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Atomic Vacancy Defect, Frenkel Defect and Transition Metals (Sc, V, Zr) Doping in Ti_4N_3 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 ($Z = \text{Sc}, \text{V}$ and Zr) doping on magnetic and electric properties of the Ti_4N_3 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 Ti_4N_3 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 ($Z = \text{Sc}, \text{V}$ and Zr) on Ti_4N_3 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 Ti_4N_3 -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; Ti_4N_3 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 ($2630 \text{ m}^2/\text{g}$) [3], high electron mobility ($1.5 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$) [4], good thermal conductivity ($5000 \text{ W/m}\cdot\text{K}$) [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/carbonitride/nitride compounds. In 2011, the Gogotsi used HF acid to selectively etch the Al atomic layer of ternary-layered carbide material Ti_3AlC_2 to obtain $\text{Ti}_3\text{C}_2\text{T}_x$ (T_x stands for the surface terminations, for example, hydroxyl, oxygen or fluorine) [10]. Ti_3AlC_2 is a MAX phase material, namely a typical ternary-layered ceramic. Generally, they may be shown as $\text{M}_{n+1}\text{AX}_n$, M meaning 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]. $\text{Ti}_3\text{C}_2\text{T}_x$ 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 $\text{M}_{n+1}\text{X}_n\text{T}_x$, where T_x is the functional group attached to the surface of MXene, such as -O, -OH and -F. M_2XT_x , $\text{M}_3\text{X}_2\text{T}_x$ and $\text{M}_4\text{X}_3\text{T}_x$ structures for $n = 1, 2$ and 3 , respectively, had been created [12]. Recently, the $(\text{M}'\text{M}')_{n+1}\text{X}_n\text{T}_x$ 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 Ti_3C_2 , Ti_2C , Nb_2C , V_2C , $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{C}$, $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{C}_2$, Ti_3CN , Ta_4C_3 , Ti_4N_3 , etc. [14]. Ti_4N_3 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 symmetry group P63/mmc structure have metallicity, but they have many advantages of a ceramic material. A covalent bond exists between M-X ion atoms-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 Ti_2C 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, Cr_2C is a half-metallic ferromagnetic. However, with F, Cl, OH or H functionalization, Cr_2C is transformed as the antiferromagnetic semiconductor [37]. The antiferromagnetic metal Cr_2N becomes a stable ferromagnetic semi-metal under the action of O functional groups [38]. $\text{Cr}_2\text{TiC}_2\text{O}_2$ is nonmagnetic, whereas $\text{Cr}_2\text{TiC}_2\text{F}_2$ and $\text{Cr}_2\text{TiC}_2(\text{OH})_2$ are antiferromagnetic, but $\text{Cr}_2\text{VC}_2(\text{OH})_2$, $\text{Cr}_2\text{VC}_2\text{F}_2$ and $\text{Cr}_2\text{VC}_2\text{O}_2$ 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 Ti_2XT_2 ($\text{X} = \text{C/N}$, $\text{T} = \text{OH, F, O}$) 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.

M_4X_3 (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 Ti_4N_3 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_4N_3 MXene nanosheet was investigated. The structure, electronic properties, and magnetism of Ti_4N_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_4N_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_4N_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_4N_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: $3d^24s^2$, N: $2s^22p^3$, Sc: $3d^14s^2$, Zr: $4p^64d^25s^2$ and V: $3d^34s^2$ valence electron configurations were specifically considered. In this work, a $3 \times 3 \times 1$ 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 $9 \times 9 \times 1$ k-point grid precision and integral Brillouin zone were used. For structural optimization, the experimental lattice constant 2.991 Å of single Ti_4N_3 [44] was set as the initial value of Ti_4N_3 nanosheet. Then for defect and doping calculation, the optimized lattice constant of Ti_4N_3 nanosheet was selected as the initial value.

3. Results and Discussion

3.1. Structure, Electronic Properties and Magnetism of Ti_4N_3 Nanosheet

Ti_4N_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_4AlN_3 precursor powder layer. Figure 1 shows the construction processing of the Ti_4N_3 MXene nanosheet by etching off the Al atomic layer from the Ti_4AlN_3 bulk. The Ti_4N_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_4N_3 nanosheet was composed of seven alternating layers of Ti and N layers. The structure was more complex than those of M_3X_2 and M_2X . Therefore, we deduced that M_4X_3 had better physical and chemical properties than M_3X_2 and M_2X .

Figure 1. Schematic of construction processing of the Ti_4N_3 MXene nanosheet by etching off the Al atomic layer from the Ti_4AlN_3 bulk. (a) Ti_4AlN_3 bulk, (b) Ti_4N_3 bulk and (c) front, (d) side and (e) top view of the Ti_4N_3 MXene nanosheet.

In our work, the spin polarization was set for the structure optimization of Ti_4N_3 nanosheet. The optimized lattice constants a and c , bond length ($d_{\text{TiX-Nx}}$) and atomic layer thickness L are listed in Table 1 for comparing them with the structural parameters of the precursor Ti_4AlN_3 [44]. The structure parameters difference between Ti_4N_3 and Ti_4AlN_3 was relatively small. For the lattice constants, the error did not exceed 2%. This indicates that the Ti_4N_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. Calculated lattice constants a and c , atomic layer thickness L , bond lengths between the N2 atom at subsurface and its neighbor Ti1 atom ($d_{\text{Ti1-N2}}$) or Ti3 atom ($d_{\text{N2-Ti3}}$) at the surface or the next subsurface, respectively.

System	a (Å)	c (Å)	L (Å)	$d_{\text{Ti1-N2}}$ (Å)	$d_{\text{N2-Ti3}}$ (Å)
Ti_4AlN_3 [44]	2.991	23.396	7.239	2.082	2.096
Ti_4N_3	2.993	23.439	7.235	2.062	2.119

Table 2 shows some structural parameters of Ti_4N_3 nanosheet. For simplicity, the surface Ti atom, the subsurface N atom, the next subsurface Ti atom and the central layer N atom are marked as Ti1, N2, Ti3 and N4, respectively. In Table 1, the bond lengths $d_{\text{Ti1-N2}}$ and $d_{\text{N2-Ti3}}$ were different, which shows that N atoms were located in a distorted octahedron. This structure was similar to the Ti_2NT_x calculated by Arkamita Bandyopadhyay et al. [40], but it is different from the single-layer Ti_4C_3 nanosheet, which is a regular octahedral structure [46].

In order to discuss electronic and magnetic properties of the Ti_4N_3 nanosheet, the total magnetic moment of Ti_4N_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_{form} and total magnetic moment M_{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-Ti1} (Å)	d_{v-N2} (Å)	d_{v-Ti3} (Å)	E_b (eV)	E_{form} (eV)	M_{tot} (μ_B)
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 Ti₄N₃ 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 Ti₄N₃ nanosheet might be a kind of candidate material in 2D spintronics because of its high spin polarizability [48].

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

Figure 2. Total density of states (TDOS) and partial density of states (PDOS) 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.

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 Ti₄N₃ nanosheet.

3.2. Atomic Vacancy Effect of Ti_4N_3 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 Ti_4N_3 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 Ti_4N_3 nanosheet, were described dramatically. Moreover, in Ti-vacancy and N-vacancy system (labeled as $\text{Ti}_4\text{N}_3\text{-Ti}$ and $\text{Ti}_4\text{N}_3\text{-N}$, 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 M_{tot} of the $\text{Ti}_4\text{N}_3\text{-Ti}$, $\text{Ti}_4\text{N}_3\text{-N}$ and Ti_4N_3 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 Ti_4N_3 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 $d_{\text{v-Ti}}$ or $d_{\text{v-N}}$) shrank compared with the Ti_4N_3 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 $\text{Ti}_4\text{N}_3\text{-Ti}$ system, the total magnetic moment increased from 1.173 to 1.817 μ_B .

Figure 3. Schematic of a vacancy defect: (a) surface Ti-vacancy and (b) subsurface N-vacancy on a Ti_4N_3 nanosheet.

In the Ti_4N_3 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 ($\text{Ti}_4\text{N}_3\text{-N}$) system, the bond length $d_{\text{v-N}}$ between the vacancy and its neighbor subsurface N atom in the subsurface layer shrank in comparison with the Ti_4N_3 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 $\text{Ti}_4\text{N}_3\text{-N}$ system, the total magnetic moment increased sharply to 2.373 μ_B .

In Table 2, the binding energies of Ti_4N_3 , $\text{Ti}_4\text{N}_3\text{-Ti}$ and $\text{Ti}_4\text{N}_3\text{-N}$ systems are listed. The binding energy can be defined as follows [49]:

$$E_b = (E_{\text{tot}} - n_{\text{Ti}}u_{\text{Ti}} - n_{\text{N}}u_{\text{N}})/n_{\text{tot}}, \quad (2)$$

where E_{tot} is the total energy of the defective and ideal system, n_{Ti} , n_{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 Ti_4N_3 , $\text{Ti}_4\text{N}_3\text{-Ti}$ and $\text{Ti}_4\text{N}_3\text{-N}$ systems have a negative value. This finding

can indicate that all systems were stable in structure. The binding energy of the $\text{Ti}_4\text{N}_3\text{-N}$ 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_{form} [48] was calculated by the following formula:

$$E_{\text{form}} = E_{\text{def}} - E_{\text{id}} - \sum n_i u_i \quad (3)$$

where E_{def} and E_{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_4N_3 system is more stable than the defective systems. A relatively small value in $\text{Ti}_4\text{N}_3\text{-Ti}$ 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 $\text{Ti}_4\text{N}_3\text{-Ti}$ and $\text{Ti}_4\text{N}_3\text{-N}$ 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_4N_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. TDOS and PDOS of vacancy defected Ti_4N_3 nanosheet: (a) $\text{Ti}_4\text{N}_3\text{-Ti}$ and (b) $\text{Ti}_4\text{N}_3\text{-N}$. $\uparrow$ 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.

3.3. Frenkel-Type Defects in Ti_4N_3 Nanosheet

Besides single atomic vacancy effects, atomic swap disordering 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” Ti_4N_3 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 Ti_4N_3 nanosheet.

Compared with the “ideal” Ti_4N_3 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 Ti_4N_3 nanosheet, the binding energy E_b and the forming energy E_{form} were calculated by the above mentioned formula. Results show that the E_b and E_{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” Ti_4N_3 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 μ_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 Ti_4N_3 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 Ti_4N_3 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 Ti_4N_3 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 Ti_4N_3 nanosheet, we detected a relatively high spin polarization (approximately 70% can be retained). The spin-polarization ratio is described by the formula [48].

Figure 6. TDOS and PDOS of the Frenkel-type defected Ti_4N_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.

3.4. Doping Effects of Transition Metal Z ($Z = \text{Sc}, \text{V}, \text{Zr}$) on the Ti_4N_3 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 ($Z = \text{Sc}, \text{V}, \text{Zr}$) on the Ti_4N_3 nanosheet. In Figure 7, a surface Ti atom was replaced by Sc, V and Zr, atoms in a Ti_4N_3 supercell to simulate possible doping behavior. Impurity atom concentration can be close to 2% in this $3 \times 3 \times 1$ supercell. After geometrical optimization, the lattice constant a , bond length d , binding energy E_b , forming energy E_{form} , the neighbor Ti atomic magnetic moment of the doped atom M_{Ti} , atomic magnetic moment of Z atom M_Z and total magnetic moment M_{tot} are listed in Table 3. The binding energy E_b is defined using the above formula. The formation energy E_{form} is defined as follows [51]:

$$E_{\text{form}} = E_{\text{Ti}_4\text{N}_3-\text{Z}} - E_{\text{Ti}_4\text{N}_3} + n_{\text{Ti}}\mu_{\text{Ti}} - n_Z\mu_Z \quad (4)$$

where $E_{\text{Ti}_4\text{N}_3-\text{Z}}$ are $E_{\text{Ti}_4\text{N}_3}$ are total energies of doped Ti_4N_3 -Z system and “ideal” Ti_4N_3 system, respectively. n_Z or n_{Ti} is the number of Z or Ti atom. μ_{Ti} or μ_Z is the chemical potential of Z or Ti atoms.

Figure 7. Schematic of doping transition metal Z ($Z = \text{Sc}, \text{V}, \text{Zr}$) on the Ti_4N_3 nanosheet.

Table 3. Calculated lattice constants a , atomic layer thickness L , binding energy E_b , forming energy E_{form} , total magnetic moment M_{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 Ti₁ or N₂ atom at the surface or subsurface, respectively.

Atom	a (Å)	L (Å)	d_{Z-Ti1} (Å)	d_{Z-N2} (Å)	E_b (eV)	E_{form} (eV)	$M_{Ti}(\mu_B)$	$M_Z(\mu_B)$	$M_{tot}(\mu_B)$
Ti ₄ N ₃	2.993	7.235	2.919	2.062	−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 Ti₄N₃-Z (Z = Sc, V, Zr), the calculated lattice barely changed, as shown by the comparison with the Ti₄N₃ nanosheet. In the Ti₄N₃-V system, the thickness of layer L tended to extend, whereas the bond length of d_{V-Ti} or d_{V-N} 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 Ti₄N₃-V was the most stable, due to the fact that the binding value of Ti₄N₃-V was the smallest among all structures. By comparing with the “ideal” Ti₄N₃ system, the doping of V element on Ti₄N₃ emitted energy because of the negative E_{form} . For Zr-doping, a relatively large forming energy indicates the difficulty of fabrication.

In Table 3, both Ti₄N₃-Sc and Ti₄N₃-V systems, which have one less electron and one more electron by comparing with the Ti₄N₃ 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 Ti₄N₃-Sc was a one-less-electron system, it can present high magnetism. For the same reason, the total magnetic moment was enhanced in the Ti₄N₃-Zr system.

Finally, for the Ti₄N₃-V system, the added electron entered the spin-up channel and resulted in a magnetic moment increment of 1 μ_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-N} in the Ti₄N₃-V system was smaller than that in the Ti₄N₃ system. More direct magnetic hybridization partly weakened the total magnetism. On the whole, surface doping of transition metal on a Ti₄N₃ 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 Ti₄N₃-Z (Z = 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 Ti₄N₃-Sc system, a high spin polarization ratio was reserved, and the spin-polarization ratio was described by Formula [48]. For the Ti₄N₃-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 Ti₄N₃-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_4N_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 translated to a primitive cell.

4. Conclusions

The atomic vacancy defect, Frenkel-type defect and transition metal Z ($Z = \text{Sc}, \text{V}, \text{Zr}$) doping in Ti_4N_3 MXene nanosheet were investigated comprehensively by the first-principles calculation

based on density functional theory. The “ideal” Ti_4N_3 had a magnetic moment of $1.173 \mu_B$ and a high spin polarization ratio of more than 80%. Firstly, atomic vacancy in the Ti_4N_3 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 Ti_4N_3 MXene nanosheet. Both atomic vacancies in Ti_4N_3 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 ($Z = \text{Sc}, \text{V}, \text{Zr}$) on the Ti_4N_3 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 $\text{Ti}_4\text{N}_3\text{-Sc}$ system, a high spin polarization ratio was reserved. The Ti_4N_3 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 Ti_4N_3 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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