Atomic Vacancy Defect, Frenkel Defect and Transition Metals (Sc, V, Zr) Doping in Ti₄N₃ MXene Nanosheet: A First-Principles Investigation

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Abstract: Using first-principles calculations based on the density functional theory, the effects of atomic vacancy defect, Frenkel-type defect and transition metal Z (Z = Sc, V and Zr) doping on magnetic and electric properties of the Ti₄N₃ MXene nanosheet were investigated comprehensively. The surface Ti and subsurface N atomic vacancies are both energetically stable based on the calculated binding energy and formation energy. In addition, the former appears easier than the latter. They can both enhance the magnetism of the Ti₄N₃ nanosheet. For atom-swapped disordering, the surface Ti-N swapped disordering is unstable, and then the Frenkel-type defect will happen. In the Frenkel-type defect system, the total magnetic moment decreases due to the enhancement of indirect magnetic exchange between surface Ti atoms bridged by the N atom. A relatively high spin polarizability of approximately 70% was detected. Furthermore, the doping effects of transition metal Z (Z = Sc, V and Zr) on Ti₄N₃ nanosheet are explored. All doped systems are structurally stable and have relatively large magnetism, which is mainly induced by the directed magnetic exchange between surface Z and Ti atoms. Especially in the doped Ti₄N₃-Sc system, the high spin polarizability is still reserved, suggesting that this doped system can be a potential candidate for application in spintronics.

Keywords: first-principles; Ti₄N₃ nanosheet; vacancy defect; doping; magnetism

1. Introduction

Graphene was discovered in 2004, breaking the classical theory that thermodynamic fluctuations do not happen in any two-dimensional (2D) crystal at a finite temperature [1,2]. Graphene had shown many excellent physical and chemical properties into wide material applications, such as big specific surface area is (2630 m²/g) [3], high electron mobility (1.5 × 10⁵ cm²/v·s) [4], good thermal conductivity (5000 W/m·K) [5], high Young’s modulus (1.0 TPa) [6] and visible light transmittance (approximately 97.7%) [7]. However, the zero-band gap of graphene limits its application in the field of electronic devices, leading to a series of studies on graphene-like 2D materials [8], such as hexagonal boron nitride, transition metal sulfur compounds, transition metal oxides, black phosphorus and various MXenes. Many graphene-like materials making up for the inadequacy of graphene materials showed better physical and chemical properties, and then were applied in optoelectronics, spintronics, catalysis, biological and chemical sensors, lithium/sodium ion batteries, supercapacitors, fuel cells, polymer composite materials and other fields [9].
MXene is a new kind of graphene-like nanosheet, which is composed of transition metals and carbon/ternary-compounds. In 2011, the Gogotsi used HF acid to selectively etch the Al atomic layer of ternary-layered carbide material Ti₃AlC₂ to obtain Ti₃C₂Tx (Tₓ stands for the surface terminations, for example, hydroxyl, oxygen or fluorine) [10]. Ti₃AlC₂ is a MAX phase material, namely a typical ternary-layered ceramic. Generally, they may be shown as M₄ₓ+1AXₙ, where M is the early transition metal, such as Sc, Ti, V, Zr, Hf, Nb, Ta, Cr and Mo, A meaning the main group 13–14 elements in the periodic table, such as Al, Si, P, S, Ga, As, In and Sn and X meaning C or N. n is generally 1, 2 or 3 [11]. Ti₃C₂Tx has the precursor MAX structure and its properties are similar to the graphene. Thus, it was named MXene. The graphene-like MXene nanosheet may be shown as M₄ₓ+1X₂nTx, where Tₓ is the functional group attached to the surface of MXene, such as -O, -OH and -F. M₂XTₓ, M₃X₂Tₓ and M₄X₃Tₓ structures for n = 1, 2 and 3, respectively, had been created [12]. Recently, the (M′M″)₄X₂nTₓ structure was found, meaning that M may also be composed of two transition metal elements [13]. Currently, more than 70 precursors of MAX phase have been reported, and an increasing number of graphene-like MXene nanosheets have been experimentally fabricated, including Ti₃C₂, Ti₂C, Nb₂C, V₂C, (Ti₃.5Nb₀.5)₂C, (V₀.5,C₀.5)₃C, Ti₃CN, Ta₄C₃, Ti₄N₃, etc. [14]. Ti₄N₃ nanosheet is one of the first nitrogen series of MXene obtained experimentally [15]. The graphene-like MXene nanosheet family with the unique hexagonal lattice and space symmetry group P6₃/mmc structure have metallicity, but they have many advantages of a ceramic material. A covalent bond exists between M-X atom-mixed valence metallic bonding in MXene, whereas only a C–C bond exists in graphene. The graphene-like MXene nanosheet had been predicted to have more adjustable performances than the graphene [16]. Therefore, the graphene-like MXene nanosheet has a broad application prospect in transparent conductive film, supercapacitors, polymer reinforcement phase, purifying agent, field effect tube, hybrid nanocomposite and electromagnetic shielding [17]. They may be also used widely in many areas such as electronic devices [18], optical devices [19], magnetic materials [20–24], thermoelectric materials [25–28] and biosensors [29].

The miniaturization and portability of modern electronic devices has put forward higher requirements about the magnetism of electronic materials. As emerging materials at present, 2D materials have become the focus of experimental and theoretical research [30–32]. However, most 2D materials themselves are non-magnetic. How to induce and regulate magnetism in 2D non-magnetic materials is increasingly becoming the focus of research [33]. On the other hand, prepared materials always have defects such as atomic disorder, swap, vacancy and impurity. They all cause important influences on the electronic structure, and then magnetic and optical properties of 2D materials [34,35]. The doping of elements B and V on different positions of the Ti₃C₂ MXene nanosheet had resulted in great changes in the electronic structure, and then magnetic properties of this nanosheet so that some novel semiconductor properties were added [36]. Similar magnetic behavior had been also observed in different MXene decorated by some functional groups. For examples, Cr₂C is a half-metallic ferromagnetic. However, with F, Cl, OH or H functionalization, Cr₂C is transformed as the antiferromagnetic semiconductor [37]. The antiferromagnetic metal Cr₂N becomes a stable ferromagnetic semi-metal under the action of O functional groups [38]. Cr₂TiC₂O₂ is nonmagnetic, whereas Cr₇Ti₇C₂F₂ and Cr₇Ti₇C₂(OH)₂ are antiferromagnetic, but Cr₂VC₃(OH)₂, Cr₂VC₃F₂ and Cr₂VC₃O₂ are ferromagnetic [39]. Few research had been carried on the surface doping and defects. The influence of point defects on the electronic structure, formation energy and magnetism of Ti₂X₇ (X = C/N, T = OH, F, O) had been studied. Results showed that small quantities of point defects might cause much variation of magnetic and electronic properties in the above material [40]. Therefore, although the defect has not become the research focus of new materials, it is still urgent to carry on the defect research for ensuring the practical application of 2D MXene materials in spintronic devices.

M₄X₃ (M meaning the transition metal element and X meaning C/N) MXene nanosheet is an ordinary 2D material in the MXene family. It has a large atomic layer thickness (seven layers, with a thickness greater than 7 Å), and a complex structure comprising overlapping and staggered layers. Furthermore, the Ti₄N₃ nanosheet is the first prepared N-based MXene and it has an intrinsic magnetic
moment, which is weak, and then may be eliminated by surface functional groups [15]. In this paper, to understand influences of the atomic defect, swap disordering and vacancy on the structural, magnetic and electronic properties of 2D MXene material, the Ti$_4$N$_3$ MXene nanosheet was investigated. The structure, electronic properties, and magnetism of Ti$_4$N$_3$ nanosheet without functional groups were analyzed firstly. Subsequently the Ti or N vacancy defect was investigated for the surface or subsurface layer of the Ti$_4$N$_3$ nanosheet. Secondly, a swap defect (named as Frenkel-type defect) between the N atom on the subsurface layer and Ti atom on the surface layer was studied. The structure change, electronic properties and magnetism of atoms around the defect atom were calculated and analyzed. In the end, the surface Ti atom of Ti$_4$N$_3$ nanosheet was replaced by Sc, V and Zr atoms, respectively. The effects of doping on the structure, electronic properties and magnetism of the atoms, and then the Ti$_4$N$_3$ nanosheet were discussed. We hope our results are useful to elucidating the various electronic and magnetic behaviors of 2D materials and the application research of new 2D Ti-based MXene nanosheet in spintronics.

2. Calculation Method

All calculations were performed using the Vienna ab initio simulation package (VASP) based on the density functional theory (DFT). The Perdew–Burke–Ernzerhof (PBE) exchange correlation function under the generalized gradient approximation (GGA) is used in calculations [41–43]. To treat the electron-ion properly, the interaction between the core electron and the valence electron is described by plane wave super-soft pseudopotential. Ti: 3d$^2$4s$^2$, N: 2s$^2$2p$^3$, Sc: 3d$^1$4s$^2$, Zr: 4p$^6$4d$^2$5s$^2$ and V: 3d$^3$4s$^2$ valence electron configurations were specifically considered. In this work, a 3 × 3 × 1 supercell was used and spin polarization was selected for structural optimization and single point energy calculation.

In the self-consistent field calculation, a global convergence standard of 1 × 10$^{-6}$ eV, cutoff energy of 500 eV, force per each atom of no more than 0.02 eV/Å, and 9 × 9 × 1 k-point grid precision and integral Brillouin zone were used. For structural optimization, the experimental lattice constant 2.991 Å of single Ti$_4$N$_3$ [44] was set as the initial value of Ti$_4$N$_3$ nanosheet. Then for defect and doping calculation, the optimized lattice constant of Ti$_4$N$_3$ nanosheet was selected as the initial value.

3. Results and Discussion

3.1. Structure, Electronic Properties and Magnetism of Ti$_4$N$_3$ Nanosheet

Ti$_4$N$_3$ nanosheet is experimentally prepared as the first N-based series MXene nanosheet [15] by melting fluoride salt in argon gas environment and the temperature was 550 °C. The nanosheet was etched away from Ti$_4$AlN$_3$ precursor powder layer. Figure 1 shows the construction processing of the Ti$_4$N$_3$ MXene nanosheet by etching off the Al atomic layer from the Ti$_4$AlN$_3$ bulk. The Ti$_4$N$_3$ nanosheet had a hexagonal structure with sandwich layers. The N atomic layer was sandwiched between the upper and lower Ti atomic layers. Each N atom was bonded with six nearest Ti atoms. Three Ti atoms were located on the upper layer and the other three Ti atoms were on the lower layer. The whole Ti$_4$N$_3$ nanosheet was composed of seven alternating layers of Ti and N layers. The structure was more complex than those of M$_3$X$_2$ and M$_2$X. Therefore, we deduced that M$_4$X$_3$ had better physical and chemical properties than M$_3$X$_2$ and M$_2$X.
which shows that N atoms were located in a distorted octahedron. This structure was similar to the structure parameters difference between Ti$_4$N$_3$ and Ti$_4$AlN$_3$ was relatively small. For the lattice constants, the error did not exceed 2%. This indicates that the Ti$_4$N$_3$ nanosheet was stable. There was no significant change between bonds due to etching, which also proves that the bond length of M-X is stronger than that of M-A [45].

Table 1 shows some structural parameters of Ti$_4$N$_3$ nanosheet. For simplicity, the surface Ti atom, the subsurface N atom, and the central layer N atom are marked as Ti1, N2, Ti3 and N4, respectively. In Table 1, the bond lengths $d_{Ti1-N2}$ and $d_{N2-Ti3}$ were different, which shows that N atoms were located in a distorted octahedron. This structure was similar to the Ti$_2$NT$_x$ calculated by Arkamita Bandyopadhyay et al. [40], but it is different from the single-layer Ti$_4$C$_3$ nanosheet, which is a regular octahedral structure [46].

In order to discuss electronic and magnetic properties of the Ti$_4$N$_3$ nanosheet, the total magnetic moment of Ti$_4$N$_3$ nanosheet is calculated as 1.173 $\mu_B$, which may be weakened, even eliminated by the action of the functional groups. This result accords with the conclusion that the magnetism may be removed by functionalization [47]. The atomic magnetic moment of Ti atoms on the surface and the next subsurface was 0.924 and 0.212 $\mu_B$, respectively, whereas the atomic magnetic moment of the N atom on the subsurface and central layers were 0.030 and 0.010 $\mu_B$, respectively. Therefore, the total magnetic moment was mainly contributed by the spin-polarized $d$-electrons of Ti atoms in the surface.
layer, which was similar to results in Reference [47], in which MXenes are magnetic and the magnetism is primarily due to surface Ti atoms.

Table 2. Calculated lattice constants $a$, atomic layer thickness $l$, binding energy $E_b$ and formation energy $E_{\text{form}}$ and total magnetic moment $M_{\text{tot}}$, where bond lengths between the vacancy atom at surface (or subsurface) and its neighbor Ti1, N2 or Ti3 atom at surface, subsurface or next subsurface, respectively.

| System   | $a$ (Å) | $l$ (Å) | $d_{v-Ti}$(Å) | $d_{v-N}$ (Å) | $d_{v-Ti}$ (Å) | $E_b$ (eV) | $E_{\text{form}}$ (eV) | $M_{\text{tot}}$ (µB) |
|----------|---------|---------|---------------|---------------|---------------|-----------|------------------------|----------------------|
| Ti$_4$N$_3$ | 2.993   | 7.235   | 2.993(2.062)  | 2.062(2.993)  | 2.918(2.119)  | 1.295     | -                      | 1.173                |
| Ti$_4$N$_3$-Ti | 2.995   | 7.176   | 2.986         | 2.045         | 2.841         | 1.281     | 2.167                  | 1.817                |
| Ti$_4$N$_3$-N | 2.988   | 7.368   | 2.063         | 2.988         | 2.161         | 1.201     | 7.118                  | 2.373                |

In Figure 2, the total density of states (TDOS) and partial density of states (PDOS) are shown. From Figure 2, near the Fermi surface the spin-up channel had a large valley and the Fermi level was located at the valley bottom. However, for the spin-down band a relatively large peak crossed over the Fermi level. This results in a great spin-polarization (more than 80%) in the Ti$_4$N$_3$ nanosheet from the spin-polarizability Equation (1), where $N_\uparrow$ and $N_\downarrow$ were spin-up and spin-down TDOS at the Fermi level, respectively. Therefore, the Ti$_4$N$_3$ nanosheet might be a kind of candidate material in 2D spintronics because of its high spin polarizability [48].

$$P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \times 100\%$$  \hspace{1cm} (1)

![Figure 2](image-url). Total density of states (TDOS) and partial density of states (PDOS) Ti$_4$N$_3$ nanosheet. $\uparrow$ and $\downarrow$ indicate the spin-up and spin-down orbitals, respectively. The Fermi level (dashed vertical line) is set to zero. The TDOS is transited to a primitive cell.

From Figure 2, TDOS near the Fermi level mainly originated from the surface Ti atoms, meaning that localization of $d$-electrons of surface Ti atoms played an important role in magnetism. The main reason was that the strong direct exchange magnetic coupling caused a remarkable spin split of energy bands near the Fermi level. This finding is in agreement with the above mentioned discussion on the total magnetic moment. Furthermore, the subsurface N2 atom was also spin polarized, which was induced by the neighbor magnetic atoms. This means that the indirect magnetic exchange between Ti1 atoms on the surface and the next subsurface Ti2 atoms might be bridged by the N2 atoms on the subsurface. Such a layer interaction could help stabilizing the whole structure of the Ti$_4$N$_3$ nanosheet.
3.2. Atomic Vacancy Effect of Ti₄N₃ Nanosheet

The atomic vacancy defect is an ordinary phenomenon in 2D materials. In general, high proportion vacancy may destruct properties of materials. We focused on the atomic vacancy defect of the Ti₄N₃ nanosheet. In Figure 3, the structure of the surface Ti-vacancy (a) and subsurface N-vacancy (b), which are the two types of vacancy effects that possibly have a relatively great impact on Ti₄N₃ nanosheet, were described dramatically. Moreover, in Ti-vacancy and N-vacancy system (labeled as Ti₄N₃-Ti and Ti₄N₃-N, respectively) in Table 2, the lattice constants a, the atomic layer thickness L, the bond length d between the vacancy and its neighbor atoms, the binding energy $E_b$ and the forming energy $E_{form}$, and the total magnetic moment Mtot of the Ti₄N₃-Ti, Ti₄N₃-N and Ti₄N₃ system are listed. As far as Ti-vacancy is concerned, a surface Ti atom had 3 neighbor N atoms and 4 neighbor Ti atoms in the Ti₄N₃ system respectively, as shown in Figure 3a. When a surface Ti atom was lost, the bond length between Ti-vacancy and its neighbor surface Ti or subsurface N atom (labeled as $d_{v−Ti}$ or $d_{v−N}$) shrank compared with the Ti₄N₃ system. Therefore, the atomic layer thickness L decreased slightly. Atomic vacancy could cause the surrounding space to collapse in the same way as the atom vacancy in other materials. The magnetic moment of surface Ti atom near the vacancy increased, owing to the enhancement of localization of d-electrons of the Ti atom. Four coordination numbers between Ti-vacancy and its neighbor Ti atoms were lost. Thus, in the Ti₄N₃-Ti system, the total magnetic moment increased from 1.173 to 1.817 µB.

![Figure 3. Schematic of a vacancy defect: (a) surface Ti-vacancy and (b) subsurface N-vacancy on a Ti₄N₃ nanosheet.](image-url)

In the Ti₄N₃ system, a subsurface N atom had four neighboring N atoms and six neighboring Ti atoms. In Table 2, we could see that in the N-vacancy (Ti₄N₃-N) system, the bond length $d_{v−N}$ between the vacancy and its neighbor subsurface N atom in the subsurface layer shrank in comparison with the Ti₄N₃ system. The atomic layer thickness L was stretched slightly due to the fact that the bridging interaction between two Ti-atomic layers supplied by N atoms was weakened. The system looks fluffy. Moreover, when a subsurface N atom was replaced by vacancy, six coordination numbers between N-vacancy and its neighbor Ti atoms at surface or the next subsurface might be lost. These atoms near the N-vacancy were far from each other. In the Ti₄N₃-N system, the total magnetic moment increased sharply to 2.373 µB.

In Table 2, the binding energies of Ti₄N₃, Ti₄N₃-Ti and Ti₄N₃-N systems are listed. The binding energy can be defined as follows [49]:

$$E_b = (E_{tot} - n_{Ti}u_{Ti} - n_{N}u_{N})/n_{tot},$$

where $E_{tot}$ is the total energy of the defective and ideal system, $u_{Ti}$, $u_{N}$ and $n_{tot}$ indicate the number of Ti, N and total atoms, respectively. $u_{Ti}$ and $u_{N}$ are the chemical potential of Ti and N atoms, respectively. All the binding energies of Ti₄N₃, Ti₄N₃-Ti and Ti₄N₃-N systems have a negative value. This finding
can indicate that all systems were stable in structure. The binding energy of the Ti$_4$N$_3$-N system was
the largest, which implies that the system had lost N atoms and might become unstable. Moreover,
in Table 2 the formation energy $E_{\text{form}}$ [48] was calculated by the following formula:

$$E_{\text{form}} = E_{\text{def}} - E_{\text{id}} - \Sigma n_i u_i \tag{3}$$

where $E_{\text{def}}$ and $E_{\text{id}}$ were the total energy of the defective and “ideal” system, $n_i$ is the number of
removed or added atoms and $u_i$ is the chemical potential of the corresponding atoms. The positive
formation energies imply that the “ideal” Ti$_4$N$_3$ system is more stable than the defective systems.
A relatively small value in Ti$_4$N$_3$-Ti system indicates that eliminating a surface Ti atom is easier than
losing a subsurface N atom.

In Figure 4, the total TDOS in a unit cell and PDOS of the neighbor Ti or N atom for Ti-vacancy and
N-vacancy were plotted dramatically in Ti$_4$N$_3$-Ti and Ti$_4$N$_3$-N nanosheets. From Figure 4a, a relatively
large spin-up peak appeared near the Fermi level in the Ti-vacancy system. The peak was mainly
derived from spin-up $d$-orbitals of surface Ti neighboring vacancy. The high spin polarizability in
Ti$_4$N$_3$ was damaged. The subsurface N atom and the next subsurface Ti atom underwent a little change
owing to the missing surface Ti atom. For the N-vacancy system, as shown in Figure 4b, the TDOS
near Fermi level was contributed by the surface or the next subsurface Ti. A spin polarizability of more
than 50% was still detected. In the two atomic vacancy systems, the middle layer N atom was not
polarized visibly.

![Figure 4](image-url)

**Figure 4.** TDOS and PDOS of vacancy defected Ti$_4$N$_3$ nanosheet: (a) Ti$_4$N$_3$-Ti and (b)Ti$_4$N$_3$-N. ↑ and ↓
indicate the spin-up and spin-down orbitals, respectively. The Fermi level (dashed vertical line) is set
to zero. The TDOS is transited to a primitive cell.
3.3. Frenkel-Type Defects in Ti₄N₃ Nanosheet

Besides single atomic vacancy effects, atomic swap disordered effect, namely a potential atomic disordering phenomenon in 2D MXene materials, is also studied in this work. In Figure 5a, the surface Ti atom and its neighboring N atom at the subsurface layer were swapped. Unfortunately, such a Ti-N swapped structure was unstable, and then it would evolve into the configuration shown in Figure 5b after structure optimization. In Figure 5b, one of the N atoms at the subsurface moved to the hole-site of three surface Ti atoms in that the Ti-N bond moved from swapped atoms slides along the original crystalline direction to the surface of the 2D material. The disordering configuration shown in Figure 5b was called as a Frenkel-type defect. In the optimized Frenkel-type defect structure, the bond length of Ti-N was 1.896 Å, the lattice constant was 2.995 Å and the atomic layer thickness was 7.329 Å. Compared with the “ideal” Ti₄N₃ structure, the outer Ti-N bond was evidently decreased owing to surface effect. The whole system looked more relaxed.

![Figure 5. Schematic of the Ti-N swapped (a) before and (b) after geometric optimization on the Ti₄N₃ nanosheet.](image)

Compared with the “ideal” Ti₄N₃ system, the outside N atom was shown to stick to the surface and exhibited a slightly inward contraction. However, for the whole system, the interlayer spacing increased, which was similar to the behavior of the N-vacancy system discussed above, which led to a decrease of the vacuum layer thickness. To focus on the structure stability of the disordering Ti₄N₃ nanosheet, the binding energy $E_b$ and the forming energy $E_{\text{form}}$ were calculated by the above mentioned formula. Results show that the $E_b$ and $E_{\text{form}}$ were equal to $-1.300$ and $-0.347$ eV, respectively. The negative value indicates that these Frenkel-type defects were more stable than the “ideal” Ti₄N₃ system. This result is not surprising, because most MXenes decorated by some functional groups are more stable [50]. The atomic magnetic moment in the Frenkel-type disordering structure was also calculated. The total magnetic moment decreased from 1.173 to 1.084 $\mu_B$ due to the enhancement of indirect magnetic exchange between surface Ti atoms bridged by the outside N atom.

More information on the electronic properties of Frenkel-type defective Ti₄N₃ nanosheet is needed. In Figure 6, the TDOS and the PDOS of the outside N and its neighbor Ti atom in Frenkel-type defect structure are given and are compared with the Ti₄N₃ configuration. The outer N was located at the hole-site of three surface Ti atoms, the surface Ti atom neighbor of the N atom would increase, and the spin split near the Fermi level in the defective structure would decrease. As a result, the high spin polarization in Ti₄N₃ nanosheet was reduced sharply. The contribution of surface Ti atoms to TDOS was most significant from surface Ti atomic PDOS. The outside N and subsurface N provided little support. In this Frenkel-type defective Ti₄N₃ nanosheet, we detected a relatively high spin polarization (approximately 70% can be retained). The spin-polarization ratio is described by the formula [48].
3.4. Doping Effects of Transition Metal Z (Z = Sc, V, Zr) on the Ti4N3 Nanosheet

Impurities in materials are unavoidable in the preparation process and can easily affect physical and chemical properties. We implemented a theoretical calculation to reveal the doping properties of transition metal Z (Z = Sc, V, Zr) on the Ti4N3 nanosheet. In Figure 7, a surface Ti atom was replaced by Sc, V and Zr, atoms in a Ti4N3 supercell to simulate possible doping behavior. Impurity atom concentration can be close to 2% in this 3 × 3 × 1 supercell. After geometrical optimization, the lattice constant \( a \), bond length \( d \), binding energy \( E_b \), forming energy \( E_{\text{form}} \), the neighbor Ti atomic magnetic moment of the doped atom \( M_{\text{Ti}} \), atomic magnetic moment of Z atom \( M_Z \) and total magnetic moment \( M_{\text{tot}} \) are listed in Table 3. The binding energy \( E_b \) is defined using the above formula. The formation energy \( E_{\text{form}} \) is defined as follows [51]:

\[
E_{\text{form}} = E_{\text{Ti4N3-Z}} - E_{\text{Ti4N3}} + n_{\text{Ti}} \mu_{\text{Ti}} - n_{Z} \mu_{Z} \tag{4}
\]

where \( E_{\text{Ti4N3-Z}} \) are \( E_{\text{Ti4N3}} \) are total energies of doped Ti4N3-Z system and “ideal” Ti4N3 system, respectively. \( n_{Z} \) or \( n_{\text{Ti}} \) is the number of Z or Ti atom. \( \mu_{\text{Ti}} \) or \( \mu_{Z} \) is the chemical potential of Z or Ti atoms.

![Figure 6. TDOS and PDOS of the Frenkel-type defected Ti4N3 nanosheet. ↑ and ↓ indicate the spin-up and spin-down orbitals, respectively. The Fermi level (dashed vertical line) is set to zero. The TDOS is transited to a primitive cell.](image)

![Figure 7. Schematic of doping transition metal Z (Z = Sc, V, Zr) on the Ti4N3 nanosheet.](image)
Table 3. Calculated lattice constants $a$, atomic layer thickness $L$, binding energy $E_b$, forming energy $E_{\text{form}}$, total magnetic moment $M_{\text{tot}}$, magnetic moment of Z atom or its neighbor Ti atom at the surface, bond length between the doping Z atom at surface and its neighbor Ti$_1$ or N$_2$ atom at the surface or subsurface, respectively.

| Atom      | $a$ (Å) | $L$ (Å) | $d_{Z-Ti}$ (Å) | $d_{Z-N2}$ (Å) | $E_b$ (eV) | $E_{\text{form}}$ (eV) | $M_{\text{Ti}}$ ($\mu_B$) | $M_Z$ ($\mu_B$) | $M_{\text{tot}}$ ($\mu_B$) |
|-----------|---------|---------|----------------|----------------|-----------|------------------------|--------------------------|----------------|--------------------------|
| Ti$_4$N$_3$ | 2.993   | 7.235   | 2.919          | 2.062          | $-1.295$  | $-1.295$               | 0.490                    | 0.389           | 1.173                    |
| Ti$_4$N$_3$-Sc | 2.999   | 7.217   | 3.029          | 2.217          | $-1.280$  | 0.930                  | 0.594                    | 0.356           | 1.649                    |
| Ti$_4$N$_3$-Zr | 2.999   | 7.211   | 3.090          | 2.220          | $-1.220$  | 4.715                  | 0.522                    | 0.294           | 1.772                    |
| Ti$_4$N$_3$-V | 2.991   | 7.241   | 2.802          | 1.985          | $-1.335$  | $-2.505$               | 0.668                    | 1.315           | 2.365                    |

For the doped systems of Ti$_4$N$_3$-Z ($Z = \text{Sc, V, Zr}$), the calculated lattice barely changed, as shown by the comparison with the Ti$_4$N$_3$ nanosheet. In the Ti$_4$N$_3$-V system, the thickness of layer $L$ tended to extend, whereas the bond length of $d_{V-Ti}$ or $d_{V-N2}$ tended to shrink. Moreover, to focus on structure stability, we show that all of the binding energies were negative in Table 3. This finding implies that this structure was stable. We predicted that Ti$_4$N$_3$-V was the most stable, due to the fact that the binding value of Ti$_4$N$_3$-V was the smallest among all structures. By comparing with the “ideal” Ti$_4$N$_3$ system, the doping of V element on Ti$_4$N$_3$ emitted energy because of the negative $E_{\text{form}}$. For Zr-doping, a relatively large forming energy indicates the difficulty of fabrication.

In Table 3, both Ti$_4$N$_3$-Sc and Ti$_4$N$_3$-V systems, which have one less electron and one more electron by comparing with the Ti$_4$N$_3$ system separately, show high magnetism. Localization of the surface transition metal atoms was increased due to the relatively large bond length between surface impurity atoms and surface Ti atom or subsurface N atom. Although Ti$_4$N$_3$-Sc was a one-less-electron system, it can present high magnetism. For the same reason, the total magnetic moment was enhanced in the Ti$_4$N$_3$-Zr system.

Finally, for the Ti$_4$N$_3$-V system, the added electron entered the spin-up channel and resulted in a magnetic moment increment of 1 $\mu_B$. In Table 3, the total magnetic moment derived from the surface V atom. However, the bond length of $d_{V-Ti}$ or $d_{V-N2}$ in the Ti$_4$N$_3$-V system was smaller than that in the Ti$_4$N$_3$ system. More direct magnetic hybridization partly weakened the total magnetism. On the whole, surface doping of transition metal on a Ti$_4$N$_3$ nanosheet can mediate magnetism. This result provides a controlled way for us to design 2D MXene materials with high magnetic properties.

In Figure 8, the TDOS of the doped system Ti$_4$N$_3$-Z ($Z = \text{Sc, V, Zr}$) and the PDOS of surface Z atom and its neighbor surface Ti and subsurface N atom are presented. In Figure 8a, because Sc is one electron less than the Ti atom, the TDOS near the Fermi level decreased and presented a large spin valley. The PDOS of surface Ti atom neighboring the Sc atom shifted toward low-energy orientation due to the fact that the whole system was one electron less. For subsurface N atom, the contribution to TDOS was extremely small. As a result, in the doped system Ti$_4$N$_3$-Sc system, a high spin polarization ratio was reserved, and the spin-polarization ratio was described by Formula [48]. For the Ti$_4$N$_3$-V system, as shown in Figure 8b, we can see that near the Fermi level, some spin-peaks appeared in the spin-up channel because of one more electron. Similar behaviors were detected in the PDOS of surface Ti atoms owing to rehybridization. However, for the doped Ti$_4$N$_3$-Zr system, as shown in Figure 8c, the strong Zr-Ti interaction could widen the spin split near the Fermi level owing to the short bond length of Zr-Ti. In the PDOS of surface Ti and V atoms, some peaks appeared near the Fermi level. This system presented a relatively low spin polarization but a large magnetism.
Figure 8. The TDOS and PDOS of transition metal (a) Sc, (b) V and (c) Zr doped Ti$_4$N$_3$ nanosheet. ↑ and ↓ indicate the spin-up and spin-down orbitals, respectively. The Fermi level (dashed vertical line) is set to zero. The TDOS is transited to a primitive cell.

4. Conclusions

The atomic vacancy defect, Frenkel-type defect and transition metal $Z$ ($Z = \text{Sc, V, Zr}$) doping in Ti$_4$N$_3$ MXene nanosheet were investigated comprehensively by the first-principles calculation
based on density functional theory. The “ideal” Ti₄N₃ had a magnetic moment of 1.173 µB and a high spin polarization ratio of more than 80%. Firstly, atomic vacancy in the Ti₄N₃ MXene was studied. Although the system was stable even with the absence of a surface Ti or subsurface N atom, the Ti-vacancy appeared easier than the N-vacancy in the Ti₄N₃ MXene nanosheet. Both atomic vacancies in Ti₄N₃ could increase magnetism. Secondly, detection from swapped atom disordering indicates that the surface Ti-N swapped disordering was unstable and evolved into a Frenkel-type defect. In the Frenkel-type defect system, the total magnetic moment was decreased due to the enhancement of indirect magnetic exchange between surface Ti atoms bridged by the outside N atom and presented a relatively high spin polarization of approximately 70%. Finally, the doping effects of transition metal Z (Z = Sc, V, Zr) on the Ti₄N₃ nanosheet were systematically investigated. The results revealed that all of the doped systems were structurally stable and had relatively large magnetism, which was derived from the directed magnetic exchange between surface Z and Ti atoms. Surface atomic relaxation also played an important role in magnetism and electronic properties. Especially in the doped system Ti₄N₃-Sc system, a high spin polarization ratio was reserved. The Ti₄N₃ MXene nanosheet doped by Sc atom could be a potential candidate for application to spintronics. Studies on atomic defects and doping from transition metals (Sc, V, Zr) in MXene nanosheet Ti₄N₃ can help elucidate the various electronic and magnetic behaviors of real 2D materials and contribute to the development of new 2D Ti-based MXene.

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