Composition and temperature dependences of site occupation for Al, Cr, W, and Nb in $MoSi_2$*

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The composition and temperature dependences of site occupation for Al, Cr, W, and Nb in $MoSi_2$ are investigated by using a thermodynamics model and first principles calculations. A simple parameter measuring the substitution energy difference between Si and Mo sites reflects the nature of site occupancy. At 0 K, these elements prefer Si sites in Mo-rich and Mo sites in Si-rich, and show no site preference in stoichiometric $MoSi_2$. At elevated temperature, the site occupation behaviors show strong dependence on both composition and temperature. Some calculated results have been certified in previous experiments.

Keywords: molybdenum silicides, site occupancy, first principles calculations

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1. Introduction

Molybdenum disilicide ($MoSi_2$) is a promising candidate material for high temperature structural applications, such as in aircraft gas turbine engines, for its high melting temperature ($T_m = 2293$ K), relatively low density, excellent high temperature oxidation resistance, and high thermal conductivity.[1–5] However, $MoSi_2$ has a low fracture toughness at room temperature (2 MPa·$m^{1/2}$–3 MPa·$m^{1/2}$) and low creep strength at elevated temperature. It is observed that the creep stress exponents of polycrystalline $MoSi_2$ with different grain sizes under stress 50 MPa–200 MPa at 1473 K are in a range of 2–9,[6] and the creep activity energy is about 430 kJ/mol.[7] The creep resistance of $MoSi_2$ drops sharply beyond 1473 K due to enhanced plasticity from the activation of more than five independent slip systems.[6] These disadvantages greatly hinder the applications of $MoSi_2$ for load-bearing, hot section components.

It has been recently reported that these mechanical properties can be improved by alloying with certain elements, such as Al,[8–10] Cr,[11–13] W,[14,15] and Nb.[13,15–18] The addition of Al is found to reduce the yield strength of $MoSi_2$ at all temperatures, improve the low temperature deformability,[19] and increase to 4 MPa·$m^{1/2}$∼6 MPa·$m^{1/2}$ in fracture toughness at room temperature.[20] The addition of Cr has no obvious effect on the fracture toughness,[21] but can increase the yield strength at high temperatures (above 1573 K). Moreover, the additions of A1 and Cr can prevent and mitigate the pesting oxidation due to these elements having a strong affinity to oxygen.[21] W can increase the yield strength at all temperatures, and reduce effectively the high temperature (1473 K) creep rate.[22] Nb was found to be the most potent alloying element in improving the mechanical properties of $MoSi_2$.[23] Nb is the most effective in improving the low temperature deformability and high temperature strength of $MoSi_2$, and can increase obviously fracture toughness.[19]

Site occupancy behaviors of these ternary elements are believed to be critical in achieving the improvement. Owing to the extreme difficulty in directly characterizing point defects in an experiment, first-principles approaches[24–27] have emerged in recent years as an indispensable tool to provide useful insights into point defect thermodynamics.[28–31] In this paper, we focus on the site occupancy preference and thermodynamic equilibrium concentrations of Al, Cr, W, and Nb in $C11_b$ $MoSi_2$, particularly as a function of temperature and alloy composition, through integrating the statistical mechanical thermodynamics model and first-principles calculations.

2. Computational methods

All first-principles calculations are performed based on density functional theory (DFT) as implemented in the VASP code.[32,33] The electron-core interaction is described by the projector augmented wave method (PAW)[34] within the frozen-core approximation. According to our previous work,[28] the generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE)[35] approach is regarded as an appropriate exchange-correlation functional and then em-

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ployed in this work. The plane-wave basis sets are generated with valence configurations of Mo-$4p^6 4d^5 5s^1$, Si-$3s^2 3p^2$, Al-$3s^2 3p^1$, Cr-$3d^5 4s^1$, W-$5p^6 6s^2 5d^4$, and Nb-$4s^2 4p^6 5s^1 4d^4$, respectively. The plane wave cutoff energy of 400 eV was found to be sufficient and also efficient in our previous work,[28] and thus is used throughout this work. The computations are performed based on a 48-atom $2\times2\times2$ periodic simulation cell. In order to test the cell size effects, we also calculate the formation enthalpies of isolated point defects within a 162-atom $3\times3\times3$ periodic cell. The obtained formation enthalpies of Mo vacancy, Mo anti-site, Si vacancy and Si anti-site are 3.628 eV, 3.535 eV, 5.440 eV, and 2.343 eV, respectively. These values are all slightly higher than 3.536 eV, 3.470 eV, 5.309 eV, and 2.310 eV of the 48-atom system reported in our previous work.[28] These differences are generally less than 0.1 eV except for the Si vacancy (0.131 eV), and it indicates that the 48-atom cell is sufficient to give converged results. Moreover, the 32-atom system and even a system with less atoms have been used in other studies, such as Refs. [29] and [30], and it has been proved that the results of the $2\times2\times2$ periodic simulation cell in the statistic model are acceptable and credible. In this work, the point defect calculations are performed within a 48-atom (16Mo, 32Si) $C11_b$ $MoSi_2$ conventional supercell with an $8\times8\times3$ Monkhorst–Pack k-mesh[36] for the Brillouin zone integration. During calculations, both cell parameters and internal parameters are relaxed simultaneously to minimize the Hellman–Feymann force on each atom with a tolerance value of 0.02 eV/Å.

$MoSi_2$ has a body-centered tetragonal $C11_b$ structure up to 1900 °C (space group $I4/mmm$). A unit cell of $C11_b$ $MoSi_2$ consists of two Mo and four Si atoms, with Mo located at the Wyckoff $2a$ site (0,0,0) and Si at the $4e$ site $(0,0,u)$. The lattice parameters have been experimentally determined to be $a=3.2056$ Å, $c=7.8450$ Å, and $u=0.3353$ c.[37] Point defects in $C11_b$ $MoSi_2$ can be assumed to be sufficiently dilute, which allows the Wagner–Schottky model[30,31,38] to be used to predict the point defect concentrations and other relevant thermodynamic functions.

3. Results and discussion

According to the Wagner–Schottky assumption, the formation energy of the compound depends linearly on defect concentration, or alternatively, the formation enthalpies of point defects can be obtained by finite differencing from fully-ordered stoichiometric $MoSi_2$ as[28–31,38]

$$H_{i_\alpha}=\frac{\Delta H_{\rm def}-\Delta H_{\rm perf}}{c_{i_\alpha}}, \tag{1}$$

where H_{i_α} is the formation enthalpy of species i on the a sublattice with $a=\{\text{Mo, Si}\}$ and $i=\{\text{Mo, Si, }V\text{, }X\}$ (here V denotes vacancy, and X represents the alloying element, such as Al, Cr, W, and Nb), $\Delta H_{\rm def}$ is the formation enthalpy (per formula unit) of a 48-atom $C11_b$ $MoSi_2$ conventional supercell containing a single point defect ($V_{\rm Mo}$, $V_{\rm Si}$, $\rm Mo_{Si}$, $\rm Si_{Mo}$, $X_{\rm Mo}$, and $X_{\rm Si}$), $\Delta H_{\rm perf}$ is the formation enthalpy of a perfectly ordered defect-free $MoSi_2$ in its $C11_b$ structure, and c_{i_α} is the concentration of species i on a sublattice. Note that $c_{i_\alpha}=1/48$ for an anti-site defect or a ternary substitution, and 1/47 for a vacancy in the 48-atom supercell.

For a doped $MoSi_2$, $\Delta H_{\rm def}$ depends sensitively on doping concentration. The formation enthalpy of $\rm Mo_pSi_qX_r$ with an arbitrary composition can be calculated as

$$\Delta H_{\rm Mo_pSi_qX_r}=\frac{1}{p+q+r}(E_{\rm Mo_pSi_q}-p\times E_{\rm Mo}-q\times E_{\rm Si}-r\times E_X), \tag{2}$$

where $E_{\rm Mo}$, $E_{\rm Si}$, E_X, and $E_{\rm Mo_pSi_qX_r}$ are, respectively, the calculated total energies of pure Mo, Si, X, and the doped compound $\rm Mo_pSi_qX_r$; p, q, and r are the molar compositions of Mo, Si, and X. The formation enthalpies of isolated point defects used in the present calculation are listed in Table 1. In Table 1, the formation enthalpies of Si anti-site ($\rm Si_{Mo}$), Mo anti-site ($\rm Mo_{Si}$), Mo-vacancy ($V_{\rm Mo}$), and Si-vacancy ($V_{\rm Si}$) have been calculated in our previous work,[28] and the formation enthalpies of two site occupations for Al, Cr, W, and Nb are calculated in this work. From Table 1, we find that the calculated formation enthalpies are relatively high, and it may be related to the strong covalent bonds caused by the hybridization of Mo-4d and Si-3p orbitals.[28]

Micro-changes of the point defect concentrations correspond to some defect reactions, and these defect reactions can be described by

$$V_{\rm Mo}+\rm Si_{Si}\rightarrow V_{Si}+Si_{Mo}, \tag{3a}$$

$$V_{\rm Si}+\rm Mo_{Mo}\rightarrow Mo_{Si}+V_{Mo}, \tag{3b}$$

$$V_{\rm Si}+X_{\rm Mo}\rightarrow X_{\rm Si}+V_{\rm Mo}, \tag{3c}$$

$$0\rightarrow V_{\rm Mo}+2V_{\rm Si}. \tag{3d}$$

The equilibrium concentrations of point defects can be estimated by minimizing the Gibbs free energy of the system,[28–31] i.e. $\min(\Delta G)=\min(\Delta H-T\Delta S)$, in which the entropy is considered in our work according to the method in

Table 1. Formation enthalpies of isolated point defects of stoichiometric $C11_b$ $MoSi_2$ used in the present calculation (in units of eV).

Designation	$V_{\rm Mo}$	$V_{\rm Si}$	$\rm Mo_{Si}$	$\rm Si_{Mo}$	$\rm Al_{Mo}$	$\rm Al_{Si}$	$\rm Cr_{Mo}$	$\rm Cr_{Si}$	$\rm W_{Mo}$	$\rm W_{Si}$	$\rm Nb_{Mo}$	$\rm Nb_{Si}$
Formation enthalpy	3.54	2.31	3.47	5.31	3.79	0.19	0.72	2.88	0.53	3.76	0.25	2.70

Refs. [30], [31], [39]–[42]. This procedure leads to a set of non-linear equations as follows:

$$\frac{3c_{V_{\rm Si}}c_{{\rm Si}_{\rm Mo}}}{c_{V_{\rm Mo}}(2-3c_{{\rm Mo}_{\rm Si}}-3c_{X_{\rm Si}}-c_{V_{\rm Si}}+2c_{V_{\rm Mo}})}=\exp\left(-\frac{H_{\rm A}}{k_{\rm B}T}\right), \quad (4a)$$

$$\frac{3c_{V_{\rm Mo}}c_{{\rm Mo}_{\rm Si}}}{c_{V_{\rm Si}}(1-3c_{{\rm Si}_{\rm Mo}}-3c_{X_{\rm Mo}}+c_{V_{\rm Si}}-2c_{V_{\rm Mo}})}=\exp\left(-\frac{H_{\rm B}}{k_{\rm B}T}\right), \quad (4b)$$

$$\frac{c_{X_{\rm Si}}c_{V_{\rm Mo}}}{c_{X_{\rm Mo}}c_{V_{\rm Si}}}=\exp\left(-\frac{H_{\rm C}}{k_{\rm B}T}\right), \quad (4c)$$

$$\frac{27c_{V_{\rm Mo}}c_{V_{\rm Si}}^2}{4(1+c_{V_{\rm Si}}+c_{V_{\rm Mo}})^3}=\exp\left(-\frac{H_{\rm D}}{k_{\rm B}T}\right), \quad (4d)$$

$$c_{{\rm Mo}_{\rm Si}}-c_{{\rm Si}_{\rm Mo}}-c_{X_{\rm Mo}}+\frac{1+c_{V_{\rm Si}}-2c_{V_{\rm Mo}}}{3}=c_{\rm Mo}, \quad (4e)$$

$$c_{X_{\rm Si}}+c_{X_{\rm Mo}}=c_X, \quad (4f)$$

where c_{i_α} is the concentration of species i on a sublattice; $k_{\rm B}$ is the Boltzmann's constant; T is the investigated temperature; $c_{\rm Mo}$ and c_X are the concentrations of Mo and alloying element X (Al, Cr, W, and Nb), respectively; $H_{\rm A}$, $H_{\rm B}$, $H_{\rm C}$, and $H_{\rm D}$ are the enthalpy changes of the defect reactions (Eq. (3)), and can be expressed as the following equations:

$$H_{\rm A}=H_{{\rm Si}_{\rm Mo}}-H_{V_{\rm Mo}}+H_{V_{\rm Si}}, \quad (5a)$$

$$H_{\rm B}=H_{{\rm Mo}_{\rm Si}}+H_{V_{\rm Mo}}-H_{V_{\rm Si}}, \quad (5b)$$

$$H_{\rm C}=H_{X_{\rm Si}}-H_{X_{\rm Mo}}-H_{V_{\rm Si}}+H_{V_{\rm Mo}}, \quad (5c)$$

$$H_{\rm D}=2H_{V_{\rm Si}}+H_{V_{\rm Mo}}. \quad (5d)$$

Here, H_{i_α} is the formation enthalpy of species i on a sublattice, and listed in Table 1. Because of the influence of the occupation on two different sublattice sites of alloying elements, we find that equation (4) in this work is more complex than the non-linear equations in Ref. [28]. The numerical solution of Eq. (4) predicts the equilibrium concentrations of all types of point defects for a given composition at a given temperature. The fraction of X in the Mo sublattice is defined as $c_{X_{\rm Mo}}/(c_{X_{\rm Mo}}+c_{X_{\rm Si}})$, and it can reflect the site preference of the X atom. If $c_{X_{\rm Mo}}/(c_{X_{\rm Mo}}+c_{X_{\rm Si}})<1/3$, X tends to occupy the Si sublattice; if $c_{X_{\rm Mo}}/(c_{X_{\rm Mo}}+c_{X_{\rm Si}})>1/3$, X tends to occupy the Mo sublattice; if $c_{X_{\rm Mo}}/(c_{X_{\rm Mo}}+c_{X_{\rm Si}})=1/3$, X tends to occupy randomly both Mo and Si sublattices.

According to Refs. [30] and [31], the site preferences of ternary alloying elements in $C11_b$ $MoSi_2$ at $T=0$ K are governed by enthalpy only. The 0 K site occupancy behaviors of substitutional ternary elements in $C11_b$ $MoSi_2$ can be classified into the following three general types:

(i) $H_{X_{\rm Mo}}+H_{{\rm Mo}_{\rm Si}}-H_{X_{\rm Si}}<0$: X tends to occupy the Mo sublattice site due to the thermal excitation $X_{\rm Si}+{\rm Mo}_{\rm Mo}\rightarrow X_{\rm Mo}+{\rm Mo}_{\rm Si}$.

(ii) $H_{X_{\rm Mo}}+H_{{\rm Mo}_{\rm Si}}-H_{X_{\rm Si}}>H_{{\rm Mo}_{\rm Si}}+H_{{\rm Si}_{\rm Mo}}$ (or $H_{X_{\rm Mo}}-H_{X_{\rm Si}}-H_{{\rm Si}_{\rm Mo}}>0$): X tends to occupy the Si sublattice site due to the thermal excitation $X_{\rm Mo}+{\rm Si}_{\rm Si}\rightarrow X_{\rm Si}+{\rm Si}_{\rm Mo}$.

(iii) $0<H_{X_{\rm Mo}}+H_{{\rm Mo}_{\rm Si}}-H_{X_{\rm Si}}<H_{{\rm Mo}_{\rm Si}}+H_{{\rm Si}_{\rm Mo}}$: The site preference of X is composition-dependent. X prefers the Si sublattice sites in Mo-rich and the Mo sublattice sites in Si-rich, and shows no site preference in stoichiometric $C11_b$ $MoSi_2$ where X randomly occupies both Mo and Si sublattices.

Therefore, using a simple parameter defined as $E_X^{{\rm Si}\rightarrow{\rm Mo}}=H_{X_{\rm Mo}}+H_{{\rm Mo}_{\rm Si}}-H_{X_{\rm Si}}$ can be sufficient to determine the 0-K site preference nature of any ternary element in $C11_b$ $MoSi_2$. Essentially, the parameter $E_X^{{\rm Si}\rightarrow{\rm Mo}}$ characterizes the energy cost associated with the transfer of an X atom from an Si site to an Mo site in $MoSi_2$, in accordance with the reaction: $X_{\rm Si}+{\rm Mo}_{\rm Mo}\rightarrow X_{\rm Mo}+{\rm Mo}_{\rm Si}$. Figure 1 shows our first-principles calculated $E_X^{{\rm Si}\rightarrow{\rm Mo}}$ values for ternary elements (Al, Cr, W, and Nb) in $C11_b$ $MoSi_2$. The formation energy of an antisite defect pair in $C11_b$ $MoSi_2$, i.e., $H_{{\rm Si}_{\rm Mo}}+H_{{\rm Mo}_{\rm Si}}$, is calculated to be 8.78 eV. This value of $E_X^{{\rm Si}\rightarrow{\rm Mo}}$ would differentiate between the site preference behaviors (type-II and type-III) of X in $C11_b$ $MoSi_2$. According to Fig. 1, doping $MoSi_2$ with Al, Cr, W, or Nb shall fall into type-III at 0 K. In other words, the site preferences of these elements are all composition dependent when the temperature effect can be ignored.

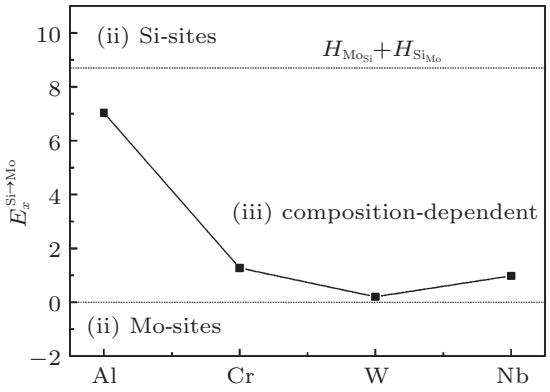


Fig. 1. Classifications of the 0-K site preference behavior of Al, Cr, W, and Nb in $C11_b$ $MoSi_2$ according to the parameter $E_X^{{\rm Si}\rightarrow{\rm Mo}}$.

At elevated temperatures, we adopt the statistical–mechanical thermodynamics model in combination with first-principles formation enthalpies to revisit the site preference problem. The site preferences of these ternary elements at elevated temperature are sensitively dependent on the composition of $MoSi_2$. The equilibrium partitioning of ternary elements between Mo and Si sites is predicted as a function of concentrations at $T=1873$ K, and the results for Mo-rich, Si-rich, and stoichiometric $C11_b$ $MoSi_2$ are compared in Fig. 2. The horizontal dashed lines represent the case of type-III (no site preference), i.e., X atoms can randomly occupy both Mo and Si sites. As seen for Si-rich $C11_b$ $MoSi_2$ in Fig. 2(a), Cr, W, and Nb all tend to substitute only for the Mo sublattice in $MoSi_2$. The number fraction of $X_{\rm Mo}$ (X = Cr, W, and Nb) reaches almost 1 at any concentration of interest. Al also shows strong Mo-site preference in Si-rich $MoSi_2$, but the initial fraction of $Al_{\rm Mo}$ is ~0.6 only. Its strong preference

becomes more prominent with increasing the Al concentration. These conclusions have been approved by many available studies. Our previous experiments[13] have proposed the Mo-site preferences of Cr and Nb for Si-rich alloy. Feng *et al.*[11] have also shown that the intensity of C40-type $(Mo_{1-x}Cr_x)Si_2$ phase diffraction peaks gradually increases with the increase of Cr content of a Si-rich alloy in the mode of self-propagating high-temperature synthesis. Xu *et al.*[21] have reported the Mo-site preference of Cr detected by x-ray diffraction in a Si-rich alloy (Cr-alloyed $MoSi_2$-based nanocomposite coatings). Meanwhile, Yang *et al.*[43] and Sharif *et al.*[23] have pointed out the Mo-site preference of Nb for Si-rich alloy with 1 at.% (atom percent) Nb and 5 at.% Nb by arc-melting at various high temperatures, respectively.

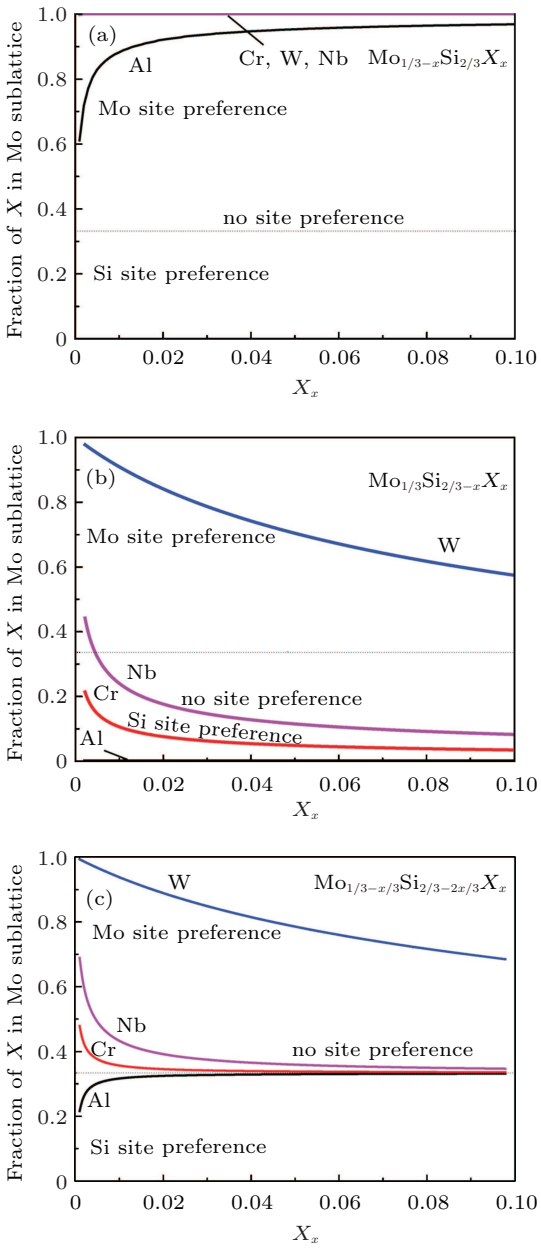


Fig. 2. (color online) Predicted fractions of X substitution in the Mo sublattice in (a) Si-rich, (b) Mo-rich, and (c) stoichiometric $C11_b$ $MoSi_2$ at 1873 K, as a function of X concentration.

The situation is totally different in Mo-rich $MoSi_2$ as seen in Fig. 2(b). Al, Cr, and Nb each have a predominant preference for the Si sublattice sites at all concentrations, while W has a strong tendency to substitute Mo. For each element, the Si-site preference increases rapidly with concentration increasing. Yanagihara *et al.*[44] have pointed out that Al prefers a Si site for Mo-rich alloy with 10 at.% Al prepared by arc-melting. Hou *et al.*[45] have also considered that $Mo(Si, Al)_2$ increased with increasing the content of Al for each of these Mo-rich alloys ($MoSi_2$-0, 15.3, 22, and 29.3 at.% Al coatings) prepared by electrothermal explosion ultrahigh speed spraying technology. Moreover, the Si-site preference of Al for Mo-rich alloy has been approved by a number of previous experiments.[46–49]

The most complicated situation is for the stoichiometric $C11_b$ $MoSi_2$ (Fig. 2(c)). At almost all concentrations, W has a strong site preference for Mo sublattices. Cr and Nb show a very weak Mo-site preference while Al shows a very weak Si-site preference. As the concentration increases, Cr, Nb, and Al tend to randomly substitute for both Mo and Si sites. Mitra and Rao[50] have shown that 3.1-at.% Al replaced Si in $MoSi_2$, forming a solid solution or $Mo(Si,Al)_2$ in the oxidation of $MoSi_2$–9 at.% Al alloy at 1200 °C. Xu *et al.*[51] have also reported the Mo-site preference of W detected by x-ray diffraction in a stoichiometric alloy prepared by a mechanical-assistant combustion synthesis method. The extensive experimental results show that WSi_2 also possesses the $C11_b$ structure and often forms a complete solid solution with $MoSi_2$, which can indicate the Mo-site preference of W for W-alloyed $MoSi_2$-based alloys with different stoichiometric ratios.[52]

Figure 3 further comparatively shows the site preference of 1 at.% X in $C11_b$ $MoSi_2$ at 1873 K, as a function of Mo concentration. The doped $Mo_xSi_{0.99-x}X_{0.01}$ is Si-rich for $x < 1/3$, and Mo-rich for $x > 1/3$. Clearly, at 1873 K, Al, Cr, and Nb can be classified as type-III elements, exhibiting strongly composition-dependent site preference at around $x = \sim 1/3$. The site preferences of Al, Cr or Nb change drastically when the compound deviates from its stoichiometric composition. The ternary element partitions into the Mo sublattice in the Si-rich composition range, and into the Si sublattice in the Mo-rich composition range. It is worth noting that W shows a consistent preference for the Mo sublattice over the whole composition range. Recall that the value of $E_W^{Si\to Mo}$ is very small and positive but nearly zero in Fig. 1, thus the site preference of W in $MoSi_2$ shows very weak composition dependence (i.e., the type-III behavior) at low temperature, but tends to follow the type-II behavior to substitute for Mo sites under the increased entropy effects at elevated temperatures. The conclusion again indicates the Mo-site preferences of W for W-alloyed $MoSi_2$-based alloys with different stoichiometric ratios, which are in accordance with the previous experimental results.[52]

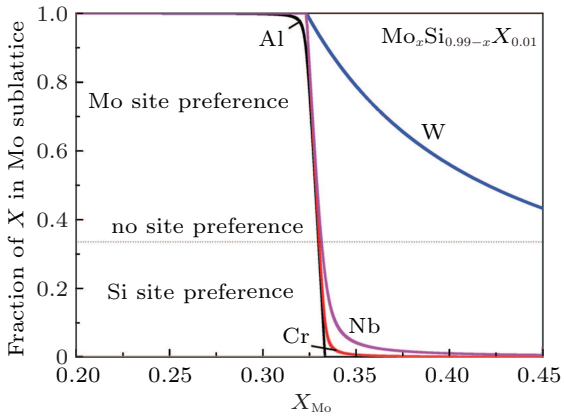


Fig. 3. (color online) Predicted site preferences of 1% X in $MoSi_2$ as a function of Mo concentration at 1873 K.

To manifest the temperature effect on site preference, we predict the equilibrium partitioning of 1% X between Mo and Si sites in the doped $MoSi_2$ as a function of temperature in Fig. 4. In Si-rich $MoSi_2$ (Fig. 4(a)), Al, Cr, W, and Nb each have a predominant preference for the Mo sublattice over the whole temperature range. The fraction of Al in the Mo sublattice starts to decrease rapidly above 1200 K. This happens because the value of $E_{Al}^{Si\to Mo}$ predicted at 0 K is so close to $H_{Si_{Mo}} + H_{Mo_{Si}}$ (see Fig. 1) that the entropy effect at high temperature facilitates the change of the site preference behavior from type-III to type-I. Just a few experimental data are available for the site preferences of ternary elements in $MoSi_2$ as a function of temperature. Sharif *et al.*[23] have also considered the case that Nb atoms occupied the Mo sublattices from 400 °C to 1600 °C for Si-rich alloy with 1 at.% Nb by arc-melting. In contrast, in Mo-rich $MoSi_2$ (Fig. 4(b)), Al has a predominant preference for the Si sublattice over the whole temperature range. The partition of Cr, W, and Nb to the Mo sublattice is strongly dependent on temperature. Cr, W, and Nb each show a preference for the Si sublattice at low temperatures, but start to choose Mo sites as temperature increases. In particular, the fractions of W and Nb in the Mo sublattice increase to such an extent that their preferences are reversed. The increase of the extent of X fractions in the Mo sublattice with increasing temperature follows the same ordering of $E_X^{Si\to Mo}$ values as seen in Fig. 1. Zhang *et al.*[53] have proposed that Al atoms occupied the Si sublattices determined by x-ray diffraction for Mo-rich alloy with 1 at.% Al prepared by direct current hot pressing from 1300 °C to 1700 °C. Dasgupta and Umarji[19] have considered the fact that Nb prefers the Mo site and Al prefers the Si site for a $MoSi_2$-based with 1 at.% Nb ($(Mo_{0.97}Nb_{0.03})(Si_{0.96}Al_{0.04})_2$) prepared by arc-melting at 1800 K. Finally, in stoichiometric $MoSi_2$ (Fig. 4(c)), all elements are partitioned randomly between Mo and Si sites at low temperatures. As the temperature increases, Cr, Nb, and W each show a preference for the Mo sublattice, while Al for the Si sublattice. In conclusion, the site preference behaviors show strong dependence on both composition and temperature at elevated temperature. Our conclusion is in good agreement with the available experimental data, and more experimental data are demanded in order to verify our proposed cause.

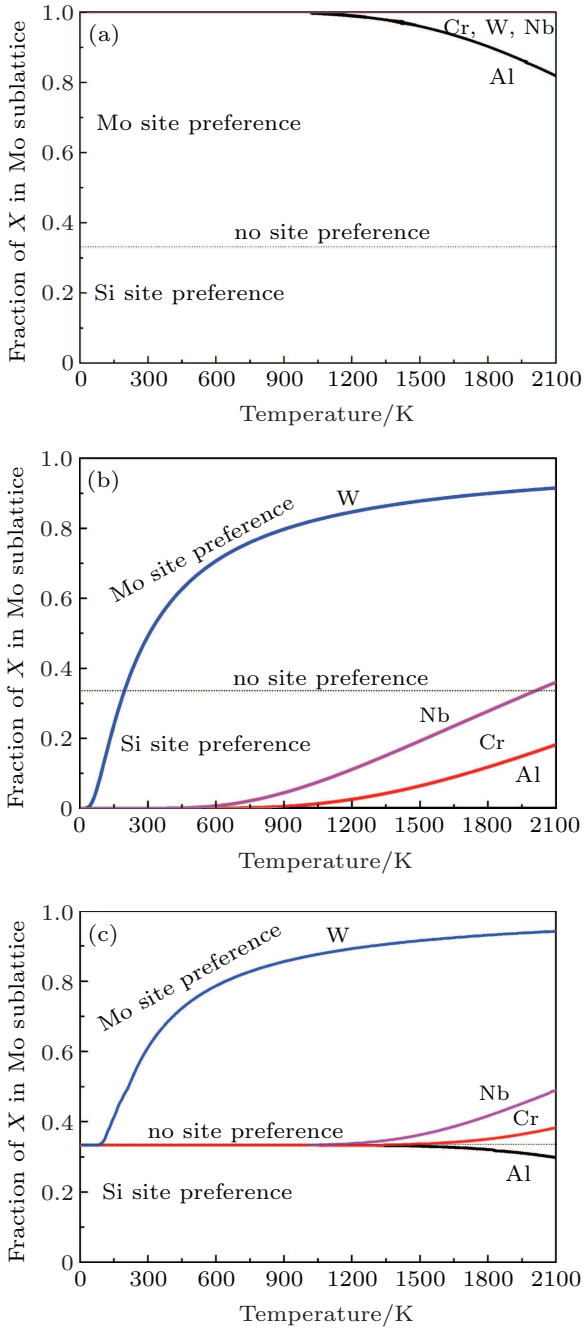


Fig. 4. (color online) Predicted site preferences of X in (a) Si-rich $Mo_{0.3233}Si_{0.6667}X_{0.01}$, (b) Mo-rich $Mo_{0.3333}Si_{0.6567}X_{0.01}$, and (c) stoichiometric $Mo_{0.33}Si_{0.66}X_{0.01}$, at different temperatures.

Site occupancy of alloying elements is related to the mechanical properties of $MoSi_2$. It is reported that the additions of alloying elements in $MoSi_2$ can improve the fracture toughness at room temperature, which is attributed to alloying elements weakening the Mo–Si bonds and introducing more metallic nature to the bonding.[54] The effects of these alloying substitutions on the service performance of $MoSi_2$ are desired to be developed in future work.

4. Conclusions

The site occupation behaviors of ternary elements (X = Al, Cr, W, and Nb) in $C11_b$ $MoSi_2$ are investigated as a function of composition and temperature by using first-principles calculations with the statistical mechanical thermodynamics model. A simple parameter defined as $E_X^{Si\to Mo} = H_{X_{Mo}} + H_{Mo_{Si}} - H_{X_{Si}}$ can be used for roughly estimating the nature of the site preference at high temperature. Our calculations manifest the strong composition and temperature dependence of the site occupation behaviors of these ternary elements in $C11_b$ $MoSi_2$. Some calculated results have been verified in previous experiments.

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