of the maintained $S_{4z}$ screw symmetry, the Dirac points of the DSM phase present on this axis will survive also in this doped system.

Furthermore, the breaking of IS gives rise to the possibility of two-fold degenerate nodes, possibly Weyl points, away from the tetragonal axis. These nodes cannot be directly generated from the original Dirac points, as in the case of a single Zn doping, because in this case the original Dirac nodes are still present in the system. Therefore, this particular implementation of the impurities, opens up the possibility of observing a Dirac + Weyl coexisting phase, similar to the one recently discovered in polar hexagonal $ABC$ Crystal SrHgPb$_4$.

In order to realize such a coexisting phase, we need to consider an additional degrees of freedom, which can induce additional accidental double degeneracies away from the $Z$-$\Gamma$-$Z$ axis. In our case this extra parameter is provided by an applied strain. For a detailed analysis, we have performed calculations for both relaxed and unrelaxed structures. Fig. 7 shows the bandstructure and DOS for the unrelaxed structure. Here by unrelaxed we mean the system where the impurities have been inserted in the relaxed pure $Cd_3As_2$ crystal, without carrying out any further relaxation. Since the double degeneracy is preserved and the valence and conduction bands are inverted along $Z$-$\Gamma$-$Z$ high symmetry path, we can clearly see the presence of a four-fold Dirac node along this path, just like in pure $Cd_3As_2$. However, we point out that this Dirac node differs from the ones present in pure $Cd_3As_2$ in an important way. In pure $Cd_3As_2$, the linearly dispersed states emanating the Dirac node form a doubly-degenerate 3D Dirac cone. But in this case, it can only form a doubly-degenerate cone on a 2D plane (the shaded plane shown in the inset of Fig. 7a) for the states along the $k_z$-axis. Away from $Z$-$\Gamma$-$Z$ path the bands are no longer doubly degenerate and split into two nondegenerate cones (the gray cone, and the yellow cone inside it as shown in the inset).

To search for the Weyl nodes, we need to look for band-touching points at generic points in the full BZ, not necessarily on high-symmetry axis, which is difficult to achieve using DFT. To facilitate this search, we have constructed the TB model in the Wannier function basis using the Wannier90 code, and then have used WannierTools to search for nodes. We found two band-touchings along the tetragonal axis, namely the expected Dirac points, and eight new two-fold degenerate nodes in the $k_z=0$ plane, as shown in Fig 8. To investigate whether these eight nodes are Weyl nodes, we have calculated the chirality of the each node, which shows that four of the nodes have chirality $+1$ (red dots) and the remaining four have chirality $-1$ (blue dots), suggesting that they are indeed Weyl nodes. For further evidence, we have plotted the Berry curvature on the $k_z=0$ plane, zoomed around two nodes of opposite chirality, as shown in Fig 8. which clearly shows source-like and sink-like divergences of the curvature around each node, a characteristic feature of the Weyl nodes. These results indicate that this unrelaxed $(Cd_{1-x}Zn_x)_3As_2$ ($x=0.5$) system is a very unusual and interesting topological system in which both Dirac and Weyl nodes coexist, resulting in a new topological phase that is a mixture of DSM-like and WSM phases.

To investigate whether this mixed phase is stable, we have relaxed the structure for both the cell parameters and the atomic positions. Relaxation reduces the cell parameter to $a = b = 16.567031$ angstrom and $c = 23.487859$ bohr and brings the As layer closer to the Zn layer (further away from the Cd layer). There is no substantial change in the DOS. The bandstructure is also similar to that of unrelaxed case, except that the lowest hybrid sp band now is higher than the $p_{1/2}$ valence band. The four-fold

![Fig 7](image1)

![Fig 8](image2)
band touching point along Z-Γ is still present but slightly moved along the line. To search for nodes in the full BZ, we have followed the same procedure used above for the unrelaxed case. In this case we have found only the Dirac nodes along the tetragonal axis, whereas the Weyl nodes on the \( k_z = 0 \) plane have disappeared. Since the bands are now gapped on \( k_z = 0 \) plane, we have calculated the \( \mathbb{Z}_2 \) invariant, which shows the plane is topologically trivial, contrary to the nontrivial topology of the corresponding plane for the pure \( \text{Cd}_3 \text{As}_2 \). Therefore, in this particular case the non-trivial topology related to the Dirac phase is broken: although the four-fold degenerate nodes are still present in the system protected by the \( S_{12} \) screw symmetry, no other topological aspects are found in the system, resulting in a trivial semimetal.

4. The effect of external strain

Summarizing the main results of the previous session, we found that the \( (\text{Cd}_{1-x} \text{Zn}_x)\text{As}_2 \) (x=0.5) system display two different topological phases: (i) a trivial phase for the totally relaxed structure; (ii) a coexisting or mixed Dirac+Weyl phase for the unrelaxed structure, namely for the system where both lattice parameters and atomic positions were the ones of the relaxed pure \( \text{Cd}_3 \text{As}_2 \) DSM.

Obviously the latter can not be considered to be a stable physical system. The relevant question now is whether or not the Dirac+Weyl mixed phase can exist in more general conditions, in particular for physical configurations where the atomic positions are relaxed, which can be realized experimentally.

Since the unit-cell lattice constants \( a, b, \) and \( c \) of the relaxed system are smaller than the ones of the unrelaxed structure, we have investigated whether or not the coexisting Dirac+Weyl phase reappears when the unit cell size is progressively increased from the relaxed one. This procedure is supposed to describe an applied external strain. Specifically, in these calculations we have simulated an external strain acting on the cell in the following way: we first modify \( a = b \) (bohr) and the ratio \( c/a \) take the value of the unrelaxed \( a, b, c \) while keeping the ratio \( c/a \) equal to the value of the relaxed doped structure, 1.417747. In the first row (strain I) \( a = b = 17.273283 \), which is the value of the unrelaxed system.

Since the change in the cell parameters are quite small, the general behavior of DOS and bands are very similar for different values of the strain, but small differences arising in the bands structure lead to topological phase transitions. In particular, as we will see below, the strained systems I and V in Table III show different topology and so we expect to see an intermediate phase with some new band closings somewhere in the bulk, very similar to the ones arising in the unrelaxed cell.

In Fig. 9 the bandstructure of “strained system I” is plotted along the Z-Γ-Χ-Μ-Γ path. This strain corresponds to the case where the lattice constants \( a \) and \( b \) are equal to the value of the relaxed pure \( \text{Cd}_3 \text{As}_2 \) (which we therefore refer to as unrelaxed for the doped system). Away from the Fermi level, the bands are similar for different values of the strain, but small differences arising in the bands structure lead to topological phase transitions. In particular, as we will see below, the strained systems I and V in Table III show different topology and so we expect to see an intermediate phase with some new band closings somewhere in the bulk, very similar to the ones arising in the unrelaxed cell.

| Structure | Lattice constant \( a = b \) (bohr) | Stress (Kbar) along x, y, z | phase |
|-----------|-----------------------------------|-----------------------------|-------|
| I         | 17.273283                         | -44.90 -43.43               | Trivial |
| II        | 17.300000                         | -45.00 -42.56               | DSM   |
| III       | 17.342376                         | -47.09 -44.47               | DSM   |
| IV        | 17.446016                         | -51.19 -47.97               | DSM   |
| V         | 17.618749                         | -55.36 -50.23               | DSM   |
total relaxed system. Furthermore, the node search with WannierTools did not find any new nodes in the BZ. The $Z_2$ calculations on the $k_z = 0$ TRIP, whose WCC evolution plot is shown in Fig. 9b, reveals that the system has the same trivial topology of the fully relaxed system. This is because a generic horizontal line cuts the WCC branches in an even number (two) or zero times.

In order to see how these gaps along the $\Gamma-X$ and $\Gamma-M$ change with different strains, in Figs. 10 and 11 we plot the evolution of the bands along the paths $\Gamma-X$ and $\Gamma-M$ respectively, zoomed around the gaps, for all the five strained systems of Tab. III. We note that the gaps are very small until the third case, after which they start to increase signaling that, if there is any band closings, this must happen at an intermediate value of the strain, between the first and the last system. Furthermore, the topological analysis of the last strained structure $V$, found no other nodes beside the Dirac points along $Z-\Gamma$. The calculation of $Z_2$ invariant on the $k_z = 0$ TRIP, finds a non-trivial topology on this plane, which implies that for this value of the strain the system is a topological DSM, similar to the case of pure $Cd_3As_2$.

Among the intermediate strained systems (II-IV in Table III), the strained system II gives the smallest gap of 0.4 meV between the conduction and the valence band along the $\Gamma-X$ and $\Gamma-M$ lines.

The topological analysis shows that the strained systems II-IV are all already in the non-trivial DSM phase of the pure $Cd_3As_2$ system (see Table III). Since the topology changes from the trivial semimetal phase of strain I to the non-trivial DSM phase of strain II, we deduce that a band gap closing must necessarily take place for an intermediate value of the strain. Because of the maintained $S_4\zeta$ for this doped system, such a node in the band structure will have three other copies at rotated positions, and we expect these 4 nodes to be of Weyl type. Being unable to point-point the exact value of the strain corresponding to the band closing, we are unable to conclusively confirm via a topological analysis that the transition between the two phases indeed takes place via the mixed Weyl+Dirac phase that we have discovered for the unrelaxed system. However all these features indicate that this seems to be the most likely occurrence.

A phase diagram summarizing the topological evolution of $(Cd_{1-x}Zn_x)_3As_2$ ($x=0.5$) as a function of applied strain is shown in Fig. 12. Here the value of the applied strain is expressed in terms of the ratio $r = a_{\text{strained}}/a_{\text{relaxed}}$, which tells us how much the first lattice parameter of the strained cell ($a_{\text{strained}}$) is enlarged relatively to the one of the totally relaxed system ($a_{\text{relaxed}}$).

Summarizing the results for the $(Cd_{1-x}Zn_x)_3As_2$ ($x=0.5$) system, we found that this doped system that breaks IS but maintains both the $S_4\zeta$ symmetry and TRS can exist in three distinct topological phases: (i) a topologically trivial semimetal phase, still possessing two
four-fold nodal points on the $\Gamma-Z$ axis; (ii) a topological nontrivial DSM phase, characteristic of the pure system; (iii) a novel mixed Weyl+Dirac phase, first found in the unrelaxed $(Cd_{1-x}Zn_x)_3As_2$ system, where lattice constants and atomic positions of pure $Cd_3As_2$ were used. This mixed Weyl+Dirac phase also appears at the topological phase transition point between the trivial and DSM phase, induced by an applied external strain, as shown in Fig. 12.

At this point we are not able to assess whether or not the mixed phase can exist for a finite albeit small range of the parameters that we use to model the strain in the system. Note, for example that for the systems considered in Table III the value of $c/a$ is kept fixed and equal to the value of relaxed doped $(Cd_{1-x}Zn_x)_3As_2$. Changing this parameter can allow further flexibility to induce nodal points leading to a mixed Weyl+Dirac phase.

**FIG. 12.** Phase diagram of the topological evolution of the system, in terms of the ratio $r = a_{\text{strained}}/a_{\text{relaxed}}$. $a_{\text{strained}}$ and $a_{\text{relaxed}}$ are the first lattice constants of the totally relaxed ($a_{\text{relaxed}} = 16.567031$ bohr) and of a strained system, respectively.

C. Magnetic impurity in $Cd_3As_2$

In this section we discuss the effects of magnetic doping in the relaxed pure $Cd_3As_2$ system. Magnetic doping of the topological DSM may be of interest for practical uses since a magnetic Weyl phase may arise, supporting topological phenomena such as the quantum anomalous Hall effect. We have introduced magnetic impurities in $Cd_3As_2$ by substituting one Manganese (Mn) atom at a Cd site in a 40-atom cell, corresponding to $\sim 4\%$ impurity concentration. In order to consider a smaller and more isotropic effect of doping, we have constructed a quasi-cubic supercell made of 80 atoms from the original $Cd_3As_2$ system, in which one Mn substitution corresponds to $\sim 2\%$ of doping. As in the case of the Zn doping, this type of magnetic doping corresponds to a kind of random doping, which could be realized in experiments.

In either the 40- or 80-atoms supercell cell, we break all the important symmetries, namely the TRS, the IS and $S_{4z}$ screw symmetry. As before, after adding the Mn impurity, which reduces the crystal to the $Pm$ space group, we have performed a spin-polarized relaxation of the atomic positions using Quantum Espresso, followed by electronic structure calculations by Wien2k. Although we were able to calculate the electronic and magnetic properties of the 80-atom supercell, the topological analysis requires a much larger set of Wannier functions than the for 40-atom case, and it is difficult to obtain reliable results from all electron calculations. For this reason we will discuss the results only for a 40-atom supercell.

Since the TRS is broken, the degeneracies of the bands are lifted at the TRIM points and more bands appear near the Fermi level, compared to the case of pure $Cd_3As_2$ and non-magnetic doping, as evident from the bandstructure plot shown in Fig. 13(a). Furthermore, the lack of screw symmetry also breaks the degeneracy along the tetragonal axis. Consequently, the original four-fold degenerate Dirac points along $Z-\Gamma$ line disappear. The valence band closest to the Fermi energy now displays a hybrid $p-d$ character, mainly coming from the $p$-majority states of arsenic atoms hybridized with the $d$ majority states of manganese. On the other hand, the bands coming from the conduction region, which switch with the valence band around $\Gamma$ (band inversion is still present), has still a prevalent $s-p$ character, but slightly hybridized with the $d$ orbitals of the manganese.

**FIG. 13.** (a) Bandstructure of Mn doped $Cd_3As_2$ showing the main characters of the two bands closest to the Fermi energy. (b) and (c) Spin resolved total DOS and projected DOS, respectively.

The DOS in Figs. 13(b) and (c) show the exchange splitting between the majority and minority spins. The two different channels present regions of low occupancies close to the Fermi energy. Just below the Fermi level, the occupancy of the minority states has a gap whereas the
majority states have a metallic behavior and just above the Fermi level majority spin states are gapped whereas minority spin states are metallic. This half metallic feature could be very interesting for spintronic applications, since it allows one to exploit separately the different spin channels. The calculated total moment of the cell is about 5 $\mu_B$ with main contribution coming from Mn and neighboring As atoms, which is close to the atomic moment of an isolated Mn. The local moment of Mn ion in this system is about 4 $\mu_B$, which results from the hybridization of Mn d orbitals with the p orbitals of the four closest As atoms, which is evident from projected DOS plotted in Fig. 13(c). Furthermore, the induced moment in As atoms are of the same sign as the Mn moment, suggesting a ferromagnetic coupling resulting from $p-d$ exchange, which is consistent with previous work [50].

Finally, we have investigated the topological properties of Mn doped $Cd_3As_2$. Since all the two-fold degeneracies are removed, there are no Dirac nodes in this system. But the presence of the Mn impurity introduces a splitting of the bands and new bands appear, which when they cross may give rise to nodes at generic points. We first look for nodes in the whole BZ within the energy between $E_1 = -0.1 \ eV$ to $E_2 = 0.05 \ eV$, since we expect the relevant Weyl points to be close to the Fermi level. We found many nodes present at different energies, but not all of them have non-trivial chiralities. In Table IV we have listed the position of the 10 non-trivial nodes along with their energies and chiralities that are closest to the Fermi level. All the nodes are slightly below the Fermi energy. Among the 10 Weyl nodes, 5 nodes are above the $k_z=0$ plane and the remaining 5 are below the plane with the total chirality above and below the $k_z=0$ plane are $C_{top} = +1$ and $C_{bottom} = -1$, respectively.

TABLE IV. Crystal positions of the 10 Weyl points, along with their energies and chiralities.

| WP | Kx (Å) | Ky (Å) | Kz (Å) | E-Ef (eV) | Chir. |
|----|--------|--------|--------|-----------|-------|
| WP1 | 0.046  | -0.135 | -0.032 | -0.032    | +1    |
| WP2 | -0.033 | -0.167 | -0.050 | -0.002    | +1    |
| WP3 | -0.107 | -0.001 | -0.088 | -0.097    | -1    |
| WP4 | 0.039  | 0.114  | -0.103 | -0.044    | +1    |
| WP5 | 0.029  | 0.009  | -0.180 | -0.057    | -1    |
| WP6 | 0.036  | -0.160 | 0.032  | -0.005    | -1    |
| WP7 | -0.046 | -0.129 | 0.043  | -0.037    | -1    |
| WP8 | 0.105  | 0.007  | 0.092  | -0.095    | +1    |
| WP9 | -0.039 | 0.109  | 0.098  | -0.056    | -1    |
| WP10| -0.033 | -0.012 | 0.178  | -0.058    | +1    |

Since the chiralities above and below the $k_z=0$ plane are different, we expect a non-trivial topological behavior on this plane. Because of the broken TRS, such topological character cannot be described by the $Z_2$ invariant. Instead, we have calculated the Chern number for the plane using WCC methods, which is similar to the calculation of $Z_2$ invariant, except that in this case we use a full path in momentum plane for both $k_x$ and $k_y$. Our calculation shows that the Chern number $C = |1|$ on the plane, which signifies that this plane can be viewed as a 2D Chern insulator and therefore, we expect this particular system to support a quantum anomalous Hall effect, as discussed in section IV. Based on these results it is reasonable to conclude that Mn doping in $Cd_3As_2$ DSM induces a topological transition to a magnetic WSM phase.

A concise summary of all the results for doped $Cd_3As_2$ obtained in this work is presented in Table V.

TABLE V. Summary of the results for different topological phases induced by different impurity realization in $Cd_3As_2$.

| Impurity | Symmetry | Topological properties |
|----------|----------|------------------------|
| 0        | TRS + IS | DSM phase, two DPs on the $k_z$ axis, $Z_2=1$ only at $k_z = 0$ TRIP. |
| 4 Zn (17%) | TRS + IS | Topological insulator phase, a gap of 12 meV at the original DPs, $Z_2=1$ for $k_z$, $k_y$, $k_z = 0$ TRIPs. |
| 1 Zn (4%) | TRS | WSM phase, 2 DPs splits into 4 Weyl nodes, $Z_2=1$ only at $k_z = 0$ TRIP |
| 12 Zn (Unrelaxed) (50%) | TRS + C4 | Coexisting DSM and WSM phase, two Dirac nodes on $k_z$, eight Weyl nodes $k_z=0$ plane. |
| 1 Zn (Relaxed) (4%) | TRS + C4 | Trivial semi-metal phase, two Dirac nodes on $k_z$. |
| 1 Mn (4%) | All broken | Magnetic WSM phase, 5 Weyl nodes above $k_z = 0$ plane, with net chirality $+1$ and 5 nodes below with net chirality $-1$. |

IV. TOPOLOGICAL PHASE TRANSITIONS IN $Na_3Bi$ DSM

In this section we turn our attention to the topological properties and to the impurity-induced phase transitions of $Na_3Bi$ DSM. Pure $Na_3Bi$ belongs to the hexagonal $P6\bar{3}/mmc$ ($D_{6h}$) space group and has IS, 63 screw symmetry $S_{6z}$, which is a 6-fold rotation about the $z$-axis followed by a half lattice translation along the $z$-axis. Therefore, the $C_3$ symmetry is also present, and, as discussed below, the permanence of this $C_3$ symmetry has the important consequence of preserving the degeneracy of the bands when the $S_{6z}$ symmetry is lifted by doping. The unit cell of $Na_3Bi$ (see Fig. 14b) contains eight atoms and the crystal structure is such that in order to break one specific symmetry without breaking the remaining symmetries requires a large supercell, which makes it difficult to study the topological properties. For this reason, we will discuss here two impurity cases only: (i) breaking of IS; (ii) breaking of IS and TRS.
A. Electronic and topological properties of pure \(Na_3Bi\) DSM

The electronic properties of pure \(Na_3Bi\) are well studied\[13\]. Here we have recalculated the bandstructure and the topological properties which we will then use as a benchmark to study the effect of impurity doping. After relaxation, the lattice constants increase from the experimental value of \(a=b=10.295228\) and \(c=18.245306\) bohr to \(a=b=10.342074\) and \(c=18.377058\) bohr. The bandstructure in Fig 14(b) shows that the two-fold degenerate valence band crosses with conduction band on the \(k_z\) axis (A-\(\Gamma\) path) and forms a Dirac node, in agreement with previous work\[13\].

![Image](55x399 to 298x566)

**FIG. 14.** (a) The hexagonal crystal structure of \(Na_3Bi\) DSM (b) Bandstructure of \(Na_3Bi\) DSM indicating the position of Dirac point in the \(k_z\) axis along A-\(\Gamma\) path. (c) The Fermi arc surface state on [011] surface.

For the topological analysis, we have first constructed the real space TB Hamiltonian using the Wannier90 code. The Bloch states are projected onto \(p\) orbital of Bi and \(s\) orbital of Na and have chosen a total of 24 Wannier functions for calculations with spin-orbit coupling. Using this Hamiltonian, we have searched for nodes in the full BZ using the WannierTools code, both for unrelaxed and relaxed structures. In both cases we have obtained two Dirac nodes symmetrically placed around the \(\Gamma\) point on the hexagonal axis (\(c\) axis). However, since the relaxed structure is elongated along the \(c\)-axis, the Dirac nodes shift away from the \(\Gamma\) point from \(\pm 0.125\) in the unrelaxed case to \(\pm 0.132\) (\(2\pi/c\)) in the relaxed case. The chirality of each Dirac node is found to be zero. Fig 14 shows the projection of the Dirac nodes onto the [011] surface of the BZ, demonstrating the existence of the characteristic Fermi arc surface states of the DSM, similar to \(Cd_3As_2\).

![Image](318x283 to 561x442)

**FIG. 15.** (a) \(Na_3Bi\) doped with a nonmagnetic Sb impurity (b) Bandstructure of \(Na_3Bi\) DSM indicating the Dirac point in the \(k_z\) axis along \(A-\Gamma\) path (c) The Fermi arc surface state on [011] surface. The curvature of the arc is reduced compared to the arc of the pure \(Na_3Bi\).

B. Sb doped \(Na_3Bi\) DSM

To study the effect of non-magnetic impurities on the topological properties, we have substituted a Bi atom with a Sb, which is isoelectric to Bi (see Fig 15(a). Since there are only two Bi atoms in the unit cell, this doping corresponds to 50% impurity concentration. The space group of the system, consequently, changes to \(P6m2\) (or \(D_{3h}^1\)), which lacks IS and contains a Mirror plane \(M_{110}\) perpendicular to \((110)\) direction as well as \(C_3\) rotational symmetry. These symmetries play crucial role in the topological properties, since the anti-commutation of \(\{M_{110}, C_3\}\) ensures the double degeneracy along the A-\(\Gamma\) line \((0,0,k_z)\).

Unlike pure \(Na_3Bi\), the relaxation of the doped structure reduces the cell parameters to \(a = b = 10.228426\) and \(c = 18.210308\) bohr compared to the experimental cell parameters of pure \(Na_3Bi\) mentioned above. Fig. 15(b) shows the bandstructure along the same path as the one plotted for pure \(Na_3Bi\) DSM (Fig. 14(b)). Since IS is broken, the double degeneracy of the bands are lifted, in general. It is evident from the figure that the double degeneracy is preserved along \(A-\Gamma\) line, and because of the band inversion around the \(\Gamma\) point, the doubly degenerate valence and conduction bands cross on this line, forming a node. However, we note that the band crossing along the \(A-\Gamma\) line is much flatter compared to the pure \(Na_3Bi\), suggesting that at this concentration the system is close to reverting the band inversion.

We have further verified, by constructing a real space Hamiltonian in the Wannier basis and using WannierTools, that these are the only two nodes in the entire BZ. The topological analysis confirms that the chirality of the nodes is zero. As in the case of pure \(Na_3Bi\), the \(Z_2\) invariant of \(k_z = 0\) plane is 1. To complete the analysis, we have calculated Fermi arc surface states as shown in Fig. 15(c). In this case the curvature of the arc is smaller than the arcs of the pure system. Therefore, our analysis shows that this system with 50% impurity is still a DSM. However, we would like to emphasize that although this phase is considered as a DSM phase because of the
presence of two doubly-degenerate Dirac nodes, the dispersion around the DPs is different from that of the pure Na$_3$Bi for the same reason as explained in section [III.B.3].

When both Bi atoms are replaced by Sb atoms to construct the Na$_3$Sb crystal, a gap opens up at the Fermi level. A trivial $Z_2$ invariant confirms that the system is a trivial insulator. The results shown in this section is consistent with the previous work done using CPA approximation [42].

To check the effect of relaxation we have performed a calculation with unrelaxed cell (experimental lattice constants) corresponding to Fig. 15a where IS is broken by Sb doping. As mentioned above, the lattice parameters of the unrelaxed cell is larger than the corresponding relaxed cell, and therefore, it is a strained system. Consequently, breaking of IS splits each Dirac node into two Weyl nodes of opposite chirality, causing a transition to a WSM phase. This calculation indicates that strain can play an important role on the stability of the Dirac nodes.

C. Mn doped Na$_3$Bi DSM

Finally, we discuss the consequences of breaking the TRS by introducing magnetic impurities in the system. The substitution of a Bi by a Mn atom in the unit cell not only breaks TRS, it breaks IS as well. As with the previous cases, we have performed a full atomic relaxation, which changes the cell parameter to $a=b=10.237421$ and $c=18.505238$ bohr. The local moment of the Mn atom is $4.3 \mu_B$. The Fig. 16 shows the band structure of Mn-doped Na$_3$Bi. The states just above the Fermi level are predominantly of Mn $d$ character (minority spin) and just below the Fermi level the bands are mixed states of Bi $p$ and Mn $d$ states. Comparing with Fig. 15 we note that the Bi $p$ states that contributed to the DP on the $A - \Gamma$ path is now pushed down about 0.3 eV below the Fermi level with Mn impurity.

Since both IS and TRS are broken, this system cannot host any Dirac node but the presence of Weyl nodes cannot be ruled out. To explore this possibility we have once again constructed a real space Hamiltonian in the Wannier basis using the Mn $d$, the Bi $p$ and the Na $s$ orbitals. We then searched for the nodes using Wannier-Tools, which shows that there are six Weyl nodes close to the Fermi level: three with net chirality +1 above the $k_z = 0$ plane and three with net chirality -1 above the $k_z = 0$ plane. It should be noted that a large concentration of impurities may create many nodes in the BZ. However, we have considered only those nodes that are close to Fermi energy, since they are most relevant for the topological characterization of the system. As in the case of Cd$_3$As$_2$, the Chern number of the $k_z = 0$ plane of Na$_3$Sb is also 1, indicating that magnetic impurity causes a transition to a Chern insulator phase.

FIG. 16. Bandstructure of Mn-doped Na$_3$Bi DSM. The breaking of both IS and TRS lifts the degeneracy of the bands. The states closer to the Fermi level are highlighted with colored bands.

V. CONCLUSIONS

In this work we have used first-principles DFT methods to study the electronic, magnetic and topological properties of doped DSMs. In particular, we have focused on the Cd$_3$As$_2$ and Na$_3$Bi DSMs with the goal of investigating whether it is possible to trigger topological phase transitions, for example, from the Dirac phase to the WSM phase, by chemical doping. Three symmetries are important for the non-trivial topological Dirac phase, namely IS, TRS and a rotational symmetry.

Therefore we studied the effect of breaking them in different ways, by adding non-magnetic impurities (Zn at the Cd site of Cd$_3$As$_2$ and Sb at the Bi site of Na$_3$Bi) or magnetic Mn impurities in the pure systems. Such doping leads to different types of phase transitions depending on the type of the symmetry breaking.

We found that when the rotational screw symmetry of Cd$_3$As$_2$ is broken while preserving IS, a gap of 12 meV opens up at the original Dirac points, confirming the expectation that the rotational symmetry is crucial for the stability of the Dirac points. Although the system is still a semimetal due to the presence of electron and hole pockets, the valence band is completely separated from the conduction band everywhere in the BZ (see Fig 14) and the $Z_2$ calculation shows that the $k_x$, $k_y$, $k_z = 0$ TRIPs are all topologically nontrivial. If both IS and rotational symmetries are broken, then each Dirac node splits into two Weyl nodes with opposite chirality i.e. the system makes a transition to Weyl phase.
The most interesting topological phase in Cd$_3$As$_2$ arises when IS is broken while the rotational screw symmetry is preserved. Due to the presence of the crystal symmetries such as the mirror plane and the rotational screw axis, along with the TRS, the two-fold degeneracy of the bands is still maintained along the tetragonal axis. Since the band inversion still occurs at the $\Gamma$ point, the original Dirac points survive despite the broken IS. At generic points away from the tetragonal axis, double degeneracy is lifted and our calculation shows the occurrence of band crossings at eight different points in the $k_z = 0$ plane, close to the Fermi level. The topological analysis confirmed that they form four pairs of Weyl nodes, each pair consisting of nodes with opposite chirality. Therefore, this particular realization of impurity doping results in a mixed Dirac + Weyl phase. Although this interesting result was explicitly obtained for an unrelaxed system, we showed that in the presence of an additional external strain such a phase should emerge at the strain-induced topological phase transition point separating a trivial semimetal phase from a DSM phase. It is also possible that this mixed phase could be present in a relaxed system for a small range of external stress around this transition point. In Na$_3$Bi, we also obtained the Dirac phase when IS is broken but we found no band touching point at other generic $k$-point in the BZ at the Fermi energy. Therefore, there is no Dirac-Weyl coexisting phase in Na$_3$Bi at 50% concentration, although this special phase may appear at lower impurity concentrations.

We have also investigated the consequence of breaking TRS by introducing Mn impurities. Since we have used only one Mn in the unit for this study, this impurity doping breaks all the other crystal symmetries as well. Since both IS and TRS are broken, the system cannot host any Dirac node. However, in Cd$_3$As$_2$, a total of ten Weyl nodes are formed close to the Fermi level, five above the $k_z = 0$ plane with net chirality +1 and five below the $k_z = 0$ plane with net chirality -1, turning the system into a magnetic WSM. The difference in chirality above and below the $k_z = 0$ plane reflects the nontrivial character of this plane and our topological analysis shows that the Chern number for this plane, $C = [1]$, which signifies that this plane may be viewed as 2D Chern insulator. Similarly for Na$_3$Bi, we obtained a Weyl phase in Mn-doped Na$_3$Bi, with three Weyl nodes with net chirality +1 and three nodes with net chirality -1, above and below the $k_z = 0$ plane, respectively. Therefore, these magnetically-doped DSMs that transform into WSMs provide a possible platform to realize the quantum anomalous Hall effect.

One final important remark regards the experimental realization of the different doping cases that we have analyzed in this work. We recognize that achieving the precise breaking of one particular symmetry while preserving others in a bulk system is a highly nontrivial endeavor from the experimental point of view. However, we believe that some of the cases that we have investigated in this work, such as the one with a single impurity (both magnetic and nonmagnetic) can be realized experimentally, since for a large enough unit cell this essentially represents a random doping. We also believe that the impurity case displaying coexisting Weyl+Dirac phase (IS broken but rotational symmetry preserved) can be realized, since this particular system has a layered structure (see Fig. 1) which is suitable for molecular beam epitaxy techniques. Therefore, we hope that our work will encourage experimental investigations of impurity-induced phase transitions in these topological semimetal materials.

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