First-Principles Study of Vacancies in Ti₃SiC₂ and Ti₃AlC₂

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Abstract: MAX phase materials have attracted increased attention due to their unique combination of ceramic and metallic properties. In this study, the properties of vacancies in Ti₃AlC₂ and Ti₃SiC₂, which are two of the most widely studied MAX phases, were investigated using first-principles calculations. Our calculations indicate that the stabilities of vacancies in Ti₃AlC₂ and Ti₃SiC₂ differ greatly from those previously reported for Cr₂AlC. The order of the formation energies of vacancies is V⁰Ti(a) > V⁰Ti(b) > V⁰C > V⁰A for both Ti₃SiC₂ and Ti₃AlC₂. Although the diffusion barriers for Ti₃SiC₂ and Ti₃AlC₂ are similar (~0.95 eV), the properties of their vacancies are significantly different. Our results show that the vacancy–vacancy interaction is attractive in Ti₃AlC₂ but repulsive in Ti₃SiC₂. The introduction of V⁰Ti and V⁰C vacancies results in the lattice constant c along the [0001] direction increasing for both Ti₃SiC₂ and Ti₃AlC₂. In contrast, the lattice constant c decreases significantly when V⁰A are introduced. The different effect of V⁰A on the lattice constants is explained by enhanced interactions of nearby Ti layers.

Keywords: MAX phases; vacancies; diffusion barrier; density functional theory

1. Introduction

The MAX phases form a large family of ternary carbides/nitrides with the general formula Mn+1AXn, where n varies from 1 to 3, M is an early transition metal, A is an A-group element, and X is C or N [1–3]. The MAX phases have a unique combination of the properties of ceramics and metals. Similar to metals, they are electrically and thermally conductive, easy to machine, ductile at high temperatures, and exceptionally resistant to damage and thermal shock. Like ceramics, they are elastically rigid, lightweight, and oxidation resistant.

Titanium aluminum carbide (Ti₃AlC₂) and titanium silicon carbide (Ti₃SiC₂) are 312 MAX phases. Like most MAX phases, Ti₃SiC₂ is stiff (Young’s modulus 352 GPa [4], tough (toughness 9 MPa m¹/² [5]), thermally conductive (37 W·m⁻¹·K⁻¹ [6]), and electrically conductive (4.5 × 10⁶ Ω⁻¹·m⁻¹ [7]). The properties of Ti₃AlC₂ differ slightly from those of Ti₃SiC₂; for example, it has a lower Young’s modulus (297 GPa) and electrical conductivity (2.9 × 10⁶ Ω⁻¹·m⁻¹). Both materials are readily machinable and tolerant to damage and thermal shock [8]. Ti₃SiC₂ has two polymorphs, i.e., α and β phases [9]. α-Ti₃SiC₂ has the same structure as Ti₃AlC₂, but the Si layer in β-Ti₃SiC₂...
is shifted. $\beta$-$\text{Ti}_3\text{SiC}_2$ is a metastable phase, therefore $\alpha$-$\text{Ti}_3\text{SiC}_2$ has been more widely studied [8,10]. For simplicity, only $\alpha$-$\text{Ti}_3\text{SiC}_2$ is considered in this work.

On one hand, defects can be unintentionally introduced into $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ during their synthesis. These materials are refractory ceramics and considerable concentrations of vacancies and impurities are introduced during their multi-component nanolaminate formation. On the other hand, $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ are potential structural materials for nuclear applications. Defects are created in the lattices of $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ by irradiation when the incident particles displace atoms from their substitutional positions. As mentioned above, their unique properties make $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ suitable candidates to be adopted in applications where materials are subject to extreme environments, such as nuclear reactors [11–14]. Amorphization is an important factor to evaluate the irradiation-resistant of a material. The resistance of amorphization is dependent on the competing effects between the defect production and annihilation rate. Vacancies are the simplest defects in MAX phases. A deeper knowledge of the properties of them in $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ is crucial for the understanding of the defect production, annihilation process, and phase stability [15–23].

A large number of experimental studies [11–14,24–31] have investigated the properties of $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ when subjected to irradiation with heavy ions and neutrons. Nappé et al. [11] studied the defect properties of $\text{Ti}_3\text{SiC}_2$ under Au-, Kr-, and Xe-ion irradiation. They observed generation of many defects in the structure and an expansion along the $c$ axis. Liu et al. [12] reported that atomic disorder appeared in $\text{Ti}_3(\text{Si,Al})\text{C}_2$ after Kr-ion irradiation, but the typical layered structure was preserved. Whittle et al. [13] reported that $\text{Ti}_3\text{AlC}_2$ and $\text{Ti}_3\text{SiC}_2$ showed high tolerance to damage from Xe-ion irradiation. Hoffman et al. [14] compared the neutron irradiation tolerances of $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ with those of SiC and alloy 617. They concluded that $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ have good irradiation tolerances.

Compared with experimental methods, first-principles calculations have the advantage of enabling the study of materials at the atomic scale. Such calculations have frequently been used to predict the crystal structures and stabilities of MAX phases, and to model their defects and related properties. Wang et al. [15–17] systematically studied the effects of vacancies and impurities in the $\text{Ti}_2\text{AlC}$ phase. They calculated the stabilities of $\text{Ti}_2\text{AlC}$ samples with different types of vacancies. Music et al. [18] studied the vacancies in $\text{Ti}_4\text{AlN}_3$, and reported that the introduction of about 25% N vacancies in $\text{Ti}_4\text{AlN}_3$ is energetically favorable. Tan et al. [19] studied vacancy diffusion in $\text{Ti}_3\text{AlC}$ and its impurity phase $\text{Ti}_3\text{AlC}$. Du et al. [20] studied the C vacancies in $\text{Ta}_4\text{AlC}_3$, and suggested that the introducing of C vacancies decreases the phase stability. Han et al. [21] studied defect stabilities in $\text{Cr}_2\text{AlC}$ under different magnetic orderings.

However, although $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$ are the most extensively studied MAX phases experimentally, theoretical investigations of their defect properties are rare. Medvedev et al. [22] studied the influence of disorder associated with the presence of vacancies on the electronic properties of $\text{Ti}_3\text{SiC}_2$. They found that the presence of C vacancies in $\text{Ti}_3\text{SiC}_2$ caused local perturbations of the electronic structures. Zhao et al. [23] studied the formation energies of different defects in $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$. They found that replacement of Ti by Al in $\text{Ti}_3\text{AlC}_2$ was more energetically favorable than replacement of Ti by Si in $\text{Ti}_3\text{SiC}_2$. These previous theoretical works mainly investigated point defect stabilities. In this work, we focus on the formation, stability, geometry, and diffusion properties of vacancies in $\text{Ti}_3\text{SiC}_2$ and $\text{Ti}_3\text{AlC}_2$.

### 2. Theoretical Method

Our calculations were performed under the framework of density functional theory as implemented in the Vienna ab initio simulation package (VASP) [32,33]. The projected augmented wave method (PAW) [34] and the generalized gradient approximation (GGA) [35] were used. According to our previous study on MAX phases [19,21], the exchange and correlation energies were calculated using the Perdew–Burke–Ernzerhof (PBE) functional [36]. The wave functions were expanded in a plane-wave basis set with an energy cutoff of 400 eV. The lattice constants and internal freedom
of the unit cell were fully optimized until the Hellman-Feynman forces on the atoms were less than 0.01 eV/Å. The effective charge for each atom (charge difference after bonding) is given using Bader charge analysis [37].

In order to simulate a single vacancy structure, we employed a $2 \times 2 \times 1$ supercell, which contains 48 atoms. According to our previous studies on defects properties of MAX phases [19,21,38], the supercell has been proved to be sufficient to reproduce the defect structures. The special k-point sampling integration was used over the Brillouin zone by using the $\Gamma$-centered $5 \times 5 \times 5$ for this supercell [39]. All these calculation setups were checked using a larger energy cutoff and k-mesh; the results of total energy and Hellmann-Feynman forces are convergent within 0.01 eV and 0.01 eV/Å, respectively.

To evaluate the energy barrier of an Al-vacancy, the climbing image nudged elastic band method (cNEB) [40,41] was employed to investigate the saddle points and minimum energy paths for vacancy diffusion from the initial state to the final state. In all transition state search calculations performed in this paper, a total of eight images were used (not including the initial and final images of each transition).

3. Results and Discussion

3.1. Properties of Perfect Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$

Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ are both belonging to 312 phases with the same crystal symmetries, as shown in Figure 1. They are based on layers of hexagonally close-packed Ti and Al/Si layers with C occupying octahedral centers between the Ti layers. The structures of Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ can also be regarded as alternating stacks of two layers of edge-sharing Ti$_6$C octahedra and a planar close-packed Al/Si layer. The Si/Al atoms are located in the Wyckoff 2$b$ (0, 0, 1/4) positions and the C atoms are in 4$f$ ($1/3$, $2/3$, $z_C$) positions. There are two types of non-equivalent Ti atoms, denoted by Ti(a) and Ti(b), which are located at 4$f$ ($1/3$, $2/3$, $z_{Ti}$) and $2a$ (0, 0, 0), respectively. The calculated structural parameters for Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ are listed in Table 1; the experimental results are also listed for comparison. The differences between the calculated and experimental values of the lattice constants are all smaller than 1%, indicating reliable predictions by our PBE calculations.

![Figure 1](image.png)

**Figure 1.** Crystal structures of Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$: (a) conventional cell and (b) supercell used to model defect configurations. Red, blue, and black balls represent Ti, Si/Al, and C atoms, respectively. Two types of non-equivalent Ti atoms are identified.
Table 1. Calculated (Cal.) lattice constants $a$ and $c$ (Å), $c/a$ ratio, and internal structural parameters $z_{\text{Ti}}$ and $z_{\text{C}}$ for Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$. Experimental values (Exp.) are also listed.

| Material    | Method | $a$ (Å) | $c$ (Å) | $c/a$ | $z_{\text{Ti}}$ | $z_{\text{C}}$ |
|-------------|--------|---------|---------|-------|-----------------|----------------|
| Ti$_3$SiC$_2$ | Cal.   | 3.075   | 17.734  | 5.767 | 0.135           | 0.572          |
|             | Exp.   | 3.07    | 17.67   | 5.76  | 0.135           | 0.568          |
| Ti$_3$AlC$_2$ | Cal.   | 3.082   | 18.642  | 0.648 | 0.127           | 0.569          |
|             | Exp.   | 3.075   | 18.578  | 0.641 | 0.128           | 0.564          |

After optimization of the crystal structures, the mechanical property parameters were calculated. In the Voigt–Reuss–Hill approximation [43–45], the bulk modulus $B$, and the shear modulus $G$ are the average of the values obtained by Voigt and Reuss approximations [43]. The Young’s modulus ($E$), the Poisson ratio $(\nu)$, the transverse ($V_t$), longitudinal ($V_l$), and average ($V_a$) acoustic wave velocities, and the Debye temperature ($\Theta_D$) can be obtained. Experimental values for Ti$_3$AlC$_2$ have not been reported, therefore only the calculated values for Ti$_3$SiC$_2$ are listed in Table 2 and compared with the experimental values. The results show that the calculated values are reasonably consistent with the experimental results.

Table 2. Calculated elastic properties of Ti$_3$SiC$_2$, including the bulk modulus $B$, the shear modulus $G$, the Young’s modulus $E$, the Poisson ratio $\nu$, the acoustic wave velocities ($V_t$, $V_l$, $V_a$), and the Debye temperature $\Theta_D$. The experimental values [46] are also listed for comparison.

| Properties | $B$ (GPa) | $G$ (GPa) | $E$ (GPa) | $\nu$ |
|------------|-----------|-----------|-----------|-------|
| Cal.       | 200.3     | 132.3     | 325.2     | 0.23  |
| Exp.       | 187.0     | 142.0     | 339.0     | 0.2   |
| Properties | $V_t$ (Km/s) | $V_l$ (Km/s) | $V_a$ (Km/s) | $\Theta_D$ (K) |
| Cal.       | 9.17      | 5.43      | 6.0       | 780   |
| Exp.       | 9.14      | 5.61      | 6.2       | 804   |

3.2. Formation Energies of Vacancies in Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$

The stabilities of vacancies at different atomic sites in crystals can be evaluated by the vacancy formation energy, which is defined as follows:

$$E_{\text{vac}}(V_X) = E_{\text{tot}}(V_X) - E_{\text{tot}}(\text{perf}) + \mu_X,$$

where $E_{\text{vac}}(V_X)$ is the vacancy formation energy of atom $X$ ($X = \text{Ti, Al, C}$), $E_{\text{tot}}(V_X)$ is the calculated total energy of a cell with defect $X$, $E_{\text{tot}}(\text{perf})$ is the total energy of a perfect crystal without defects, and $\mu_X$ is the chemical potential of $X$. Here, $\mu_X$ is chosen as the energy of an isolated $X$ atom for simplicity.

As shown in Figure 2, for both Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$, A-group element vacancies have the lowest formation energies, indicating that they are easily formed. The non-equivalent Ti(a) and Ti(b) atoms have different vacancy formation energies. Figure 1 shows that the Ti(a) atoms are located between Al and C layers. Ti(a) forms covalent bonds with C atoms, but forms weak metallic bonds with Al atoms. In contrast, the Ti(b) atoms are located at the center of [Ti$_6$C] octahedra, and have stronger interactions with surrounding atoms. The vacancy formation energies of the Ti(b) atoms are therefore larger than those of the Ti(a) atoms. The order of the vacancy formation energies is $V_{\text{Ti(a)}} > V_{\text{Ti(b)}} > V_{\text{C}} > V_{\text{A}}$. These results for Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ differ greatly from our previously reported results for Cr$_2$AlC, in which the Al vacancies were predicted to have high formation energies and the Cr vacancies were predicted to have low formation energies [21]. The formation energy of $V_{\text{Al}}$ is 0.9 eV lower than that of $V_{\text{Si}}$, indicating that an A-group element mono-vacancy is more easily formed in Ti$_3$AlC$_2$. 
where \( n \) is the concentration of \( V_A \) vacancies in Ti\(_3\)SiC\(_2\) and Ti\(_3\)AlC\(_2\). Figure 3 shows that for Ti\(_3\)AlC\(_2\) the vacancy formation energy decreases as the number of vacancies increases, indicating that existing vacancies can accelerate the formation of new vacancies. Therefore, decomposition of Ti\(_3\)AlC\(_2\) can be caused by formation of a large number of vacancies in the Al layers. In contrast, the relationship between the \( V_A \) content and the vacancy formation energy is different for Ti\(_3\)SiC\(_2\); the vacancy formation energy increases significantly with the increasing number of vacancies. This indicates that it is difficult to introduce a new \( V_{Si} \) near the original one because of the increased vacancy formation energy. Based on these results, it is reasonable to conclude that the interactions between nearby vacancies in Ti\(_3\)AlC\(_2\) are attractive, but are repulsive in Ti\(_3\)SiC\(_2\). The vacancies therefore tend to disperse in Ti\(_3\)SiC\(_2\) but are accommodated in Ti\(_3\)AlC\(_2\).

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**Figure 2.** Vacancy formation energies (\( E_{vac}, \text{eV} \)) of \( V_C \), \( V_{Ti(a)} \), \( V_{Ti(b)} \), and \( V_A \) (\( V_{Si}/V_{Al} \)) in Ti\(_3\)SiC\(_2\) and Ti\(_3\)AlC\(_2\).

#### 3.3. Vacancy–Vacancy Interactions of \( V_A \)

These above calculation results indicate that \( V_A \) vacancies are easily formed when Ti\(_3\)SiC\(_2\) and Ti\(_3\)AlC\(_2\) are in oxidizing, corrosive, and irradiation environments. The effects of \( V_A \) vacancies on the phase stabilities of Ti\(_3\)SiC\(_2\) and Ti\(_3\)AlC\(_2\) were explored by introducing more vacancies and calculating their vacancy formation energies:

\[
E_{vac}(V_X) = E_{tot}(V_X) - E_{tot(perf)} + \mu_X,
\]

where \( \mu \) is the formation energy of \( V_X \) in an infinite lattice. The relationship between the \( V_A \) content and the vacancy formation energy is different for Ti\(_3\)SiC\(_2\); the vacancy formation energy increases significantly with the increasing number of vacancies. This indicates that it is difficult to introduce a new \( V_{Si} \) near the original one because of the increased vacancy formation energy. Based on these results, it is reasonable to conclude that the interactions between nearby vacancies in Ti\(_3\)AlC\(_2\) are attractive, but are repulsive in Ti\(_3\)SiC\(_2\). The vacancies therefore tend to disperse in Ti\(_3\)SiC\(_2\) but are accommodated in Ti\(_3\)AlC\(_2\).

**Figure 3.** Vacancy formation energy (\( E_{vac}, \text{eV} \)) of \( V_A \) (\( V_{Si}/V_{Al} \)) dependences on A-group element atomic content of Ti\(_3\)SiC\(_2\) and Ti\(_3\)AlC\(_2\).
In order to verify this conclusion, we calculated and compared the vacancy formation energies for three configurations with two vacancies introduced at different locations. The results are shown in Figure 4. For Ti$_3$SiC$_2$, the configuration with two vacancies located in different layers has a low formation energy. Vacancy pair formation (config.1) increases the energy by ~0.2 eV compared with the other two configurations (config.2 and config.3). In contrast, config.1 is energetically more favorable for Ti$_3$AlC$_2$. Therefore, Ti$_3$SiC$_2$ should be more stable than Ti$_3$AlC$_2$ in a corrosive environment.

![Figure 4](image)

**Figure 4.** Vacancy formation energies ($E_{\text{vac}}$, eV) for $V_A$ ($V_{\text{Si}}/V_{\text{Al}}$) in three defect configurations of Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$. Yellow circles represent vacancies in Si/Al layers.

### 3.4. Diffusion of $V_A$ Vacancies

It is well known that the Al/Si atoms move in MAX phases predominantly by vacancy-mediated diffusion [19,21]. To ensure that the supercell was sufficiently large to avoid the influence of adjacent cells, a $\sqrt{3} \times 2\sqrt{3} \times 1$ supercell was used to calculate the diffusion barrier. The obtained values are consistent with those obtained using a $2 \times 2 \times 1$ supercell.

The calculated diffusion barriers ($B_{\text{diff}}$) for Si/Al in Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ are less than 1 eV; these are close to the self-diffusion barriers of many metals, as shown in Table 3. The diffusion of vacancies along the (0001) plane can therefore occur frequently in these two materials. As mentioned previously, the interactions of vacancies in Ti$_3$SiC$_2$ are repulsive, whereas they are attractive in Ti$_3$AlC$_2$. A new vacancy will therefore diffuse away from an existing vacancy in Ti$_3$SiC$_2$; this does not greatly affect the stability of the material. In contrast, the low diffusion barrier indicates that vacancies in Ti$_3$AlC$_2$ tend to be accommodated. A large number of vacancies may therefore lead to decomposition of the material. The diffusion of atoms in the corresponding free-standing Si/Al layers was also studied using the same method shown in Figure 5. The diffusion barriers in free-standing layers (~0.2 eV) are clearly different from those in the Si/Al layers of MAX phases (~0.95 eV). These results indicate that the main contribution to the barrier is the interaction between the Al/Si and Ti layers, rather than the interaction in the Si/Al layers.

### Table 3. Diffusion barriers for $V_A$ in Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$. Self-diffusion barriers of Al, C, and Ni are also listed for comparison.

| Material | Ti$_3$SiC$_2$/Ti$_3$AlC$_2$ | Cu | Al | Ni |
|----------|--------------------------|----|----|----|
| Barrier (eV) | 0.95 | 0.92 [47] | 0.61 [48] | 1.4–1.8 [49,50] |
Driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane.

3.5. Effects of Vacancies on Lattice Constants

Defects in a material can lead to changes in the lattice constants. For example, irradiation of nuclear graphite increases the lattice constant in the [0001] direction, and decreases the lattice constants a and b in the (0001) plane. This is because of the large numbers of interstitial carbons in the graphite interlayers. In this work, the effects of vacancies on the lattice constants of Ti3SiC2 and Ti3AlC2 were investigated. Figure 6 shows the trends in the changes in the lattice constants of Ti3SiC2 and Ti3AlC2 with increasing the number of vacancies in the supercell. The introduction of vacancies increases the lattice constant a and decreases c. The change in a is negligible, but a significant change in c is observed along the [0001] direction. The lattice constant changes for Ti3SiC2 are larger than those for Ti3AlC2.

![Figure 5](image1.png)

**Figure 5.** Calculated energy plots for diffusion of Si/Al vacancy in Ti3SiC2 and Ti3AlC2 using cNEB method. Energy barriers (B_{diff}) for Ti3SiC2 and Ti3AlC2 are both 0.95 eV. Empty squares/circles denote energies for Si/Al vacancy diffusion in free-standing Si/Al layers; these indicate a low barrier of ~0.2 eV.

![Figure 6](image2.png)

**Figure 6.** Changes in lattice constants of Ti3SiC2 and Ti3AlC2 with respect to concentration of Si/Al vacancies. Black and red lines indicate results for Ti3SiC2 and Ti3AlC2, respectively.

The lattice constant changes induced by other types of vacancies were also calculated. The results for V_Ti and V_C are the opposite of those for V_A. As shown in Figure 7, when V_Ti and V_C vacancies are introduced, the lattice constant a decreases and c increases. The effects of V_A and V_Ti/V_C on the lattice constants differ because the interactions between the corresponding atoms and their surrounding atoms are different. In the formation of V_Ti and V_C, the strong Ti–C covalent bond is broken; this is the driving force behind the decrease in the lattice constant in the (0001) plane. In the formation of V_A, the bonds between Al/Si atoms and the surrounding atoms are broken. According to our previous...
analysis of diffusion barriers, the interactions between the Al/Si layer and the two neighboring Ti layers are stronger than the in-plane interactions for VA. The formation of VA therefore contracts the materials along the [0001] direction.

![Figure 7. Lattice constant changes for Ti$_3$SiC$_2$ (black bar) and Ti$_3$AlC$_2$ (red bar) with respect to three types of on-site vacancies at a concentration of 12.5%. The difference between the results for Ti(a) and Ti(b) is very small, therefore the values are averaged as VTi for clarity.](image)

To verify this conclusion, the interactions between atoms in Ti$_3$SiC$_2$ with vacancies were analyzed based on the deformation charge densities. As shown in Figure 8, unlike the electron density distributions in the configurations of VTi and VC, there is an electron accumulation area around the two Ti atoms neighboring VA. The electron accumulation of these two Ti atoms along the [0001] direction indicates that the interaction between them is enhanced by the Si vacancy. The effects of VSi on the lattice constants are therefore different from those of VTi and VC.

![Figure 8. Deformation charge density (difference between crystal charge and atomic charge distribution) on (1, 1, 2, 0) plane of Ti$_3$SiC$_2$ with (a) VTi$_{\text{b}0\text{b}}$; (b) VTi$_{\text{d}0\text{d}}$; (c) VC; and (d) VSi vacancies. Contours added with intervals of 0.005 electrons/Bohr$^3$. Red and blue isosurfaces correspond to electron-depleted and electron-enriched zones, respectively. White circles indicate positions of vacancies. Electron accumulation areas around two Ti atoms neighboring VA in (d) are indicated by red arrows.](image)
4. Conclusions

In this study, the properties of vacancies in Ti$_3$AlC$_2$ and Ti$_3$SiC$_2$, which are two of the most widely studied MAX phases, were investigated using first-principles calculations. Our results show that an A-group element vacancy (V$_A$) has the lowest formation energy, therefore the vacancy–vacancy interactions, the effects of V$_A$ on the lattice constants, and the charge redistribution of V$_A$ were studied. The formation energy of V$_{Al}$ is 0.9 eV lower than that of V$_{Si}$, indicating that an A-group element mono-vacancy is more easily formed in Ti$_3$AlC$_2$. Although the diffusion barriers for Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ are similar (~0.95 eV), the vacancy properties are different. Our results show that the vacancy–vacancy interaction is attractive in Ti$_3$AlC$_2$ but repulsive in Ti$_3$SiC$_2$. The vacancies therefore tend to disperse in Ti$_3$SiC$_2$ but are accommodated in Ti$_3$AlC$_2$. Based on these results, we conclude that Ti$_3$SiC$_2$ should be more stable than Ti$_3$AlC$_2$ in a corrosive environment. The introduction of V$_{Ti}$ and V$_C$ vacancies causes the lattice constant $c$ along the [0001] direction to increase for both Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$. The changes in the lattice constants caused by V$_A$ are opposite. The effect of V$_A$ on the lattice constants is explained by enhanced interactions of nearby Ti layers.

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References

1. Ghidiu, M.; Lukatskaya, M.R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M.W. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. Nature 2014, 516, 78–81. [CrossRef] [PubMed]
2. Naguib, M.; Mochalin, V.N.; Barsoum, M.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. Adv. Mater. 2014, 26, 992–1005. [CrossRef] [PubMed]
3. Radovic, M.; Barsoum, M.W. Max phases: Bridging the gap between metals and ceramics. Am. Ceram. Soc. Bull. 2013, 92, 20–27.
4. Barsoum, M.W.; El-Raghy, T. Synthesis and Characterization of a Remarkable Ceramic: Ti$_3$SiC$_2$. J. Am. Ceram. Soc. 1996, 79, 1953–1956. [CrossRef]
5. Barsoum, M.W. The MN$_{N+1}$AX$_N$ Phases: A New Class of Solids: Thermodynamically stable nanolaminates. Prog. Solid State Chem. 2000, 28, 201–281. [CrossRef]
6. Barsoum, M.W.; El-Raghy, T.; Rawn, C.J.; Porter, W.D.; Wang, H.; Payzant, E.A.; Hubbard, C.R. Thermal properties of Ti$_3$SiC$_2$. J. Phys. Chem. Solids 1999, 60, 429–439. [CrossRef]
7. Kisi, E.H.; Crossley, J.A.A.; Myhra, S.; Barsoum, M.W. Structure and Crystal Chemistry of Ti$_3$SiC$_2$. J. Phys. Chem. Solids 1998, 59, 1437–1443. [CrossRef]
8. Zhang, H.; Bao, Y.; Zhou, Y. Current Status in Layered Ternary Carbide Ti$_x$SiC$_2$, a Review. J. Mater. Sci. Technol. 2009, 25, 1–38.
9. Farber, L.; Levin, I.; Barsoum, M.W.; El-Raghy, T.; Tzenov, T. High-resolution transmission electron microscopy of some Ti$_{x-1}$Al$_x$ compounds ($n = 1, 2$; A = Al or Si; X = C or N). J. Appl. Phys. 1999, 86, 2540–2543. [CrossRef]
10. Wang, J.-Y.; Zhou, Y.-C. Polymorphism of Ti$_3$SiC$_2$ ceramic: First-principles investigations. Phys. Rev. B 2004, 69, 144108. [CrossRef]
11. Nappé, J.C.; Monnet, I.; Grosseau, P.; Audubert, F.; Guilhot, B.; Beauvy, M.; Benabdesselam, M.; Thomé, L. Structural changes induced by heavy ion irradiation in titanium silicon carbide. J. Nucl. Mater. 2011, 409, 53–61. [CrossRef]
12. Liu, X.M.; Le Flem, M.; Béchade, J.L.; Monnet, I. Nanoindentation investigation of heavy ion irradiated Ti(Si,Al)C2. *J. Nucl. Mater.* **2010**, *401*, 149–153. [CrossRef]

13. Whittle, K.R.; Blackford, M.G.; Aughterson, R.D.; Moricca, S.; Lumpkin, G.R.; Riley, D.P.; Zaluzev, N.J. Radiation tolerance of M_{n+1}AX_{n} phases, Ti3AlC2 and Ti3SiC2. *Acta Mater.* **2010**, *58*, 4362–4368. [CrossRef]

14. Hoffman, E.N.; Vinson, D.W.; Sindelar, R.L.; Tallman, D.J.; Kohse, G.; Barsoum, M.W. MAX phase carbides and nitrides: Properties for future nuclear power plant in-core applications and neutron transmutation analysis. *Nucl. Eng. Des.* **2012**, *244*, 17–24. [CrossRef]

15. Wang, J.; Zhou, Y.; Liao, T.; Zhang, J.; Lin, Z. A first-principles investigation of the phase stability of Ti2AlC with Al vacancies. *Scr. Mater.* **2013**, *84*, 227–230. [CrossRef]

16. Marion, L.F.; Monnet, I. Saturation of irradiation damage in (Ti,Zr)3(Si,Al)C2 compounds. *Comp. Mater. Sci.* **2013**, *64*, 268–274. [CrossRef]

17. Liao, T.; Wang, J.; Zhou, Y. First-principles investigation of intrinsic defects and (N, O) impurity atom stimulated Al vacancy in Ti2AlC. *Appl. Phys. Lett.* **2008**, *93*, 261911. [CrossRef]

18. Music, D.; Ahuja, R.; Schneider, J.M. Theoretical study of neutron vacancies in Ti4AlN3. *Appl. Phys. Lett.* **2005**, *86*, 031911. [CrossRef]

19. Jie, T.; Han, H.; Darshana, W.; Wenguan, L.; Mingwen, Z.; Ping, H. A comparative first-principles study of the electronic, mechanical, defect and acoustic properties of Ti2AlC and Ti3AlC. *J. Phys. D Appl. Phys.* **2014**, *47*, 215301.

20. Du, Y.L.; Sun, Z.M.; Hashimoto, H.; Tian, W.B. First-Principles Study of Carbon Vacancy in Ta3AlC3. *Mater. Trans.* **2008**, *49*, 1934–1936. [CrossRef]

21. Han, H.; Wickramarathne, D.; Huang, Q.; Dai, J.; Li, T.; Wang, H.; Zhang, W.; Huai, P. A first-principles study on the defective properties of MAX phase Cr2AlC: The magnetic ordering and strong correlation effect. *RSC Adv.* **2016**, *6*, 84262–84268. [CrossRef]

22. Medvedeva, N.I.; Novikov, D.L.; Ivanovsky, A.L.; Kuznetsov, M.V.; Freeman, A.J. Electronic properties of Ti3SiC2-based solid solutions. *Phys. Rev. B* **1998**, *58*, 16042–16050. [CrossRef]

23. Zhao, S.; Xue, J.; Wang, Y.; Huang, Q. Ab initio study of irradiation tolerance for different M_{n+1}AX_{n} phases: Ti3SiC2 and Ti3AlC2. *J. Appl. Phys.* **2014**, *115*, 023503. [CrossRef]

24. Liu, X.; Le Flem, M.; Béchade, J.-L.; Onimus, F.; Cozzika, T.; Monnet, I. XRD investigation of ion irradiated Ti3(Si,Al)C2. *Nucl. Instrum. Methods B* **2010**, *270*, 6281–6287. [CrossRef]

25. Nappé, J.C.; Monnet, I.; Audubert, F.; Cousseau, P.; Beauvy, M.; Benabdessalem, M. Formation of nanosized hills on Ti3SiC2 oxide layer irradiated with swift heavy ions. *Nucl. Instrum. Methods B* **2012**, *270*, 36–43. [CrossRef]

26. Marion, L.F.; Monnet, I. Saturation of irradiation damage in (Ti,Zr)3(Si,Al)C2 compounds. *J. Nucl. Mater.* **2013**, *433*, 534–537. [CrossRef]

27. Song, P.; Sun, J.; Wang, Z.; Cui, M.; Shen, T.; Li, Y.; Pang, L.; Zhu, Y.; Huang, Q.; Liu, J. Irradiation resistance properties studies on helium ions irradiated MAX phase Ti3AlC2. *Nucl. Instrum. Methods B* **2014**, *326*, 332–336. [CrossRef]

28. Zhang, L.; Qi, Q.; Shi, L.Q.; O’Connor, D.J.; King, B.V.; Kisi, E.H.; Venkatachaliam, D.K. Damage tolerance of Ti3SiC2 to high energy iodine irradiation. *Appl. Surf. Sci.* **2012**, *258*, 6281–6287. [CrossRef]

29. Huang, Q.; Liu, R.; Lei, G.; Huang, H.; Li, J.; He, S.; Li, D.; Yan, L.; Zhou, J.; Huang, Q. Irradiation resistance of MAX phases Ti3SiC2 and Ti3AlC2: Characterization and comparison. *J. Nucl. Mater.* **2015**, *465*, 640–647. [CrossRef]

30. Wang, C.; Yang, T.; Kong, S.; Xiao, J.; Xue, J.; Wang, Q.; Hu, C.; Huang, Q.; Wang, Y. Effects of He irradiation on Ti3AlC2: Damage evolution and behavior of He bubbles. *J. Nucl. Mater.* **2013**, *440*, 606–611. [CrossRef]

31. Yang, T.; Wang, C.; Taylor, C.A.; Huang, X.; Huang, Q.; Li, F.; Shen, L.; Zhou, X.; Xue, J.; Yan, S.; et al. The structural transitions of Ti3AlC2 induced by ion irradiation. *Acta Mater.* **2014**, *65*, 351–359. [CrossRef]

32. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **1996**, *6*, 15–50. [CrossRef]

33. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186. [CrossRef]

34. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979. [CrossRef]

35. Perdew, J.P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **1992**, *45*, 13244–13249. [CrossRef]
36. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [CrossRef] [PubMed]

37. Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for bader decomposition of charge density. *Comp. Mater. Sci.* **2006**, *36*, 354–360. [CrossRef]

38. Huang, Q.; Han, H.; Liu, R.; Lei, G.; Yan, L.; Zhou, J.; Huang, Q. Saturation of ion irradiation effects in MAX phase Cr2AlC. *Acta Mater.* **2016**, *110*, 1–7. [CrossRef]

39. Pack, J.D.; Monkhorst, H.J. “Special points for Brillouin-zone integrations”—A reply. *Phys. Rev. B* **1977**, *16*, 1748–1749. [CrossRef]

40. Henkelman, G.; Uberuaga, B.P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904. [CrossRef]

41. Henkelman, G.; Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **2000**, *113*, 9978–9985. [CrossRef]

42. Onodera, A.; Hirano, H.; Yuasa, T.; Gao, N.F.; Miyamoto, Y. Static compression of Ti3SiC2 to 61 GPa. *Appl. Phys. Lett.* **1999**, *74*, 3782–3784. [CrossRef]

43. Hill, R. The Elastic Behaviour of a Crystalline Aggregate. *Proc. Phys. Soc. A* **1952**, *65*, 349. [CrossRef]

44. Han, H.; Cheng, C.; Xiong, X.-G.; Su, J.; Dai, J.-X.; Wang, H.; Yin, G.; Huai, P. Piezoelectric, Mechanical and Acoustic Properties of KNaNbOF5 from First-Principles Calculations. *Materials* **2015**, *8*, 8578–8589. [CrossRef]

45. Han, H.; Yin, G.; Wickramaratne, D. A first-principles investigation of the electronic, elastic, piezoelectric and acoustic properties of K3B6O10Cl. *Compt. Mater. Sci.* **2013**, *69*, 81–86. [CrossRef]

46. Pietzka, M.A.; Schuster, J.C. Summary of Constitutional Data on the Aluminum-Carbon-Titanium System. *J. Phase Equilib.* **1994**, *15*, 392–400. [CrossRef]

47. Kornblit, L.; Pelleg, J.; Rabinovitch, A. Self-diffusion calculation for fcc metals. *Phys. Rev. B* **1977**, *16*, 1164–1167. [CrossRef]

48. García Ortega, M.; Ramos de Debiaggi, S.; Monti, A. Self-Diffusion in FCC Metals: Static and Dynamic Simulations in Aluminium and Nickel. *Phys. Stat. Sol. (b)* **2002**, *234*, 506–521. [CrossRef]

49. Atkinson, A.; Taylor, R.I. The diffusion of Ni in the bulk and along dislocations in NiO single crystals. *Philos. Mag. A* **1979**, *39*, 581–595. [CrossRef]

50. Debiaggi, S.; Decorte, P.; Monti, A. Diffusion by Vacancy Mechanism in Ni, Al, and Ni3Al: Calculation Based on Many-Body Potentials. *Phys. Stat. Sol. (b)* **1996**, *195*, 37–54. [CrossRef]