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ABSTRACT
As one of the MAX phases, Mo$_2$GeC can also be considered as a potential material for use in next generation fission and fusion program reactors. We used first-principles calculations to investigate the formation energies, stable configuration, and interatomic bonding of intrinsic defects (mono-vacancy, self-interstitials, antisites, and Frenkel pairs). For all intrinsic defects, only the value of the formation energy for the C vacancy defect is negative, and the biggest formation energy occurs for Ge$_2$ defect. The existence of mono-vacancy shrinks the Mo$_2$GeC structure, while the existence of interstitials, antisites, and Frenkel pair defects expands the Mo$_2$GeC structure. In order to further illustrate the stability of defects, we calculated the DOS and PDOS of defects. We can find that defects have a certain effect on the density of states of Mo$_2$GeC. When mono-vacancy and antisite defects are generated, the DOS at the Fermi level decreased, while the production of self-interstitials and Frenkel defects caused the DOS at the Fermi level to increase. We also found that the C vacancy, C$_i$, and Mo–Ge antisite pair caused a small pseudo-gap energy at the Fermi level, indicating that their structure is relatively stable, which is consistent with the result of low formation energy. In addition, a small isolated peak at the point of ~13.5 eV for C$_i$ appeared, which is attributed to the C-2s orbital. We hope that our results could provide theoretical guidance for future experiments and applications of Mo$_2$GeC.

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I. INTRODUCTION
In the past 20 years, extensive research has been conducted on M$_{n+1}$AX$_n$ (where n = 1, 2, or 3, M is an early transition metal, A is an A-group element, and X is either C or N$^{1+}$), which is the generic chemical formula of the MAX phases. These materials have attracted much attention since Barsoum and co-workers succeeded to synthesize Ti$_3$SiC$_2$. So far, more than 70 MAX phases have been synthesized, and the number is still increasing. They possess a hexagonal crystal structure of sheets of metal carbide or nitride octahedra, which is weakly bonded with the interleaved planar closely packed A-group element layers. The layered crystal structure of MAX phases results in a combination of outstanding properties of both metals and ceramics such as thermal conductivity and electrical conductivity, wear and corrosion protection, irradiation damage tolerance, excellent machinability, and resistance to high-temperature oxidation. These unique properties provide a broad array of applications of MAX phases. For example, they can be used in defense materials, portable electronic devices, medical application, sensors, low-friction surfaces, and aerospace, as well as protective coatings in future nuclear reactors.\cite{1,3,6}

With the approaching energy crisis and the rapid development of nuclear power, high temperature structural materials for nuclear reactors have become a hot research topic.\cite{10,11} M$_{n+1}$AX$_n$ shows great potential in tolerating radiation damage and damage-resistant capability combined with high temperature stability, so it can also be considered as a potential high temperature structural material for use in next generation fission and fusion program reactors.\cite{12} As one of the typical M$_2$GeC phases, we found that Mo$_2$GeC exhibits good mechanical properties from theoretical calculation results. Since there is no successful synthesis in the experiment, compared to Ti$_2$GeC\cite{7,15} and V$_2$GeC\cite{15,16} only few works have been devoted to study the physical properties.\cite{10,16} However, the properties of Mo$_2$GeC are compared with the properties of the MAX phase, which has been proved to be suitable for future nuclear reactors through experiments. We thought that Mo$_2$GeC can also be considered as a potential material for protective coatings and cladding materials for the nuclear industry in the future.
MAX phases may unintentionally produce different kinds of intrinsic defects during growth or exposure to external environments of high-irradiation, which mainly consist of vacancies, exchange of atoms, and self-interstitials. Formation of defects and the interaction between them can induce various changes in the mechanical and physical properties of structural materials. For example, these defects will aggregate into clusters and migrate throughout the structure material to interact with the microstructure, including other defects and dislocations, which causes the degradation of mechanical properties, such as creep, swelling, hardening, blistering, and embrittlement. In addition, the resistance of amorphization depends on competition effects between defect production and annihilation. Therefore, as future nuclear structural materials, a deep understanding of the properties of various defects will have a crucial influence on practical applications. According to our research, despite mechanical, elastic, and electronic properties of Mo₂GeC being studied, very little evidence of the fundamental physical properties for defects in Mo₂GeC has been presented.

Motivated by this background, the goal of this work is to explore the properties of different kinds of intrinsic defects, vacancies, self-interstitials, antisites, and Frenkel defects, in Mo₂GeC. In order to understand the material structure, the stable configurations of different defects are discussed systematically by first-principles methods. To understand the stability of materials with such defects, the formation energy and bonding properties of the defects are discussed in detail. This is the first quantitative theoretical prediction of the intrinsic defects in Mo₂GeC, and it still awaits experimental confirmation.

II. MODEL AND METHOD

Mo₂GeC belongs to the 63m/mmc space group. We used a 32-atom supercell (2 × 2 × 1) to calculate the single point-defect, and the perfect crystal structure is shown in Fig. 1. The Wyckoff positions of atoms are as follows: Mo atoms—4f(1/3, 1/3, zₘo), Ge atoms—2d(1/3, 1/3, 1/3), and C—2a(0,0,0). zₘo is the internal structure parameter. All calculations were achieved by using the CASTEP code, in which the density functional theory (DFT) was employed. The electronic exchange–correlation energy was considered under the scheme of Perdew–Burke–Ernzerhof (PBE) based on the generalized gradient approximation (GGA). The ion–electron interactions are represented by the plane-wave ultrasoft pseudo-potential method. The cutoff energy of the plane wave basis set was 520 eV. The Brillouin-zone k-point sampling of the materials was set to a 7 × 7 × 3 Monkhorst–Pack mesh. To ensure adequate calculation accuracy, lattice parameters are fully relaxed. Convergence tolerances were set as follows: the total energy convergence was set to 1.06 × 10⁻⁷ eV/Å; the maximum Hellmann–Feynman force on atoms was set to 0.00453 eV/Å; the maximum stress is smaller and was set to 1.19 × 10⁻² GPa; the maximum atomic displacement is lower than 8.33 × 10⁻⁴ Å. Defect formation energy is an important quantity, which describes the probability of the defect formation and the stability of the material with defect. The formation energy of the neutral defect in MAX phases can be given by the following relation:

$$E_f[X] = E_{tot}[X] - E_{per}[bulk] \pm \sum n_i \mu_i,$$

where $E_{tot}[X]$ is the total energy for a supercell that contains the defect $X$ ($X$ is the host atom or impurity atom), $E_{per}[bulk]$ is the total energy of a perfect supercell, $n_i$ is the number of $X$ atoms that have been added to (+) or removed from (−) the supercell, and $\mu_i$ is the chemical potential of the $X$ element.

III. RESULTS AND DISCUSSION

In order to know the reliability of our parameters in our calculation, the values of equilibrium lattice constants ($a$ and $c$) and volume for defect-free Mo₂GeC were calculated and are presented in Table I, together with other theoretical data for comparison. Our results are highly satisfactory because they deviate from the previous theoretical results by less than 0.32%. It ensures accuracy and reliability for our calculation.

A. Defect formation energies

To estimate the order of defect stability, we calculated the defect formation energy, which includes vacancies, self-interstitials,
antisites, and Frenkel defects. Equilibrium lattice constants and volume would change when a defect was formed until the total energy reached the minimum. The values of equilibrium lattice constants, volume, and formation volume \((\Delta V, \Delta V = V - V_0, \text{where } V_0 \text{ is the volume of perfect } \text{MoGeC})\) for \text{MoGeC} with intrinsic defects were calculated. From calculation results, we can understand the stable configuration of and lattice change in \text{MoGeC} when the defect is present.

1. Formation energy of mono-vacancy

The mono-vacancy structure of \text{MoGeC} is formed after removing one atom from the supercell MAX phase of 32 atoms. From Table II, we can find that the lattice constants \(a\) and \(c\) will reduce if mono-vacancy appears in \text{MoGeC}. For mono-vacancy type defects, the structure of \text{MoGeC} has shrunk, and the C vacancy exhibits the largest change. The existence of Mo vacancy leads to a decrease of 0.022 Å for Mo–Ge bonds, while Mo–C bonds decrease by 0.055 Å. Meanwhile, the formation of Ge vacancy results in a 0.03 Å decrease in Ge–Ge bonds. In addition, the existence of C vacancy leads to an increase of 0.016 Å for Mo–C bonds and a decrease of 0.018 Å for Mo–Ge bonds.

The vacancy formation energies are shown in Table II. In \text{MoGeC}, the formation energy of mono-vacancy for Mo, Ge, and C is \(E_f^\text{Mo} = 0.998, E_f^\text{Ge} = 1.178,\) and \(E_f^\text{c} = -0.353,\) respectively. The formation energy can satisfy the sequence \(E_f^\text{Ge} > E_f^\text{Mo} > E_f^\text{c},\) which indicates that the C vacancy is the most energetically favorable mono-vacancy. It means that there are more C vacancies than Mo and Ge under equilibrium conditions. From Table II, we can also find that the highest mono-vacancy formation energy is found while mono-vacancy. It means that there are more C vacancies than Mo and Ge under equilibrium conditions. From Table II, we can also find that the highest mono-vacancy formation energy is found while mono-vacancy appears in Mo.

2. Interstitial formation energy

For interstitial-type defects, there are four possible interstitial positions in \text{MoGeC}. They are divided into two parts: the interstices in the open space in Mo–Ge layers and the ones in compact Mo–Mo layers, as demonstrated in Fig. 1. For Mo–Ge layers, there are three kinds of interstices, which include one octahedral site \((I_{oct-1}),\) one tetrahedral site \((I_{tetra-2}),\) and one triangle site \((I_{tri-3}).\) For Mo–Mo layers, there is only one tetrahedral site \((I_{tetra-4}).\) The interstice \(I_{oct-1}\) is the center of an octahedral surrounded by three Ge and three Mo atoms, the interstice \(I_{tetra-2}\) consists of three Mo atoms and one Ge atom, the interstice \(I_{tri-3}\) is located in the center of the triangle containing three Ge atoms, and the interstice \(I_{tetra-4}\) is surrounded by four Mo atoms. They are illustrated by 1, 2, 3, and 4, as shown in Fig. 1. Based on the abovementioned four possible stable configurations of single Mo, Ge, and C atoms, the formation energy and lattice constant are listed in Tables III and IV, respectively.

For Mo atoms, there are two types of stable interstitials in \text{MoGeC} after relaxation. The first stable interstitial is observed at an octahedral position \((I_{oct-1})\) with a formation energy of 3.99 eV. Due to the large radius of the Mo atom, the stable octahedral site is not located exactly at the position, as displayed in Fig. 1. It moves slightly down in the direction of the Z axis, which is about 0.02 Å. The second stable interstitial is observed at the triangle site \((I_{tri-3})\) in the Ge plane with a formation energy of 4.09 eV. The distance between \(I_{tri-3}\) and its nearest Ge atoms is 2.267 Å. For both stable interstitials of the Mo atom, the formation energy of Mo\(^1\) is lower than that of Mo\(^0\). This shows that Mo\(^1\) is energetically more favorable. The Mo interstitials at the tetrahedral site \((I_{tetra-2} \text{ and } I_{tetra-4})\) are not stable. For Mo\(^1\), the three Mo atoms that form the bottom surface of the tetrahedron are moved up, and the Ge atom of the vertex of the tetrahedron is moved down. For Mo\(^2\), three Mo atoms that form the bottom surface are moved down, and the Mo atoms of the vertex is moved up. Interstitial atoms Mo at different tetrahedral interstitial sites \((I_{tetra-2} \text{ and } I_{tetra-4})\) are moved up.

Among all interstitials, the Ge atom with only one stable interstitial position is observed at the triangle site \((I_{tri-3})\) in the Ge plane with a formation energy of 4.31 eV. The distance between \(I_{tri-3}\) and its nearest Ge atoms is 2.257 Å. The octahedral position \((I_{oct-1})\) is not stable, where the Ge atom will move to the adjacent \(I_{tri-3}\) site after relaxation. It shows that Ge\(^1\) is more favorable. The Ge interstitial at the octahedral site \((I_{oct-2} \text{ and } I_{oct-4})\) is not stable after relaxation. For Ge\(^2\), three Mo atoms that form the bottom surface of the tetrahedron and the Ge interstitial atom are moved up, while the Ge atom of the vertex for the tetrahedron is moved down. For Ge\(^3\), three Mo atoms that form the bottom surface are moved down.

### Table II. The values of \(a, c, V, \Delta V,\) and \(E_f\) for vacancy defects.

| Phase     | \(a\)  | \(c\)  | \(V\)  | \(\Delta V\) | \(E_f\) |
|-----------|--------|--------|--------|-------------|--------|
| \text{MoGeC} | 3.12   | 12.62  | 106.58 | \ldots      | \ldots |
| \text{MoGeC(Mo)} | 3.10   | 12.62  | 105.25 | -1.33       | 0.998  |
| \text{MoGeC(Ge)} | 3.11   | 12.56  | 105.20 | -1.38       | 1.178  |
| \text{MoGeC(C)}  | 3.10   | 12.58  | 104.76 | -1.82       | -0.353 |

### Table III. The formation energy of \(I_{oct-1}, I_{tetra-2}, I_{tri-3},\) and \(I_{tetra-4}\) for Mo, Ge, and C.

| Atomic layer | \(I_{oct-1}\) | \(I_{tetra-2}\) | \(I_{tri-3}\) | \(I_{tetra-4}\) |
|--------------|---------------|----------------|---------------|---------------|
| Mo           | 3.99          | Unstable       | 4.09          | Unstable      |
| Ge           | Unstable      | Unstable       | 4.31          | Unstable      |
| C            | 3.51          | Unstable       | 4.33          | Unstable      |

### Table IV. Values of \(a, c, V,\) and \(\Delta V\) for \text{MoGeC}, Mo\(^1\), Mo\(^2\), Ge\(^1\), C\(^1\), and C\(^2\).

| Phase     | \(a\)  | \(c\)  | \(V\)  | \(\Delta V\) |
|-----------|--------|--------|--------|-------------|
| \text{MoGeC} | 3.12   | 12.62  | 106.58 | \ldots      |
| Mo\(^1\)   | 3.21   | 12.55  | 111.76 | 5.18        |
| Mo\(^2\)   | 3.17   | 12.83  | 111.99 | 5.41        |
| Ge\(^1\)   | 3.20   | 12.51  | 111.05 | 4.47        |
| C\(^1\)    | 3.11   | 12.95  | 108.22 | 1.64        |
| C\(^2\)    | 3.14   | 12.61  | 107.92 | 1.43        |
while the Mo atoms of the vertex and the Ge interstitial atom are moved up.

As for the C interstitial in Mo₂GeC, the stable interstitial positions are the octahedral position (I_{oct-1}) and the triangle site (I_{tri-3}) with a formation energy of 3.51 eV and 4.33 eV, respectively. For the octahedral position, the C interstitial atom occupies the center of the octahedral and forms C–Ge bonds with its nearest Ge atoms with a bond length of 2.062 Å, while the distance between C and the nearest Mo atoms is 2.182 Å. For the triangle site, C is located at the center of the triangle and forms three C–Ge bonds with three Ge atoms with a distance of 2.002 Å. The ordering of C stable interstitial’s formation energy is C_i^1 < C_i^3, and it can be noted from the result that formation of C_i^1 is more difficult. The C interstitial at the tetrahedral site (I_{tetra-2}, I_{tetra-4}) is not stable. For C_i^2, the three Mo atoms that form the bottom surface of the tetrahedron are moved up, while the C atom of the vertex for the tetrahedron is moved down. For C_i^3, the three Mo atoms that form the bottom surface are moved down, while the Mo atom of the vertex is moved up. Both interstitial atoms at different octahedral interstitial sites are moved up.

In Table IV, the values of volume and the lattice constant are provided after full structural relaxation. We can see from the results that formation volumes are all positive, so these interstitials lead to the expansion of the crystal size. The reason for formation volumes are all positive and can be attributed to the fact that the self-interstitial shows a strong repulsion with neighboring atoms. For all interstitials, formation energies are all positive, which indicates that interstitials cannot incorporate spontaneously at the interstitial position, which also infers that the formation of the self-interstitial is quite difficult in Mo₂GeC.

### 3. Antisite formation energy

Structural disorder caused by accumulation of point defects is the main consequence of radiation damage. The main factor preventing amorphization is the ability to adapt to structural disorder, and formation energies of cation antisite pairs can be used to judge the resistance to radiation-induced amorphization. Due to the important role of antisite pairs’ defect in the radiation properties of MAX phases, we calculated the formation energy and lattice constant of antisite pairs’ defect for Mo₂GeC, as shown in Table V. Since the Mo layer is adjacent to C and Ge layers, we mainly focus on the formation energy between the nearest Mo–C and Mo–Ge atom pairs. We can find all the formation energies of antisite defects to be positive, which means the defects are not easily formed. Meanwhile, the existence of antisite defects leads to volume expansion.

The formation energies of antisite pairs are 2.63 eV and 3.00 eV for Mo₃Mo + Ge₃Ge → Mo₃Ge + Ge₃Mo and Mo₃Mo + C₃C → Mo₃C + C₃Mo, respectively. Therefore, the most likely antisite pair to form in the case of radiation is Mo₃Mo + Ge₃Ge → Mo₃Ge + Ge₃Mo for Mo₂GeC. For MAX phases, cation antisite pairs are associated with M–A antisite pairs, and their formation energy has proved to be useful for estimating MAX phases’ radiation damage tolerance. Xiao et al. theoretically observed that the most possible antisite pairs are M_i → A_M for Ti₃SiC₂ (3.52 eV), Ti₃AlC₂ (3.13 eV), Cr₂AlC (2.40 eV), Cr₂GeC (4.04 eV), Ti₃AlC (2.96 eV), and Ti₃AlN (2.52 eV). These low formation energies indicate that antisite pairs are beneficial to the radiation tolerance of these compounds, and they provide an additional channel to accommodate radiation-induced point defects.

From the previous literature, we know that electronegativity differences between cation elements M and A are strongly related to the corresponding antisite formation energies and the formation energy of M–A increases with increasing electronegativity difference. The electronegativity difference between Ge and Mo atoms is 0.15, and this may be the reason for the formation energy of Mo–Ge to be relatively small. Hence, we can also conclude that Mo₂GeC should have a good irradiation tolerance. This result requires verification through experiments.

### 4. Frenkel pair formation energy

The formation of Frenkel defects is due to the thermal vibration of atoms on the lattice. Some atoms with a higher energy leave the normal position, enter the gap, and become interstitial atoms, leaving the original position vacant. We have studied the formation energy and lattice constant of Frenkel defects for Mo₂GeC, as provided in Table VI. For Mo₂GeC, the existence of Frenkel defects expands the structure, and the Mo Frenkel defect exhibits the largest change. Formation of Mo₂FP causes a Mo atom to leave its original position and move to an octahedral, which is surrounded by three Ge and three Mo atoms. However, Mo is not located at the center of the octahedron but slightly moves down 0.03 Å in the Z-axis direction relative to the center position. The existence of Ge₂FP makes a Ge atom leave its original position, move to the center of a triangle containing three Ge atoms, and form three Ge–Ge bonds with a bond length of 2.251 Å with the surrounding Ge atoms. For C₂FP, after optimization, C returns to the original lattice position, so it cannot exist stably. Table VI also shows the formation energy of Frenkel defects. The formation energy for Mo₂FP and Ge₂FP are 5.52 eV and 5.82 eV, respectively. We can see that all values are positive, which indicates that the formation of Frenkel defects for Mo₂GeC is relatively difficult.

### B. Effect on electronic properties

In the past few years, many criteria were proposed to explain the stability of defects. From the experimental results, we can

| TABLE VI: Values of a, c, V, ΔV, and E_f for Frenkel pair defects. |
|---------------------|-----------------|-----------------|-----------------|-----------------|
| Phase              | a    | c    | V – V₀ | E_f  |
| Mo₂GeC            | 3.12 | 12.62| 106.58 | 3.60 |
| Mo₃Mo + Ge₃Ge → Mo₃Ge + Ge₃Mo | 3.09 | 12.98| 107.61 | 1.03 |
| Mo₃Mo + C₃C → Mo₃C + C₃Mo | 3.11 | 13.24| 109.55 | 2.97 |

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conclude that the nature of interatomic bonding is an important factor.\textsuperscript{12,32} In order to better understand the electronic properties of materials when defects occur, we calculated the total density of states (TDOS) of perfect and defect Mo\textsubscript{2}GeC as well as the projected density of states (PDOS). DOS is quite helpful to deeply understand the electronic structure and nature of atomic bonding of the MAX phase. The valence electron states of Mo, Ge, and C were set to 4p\textsuperscript{6}4d\textsuperscript{5}5s\textsuperscript{1}, 4s\textsuperscript{2}4p\textsuperscript{2}, and 2s\textsuperscript{2}2p\textsuperscript{2}, respectively.

First, we studied the electronic structure of stoichiometric Mo\textsubscript{2}GeC. Figure 2 shows the density of states of Mo\textsubscript{2}GeC without defects. The non-zero density of states at the Fermi level validates the metallic nature of Mo\textsubscript{2}GeC. The results also show that the states in the vicinity of \(E_f\) are dominated by Mo’s d-orbital, which contribute to electronic conductivity.\textsuperscript{33} The contribution of the Ge atom to the Fermi level is slight, and it is almost negligible for the C atom. The results are in agreement with other previous calculations.\textsuperscript{16} It can also be seen from Fig. 2, near \(-6\) eV, that Mo’s d-orbital overlaps with the C’s p-orbital and they also have strong hybridization, while C’s s-orbital and Mo’s d-orbital have hybridization in the energy range of \(-14\) eV to \(-11.20\) eV. The hybridization lying in the largest energy range of \(-2.56\) eV to \(-4.61\) eV originates mainly from Ge’s p-orbital and Mo’s d-orbital, which suggests a relatively weaker bond than Mo–C. This indicates the formation of a strong bond and strong interaction between C and Mo, and Ge and Mo, so Mo\textsubscript{2}GeC shows a covalent feature.

### 1. Density of states of mono-vacancy

Figure 3 shows the calculated DOS of mono-vacancy defects. It can be seen that the existence of vacancy has little effect on the density of states. The hybridization of bonding is almost unchanged. In order to clearly understand the change in the density of states of Mo\textsubscript{2}GeC with or without defects, we listed the total density of states at \(-12\) eV, \(-5\) eV, and the Fermi level in Table VII. From Fig. 3 and Table VII, we find that, compared with the density of states for perfect Mo\textsubscript{2}GeC, the change in the DOS for Mo vacancy is the most obvious. The formation of Mo vacancy results in a significant decrease in the density of states around \(-12\) eV, which is mainly due to the decrease in Mo-4d.\textsuperscript{11,34} It is noted that the hybridization energy peak around \(-5\) eV has reduced because of vacancy defects, especially for C vacancy. The reason is that the number of Mo–C bonds is reduced. Among the vacancies, the most obvious decrease in the density of states at the Fermi level is Ge vacancy, so the existence of Ge vacancy has the greatest impact on conductivity. On the contrary, when a single Mo vacancy is formed, adjacent atoms near the center of the vacancy combine with other adjacent atoms, and within the same energy range, the reduction in the energy peak of hybridization is minimal. Meanwhile, there is a pseudo-gap around the Fermi level, which appears for C vacancy. This means that C vacancy is relatively stable, which is in agreement with its lowest formation energy.

### 2. Density of states of interstitials

As for self-interstitial defects, we only show the density of states for stable defects, including Mo\textsubscript{i}, Ge\textsubscript{i}, and C\textsubscript{i}. Figure 4 shows the DOS for three stable interstitials. From Table VIII, we can clearly obtain a result that the presence of all interstitials increases the density of states at the Fermi level, so the existence of interstitials enhances the conductivity of the material. Compared with Mo\textsubscript{i} and C\textsubscript{i}, the production of Ge\textsubscript{i} results in a larger change for the density of states of the Fermi level. It is noted that there is a small
isolated peak at the point of $-13.5$ eV for the $C_{1i}$, which is attributed to the C-2s orbital. Meanwhile, the energy peak of $Mo_{1i}$, $Ge_{3i}$, and $C_{1i}$ around $-5$ eV slightly drops. Therefore, if there is an interstitial, the bond between atoms will be changed. $C_{1i}$ caused a small pseudo-gap energy at the Fermi surface, indicating that its structure is relatively stable, which is consistent with the result of the low formation energy mentioned.

3. Density of states of antisites

The density of states was calculated to observe the change when antisites are formed. Figure 5 shows the density of states for antisites. It can be found that these two defects lead to the reduction in the density of states at the Fermi level. Meanwhile, as soon as antisites are introduced, the energy peak at $-12$ eV is decreased, especially for the Mo–Ge antisite pair. According to Table IX, we can find that the TDOS of the Mo–C antisite pair at the Fermi level is smaller than the TDOS of the Mo–Ge antisite pair. It means that when the Mo–C antisite pair occurs, the conductivity of Mo$_2$GeC will be significantly reduced, while the Mo–Ge antisite pair has a relatively small effect on the conductivity of Mo$_2$GeC. It is noted that the hybridization between the C-2p and Mo-4d orbital lightly reduces. In addition, a wide pseudo-gap energy around the Fermi level appears for the Mo–Ge antisite pair, which suggests that the Mo–Ge antisite pair has a relatively stable configuration. This is in agreement with its lowest formation energy.

4. Density of states of the Frenkel pair

In order to disguise the effect of various Frenkel pairs on the electronic structure, we calculated the DOS, as shown in Fig. 6. We can see that the introduction of Mo$_{FP}$ and Ge$_{FP}$ has a significant influence on the DOS of Mo$_2$GeC. Meanwhile, we have listed the

![FIG. 4. The density of states (DOS) of (a) perfect Mo$_2$GeC, (b) the Mo interstitial, (c) the Ge interstitial, and (d) the C interstitial.](image)

![FIG. 5. (a) The density of states (DOS) of perfect Mo$_2$GeC, (b) Mo–Ge antisites in Mo$_2$GeC, and (c) Mo–C antisites in Mo$_2$GeC.](image)

![FIG. 6. (a) The density of states (DOS) of perfect Mo$_2$GeC, (b) the Mo Frenkel pair in Mo$_2$GeC, and (c) the Ge Frenkel pair in Mo$_2$GeC.](image)
that there is a small isolated peak at the point of 
result of low formation energy mentioned. In addition, it is noted 
that their structures are relatively stable, which is consistent with the 
pair caused a small pseudo-gap energy at the Fermi level, indicating 
formation energy of Ge
is most likely to be initiatively produced. This result also shows that 
the C vacancy defect is negative, indicating that the C vacancy defect 
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Defects have a certain effect 
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