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A density functional theory assessment of the clustering behaviour of He and H in tungsten

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ABSTRACT

We have used density functional theory based ab initio calculations to investigate the tendency of He and H to form clusters. For both species the most stable interstitial configuration is in a tetrahedral site, however their clustering tendencies are totally different. The He–He interaction is purely elastic in nature and as such highly binding at close separation distances. The H–H interaction on the other hand is almost negligible since the elastic binding effect is compensated for by the change in effective position of the H states in the density of states. He atoms always bond more strongly to He_xH_y complexes in a vacancy than H atoms.

1. Introduction

One of the promising candidate for the divertor plate in ITER is tungsten, because of its high melting temperature, high thermal conductivity and low sputtering erosion. In the surface of plasma facing materials, high concentrations of hydrogen, hydrogen isotopes and helium can build up, which will interact with the point defects resulting from the bombardment of the surface as well as with the impurities of the materials. These interactions will induce changes in the microstructure and thus in the mechanical properties. In order to predict the evolution of the tungsten microstructure and the possibility of swelling, modelling at the atomistic level is necessary. Even though recently developed empirical potentials are available [1,2] with which the hydrocarbon interactions with tungsten were investigated for instance, they cannot handle the intricacies of the electronic structure. We have thus used a density functional theory approach to investigate the properties of He and H clusters in tungsten.

2. Methods

Our calculations have been performed using the Vienna Ab initio Simulation Package VASP [3]. They were performed in the framework of Blöchl's projector augmented-wave (PAW) method [4] within the Generalised Gradient Approximation (GGA) of Perdew and Wang [5,6]. The pseudopotentials were taken from the VASP library. The supercell approach with periodic boundary conditions (PBC) was used to simulate point defects as well as pure phases. Brillouin zone (BZ) sampling was performed using the Monkhorst and Pack scheme [7]. The plane wave cut-off energy was taken to be 350 eV in order to get converged results. All the calculations presented have been performed with 128 atom supercells and a $3 \times 3 \times 3$ k-point sampling. All the structures have been relaxed by conjugate gradient, at constant volume.

The binding energy $E_b(A_1,A_2)$ between two entities A_1 and A_2 is obtained as

$$E_b(A_1,A_2) = [E(A_1) + E(A_2)] - [E(A_1 + A_2) + E_{ref.}] \quad \text{(I)}$$

where $E_{ref.}$ is the energy of the supercell without A_1 and A_2, $E(A_j)$ is the energy of the supercell containing A_j only and $E(A_1 + A_2)$ is the energy of the supercell containing both A_1 and A_2 in interaction with each other. All the supercells contain the same number of metal sites, i.e., have the same size. With such a scheme a positive binding energy means attraction.

3. Results

3.1. Pairs of light elements

We have determined the binding energy between pairs of light elements (LE) both positioned initially in a tetrahedral (T) site according to the labelling of Fig. 1. Indeed, the most stable configuration for both He or H is the tetrahedral site, the energy difference between the two possible interstitial sites ΔE_{T-O}, where O stands for octahedral, being equal to 0.22 eV for He and to 0.38 eV for H. The results are presented in Table 1. Despite being both light elements, the difference between He and H was found to be spectacular as two He atoms bind with an energy as large as 1 eV, while two H atoms repel each other. The mixed He–H

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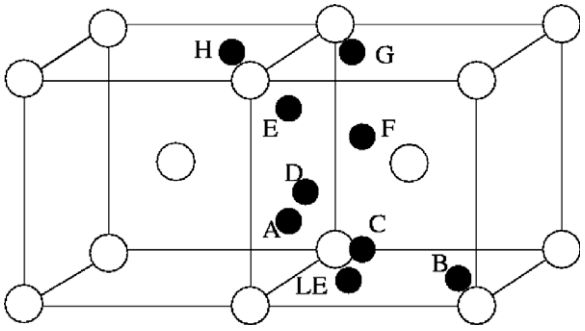

Fig. 1. Possible configurations for two LE in tetrahedral sites. The first light element is in the site labelled LE, the second one in the site labelled with an alphabetical character.

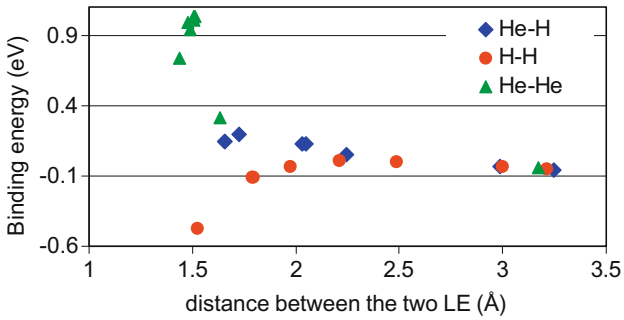

Fig. 2. Binding energy (eV) versus distance (Å).

interactions are in most cases attractive, however less attractive than the He–He interactions. The strong interaction observed between two He atoms is certainly at the origin of the difficulty to obtain information about single He atoms in the tungsten matrix [8]. The most stable configuration corresponds to the relaxed configuration of case E in Table 1, for both He–He and He–H interactions. However as could be expected the positions of the light elements are not identical. The two He atoms in the He_2 complex are oriented along a direction close to a ⟨012⟩ direction, while the He–H atoms are oriented along a direction close to a ⟨027⟩ direction.

When exploring the different configurations involving tetrahedral sites situated at different distances, it appears that in most of the configurations, the light element atoms relax by quite a large amount, especially the He atoms, moving away from their initial tetrahedral site. For the HeH configurations, the H atoms always remain much closer to a tetrahedral site, while the He atoms can move very far from any interstitial site. Fig. 2 represents the binding energy versus distance after relaxation for the He_2, HeH and H_2 complexes. It shows very clearly that for the light element pairs, the distance between the two light elements is the smallest for the He_2 complex, it converges towards 1.5 Å. For H, H–H length smaller than 1.8 Å leads to repulsion larger than −0.1 eV, whereas for larger interaction distances, the binding energy is close to zero. The HeH complex behaviour is intermediate between the two cases above, the distance between He and H in the most stable complex being close to 1.7 Å.

The He–He interaction is purely elastic in nature and, as such, highly binding at close separation distances in the low compressibility W matrix. The H–H interaction on the other hand is almost negligible since the elastic binding effect is compensated for by the change in effective position of the H states in the electronic structure. If the H ions are at short separation distances, the bonding and antibonding states are asymmetrically shifted upwards in energy, thus raising the interaction energy to result in a weak repulsion instead of the weak attraction suggested by a pure elastic analysis. The asymmetric split depends on distance in the same manner as the elastic interaction does. The interaction between one H and one He can be described by a linear mixing of the two LE behaviours.

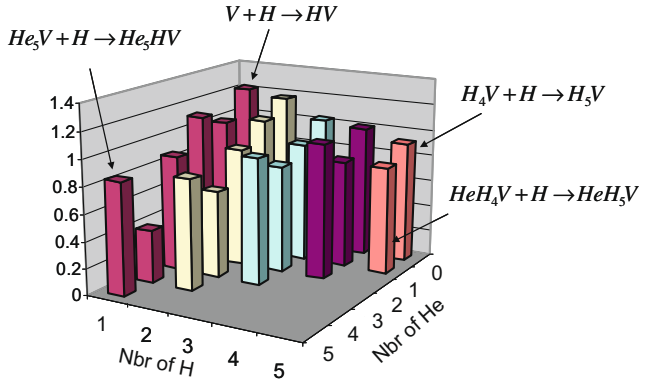

Fig. 3a. Binding energies (eV) for the reaction: $He_xH_yV + H \rightarrow He_xH_{y+1}V$.

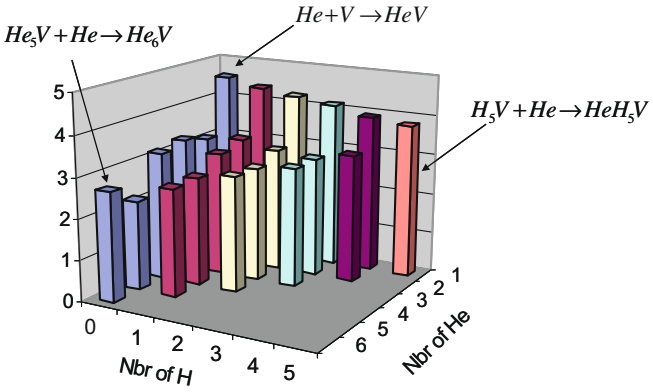

Fig. 3b. Binding energies (eV) for the reaction: $He_yH_xV + He \rightarrow He_{y+1}H_xV$.

Table 1
Binding energies (eV) and relaxed distance (in lattice parameter a units) between light elements.

Configurations	Initial distance between the two LE	He–H binding energy (eV)	Final distance between the two LE	He–He binding energy (eV)	Final distance between the two He	H–H binding energy (eV)	Final distance between the two H
A	$\frac{a}{4}\sqrt{2} = 0.354a$	0.13	0.64a	0.74	0.45a	−0.47	0.48a
B	a/2 = 0.5a	0.14	0.52a	0.94	0.47a	−0.11	0.56a
C	$\frac{a}{4}\sqrt{6} = 0.612a$	0.13	0.52a	1.01	0.47a	−0.03	0.62a
D	$\frac{a}{2}\sqrt{2} = 0.707a$	0.05	0.71a	0.31	0.52a	**0.01**	0.70a
E	$\frac{a}{4}\sqrt{10} = 0.791a$	**0.20**	0.54a	**1.03**	0.47a	0.00	0.78a
F	$\frac{a}{4}\sqrt{14} = 0.935a$	−0.03	0.94a	0.99	0.47a	−0.03	0.94a
G	a	−0.06	a	−0.01	a	−0.05	a
H	$\frac{a}{2}\sqrt{5} = 1.116a$	0.14	0.52a	1.03	0.48a	−0.11	0.56a

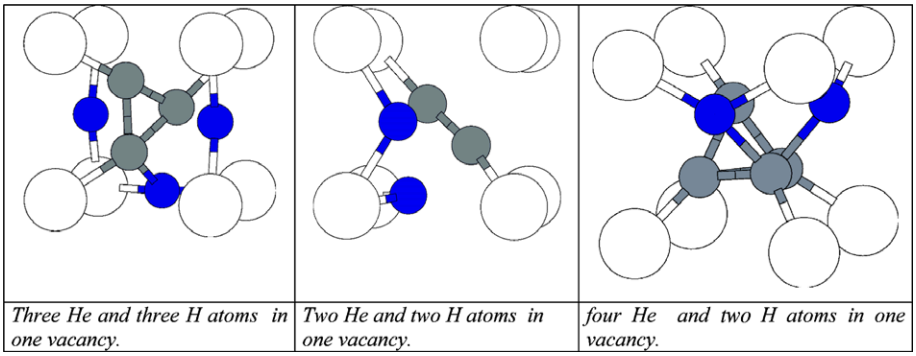

Fig. 4. Three typical configurations for mixed He and H clusters in a vacancy. He atoms are grey, H atoms are blue. The white spheres are the W atom and the vacancy is located at the centre of the 8 W atoms.

3.2. Mixed He and H clusters in the presence of a single vacancy

In a second part, we determined the binding energies for He_xH_yV ($x + y \leqslant 6$), mixed clusters, i.e. He and H atoms filling one vacancy. The results for the most stable configurations are presented in Fig. 3a in the perspective of H trapping, (i.e., with the aim of determining the possible traps for H created during an helium pre-irradiation similar to the one performed by Iwakiri et al. [9]) and in Fig. 3b in the perspective of He trapping. The light elements (essentially He) do not relax close to any geometrical site (such as the tetrahedral or the octahedral sites) and consequently the ground state of each configuration is not trivial to find. In order to get the most stable configuration, we investigated, for each complex, different configurations starting from different initial positions of the light elements, sometimes as many as seven different possible ones. In addition, for a few cases, some ab initio molecular dynamics simulations at 600 K followed by conjugate gradient relaxation were performed in order to check that more stable new configurations could not be obtained. Fig. 4 presents three typical configurations for mixed He and H clusters in a vacancy.

For the cluster sizes investigated, the binding energy, for He as well as for H, does not depend very much on the number of He and H present within the vacancy. The He binding energy is in the range 3–4 eV and the H binding energy is around 0.8–1 eV. The results indicate that removing an He atom from a mixed He_xH_yV cluster requires always more energy (between 2 and 3 eV more) than removing an H atom from a cluster of identical size.

The binding energy of the HeHV complex indicates that when a moving H atom comes close to an HeV complex, the H atom will bind strongly to the HeV complex, as the reaction HeV + H → HHeV will lead to an energy gain close to 1 eV.

Furthermore, an H atom cannot destroy an HeV complex, which is very stable. Indeed, the reaction HeV + H → HV + He is not possible (the reaction energy is 3.36 eV). Lee et al. [10] studying hydrogen and helium trapping in tungsten under single and sequential irradiations interpret their results by a possible de-trapping of He by H^+ and D^+ ions from energetic traps. Our calculations indicate that the de-trapping of He from an HeV complex by an H atom is not possible.

4. Conclusion

We have investigated the tendency of He and H to form clusters using the density functional theory implemented in the VASP code. The tetrahedral site is for both element the most stable interstitial configuration. The He–He interaction is purely elastic in nature and close to 1 eV. The elastic binding effect is compensated for by the change in effective position of the H states in the density of states for the H–H interaction leading to almost negligible interaction. The He–H interaction corresponds simply to a combination of both cases. These trends are emphasized in mixed He and H complexes in a vacancy: it costs 2–3 eV more energy to remove an He atom from a mixed He and H complex than to remove an H atom from a complex of identical size.

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