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Theoretical calculation on electronic excitation and compression effect in tungsten

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ABSTRACT

The vacancy formation enthalpy of tungsten under the condition of intense laser irradiation and compression has been investigated from first-principles, respectively. The results show that the monovacancy formation enthalpy of tungsten tends to increase as the electronic temperature is increased, which can explain the fact that the melting process becomes more difficult under high electronic temperature. In addition, the monovacancy formation enthalpy of tungsten is found to increase from 3.198 eV at 0 GPa to 4.184 eV at 100 GPa, which results in the retardation of diffusion under the condition of compression.

1. Introduction

It is a well-known fact that monovacancies and divacancies in metals have important influence on physical properties as diffusion [1,2], electrical conductivity [3] and heat capacity [4] of materials. Over the past few decades, a lot of investigations have been done to study the monovacancies of metals experimentally and theoretically [5–13]. Under compression or intense laser irradiation conditions, materials phenomena such as phase transformations where diffusion plays a key role often occur. Thus, it is necessary to investigate the effects of compression and intense laser irradiation on the monovacancy formation enthalpies of transition metals. Mukherjee et al. [14] investigated the pressure dependence of the enthalpy of vacancy formation in tantalum, the results showed that the value of the formation energy of monovacancy H_{vac} in tantalum increased with the increment of the external pressure. Using a molecular dynamics method, Jang et al. [15] investigated the effect of stress on self-diffusion in body-centered cubic Fe in 2010. By means of ab initio calculations, Bottin and Zérah [16] studied how the monovacancy formation enthalpies change in gold and aluminum at high electronic temperature. In our previous work [17], first-principle theory was carried out on metal tantalum to investigate the effect of electronic excitation on metal monovacancy formation enthalpies.

As far as we know, few investigations have been reported on the monovacancy of the formation enthalpy for tungsten at high pressure or under the intense laser irradiation. In order to investigate the influence of electronic excitation and high pressure on transition metals W, we perform finite-temperature DFT calculations on a lattice of W under the effect of electronic excitation and compression.

2. Computational method and technical details

2.1. Monovacancy formation enthalpy

A vacancy forms in an ideal lattice when an atom is removed from its bulk position and replaced in a new bulk lattice site. The value of vacancy formation enthalpy can be calculated by following formula:

$$H_f^v = E_f^v + V_f^v \times P \tag{1}$$

where E_f^v is the vacancy formation energy, V_f^v is the vacancy formation volume and P is the pressure. The value of E_f^v and V_f^v can be obtained by following equations:

$$E_f^v = E(N-1;1;P) - \frac{(N-1)}{N}E(N;0;P) \tag{2}$$

$$V_f^v = V(N-1;1;P) - \frac{(N-1)}{N}V(N;0;P) \tag{3}$$

where $E(N;0;P)$ and $V(N;0;P)$ are the energy and volume of an ideal supercell with N atoms at pressure P, respectively; while

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$E(N-1;\ 1;\ P)$ and $V(N-1;\ 1;\ P)$ are the energy and volume of a supercell with $N-1$ atoms and a vacancy at pressure P, respectively.

Based on the work of Hohenberg and Kohn, the DFT energy may be expressed in the form

$$E = E_k + E_{eZ} + E_H + E_{xc} + E_{ZZ} \quad (4)$$

The contributions of DFT energy depend on the electronic temperature T_e except the core–core interaction energy E_{ZZ}. Thus the DFT energy can be considered as a function of electronic temperature T_e.

Combined with above formulas (1)–(3), the vacancy formation enthalpy of transition metals under different electronic temperatures T_e and different pressures P can be obtained.

2.2. Technical details

In this paper, finite-temperature DFT calculations are performed on an ideal lattice of W involved different atoms with electronic temperature ranging from 0 to 5 eV and pressure ranging from 0 to 300 GPa, respectively. The generalized gradient approximation designed by Perdew, Burke, and Ernzerhof (PBE) [18–20] is adopted as the exchange–correlation function E_{xc}. The projector-augmented wave (PAW) method is employed to describe the interaction between ions and electrons by using the Vienna ab initio simulation package (VASP) [21–23]. A cutoff energy of 223 eV and a suitable Monkhorst–Pack mesh [24] of k points are used to obtain accurate energy of ideal systems and defective systems at different electronic temperatures and different pressures. Moreover, suitable bands are employed to ensure that there are enough states for electrons to occupy even at high electronic temperatures. The calculations of the vacancy formation enthalpy are performed in supercells. To ensure the simulations performed at a constant pressure, the supercell structures are optimized to relax the ion positions around the vacancy.

3. Result and discussion

3.1. Monovacancy formation energy without regard to the electronic excitation and compression effect

In order to further study the effect of electronic excitation and compression on the transitional metal, first of all, we calculated the monovacancy formation energy of metal W at ambient pressure and electronic temperature $T_e = 300$ K, and listed this information in Table 1.

From Table 1, it can be seen that the monovacancy formation enthalpy of W we obtained is 3.198 eV. It is slight lower than previous theoretical results 3.27 eV (obtained by FP-LMTO method), 3.44 eV (obtained at ambient pressure and electronic temperature $T_e = 0$ K), 3.35–3.69 eV (FP-LMTO and PP method) and the experimental values at finite electron-temperature. This result shows that our present work slightly underestimates the monovacancy formation enthalpy of W. In addition, it is larger than the corresponding value of metal Ta we obtained in our previous work [17]. This result is in accord with the conclusion obtained by Soderlind et al. [27] that the bcc transition metals W has the highest vacancy formation volume.

Table 1
Theoretical and experimental values of monovacancy formation energy of metal W at zero-pressure.

	Present work	Previous work	Experimental values
H_f^v (eV)	3.198	3.27[a] 3.44[b] 3.35–3.69[e]	3.61 ± 0.2 (2400 K $\leq T \leq$ 3400 K)[c] 3.51 ± 0.2 (2400 K $\leq T \leq$ 3400 K)[d]

[a] Ref. [10].
[b] Ref. [11].
[c] Ref. [25].
[d] Ref. [26].
[e] Ref. [27].

3.2. Convergence test

To obtain accurate monovacancy formation enthalpies of tungsten under high electronic temperatures and pressures, convergence test of three factors should be carried out carefully. The first parameter is the size of the supercell we used, i.e., the number of atoms. In previous studies [10,11], 16, 27 and 54-atom supercells were employed to calculate the monovacancy formation enthalpy for tungsten. To ensure the accuracy of our calculation, we choose 54-atom supercell in our work. In Table 1 of Section 3.1, the values of monovacancy formation enthalpy obtained in 54-atom supercell is listed, and our calculated result is close to previous experimental and theoretical results.

The second parameter is the Monkhorst–Pack mesh which determines the number of k-points used for Brillouin zone sampling. Convergence tests for the k-point grid are performed in a 54-atom supercell, and the absolute differences of the formation enthalpy with different sets of k-points at different electronic temperatures are presented in Table 2. In order to ensure the precision of the vacancy formation enthalpy, we do not stop the convergence until the formation enthalpy converged to an accuracy of 20 meV.

3.3. The effect of electronic excitation on vacancy formation enthalpy

Due to the electron at high electronic temperature that will occupy the high energy bands, the bands at different electronic temperatures should be carefully select to ensure that a considerable number of empty bands is still included in our calculations. The bands we employed at different electronic temperatures are listed in Table 3.

In addition, it is known that the highly excited electrons can strongly modify the inter-atomic forces by weakening the crystal covalent bonds. And the modification of the inter-atomic forces in materials would further result in the variation of the internal pressure of materials. So the monovacancy formation enthalpy of metals would be changed as the electronic temperature change. To study the effect of electronic excitation on transition metal

Table 2
The absolute differences of the formation enthalpies (meV) with different sets of k-points under different electronic temperature conditions. The 54-atom supercell lattices $2\times2\times2$, $4\times4\times4$, $6\times6\times6$ and $8\times8\times8$ k-point meshes are used, giving 1, 4, 10 and 20 k-points in the irreducible Brillouin zone, respectively.

MP meshes	$T_e = 0.01$ eV	$T_e = 0.5$ eV	$T_e = 1.0$ eV
$4\times4\times4-2\times2\times2$	−752	17	1
$6\times6\times6-4\times4\times4$	226	–	–
$8\times8\times8-6\times6\times6$	−16	–	–

Table 3
The bands we used at different electronic temperatures.

T_e (eV)	0.01	0.5	1.0	3.0	4.0	5.0
Bands	200	350	500	1500	2200	3500