Unraveling Electronic Structure, Magnetic States, and Topological Phenomena in Pristine, Defected, and Strained Ti$_2$N MXene

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ABSTRACT: We unravel the evolution of structural, electronic, magnetic, and topological properties of graphene-like pristine, defected, and strained titanium nitride MXene with different functional groups (-F, -O, -H, and -OH) employing first-principles calculations. The formation and cohesive energies reveal their chemical stability. The MAX phase and defect free functionalized MXenes are metallic in nature except for oxygen terminated one, which is 100% spin polarized half-metallic. Additionally, the bare MXene is nearly half-metallic ferromagnet. The spin-orbit coupling significantly influences the bare MXene possessing band inversion. The strain effect sways the Fermi energy state under compression and toward higher energy state under tensile strain in Ti$_2$NH$_2$. These properties are reversed in Ti$_2$N, Ti$_2$NF$_2$, and Ti$_2$N(OH)$_2$. The half-metallic nature changes to semi-metallic under 1% compression and is completely destroyed under 2% compression. In single vacancy defect, the band structure of Ti$_2$NO$_2$ remarkably transforms from half-metallic to semi-conducting (with large band gap of 1.73 eV) in 12.5% Ti, weakly semi-conducting in 5.5% Ti, and topological semi-metal in 12.5% oxygen. The 25% N defect changes the half-metallic to the metallic with certain topological features. Further, the 12.5% Co substitution in Ti$_2$NO$_2$ preserves the half-metallic character, whereas Mn substitution allows to convert half-metallic into weak semi-metallic preserving ferromagnetic character. However, Cr substitution converts half-metallic ferromagnetic to half-metallic anti-ferromagnetic state. The understanding made here on collective structural, stability, and magnetic and topological phenomena in novel 2D MXenes open up their possibility in designing them for synthesis and thereby taking to applications.

KEYWORDS: MXenes, Structural Stability, Electronic Structure, Magnetic States, Topological Phenomena, Strain, and Defect
INTRODUCTION

After the discovery of graphene by the group of Novoselov and Geim in 2004,1 many researchers are focusing on two-dimensional (2D) materials with diverse physical phenomena. Many 2D materials go beyond the graphene.2,3 Atomically-thin 2D materials have unique physical, chemical, electronic, and optical properties,4 as well as their various potential applications compared to their conventional three-dimensional (3D) counterparts. Graphene is limited to just carbon atoms in its composition, whereas the rapidly growing area of 2D materials include large set of transition metal (TM) carbides and nitrides (MXenes).5 These materials have wide range of applications in diverse field such as energy storage, water electrolyzers, super-capacitor, lithium ions batteries,6 biomedical applications,7 sensors,8 catalysis,9 and spintronic devices.10

In 2011, a new group of 2D materials based on TM carbides were synthesized.11 These 2D MXenes (Figures 1b and 1c) are obtained from 3D MAX phase (Figure 1a), having general chemical formula $M_{n+1}AX_n$ where $n = 1$ to 3, M is TM, A is an A-group (basically IIIA and IVA or group 13 and 14) elements and X is either carbon or nitrogen. The unit cell of the MAX phase is characterized by near close-packed M layers interleaved with the layers of a pure A-group elements and with the X atoms filling the octahedral sites. The A-group elements are positioned at the center of trigonal prism.12 Currently, investigators are paying attention to theoretical modeling of the MAX phases. Unlike the MX phases, bonding in the MAX phases are combination of metallic, covalent, and ionic. In the MX phase, there is a strong overlap between the $p$ orbitals of the X elements and the $d$ orbitals of the M atoms, making strong covalent bonds that are comparable to those in the MX binaries.13 The 2D materials (MXene) offer a large variety of chemical compositions compared to graphene.14 MXenes can be thought of as conductive clays in which cation intercalation and exchange easily occur.15 Among all experimentally synthesized and theoretically predicted MXenes, the carbide based MXenes are widely studied especially Ti$_3$C$_2$T$_2$ (T= surface termination).16 The synthesis of titanium nitride based MXene is quite difficult due to large value of formation energy in their 3D MAX phase and its poor stability in etchant, typically in hydrofluoric acid (HF).17 The Ti$_4$N$_3$ MXene was successfully synthesized from precursor Ti$_4$AlN$_3$ using molten fluoride salt to etching Al elements.18

![Figure 1: (Color online) (a) Hexagonal closed packed structure of MAX phase $M_2AX$, and (b) and (c) are corresponding side and top views of MXene $M_2X$ in $3 \times 3 \times 1$ super-cell.](image)

The Ti$_2$N MXene was successfully synthesized with functionalized fluoride by immersing Ti$_2$AlN in a mixture of potassium fluoride (KF) and hydrochloric acid (HCl).17 Thus, surface terminated mono-layer may get significant changes in structural stability, electronic, and magnetic properties as compared to bare MXene.19 The nitride MXenes exhibit better pseudocapacitive performance than carbide based MXenes.20 This type of 2D materials have high value of electrical conductivity and wide range of absorption applications, which are key to their success in the aforementioned applications.21 The 2D materials are highly flexible and extremely sensitive to the applied strain to modulate electronic band structure.22–24 The nature of band structure changes from indirect band gap to direct band gap under tensile strain and the band gap closes under compression strain in Ti$_2$CO$_2$ MXene.25

Despite having all fascinating properties, the defect in MXenes severely alter the structural sta-
bility, electronic, and magnetic properties. The presence of intrinsic Ti defects in Ti$_2$C$_2$T$_2$ layers was experimentally determined (using scanning tunneling microscopy) in Ref. However, the detail explanation of structural defect in MXene is missing, which is addressed here.

Beside the major astonishing properties and applications of MXenes, there was a limitation in the field of storage capacity. This was solved by doping nitrogen atom in Nb$_2$CT$_2$ MXenes, which increases storage capacity in lithium ion batteries. The Nb doping can change electronic properties by shifting the Fermi level towards the conduction band that enhances the electronic conductivity in Ti$_2$C$_2$T$_2$. Further, the B doping in oxygen terminated Ti$_2$C MXene improves the elastic properties with reasonably high critical strain making suitable for the flexible device applications.

Furthermore, the realization of free-standing single atomic layers of graphene opened a new route towards the topological phenomena in 2D materials. The coexistence of electron and hole packets with Dirac cone is responsible for quantum oscillation in 3D topological materials beyond the graphene. Similarly, the Zr$_2$Si also exhibits anisotropic Dirac cones. Theoretically, the titanium carbide based MXenes can also be predicted to exhibit the Dirac topology in their electronic band structure. In the similar vein, the topological and associated properties are expected in the Ti$_2$N MXene.

In this paper, we have studied the electronic and magnetic properties of the MAX phase, and bare and its corresponding functionalized MXenes. The chemical stability of all MXenes and MAX phase were studied with the help of cohesive and formation energies. The -O terminated MXene is relatively stable as compared to all other MXenes. The MAX phase and functionalized MXenes exhibit the non-magnetic (NM) metallic except for O terminated one, which is predicted to be half-metallic ferromagnet. The strain effect in the mono-layer MXene influences the position of the Fermi level with different topological nature. The defect in Ti$_2$NO$_2$ brings significant changes in the electronic properties with various topological nature. The electronic properties of Ti defect strongly depend upon vacancy concentration. The half-metallic nature changes to strong and weak semi-conductor depending upon the concentration. Similarly, the half-metallic property changes to topological semi-metal and also remains metallic with Dirac topology depending on different defects. Interestingly, the TM substitution introduces peculiar magnetic to semimetallic to topological phenomena in Ti$_2$NO$_2$ MXene.

According to the best of our knowledge, the topological features, effect of spin-orbit coupling (SOC) in the band structure, vacancy concentration dependent semi-conducting nature, doping, and detail explanation of half-metallicity are new finding of this work.

RESULTS AND DISCUSSION

Structural Properties

The Ti$_2$N MXene is obtained by removing Al from hexagonal structure with space group number 194 ($P6_3/mmc$) of Ti$_2$AlN MAX phase. The MAX phase is formed due to mixed combination of ionic/covalent/metallic bonding between Ti, Al, and N atoms thereby hybridizing Ti 3$d$-N 2$p$, Ti 3$d$-Al 3$s$, and Ti 3$d$-Al 3$p$ states. The Al components in MAX phase are chemically reactive and the bonding between Ti and Al is purely metallic. So, the relatively weak bond and reactive A element can be selectively etched with suitable chemical composition leaving behind the chemically stable closely packed Ti$_2$N MX phase, where the N atom filling the octahedral side of Ti$_2$N. The chemical exfoliation of Ti$_2$N from Ti$_2$AlN usually leaves some -O, -F, -H, and -OH on the surface, and these groups may have significant influence on the electronic and magnetic properties of MXenes. There are three possible sites of surface termination (Figure 2c), on the top of Ti(1) (site a), on the top of N (site b), and on the top
of Ti(2) (site c). On the basis of these three sites, there are four possible configurations for the position of terminated species. In model I, at site a, in model II, at site b, in model III, at site c, and in model IV (mixed model II and III), one termination at site b and other termination at site c, are considered. The most preferential position for termination is in model III.\(^{42}\) In the case of -OH termination, the favorable position of the hydrogen atom is on the top of oxygen atom, as a result, the structure becomes symmetrically equivalent to a mono-atom termination.\(^{37}\) After the surface termination, there are electronic reconstruction of new energy states between Ti atoms with the terminated species.

Figure 2: (Color online) (a) The top view of Ti\(_2\)NO\(_2\), and (b) and (c) are side views of Ti\(_2\)N(OH)\(_2\) and Ti\(_2\)N in 3 × 3 × 1 super-cell, respectively, (d) the side view of mono-layer Ti\(_2\)N. The up and down arrows indicate the up and down spins.

To investigate the stability of bulk Ti\(_2\)AlN MAX phase, and bare Ti\(_2\)N and its corresponding functionalized Ti\(_2\)NT\(_2\) (T = -OH, -H, -O, -F) MXenes, formation energy is calculated using formula,

\[
E_f(Ti_2NT_2) = E_{tot}(Ti_2NT_2) - 2E_{bulk}(Ti) - E_{bulk}(N) - 2E_{bulk}(T)
\]

where \(E_{tot}(Ti_2NT_2)\), \(E_{bulk}(Ti)\), \(E_{bulk}(N)\), and \(E_{bulk}(T)\) represent total energy of optimized systems, bulk energies of Ti, N, and T atoms, respectively.\(^{43}\) In the similar way, cohesive energy is calculated as

\[
E_c(Ti_2NT_2) = E_{tot}(Ti_2NT_2) - 2E_{iso}(Ti) - E_{iso}(N) - 2E_{iso}(T)
\]

where \(E_{tot}(Ti_2NT_2)\), \(E_{iso}(Ti)\), \(E_{iso}(N)\), and \(E_{iso}(T)\) represent total energy of optimized systems, energies of isolated Ti, N, and T atoms, respectively. The energy of isolated atoms are calculated by adding single atom at the center of defined large super-cell.\(^{44}\) The negative value of the cohesive and formation energies indicate that our systems are stable and the oxygen terminated MXene is relatively more stable as compared to all other MXenes and MAX phase. This is mainly due to the strong hybridization between Ti-3\(d\) and O-2\(p\) atoms. The formation energy is very large as compared to the cohesive energy of nitride based MXenes (Ti\(_2\)N and Ti\(_2\)NT\(_2\)), which is consistent with previously reported values.\(^{45}\) So, it is difficult to extract nitride based MXene from its parent precursor MAX phase. The stability of MAX phase and MXenes are in increased sequence of Ti\(_2\)NH\(_2\) < Ti\(_2\)N(OH)\(_2\) < Ti\(_2\)N < Ti\(_2\)AlN < Ti\(_2\)NF\(_2\) < Ti\(_2\)NO\(_2\) (Table1).\(^{46}\) But this sequence is quite different for the formation energy: Ti\(_2\)N < Ti\(_2\)AlN < Ti\(_2\)NH\(_2\) < Ti\(_2\)N(OH)\(_2\) < Ti\(_2\)NO\(_2\) < Ti\(_2\)NF\(_2\) (Table1). The bare MXene is less stable than the parent precursor MX phase. We found that, the values of the formation and cohesive energies are significantly decreased after the surface terminations, particularly in -O and -F groups indicating the functionalized MXenes more stable than their bare MXene. The Ti\(_2\)N MXene and its derivative structures have slightly lower formation energies than that shown in the Open Quantum Materials Database.\(^{47,48}\) Furthermore, the dynamical stability of Ti\(_2\)N mono-layer was investigated by Wang et al. (Ref.\(^{42}\)). They performed lattice phonon calculations and found well separated optical and acoustic branches with no imaginary frequency phonon at any wave vector. With this finding and information, we use here the optimized mono-layered hexagonal structure.\(^{19}\) We first optimize our material systems,
Table 1: Calculated values of mono-layer thickness (L) and distance between Ti-T, Ti-Ti, and Ti-N atoms. $E_c$ and $E_f$ are calculated values of cohesive and formation energies for MAX phase, bare and its corresponding functionalized MXenes. The negative values of cohesive and formation energies reveal their chemical stability. The values in parenthesis are from Ref.\textsuperscript{19}

<table>
<thead>
<tr>
<th>Crystals</th>
<th>L(Å)</th>
<th>$d_{Ti-T}(\text{Å})$</th>
<th>$d_{Ti-Ti}(\text{Å})$</th>
<th>$d_{Ti-N}(\text{Å})$</th>
<th>$E_c$(eV)</th>
<th>$E_f$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$AlN</td>
<td>....</td>
<td>2.90</td>
<td>2.08</td>
<td>-6.14</td>
<td>-2.51</td>
<td></td>
</tr>
<tr>
<td>Ti$_2$N</td>
<td>2.31</td>
<td>....</td>
<td>2.87</td>
<td>2.06</td>
<td>-6.04</td>
<td>-2.36</td>
</tr>
<tr>
<td>Ti$_2$NF$_2$</td>
<td>4.57 (4.63)</td>
<td>2.18 (2.16)</td>
<td>2.77</td>
<td>2.08 (2.07)</td>
<td>-6.30</td>
<td>-3.86</td>
</tr>
<tr>
<td>Ti$_2$NO$_2$</td>
<td>4.24 (4.35)</td>
<td>2.00 (1.98)</td>
<td>3.09</td>
<td>2.20 (2.15)</td>
<td>-8.18</td>
<td>-3.44</td>
</tr>
<tr>
<td>Ti$_2$NH$_2$</td>
<td>4.23 (4.20)</td>
<td>2.00, 2.01 (2.00)</td>
<td>2.84</td>
<td>2.08 (2.07)</td>
<td>-5.05</td>
<td>-2.84</td>
</tr>
<tr>
<td>Ti$_2$N(OH)$_2$</td>
<td>6.66 (6.66)</td>
<td>2.17 (2.17)</td>
<td>2.82</td>
<td>2.08 (2.07)</td>
<td>-5.57</td>
<td>-3.06</td>
</tr>
</tbody>
</table>

that makes easier to study the electronic and magnetic properties. Table 1 shows optimized values of mono-layer thickness (L), bond length between titanium atom Ti and terminated species T ($d_{Ti-T}$), titanium-titanium atoms ($d_{Ti-Ti}$), and titanium to nearest N atoms ($d_{Ti-N}$) thereby calculating cohesive and formation energies of selected functionalized MXenes. The calculated values are compared with previously reported theoretical values (shown in parenthesis).\textsuperscript{19}

Our optimized lattice parameters are in general consistent with the previously reported theoretical values (Figure 3).\textsuperscript{19} The extracted 2D MXenes from 3D MAX phase have decreased cell size, and bond length between Ti-Ti and Ti-N. But after the surface termination, the cell size and thickness of mono-layers are increased due to the addition of extra atoms in the bare Ti$_2$N MXene.

The thickness of mono-layer strongly depends on terminating species. The thin mono-layer was found in hydrogen termination while thick mono-layer was found in hydroxyl termination in the bare MXene. Interestingly, the bond length between Ti-N and Ti-T in Ti$_2$N, Ti$_2$NO$_2$, Ti$_2$NF$_2$, and Ti$_2$N(OH)$_2$ follow symmetrical bond nature except for Ti$_2$NH$_2$. In hydrogen termination, Ti-T bond length at the top side is slightly shorter than the bottom side. Meanwhile, the bond length between Ti and N atoms show symmetrical nature 1.

The oxygen termination on MXene layers plays a remarkable role as compared to other terminated species. In oxygen termination, the bond length between Ti-Ti atoms increases by 0.22 Å and decreases by 0.1 Å in F termination but only slight change occurs in the case of -OH, -H terminations. Also, relatively shortest bond length $d_{Ti-T}$ and longest bond length $d_{Ti-N}$ represent strong interaction between surface of Ti and O atoms. The bond length between Ti-F is is larger as compared to the other terminations, which shows weak inter-
action between Ti and F. Figure 2a and 2b represent top and side views of the optimized structure of Ti$_2$NO$_2$ and Ti$_2$N(OH)$_2$ in 3 × 3 × 1 super-cell. The terminated atoms are filling the vacant space on the top and bottom sides of Ti layers forming alternate position with titanium atoms in the stable configuration (Figure 2b).

Electronic and Magnetic Properties Without Vacancy Defect

The energetically stable configurations of MAX phase, bare MXene and its corresponding functionalized MXenes have been studied with the full relaxed calculations corresponding to possible NM, ferromagnetic (FM), and anti-ferromagnetic (AFM) configurations. The MAX phase is energetically stable in NM configuration. In the case of bare MXene, the relaxation calculations with AFM configuration show zero net total magnetization with 0.33 $\mu_B$ magnetic moment for individual Ti atoms. Similarly, the relaxation calculations with FM configuration show total magnetization 1.10 $\mu_B$ per unit cell (with 0.25 $\mu_B$ magnetic moment for each Ti) which is closely comparable to 1.00 $\mu_B$ per unit cell found in Ref. 45. The energy of FM and AFM configurations with reference to NM configuration are -39 meV and -36 meV, respectively. This shows, the FM configuration is energetically more stable than the AFM configuration.

It is interesting to point out that a few published papers (as for example Ref. 42), especially in bare Ti$_2$N, indicate the AFM ground state by using onsite electron-correlation (Hubbard U) on the top of PBE functional. They consider Hubbard parameter for titanium by using the strong correlation effect of TiO$_2$ 49 in Ti$_2$N. We believe that MXenes are not similar materials as those of oxides where the strong correlation plays a role to identify insulating behavior. Here, we focus on topology due to 2D nature and variable magnetism where the role of strong correlation may not be fully relevant. We, in fact tested Ti$_2$N with applying Hubbard parameter (4.2 eV as suggested by Ref. 42) and found that the ground state becomes AFM with total loss of expected topological features in 2D materials. We used 1 × 1 × 1, 2 × 2 × 1, and 3 × 3 × 1 cells to study the electronic band structure (with SOC) and the DOS without SOC. The surface termination on bare MXene mono-layer results the complete removal of magnetism except for the oxygen terminated one, which is 100% spin polarized half-metallic.

On moving from 3D bulk states (Ti$_2$AlN) to 2D surface states (Ti$_2$N), there are myriad changes in the electronic structure properties from metallic to nearly half metallic 45 with topological characters. Interestingly, at the region between high symmetry points of K and Γ, there are two Dirac cones (a) (linear 50) and (b) (distorted 50) below the Fermi level in spin up channel, and two Dirac cones (c) (distorted) and (d) (linear) above the Fermi level in spin down channel (Figure 4P). The formed gapless linear Dirac cones (a) and (d) uncover the zero mass parameter but the distorted Dirac cones reveal the non-zero mass parameter, it may be positive or negative, depending upon the nature of the distortion. The distorted Dirac cones (b and d) are expected to have positive mass parameter 50. The formation of distorted Dirac cone apparently diminishes the characteristic of the quantum oscillation. 35 The formation of Dirac cone (b) just below the Fermi level reveals the idea of n-type self doping character informing the presence of electron carriers even without transforming the electrons from surrounding environment. 31 The spin down bands show the metallic character whereas the spin up bands show nearly half-metallic character. This indicates that Ti$_2$N is nearly half-metallic, which is supported by Ref. 45. The same band crosses the Fermi level multiple-times forming multiple Dirac cones at and near the Fermi level, which reveals the characteristic of multi-nodal properties in Ti$_2$N. 51 The bottom of unoccupied states in the spin down and top of occupied states in the spin up channels lie just above and below the Fermi level, which reveal the exchange splitting energy of 0.16 eV (Figure 4P). 52
This exchange splitting is caused by the 3d states of Ti atom. The band structure corresponding to SOC in Ti$_2$N is shown in Figure 4Q. The overlapped bands (without SOC) near the Fermi level in region Γ-M are separated and form Dirac topological features under the presence of SOC without disturbing the multi-nodal properties. Interestingly, the SOC allows to make two gapped linear Dirac cones (e) and (f) below and above the Fermi level (Figure 4Q). The formation of Dirac cone below the Fermi level reveals the self n-type of doping character, whereas the formation of Dirac cone just above the Fermi level reveals the self p-type doping character indicating the electrons and holes carriers even without transforming the electrons from surrounding environment.\textsuperscript{31,35} The origin of gap opening in the Dirac cones are due to hybridization of the electronic wave function between the top and bottom surfaces with the same quantum numbers.\textsuperscript{53} In our case, the hybridization causes the time reversal symmetry breaking under SOC\textsuperscript{54} and the Dirac cones behave massive states\textsuperscript{55,56}. Similarly, linear gapped Dirac cone (i) and distorted gapped Dirac cone (j) are found near the Fermi level (above and below) in region K-Γ (Figure 4Q). In the same region, a linear gapped Dirac cone (l) and distorted gapped Dirac cones (g), (h), and (k) are found above the Fermi level.

Figure 5 shows the zoomed view (A and B) of Figure 4 with spin polarized projected 3d band structure of Ti atom in Ti$_2$N MXene. The Ti$_2$N MXene has octahedral symmetry (D$_{3h}$), where the t$_{2g}$ (d$_{xz}$, d$_{yz}$, and d$_{xy}$) and e$_g$ (d$_{x^2-y^2}$ and d$_{z^2}$) are lower and higher energy states, respectively.\textsuperscript{26,57} The d$_{xy}$ of t$_{2g}$ and d$_{z^2}$ of e$_g$ states juxtapose each other and in the absence of SOC, the spin up and down bands cross at two points (I and II) (Figure 5A). The SOC couples the opposite spin components forming the topologically non-trivial gap at the band crossing points (I and II)\textsuperscript{58–61} (Figure 5B). The gap opening results from the time reversal symmetry breaking\textsuperscript{54} and hybridization\textsuperscript{53} of the opposite spin states (Figure 5B). Here, the d$_{xy}$ state is hybridized with the d$_{z^2}$ state around...
gap opening in I is relatively larger as compared to II. The dispersion of the bands remain linear under the SOC. The non-trivial topological gap with $Z_2 = 1^{62,63}$ form the linear Dirac cones which are responsible for the quantum oscillations.\cite{35} Thus, Ti$_2$N is expected as a topological material.\cite{64} In the same vein, just above the Fermi level in the region $K - \Gamma$, the band inversions are uncovered indicating non-trivial topological features ($f$ and $i$ representations in Figure 5Q), whose characteristic features are already discussed above. These unprecedented multiple or double band inversions around the Fermi level are resulted from the nodal lines.\cite{65}

The overlap of the valence and the conduction bands at the Fermi level in band structure (Figure 6) of MAX phase reveals the considerable metallic character. The presence of SOC does not influence these outcomes.

After surface termination, all the functionalized Ti$_2$NT$_2$ ($T = -\text{OH}, -\text{H}, -\text{F}$) MXenes become metallic NM\cite{19} except for oxygen terminated one, which is half-metallic ferromagnet.\cite{10} The electronic properties of Ti$_2$NF$_2$ and Ti$_2$N(OH)$_2$ are similar due to the presence of electrophiles $-\text{F}$ and $-\text{OH}$, which accept one electron from Ti. However, the electronic property of Ti$_2$NO$_2$ is different due to the presence of $-\text{O}$ electrophile, which accepts
two electrons from Ti atom.\textsuperscript{41} The band structure of hydrogen terminated MXene in $1 \times 1 \times 1$ mono-layer (Figure 6).

![Figure 6](image)

**Figure 7:** (Color online) P and Q represent the spin polarized band structure corresponding to without SOC and with SOC of oxygen terminated Ti$_2$NO$_2$ MXene mono-layer. R, S, T, and U highlight the Dirac topology. The red dashed lines represent the the position of the Fermi level.

The band splitting from a $\Gamma$ point is reconstructed at another $\Gamma$ point just below the Fermi level. Further, the bands cross the Fermi level from the occupied states to the unoccupied states, thereby converting the nearly half-metallic Ti$_2$N to the metallic.

The bands cross the Fermi level from the occupied states to the unoccupied states indicating the metallic property in both -F and -OH terminated $1 \times 1 \times 1$ mono-layer MXene (Figure 6) similar to that of H terminated one. Astonishingly, gapped Dirac cones are found at K point on and above the Fermi level in the case of -F and -OH terminations, respectively (Figure 6). The charge carrier corresponding to that Dirac cone behaves like hole-packets at the conduction band.\textsuperscript{35}

Similarly, the oxygen termination in Ti$_2$N MXene converts the nearly half-metallic to 100\% spin polarized half-metallic (Figure 7). The spin up and the down bands are with similar characters (Figure 7P). The black and red colored bands correspond to the spin down and the spin up channels. The spin down channel clearly shows the semi-conducting nature whereas the spin up channel shows the metallic nature exhibiting the half-metallic character. This half-metallic FM nature is due to the exchange splitting energy of 0.42 eV, which is higher than that found in the Ti$_2$N mono-layer.

The spin down band splits from the near $\Gamma$ point above the Fermi level and reconstructs at another $\Gamma$ point above the Fermi level. Same behavior happens for the spin up band starting from below the Fermi level. The presence of SOC in Ti$_2$NO$_2$ mono-layer converts the half-metallic to topological half-metallic nature (Figure 7Q). Interestingly, four distorted gapped Dirac cones such as: three (b, c, and d) and one (a) are found at the vicinity of K and $\Gamma$ above the Fermi level, respectively. Similarly, a linear gapped Dirac cone (e) is found at the region between K - $\Gamma$ just above the Fermi level.

On moving from primitive to super-cells, the multiplex topological features of folded band structure\textsuperscript{66} have been calculated. These complex folded band structure of super-cells are unfolded to conform the band structure emerging from the primitive cell (Figure 8). The folded bands are difficult to analyze with the angle-resolved photoemission spectroscopy data.\textsuperscript{66,67} Thus, the unfolding of the band structure are important to analyze and compare with the experiment.

To get better deliberation on the electronic structure properties of MAX phase and MXenes, PDOS are shown in Figure 9. The bands of MAX phase are mainly contributed from Ti-3$d$, N-2$p$, N-2$p$, N-2$p$, and O-2$p$. The bands of MXenes are mainly contributed from Ti-3$d$, N-2$p$, O-2$p$, and Ti-2$p$. The band structure of MXene with SOC is shown in Figure 10. The bottom of the conduction band is at the $\Gamma$ point, and the top of the valence band is at the M point. The band structure of MXene without SOC is shown in Figure 11. The bands are flat and metallic at the Fermi level. The band structure of MXene with SOC is shown in Figure 12. The bands are gapped and metallic at the Fermi level. The band structure of MXene with SOC is shown in Figure 13. The bands are gapped and metallic at the Fermi level. The band structure of MXene with SOC is shown in Figure 14. The bands are gapped and metallic at the Fermi level. The band structure of MXene with SOC is shown in Figure 15. The bands are gapped and metallic at the Fermi level.
Al-3p, and Al-3s states.

Figure 8: (Color online) A and B represent the spin up and spin down band structure of unfolded $3 \times 3 \times 1$ super-cell and primitive cell to revive the effective primitive band structure of Ti$_2$NO$_2$. The colored (orange) dotted curves represent the effective bands of primitive cell and shaded spectral bands (green and yellow) represent the total spectral weight of unfolded bands of the super-cell. The sharp yellow colored bands reveal the higher spectral weight. The red dashed lines represent the position of the Fermi level.

The total DOS is dominated by Ti-3$d$ states. The 3$s$ and 3$p$ states of Al, and 2$p$ and 2$s$ states of N form a very large energy gap of 6.49 eV, which is consistent with previously reported value of 6.2 eV. This large energy gap in valence band indicates that, there is no $sp$ hybridization in Ti$_2$AlN. The value of DOS near the Fermi level $N(E_F)$ is 2.74 states per eV, which is also consistent with the previously reported value of 3.03 states per eV.

To illustrate the electronic properties vividly, we divided the valence band into two sub-bands of A and B (Figure 9P). In the sub-band A, there is a strong contribution from Ti-3$d$ and Al-3$p$ states. Similarly, in the sub-band B, the strong contribution is from the Ti-3$d$ and N-2$p$ states and weak contribution is from the Al-3$s$ states. So, the Ti-3$d$ states play a significant role in both sub-bands A and B.

After eliminating Al from MAX phase, bands become narrow and form open gap making large indirect gap of 2.40 eV in the spin up and 2.59 eV in the spin down (within the occupied part) are found between the sub-bands A and B in Ti$_2$N (Figure 9Q). The sub-band A is formed due to strong contribution from Ti-3$d$ states and weak contribution from N-2$p$ states. Similarly, the sub-band B is formed due to the combination of N-2$p$ states and Ti-3$d$ states with major contribution from N-2$p$ states. This may indicate that, the change occurring below the Fermi level influences the electronic states at the Fermi level as discussed earlier in Ref.

The termination on mono-layer MXene plays a vital role especially far below the Fermi level in the valence band. The surface termination in the bare MXene mono-layer splits the sub-band B into separate sub-bands B and C. In fluoride termination, the sub-band A is dominated by Ti-3$d$ states and the sub-bands B and C are the mixed states of Ti-3$d$, N-2$p$, and F-2$p$ states (Figure 9P). The sub-band C is significantly dominated by F-2$p$ states. The large indirect energy gap of 2.71 eV and comparatively small direct energy gap of 0.74 eV are between the sub-bands A and B, and the sub-bands B and C, respectively. Hydroxyl termination follows the similar trend in which the sub-band A is dominated by Ti-3$d$ states. The sub-band B is the mixed states of Ti-3$d$, N-2$p$, and O-2$p$ states but the sub-band C is the mixed states of O-2$p$, Ti-3$d$, and H-1$s$, and N-2$p$ states (Figure 9P). The indirect energy gap of 1.65 eV
and the direct energy gap of 1.84 eV are found between the sub-bands A and B, and B and C, respectively.

![Figure 9: (Color online) P represents the PDOS of Ti$_2$AlN MAX phase and Ti$_2$NT$_2$ (T = -F, -H, -OH) MXene mono-layers. Similarly, Q represents the spin polarized PDOS of bare Ti$_2$N and Ti$_2$NO$_2$ MXene mono-layers. The PDOS are preserved in the larger super-cells under Gaussian smearing. The colored arrows (up and down) represent the spin up and spin down channels in both Ti$_2$N and Ti$_2$NO$_2$ MXene, respectively. The red dashed line represents the position of the Fermi level. Similarly, the sub-band A in H and O terminated MXenes are also dominated by Ti-3d states (Figure 9P and 9Q). The hydrogen atom contributes only in the sub-band B (Figure 9P). In hydrogen termination, only one indirect energy gap of 1.53 eV is found between sub-bands A and B, and continuous bands are found between the sub-bands B and C indicating that the hydrogen atom does not play a significant role in the bare Ti$_2$N MXene as compared to other. Likewise, in oxygen termination, the small direct energy gap of 0.13 eV in the spin up and 0.09 eV in the spin down are found between the sub-bands B and C exhibiting the strong hybridization between Ti-3d, N-2p, and O-2p states (Figure 9Q). But the large indirect energy gap of 1.88 eV in the spin up and 2.22 eV in the spin down are found between the sub-bands A and B. The sub-band C is mainly dominated by N-2p states.

From the electronic band structure, the Fermi level is shifted down in the bare MXene obtained by etching Al from the MAX phase and is again shifted down under the surface terminations. The sub-band C is found below the sub-band B, due to electronic reconstruction between Ti and functional group. The functional group mainly contributes in both sub-bands B and C except for hydrogen termination, where hydrogen atom significantly contributes in the sub-band B (Figure 9P).

Origin of Half-metallic Gap in Ti$_2$NO$_2$

The magnetism and half-metallicity strongly depends upon the coordination environment of Ti and the number of 3d electrons associated within it. It plays a vital role in the electronic and magnetic properties. Similar to TM dichalcogenides, non-bonding 3d bands in MXenes are positioned between the bonding and anti-bonding of Ti-N and Ti-O states.\(^{71}\) Presuming all the constituent elements (N and O) are in their normal oxidation states O\(^2-\) and N\(^3-\), the Ti-N and Ti-O bonding states are completely filled, while their antibonding states are empty. So, only the presence of 3d electrons in the non-bonding states are able to contribute to the magnetism of Ti$_2$NO$_2$.

In Ti$_2$NO$_2$, the Ti atom subjected to octahedral crystal field (with symmetry D$_{3d}$) from neighboring N and O atoms. As shown in Figure 10, $E_g$ corresponds to ($x^2$-$y^2$, xy) and (xz, yz) degenerate states, whereas A$_{1g}$($z^2$) form a separate state Refs.\(^{71,72}\) The magnetism appearing in this class of materials are due to mixed localized and delocalized characters of Ti-3d instead of electron counting applied in Refs.\(^{10,71}\)

Figure 10P details the projected spin polarized 3d DOS of Ti in 1×1×1 mono-layer Ti$_2$NO$_2$.
using Gaussian smearing method. The t\textsubscript{2g} and e\textsubscript{g} are not separated in DOS. The d\textsubscript{xy} from t\textsubscript{2g} and d\textsubscript{z\textsuperscript{2}-y\textsuperscript{2}} from e\textsubscript{g} states make degenerate states, whereas the d\textsubscript{xz} and d\textsubscript{yz} states of t\textsubscript{2g} also make degenerate state. The three multiplets are formed by d\textsubscript{z\textsuperscript{2}}, d\textsubscript{xy} and d\textsubscript{z\textsuperscript{2}-y\textsuperscript{2}}, and d\textsubscript{yz} and d\textsubscript{xz}. Individually, the non-degenerate d\textsubscript{z\textsuperscript{2}} state dominates the other states in both spin channels. The d\textsubscript{z\textsuperscript{2}} state crosses the degenerated states d\textsubscript{z\textsuperscript{2}-y\textsuperscript{2}} and d\textsubscript{xy} exactly at the Fermi level. The concept of t\textsubscript{2g} and e\textsubscript{g} states breaks down due to the local symmetry, which is responsible for the half-metallic character in Ti\textsubscript{2}NO\textsubscript{2}.

The top and bottom layers of Ti provide two electrons to O atoms in respective sides and they jointly (both bottom and top of Ti layers) provide three electrons to the neighboring N atoms. Due to lattice symmetry, there is equal possibility for +4 and +3 oxidation states of Ti in the top and bottom layers. The remaining one 3d electron either fills the non-bonding states or helps to delocalize the system to have band magnetic feature and telltale the magnetic moment of 0.27 \mu_B per Ti atom. This magnetic moment splits the above mentioned states into fully occupied bands for majority spin channel and open bands for minority spin states providing the semi-conducting nature with large gap of 2.28 eV in the minority spin channel, which is also availed by Ref.\textsuperscript{10} The material with large half-metallic gap is most promising magnetic material for the next generation 2D spintronics.\textsuperscript{73,74}

**Effect of Biaxial Strain in Electronic Band Structure of MXene**

Here, we have studied the compressive strain a(1-e) and the tensile strain a(1+e) (where, e represents compression and elongation up to 5% with increment of 1%) keeping the fixed value of the vertical distance (vacuum) at 17.04 Å. Under the compression in Ti\textsubscript{2}N(OH)\textsubscript{2} (up to 5%), the Fermi level is shifted up continuously by pushing the electrons from the occupied states to the unoccupied states. The distorted Dirac cone is found at K point above the Fermi level, which remains distorted under 1% compression. Additionally, on increasing the compressive strain from 1%, the distorted gapped Dirac features change to linear gapped Dirac (in 2%, 3%, and 4%) and finally returns to Distorted gapped Dirac cone under 5% compression. Again, the complex gapped Dirac features are also found in the region between K-Γ below the Fermi level under compression from 2% to 5%.

Unlike the compression, the scenario of shifting the Fermi level is reversed during the tensile strain. The Fermi level is continuously shifted down under tensile strain indicating the electrons are pushing from the unoccupied states to the occupied states. While increasing the strength of tensile strain, the gapped Dirac cone gets enhanced. We have also studied the effect of ap-

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**Figure 10:** (Color online) P represents the projected spin polarized 3d DOS of Ti in Ti\textsubscript{2}NO\textsubscript{2} within 1 x 1 x 1 mono-layer using Gaussian smearing method. The Ti atom follows the octahedral symmetry (D\textsubscript{3d}) crystal field from neighboring N and O, which split the 3d orbital into t\textsubscript{2g} (d\textsubscript{xz}, d\textsubscript{yz}, and d\textsubscript{xy}) and e\textsubscript{g} (d\textsubscript{z\textsuperscript{2}-y\textsuperscript{2}} and d\textsubscript{xz}) states. The red dashed lines represent the position of the Fermi level.
plied compression and tensile strains in the bare Ti₂N MXene and other surface terminated MXenes such as: Ti₂NF₂, Ti₂NO₂, and Ti₂NH₂. In Ti₂N, Ti₂NF₂, and Ti₂N(OH)₂ MXenes show the same physics for shifting the Fermi level but reversed in the case of Ti₂NH₂. Under the compression, two Dirac cones have been found below the Fermi level in the region K-Γ whereas only one Dirac cone has been found under the tensile strain in Ti₂NH₂.

The half-metallic nature in oxygen termination shows peculiar electronic and magnetic properties. The half-metallicity is extremely sensitive to compression. It breaks down under 1% compressive strain.

The states represented by sub-bands A (spanning from slightly below and above the Fermi level) are significantly dominated by Ti-3d states. The sub-bands B and C are the mixed states of Ti-3d, O-2p, and N-2p with the major contribution from the O-2p states (Figure 11).

Vacancy Defect in Ti₂NO₂ MXene

Before studying the electronic and magnetic properties of defected systems, the structural stability corresponding to different super-cells has been studied. The formation and cohesive energies of mono-layer Ti₂N reveal the structural stability starting from 2×2×1 super-cell. So, the structural defects can be studied within the framework of 2×2×1 super-cell. Herein, we have studied the single vacancy defect and doping in relatively most stable configuration of Ti₂NO₂.

The vacancy concentration defects with N (25%), O (12.5%), and Ti (12.5% and 5.5%) have been investigated. The magnetic and NM calculations show NM as the ground state for all defected systems. Therefore, NM configuration was considered to investigate the properties of defected systems using 2×2×1 and 3×3×1 super-cells. The relaxed structures corresponding to N, O, and Ti in Ti₂NO₂ MXene are shown in Figure 12. In defect free Ti₂NO₂, the bond length between Ti and N follows symmetrical nature in the entire super-
Under the defect formation, the global symmetry is destroyed preserving the local symmetry structures. The formation energy of single vacancy defect is calculated by using formula,

\[ E_{SV} = E_{pure} - \left( \frac{E_{iable} + E_{bulk}}{M} \right) \]

where \( E_{pure} \) and \( E_{defect} \) are the total energy of defect free and defected systems, respectively. Similarly, \( E_{bulk} \) is the bulk energy of atom forming defect in system and \( M \) is total number of atoms in bulk.\(^{26}\) The formation energies of single vacancy defects follow the sequence \( V_{Ti} > V_{O} > V_{N} \). The Ti defect formation is more energy consuming as compared to others because it requires six bonds to break (three Ti-N and three Ti-O). In Ti(3d)-O(2p) overlap, the Ti is in +4 oxidation states. The +4 oxidation states in Ti\(_2\)NO\(_2\) lead to strong Ti-O bond.\(^{26}\) Due to this reason, Ti-O bond is relatively stronger than Ti-N bond. Similarly, in O defect, which requires only three breaking Ti-O bonds, that way it is relatively less energy consuming than Ti defect but in \( N \) defect, which requires six Ti-N bonds are breaking. These Ti-N bonds are relatively weaker as compared to Ti-O bonds, so \( N \) defect is relatively less energy consuming as compared to Ti and O defect in Ti\(_2\)NO\(_2\) MXene sheet. We have also used larger \( 3 \times 3 \times 1 \) super-cell to get more insight in the Ti defected system.

While moving from \( 2 \times 2 \times 1 \) to \( 3 \times 3 \times 1 \) super-cells, the formation energy changes to 0.96 eV designating more stable \( 2 \times 2 \times 1 \) structure as compare to \( 3 \times 3 \times 1 \) super-cell in Ti defected system. The larger (negative) value of defect formation energy in \( 2 \times 2 \times 1 \) designates the formation of a single vacancy defect. With the appropriate ground state energy, the electronic band structure and DOS were studied. Interestingly, the single vacancy defect of Ti and O atoms in Ti\(_2\)NO\(_2\) abruptly changes the electronic properties from the half-metallic to the semi-conducting with large direct band gap of 1.73 eV (Figure 13P) in 12.5% for Ti and topological semi-metal in O.
defect, which are consistent with previously reported theoretical results.\textsuperscript{26} The semi-conducting nature found in Ti defect changes to weak semi-conductor under vacancy concentration 5.5%.

Figure 14: (Color online) P and Q represent the band structure corresponding to without SOC and with SOC with 12.5% vacancy concentration of O within $2 \times 2 \times 1$ super-cell in Ti$_2$NO$_2$, respectively. R, S, T, and U highlight the Dirac topology. A slightly distorted Dirac cone (a) is found just above the Fermi level, which telltale the p-type self-doing character diminishing the quantum oscillation. Interestingly, a gapped Dirac cone (b) is found at the Fermi level, which exhibits paramount transport properties in the system. The red dashed lines represent the position of the Fermi level.

So, the concentration of vacancy defect eloquently changes the electronic properties of MXene. On decreasing the concentration of vacancy defect, the Fermi level is shifted towards conduction side exhibiting perfect semi-conductor to weak semi-conductor for Ti defect (Figure 13Q).

Figure 15: (Color online) P and Q represent the band structure corresponding to without SOC and with SOC with 25% vacancy concentration of N within $2 \times 2 \times 1$ super-cell in Ti$_2$NO$_2$, respectively. R, S, T, and U highlight the Dirac topology. V represents the PDOS of N vacancy defect in stable NM configuration. The red dashed lines represent the position of the Fermi level.

The NM solution of band structure for O defect with vacancy concentration 12.5% is shown in Figure 14. The topological semi-metal is found by forming two Dirac cones (a) just above the Fermi level and (b) at the Fermi level (Figure 14P).

The formation of Dirac cone at Fermi level enhances the transport properties of electrons in the
The Dirac cone above the Fermi level reveals the characteristic of the p-type self-doping. Here, due to the SOC, the bands split and form multiple Dirac topological features (c) and (d) below and above the Fermi (Figure 14T) level revealing the n- and p-type self doping characters, respectively.

Similarly, the split bands form multiple distorted Dirac features (e) near the Fermi level (Figure 14U), which enhance the transport properties of the system. The formation of the distorted Dirac cone diminishes the quantum oscillation. The N defect changes the half-metallic nature to the metallic nature (Figure 15), which is also consistent with previously reported theoretical results. The gapped linear Dirac cone (a) is found in the region Γ-M above the Fermi level (Figure 15P). Similarly, a linear gapless Dirac cone (b) is found at K point above the Fermi level. Applying the strength of SOC on Ti atoms, the bands get split (shown in Dirac cones (c) and (d)) and opened at about 0.01 eV in the Dirac cone (b) (Figure 15U). Thus, the SOC converted the massless Dirac feature (b) to massive gapped Dirac feature (d) by forming the gap between the top and bottom surface states.

Figure 16 shows the PDOS of N defect in Ti$_2$NO$_2$. Similar to the O defect, the valence bands are dominated by O-2$p$ and N-2$p$ states, whereas the Ti-3$d$ states dominate around and above the Fermi level.

Influence of Cr, Mn, and Co Doping in Ti$_2$NO$_2$ MXene

Here, we performed the substitutional doping (12.5%) of different transition elements such as Cr, Mn, and Co in Ti$_2$NO$_2$ MXene within $2 \times 2 \times 1$ super-cell. Under the Cr substitution, the global symmetry in bond length breaks down with slight changes. However, local symmetry is preserved near the dopant atom. The Cr-N bond length is 2.09 Å, which is slightly shorter than that of Ti-N in pristine phase, whereas the Cr-O bond is 2.09 Å, which is slightly larger than that of Ti-O in pristine. The elongation and compression of Cr-O and Cr-N bonds as compared to pristine significantly break the uniformity in the bond length throughout the super-cell, which results significant influence in the electronic and magnetic properties.
In the case of Mn dopant, same behaviors are found with slight variation in the bond length. But for Co, the bond length between Co-O is 2.27 Å, which is larger value by 0.27 Å as compared to Ti-O in pristine phase. Similarly, the Co-N bond is 2.08 Å, which is shorter by 0.12 Å than that of Ti-N. The elongation and compression in the bond length result the Co atom slightly shifted towards the bottom side (Figure 17c). The relaxed structures after substitutions of Mn, Cr, and Co in Ti$_2$NO$_2$ are shown in Figure 17. The stability of doped systems were investigated through the formation energy using formula,

$$E_f = (E_{t1} - E_{t2}) - (E_1 - E_2)$$

where $E_{t1}$ and $E_{t2}$ represent the total energies of Ti$_2$NO$_2$ with substitutional and pristine phases. $E_1$ and $E_2$ represent the free energy of single dopant and Ti atoms. The calculated value of formation energies are 4.43 eV, 3.70 eV, and 3.81 eV in Mn, Cr, and Co doped MXenes, respectively. The substitution of transition metals in MXene sheets inaugurate the significant change in the structural, electronic, and magnetic properties while favoring the magnetic configurations.

Figure 18 (P and Q) represents the spin polarized band structure and PDOS of Mn doped system. The Mn in Ti$_2$NO$_2$ allows to convert 100% spin polarized half-metallic to weakly semimetallic nature. In the spin up channel, the band splits from Γ point below the Fermi level and reconstructs at other Γ point. Interestingly, these split band forms gapped type of Dirac cone at K point.
point above the Fermi level in the spin up channel. The situation of band splitting for spin down channel is same as that of the spin up channel.

To describe the electronic band structure of Mn doped Ti$_2$NO$_2$, we divided the bands into separate sub-bands (i.e A, B, C, D, and E) in the spin up channel and three sub-bands (i.e A, B, and C) in the spin down channel, respectively. The conduction bands are significantly dominated by Ti-3$d$ states and trivially contributed from other states. The sub-bands B and C are dominated by Mn-3$d$ states. In the spin up channel, the sub-bands A and B form indirect energy gap of 0.52 eV. Similarly, the energy gaps between sub-bands B and C, and C and D are 0.62 eV (direct) and 0.19 eV (indirect), respectively. The sub-bands D and E are significantly concentrated from the O-2$p$ states along with Ti-3$d$ and Mn-3$d$ states. In the case of spin down channel, the energy gap between sub-bands A and B is 1.71 eV (direct). The same behavior is seen in sub-bands B and C.

Here, the asymmetrical nature of the PDOS corresponds to the spin up and spin down channels giving rise to ferromagnetism (3.98 $\mu_B$ per cell) preserving the weak semi-metallic nature, which originates from the 3$d$ states of Mn and Ti atoms. The intrinsic magnetic moment of Mn is 3.73 $\mu_B$ when it is doped on the top layer of Ti$_2$NO$_2$. This doping reduces the magnetic moment of Ti from 0.28 $\mu_B$ to smaller but non negligible values.

In contrast to Mn doped system, the spin up channel shows the semi-conducting nature with direct band gaps of 1.07 eV (at K point) and 0.97 eV (at M point) for Cr and Co, respectively. The 3$d$ electrons of TM are responsible for the semi-conducting behavior in both doped systems. In the spin down channel, the bands cross the Fermi level representing the metallic character. Thus, the semi-conducting nature in the spin up channel and metallic nature in the spin down channel predict the half-metallic character in both Cr and Co doped systems with 100% spin polarization (Figure 18R and 18T).

For Cr dopped system (Figure 18S), the bands above the Fermi level are mostly dominated by Ti-3$d$ with smaller contributions from Cr-3$d$, O-2$p$, and N-2$p$. To describe valence states, we divided it into four different sub-bands A, B, C, and D. The sub-band A is dominated by Cr-3$d$ states in the spin up channel and by Ti-3$d$ states in the spin down channel. The direct energy gaps between the sub-bands A and B are 1.90 eV and 0.91 eV for the spin down and spin up channels, respectively. The sub-bands B, C, and D are the mixed states with major contribution from the O-2$p$ states.

Similarly, the PDOS of Co doped system is shown in Figure 18U. In the unoccupied states, the bands are dominated by Ti-3$d$ states. Coincidentally, two energy gaps are found toward the occupied states in both spin channels. In spin up channel, the sub-bands A and B are mainly dominated by Co-3$d$ states forming an indirect energy gap of 0.47 eV. The energy gap between B and C forms indirect gap of 0.47 eV. In spin down channel, the sub-bands A and B are mainly dominated by Ti-3$d$ and Co-3$d$ states, respectively. The indirect energy gaps between sub-bands A and B, and B and C are of 0.5 eV and 1.34 eV, respectively. In both channels, the sub-bands C, D, and E show the major contribution from O-2$p$ states along with N-2$p$, Ti-3$d$, and Mn-3$d$ states.

**Origin of Half-metallic Gap in Cr and Co Doped Ti$_2$NO$_2$**

The 3$d$ electrons of Cr and Co play a significant role for half-metallicity and magnetism. Figure 19 (P and Q) represents the projected spin polarized 3$d$ DOS of Ti and Cr, respectively. The substitution of Cr allows to transform from the half-metallic FM to the half-metallic AFM. The half-metallicity is originated from both 3$d$ electrons of Ti and Cr atoms. Unlike doped free phase, the Cr substitution changes the positive exchange to negative exchange splitting (spin up - spin down) with energy of 0.42 eV. The Cr substitution allows all the components of t$_{2g}$ states (d$_{xz}$, d$_{yz}$, and d$_{xy}$) and e$_g$ (d$_{x^2-y^2}$ and d$_{z^2}$) states of Ti to be
non-degenerated states, whereas \( d_{x^2-y^2} \) of \( e_g \) and \( d_{xy} \) of \( t_{2g} \), and \( d_{xz} \) and \( d_{yz} \) of \( t_{2g} \) states are degenerated in the case of Cr. The \( d_{z^2} \) state also shows the dominant nature in both Ti and Cr atoms.

Figure 19: (Color online) P and Q represent the projected spin polarized 3\( d \) DOS of Ti and Cr following octahedral phase with \( D_{3d} \) point group corresponding to \( t_{2g} \) (\( d_{xz}, d_{yz}, \) and \( d_{xy} \)) and \( e_g \) (\( d_{x^2-y^2} \) and \( d_{z^2} \)) states in Cr doped Ti\(_2\)NO\(_2\). The red dashed lines represent the position of the Fermi level.

In Cr doped case, there are two possibilities to fill the non-bonding states. Presuming all the constituents of Ti\(_2\)NO\(_2\) are in their normal oxidation states, the top and bottom Ti atoms have either +4 or +3 oxidation states as mentioned above. Similarly, the top of Cr and the bottom of Ti have either +4 or +3 oxidation states after providing two electrons to O and three electrons to N atom.

Following Hund’s rule, the remaining 3\( d \) electrons of Ti and Cr fill partially the non-bonding states. These free 3\( d \) electrons in non-bonding

Figure 20: (Color online) P and Q represent the projected spin polarized 3\( d \) DOS of Ti and Co following octahedral phase with \( D_{3d} \) point group corresponding to \( t_{2g} \) (\( d_{xz}, d_{yz}, \) and \( d_{xy} \)) and \( e_g \) (\( d_{x^2-y^2} \) and \( d_{z^2} \)) states in Co doped Ti\(_2\)NO\(_2\). The red dashed lines represent the position of the Fermi level.

Following Hund’s rule, the remaining 3\( d \) electrons of Ti and Cr fill partially the non-bonding states. These free 3\( d \) electrons in non-bonding
states give AFM character. The individual magnetic moments of Ti and Cr align anti-parallelly. The Cr moment here is one order magnitude larger than those of Ti atoms. Furthermore, the individual magnetic moments of Cr and Ti split the non-boding states into fully occupied bands in the spin down channel and open band gap in the spin up channel revealing the semi-conducting behavior.

Similarly, Co substitution also preserves the FM half-metallic character with total magnetization of 1.05 $\mu_B$. The magnetic moment of Co in Ti$_2$NO$_2$ is 1.90 $\mu_B$, which diminishes the individual magnetic moments of Ti from 0.28 $\mu_B$ to smaller but non negligible values. The spin alignment of Co is anti-parallel with all Ti atoms except for one Ti in the bottom layer making the system overall FM. The Co substitution also favors the negative exchange splitting with energy 0.16 eV. Similarly, this substitution allows all the components of $t_{2g}$ ($d_{xz}$, $d_{yz}$, and $d_{xy}$) and $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$) states of Ti to be non-degenerate states, whereas $d_{x^2-y^2}$ of $e_g$ and $d_{xy}$ of $t_{2g}$, and $d_{xz}$ and $d_{yz}$ of $t_{2g}$ states are degenerate states in the case of Co (Figure 20P and 20Q). The $d_{z^2}$ state also shows the dominant character in both Ti and Co.

CONCLUSION

In summary, we have systematically studied the structural, electronic, and magnetic properties of MAX phase Ti$_2$AlN, bare MXene Ti$_2$N, and functionalized MXenes Ti$_2$NT$_2$ (T= -OH, -H, -O, -F). The formation and cohesive energies favor the chemical and structural stabilities in all MXenes and parent MAX phase. The Ti$_2$NO$_2$ is relatively stable among all MXenes starting from $2 \times 2 \times 1$ super-cell. The bare MXene is closely half-metallic FM but after the surface termination, FM nature is completely removed without affecting the metallic nature except for -O termination, which is half-metallic FM. The ferromagnetism in Ti$_2$N arises from Ti-3$d$ states. The region near the Fermi level is dominated by Ti-3$d$ states in all MXenes and MAX phase. The companionship of SOC influences strongly only in the bare MXene and trivially influences with O and N defects thereby forming the multiple topological features. The SOC couples the opposite spin channels forming band inversion in the bare MXene. This band inversion is caused by both time reversal symmetry breaking and hybridization of different spin components of $t_{2g}$ and $e_g$ states. The strain significantly influences the Fermi level with peculiar linear and distorted Dirac topological features. The Fermi level shifts toward the lower energy states under compression and it shifts toward the higher energy states under tensile in Ti$_2$NH$_2$. These features are reversed in the case of Ti$_2$N, Ti$_2$NF$_2$, and Ti$_2$N(OH)$_2$. The 100% spin polarized half-metallic nature changes closely to the half-metallic under 1% compression and it is completely destroyed under 2% compression in -O termination. The defect in Ti$_2$NO$_2$ completely changes the electronic properties from half-metal to semiconductor with certain band gap and fascinating topological semi-metal for Ti and O atoms, respectively. In the N defect, the material changes from the half-metallic to the metallic with paramount topological phenomena. The variable vacancy concentration allows to change the weak semiconductor to strong semiconductor in Ti$_2$NO$_2$. The 12.5% Co substitution in Ti$_2$NO$_2$ preserves the half-metallic character, whereas Mn substitution changes the electronic properties from the half-metallic to weak semi-metallic preserving the FM character. However, Cr substitution changes the magnetic properties from FM to AFM preserving the half-metallic character. The magnetism and half-metallicity are mainly due to different orbital filling configurations of 3$d$ electrons of the TM. The presence of the half-metallicity in pristine, and Cr and Co substitutions could provide magnetic functionalities in spintronic applications.
THEORETICAL BACKGROUND, COMPUTATIONAL DETAILS, AND EXPERIMENTAL INFORMATION

This study uses density functional theory (DFT) in conjunction with pseudo-potential plane wave method (Quantum ESPRESSO). Both Perdew-Burke-Ernzerhof (PBE) and hybrid (HSE06) functionals predict very similar crystal and electronic structures of Ti$_2$N and related materials. Following this, we have used only PBE functional to describe exchange-correlation potential within the generalized gradient approximation, where scalar relativistic pseudo-potential for collinear calculations and fully-relativistic pseudo-potential for non-collinear calculations are considered and focused on underlying physics involved in these materials.

We have performed non-collinear calculations to study the effect of SOC in the electronic band structure employing relativistic DFT based on fully-relativistic pseudo-potential. This pseudo-potential is constructed from the solutions of Dirac type Kohn-Sham equation for four components of pseudo wave functions. The four component spinors Dirac equation changes to two components spinors Pauli-type equation when small components of the pseudo wave functions are neglected without affecting the results. Under the Pauli-type formalism, the calculated relativistic frozen-core energy implicitly includes the spin-orbit effect.

The projected augmented wave method is used to describe the ion-electron interaction, with $1s^1$, $2s^2 2p^3$, $2s^2 2p^4$, $2s^2 2p^5$, $3s^2 3p^1$, and $4s^2 3d^2$ treated as valence electrons for H, N, O, F, Al, and Ti, respectively. A plane wave basis set with a sufficient cutoff energy of 680 eV has been used to represent valence electrons and 6800 eV for charge density, which are sufficient for these class of materials.

To model 2D-lattices, we performed electronic structure calculations for bare and terminated species of $1 \times 1 \times 1$, $2 \times 2 \times 1$, and $3 \times 3 \times 1$ cells. The underlying structural optimization is performed using small k-points grid $4 \times 4 \times 1$ with the energy convergence criterion in the order of $10^{-5}$ eV / cell. The geometries of MXenes were relaxed until force becomes less than or equal to 0.01 eV / cell. After full structural optimization, a large vacuum space more than 17 Å along the lattice vector $c$ was set to avoid any interaction between MXenes sheet and dense k-points grid $20 \times 20 \times 1$ was used for electronic calculations and $25 \times 25 \times 1$ for density of states (DOS) calculations. DOS was calculated by using Gaussian smearing method. To clearly identify the underlying topological features, we have used a large number of energy points (2000) along high symmetry directions in band structure calculations. In addition, the band structure of primitive cell is recovered from the complex band structure of super-cell by unfolding the super-cell Brillouin zone into Brillouin zone by using the bandUP (unfold.x code) computer program within the same exchange-correlation functional, which is based on the evaluation of spectral weight,

$$P_{mK}(\vec{k}) = \sum_n \left| \langle \psi^{SC}_{mK} | \psi^{PC}_{nk} \rangle \right|^2$$

where $\psi^{SC}_{mK}$ and $\psi^{PC}_{nk}$ represent eigenstates of super- and primitive-cells, respectively. Similarly, $K$ and $k$ represent the wave vector of super-cell Brillouin zone and primitive cell Brillouin zone, respectively. $P_{mK}(\vec{k})$ is the spectral weight, which gives the probability of eigenstates of super-cell will be same as the eigenstates of primitive cell. This bandUP technique is already used in graphene as well as nanowires.

Experimentally, these promising MXenes within 2D materials family also possess unique properties acquired from complex combined bonding nature and electronic structure, atomic stacking, synthesis condition, and surface termination. Despite these fascinating properties and growing interest, the field lacks a systematic ex-
The poor structural stability of surface terminated nitride based MXenes are improved by making multi-layer structure, which has great applications in biology. The scanning transmission electron microscopy imaging reveals the presence of different point defects in single-layer Ti$_3$C$_2$T$_2$. The excellent conductivity due to point defect predicted by DFT is conformed with the help of direct electrical measurements of single- and few-layer flakes of Ti$_3$C$_2$T$_2$. The robust Ti$_3$C$_2$T$_2$/S conductive paper/sheet with excellent conductivity, unique chemisorption, and mechanical properties of lithium polysulfide shuttle was fabricated through filtration-evaporation approach. Ti$_3$C$_2$T$_2$/S paper/sheet has excellent electrochemical properties. The surface de-functionalization increased the electronic conductivity through in situ vacuum annealing, electrical biasing, and spectroscopic analysis within the transmission electron microscope.

The available literature based on experimental and computational studies show the nitride based MXene has great potential in the next generation electronic applications. However, there is a lack of systematic investigation in Ti$_2$N and its derivatives. Herein, we have intensively focused on the structural, electronic, magnetic, and topological properties in pristine, strained, defected, and doped systems.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The predictive understanding, specific to electronic (band) structure, magnetism, defect, and strain induced effects, made in this work were developed by D. P. and his group in the Critical Materials Institute, an Energy Innovation Hub led by the Ames Laboratory and funded by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. D. P. would like to acknowledge Ed Moxley for maintaining computational facilities, including the RAMAN cluster and computational software. N. K. S. would like to acknowledge UGC Nepal for partial financial support.

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