Ab initio investigation of radiation defects in tungsten: Structure of self-interstitials and specificity of di-vacancies compared to other bcc transition metals

Lisa Ventelon *, F. Willaime, Chu-Chun Fu, M. Heran, I. Ginoux

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ABSTRACT

The results of DFT calculations on radiation point defects in tungsten are presented. The lowest energy configuration of the self-interstitial has exactly the (111) orientation and no tilt from this direction is observed when using appropriate cell geometry and pseudopotential. The present DFT calculations confirm that in pure tungsten the interactions between two vacancies are unexpectedly repulsive until the fifth nearest-neighbor and that the second nearest-neighbor di-vacancy is the most repulsive. The electronic entropy contribution to the free energy makes the nearest-neighbor configuration attractive at high temperature. A comparison with other bcc metals shows that the binding energies between two vacancies are strongly metal dependent and that tungsten leads to the largest deviation from empirical potential predictions. In tungsten, the effect on vacancy properties of alloying by tantalum and rhenium has been investigated using the Virtual Crystal Approximation (VCA). The effect of these alloying elements is essentially to change the filling of the d-band and the vacancy formation energy is found to be maximal and the relaxation to be minimal when the Fermi level is at the minimum of the pseudo-gap, as predicted by previous tight-binding calculations. Di-vacancies are shown to become attractive at first and second nearest-neighbor upon tantalum alloying and even more repulsive upon rhenium alloying.

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1. Introduction

The development of plasma facing components is one of the critical issues to realize next generation fusion devices. Tungsten is foreseen as one of ITER divertor armor materials, whose function is to exhaust helium impurities from the plasma, which are produced as a result of fusion reactions. Indeed tungsten has the highest melting point of all the non-alloyed metals and is the only metal, with carbon composites, that can resist to high heat fluxes, which the divertor is subject to from the plasma. Burn-up calculations on pure tungsten under first wall fusion power plant conditions have shown that a significant Re, Os and Ta production is expected from W transmutation [10]. The properties of radiation conditions have shown that a significant Re, Os and Ta production will occur as a result of fusion reactions. Indeed tungsten has the highest melting point of all the non-alloyed metals and is the only metal, with carbon composites, that can resist to high heat fluxes, which the divertor is subject to from the plasma. Burn-up calculations on pure tungsten under first wall fusion power plant conditions have shown that a significant Re, Os and Ta production is expected from W transmutation [10].

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A systematic Density Functional Theory (DFT) study of self-interstitial atom (SIA) defects in body centered cubic (bcc) transition metals showed that in all the non-magnetic bcc transition metals, including bcc–W, the most stable defect configuration has the (111) (crowdion) orientation [20]. Magnetic-Fe is an exception, with the SIA adopting the (110) dumbbell structure according to DFT and in agreement with experiments [5,8]. However in group VIB metals (Cr, Mo and W), the orientation of the SIA may not be strictly (111). Diffuse scattering experiments in Mo suggest that the symmetry of the SIA is not compatible with a (111) orientation [7]. In these metals the energy difference between the (111) and (110) orientations of the SIA is quite small [20], such that either the (111) orientation is the ground state, and the very flat energy landscape yields a very large amplitude rotation of the defect, or there is an intermediate orientation with a lower energy. DFT calculations in Mo could not discriminate between these two hypotheses [12,20], whereas in Cr and W it was found that the SIA energy is minimal for a dumbbell orientation close to (221) [21,22].

The formation and migration energies of mono-vacancies in W and other bcc transition metals is well documented [23,24]. W and other group VIB bcc metals, Cr and Mo, have the largest vacancy formation and migration energies, even after normalization by the cohesive energy. This was shown to be related to the high stability of the bcc structure with the Fermi energy lying close to the minimum of the pseudo-gap of the electronic density of states [27]. Group-specific trends were also evidenced from DFT calculations for the vacancy–vacancy binding energies. A systematic study...
showed that in group VB metals (V, Nb and Ta) and in Fe the second nearest-neighbor configuration is the most stable, whereas in group VIb metals, the nearest-neighbor configuration is the most stable [3]. However two contradictory results have been published concerning the sign of the di-vacancy binding energy in W [3,2].

The goal of the present DFT study is to investigate the properties of radiation point defects in pure tungsten, and in tungsten alloyed with Ta or Re. We have first investigated the relative stability of the various configurations of the self-interstitial atom (SIA), paying particular attention to the effect of the interaction of the SIA with its periodic images. We have then calculated the vacancy formation energies and the di-vacancy binding energies in W and in W alloyed with Ta and Re. The unexpected behavior of di-vacancies obtained in tungsten has led us to perform a systematic on all the body-centered cubic (bcc) transition metals (V, Nb, Ta, Cr, Mo, W and Fe) in order to investigate whether this behavior is specific to tungsten or not.

2. Methodology

Most of the calculations of the present study have been performed using the plane wave PWSCF code [9]. Ultrasoft pseudopotentials have been generated for all bcc transition metals, V, Nb, Ta, Cr, Mo, W and Fe [28]. In all cases except Fe, semi-core states are included in the valence band. Their accuracy has been successfully tested on bulk properties (lattice parameter, bulk modulus, C in the valence band. The calculations in Cr are performed in the non-magnetic approximation in view of its complex magnetic ground state [26], while the calculations in ferromagnetic Fe are spin-polarized. The defect calculations are performed using the supercell approximation keeping the cell geometry fixed to the bulk equilibrium geometry and relaxing the atomic positions. The k-point grids used in the 54, 128, 250 and 432-atom cells are respectively 6 × 6 × 6, 4 × 4 × 4, 3 × 3 × 3 and 3 × 3 × 3. The Hermite-Gaussian smearing technique with a 0.3 eV width was used for electronic density of state broadening. Unless otherwise specified, the PBE-GGA scheme is used for exchange and correlation.

3. Results and discussion

We have calculated the formation energies of the high-symmetry configurations of the SIA in tungsten: (111), (110) and (100) dumbbells, and the octahedral and tetrahedral configurations using 128(+1) and 250(+1) atom cells. In this study, for the (111) SIA we have not distinguished between the dumbbell and the crowdion. The results obtained from the present SIESTA and PWSCF calculations as well as from previous PLATO and VASP calculations [20,2] are summarized in Table 2. In all cases the (111) dumbbell has the lowest formation energy. Despite a small scatter on the absolute values of the formation energies, there is a quite good agreement on the energy differences and in particular the (110) dumbbell is predicted to be only approximately 0.3 eV higher in energy than the (111) dumbbell.

In order to explore the presence of possible lower symmetry configurations, we have then tilted the (111) dumbbell towards the (110) direction. First, using the conventional cubic supercell with 128(+1) atoms, we found that the result depends on the pseudopotential. For pseudopotentials without semi-core states, using either SIESTA or PWSCF, we indeed find, as reported recently

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Basic parameters of all the bcc transition metals of groups VB and VIb and Fe calculated using PWSCF within two exchange–correlation functionals (GGA and LDA in brackets) and compared to the experimentally measured values taken from Refs. [14,13] (in italics).</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>B (GPa)</td>
</tr>
<tr>
<td>C (GPa)</td>
</tr>
<tr>
<td>C_{44} (GPa)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
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</thead>
<tbody>
<tr>
<td>DFT formation energies (in eV) of SIA defects in tungsten calculated in 128(+1) and 250(+1) atom cells. For the (110), (100), octahedral and tetrahedral configurations, the energies are given relative to the (111) dumbbell.</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>(111)</td>
</tr>
<tr>
<td>(110)–(111)</td>
</tr>
<tr>
<td>(100)–(111)</td>
</tr>
<tr>
<td>Octahedral-(111)</td>
</tr>
<tr>
<td>Tetrahedral-(111)</td>
</tr>
</tbody>
</table>
in Cr and W [21,22], that after relaxation the dumbbell adopts a (111) orientation, with θ close to ½. But with PWSCF and a pseudopotential with semi-core states, no clear off symmetry minimum is found.

We have then repeated the calculation for various sizes of cubic cells using SIESTA. The angle between the (111) dumbbell and the (111) direction changes only slightly with cell size: 18.6°, 15.5°, 16.5° and 16.9° for 54, 128, 250 and 432 atoms respectively. The tilted configuration is lower in energy than the (111) dumbbell respectively by 0.18 eV, 0.04 eV, 0.06 eV and 0.04 eV. However since this defect is aligned in the dense (111) direction, its elastic strain extends over very long distances, typically more than 10 interatomic distances [4], such that even in the largest supercell the SIA is likely to interact significantly with its periodic images.

It is possible to prevent this spurious interaction by using non-cubic supercells, e.g. by duplicating the unit cell not equally in the three directions, as schematically illustrated in Fig. 1. In SIESTA calculations performed on 3 × 3 × 4, 4 × 4 × 5 and 5 × 5 × 6 cells, containing respectively 72, 160 and 300 atoms, it is found that the (111) dumbbell always relaxes towards the (111) configuration.

In summary, two arguments point towards the absence of a tilted (111) dumbbell configuration of the SIA in W: this configuration is indeed neither found when using a more accurate pseudopotential that includes semi-core states, nor when using non-cubic supercells that reduce the interaction between periodic images of the (111) configuration.

We have then investigated the formation and migration energies of the mono-vacancy and the binding energies between two vacancies in tungsten. The vacancy formation and migration energies obtained with the SIESTA and PWSCF codes and the GGA-PBE functional are in very good agreement with previous GGA PAW-VASP results [2] (Table 3). The comparison with experiments faces the difficulty of the temperature dependence of the vacancy parameters [23]. The calculated value of the migration energy agrees well with the low temperature experimental value of 1.7 ± 0.1 eV [18]. The formation energy is known only at high temperature, 2400–3400 K [17]. Its value, 3.51 ± 0.1 eV, is significantly larger than the one calculated at 0 K, namely 3.24 ± 0.01 eV. Because of the strong variations in the local density of states of the nearest-neighbors of the vacancy right below the Fermi level, close to the minimum of the pseudo-gap (see Fig. 2), electronic entropy effects are expected to induce a significant temperature dependence of the vacancy formation energy [23]. In perfect agreement

![Fig. 1. Schematic representation in two dimensions of the interaction with its periodic images of a SIA aligned along the diagonal of the unit cell: (a) (2×2) × 2 supercell and the resulting tilted configuration; and (b) (2×2) × 3 supercell reducing the interaction between periodic images.](image)

**Table 3**

Comparison of DFT results with experiments of the formation and migration energies (in eV) of the mono-vacancy in tungsten.

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>SIESTA GGA-PBE</th>
<th>PWSCF GGA-PBE</th>
<th>VASP GGA PAW [2]</th>
<th>Experiment [17,18]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 0 K</td>
<td>T = 3000 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_f (V₁)</td>
<td>3.25</td>
<td>3.22</td>
<td>3.21</td>
<td>3.11</td>
</tr>
<tr>
<td>E_m (V₁)</td>
<td>3.47</td>
<td>1.78</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 2. Comparison in tungsten between the local densities of states (LDOS) projected on the 5d orbitals of a bulk atom, a nearest-neighbor of the mono-vacancy, and two particular neighbors of di-vacancies. For the first nearest-neighbor di-vacancy, the LDOS is taken on the atom that is nearest-neighbor to one vacancy constituting the di-vacancy, and fifth nearest-neighbor to the other one. For the second nearest-neighbor di-vacancy, the LDOS is taken on one of the four atoms that is nearest-neighbor to both vacancies. The calculations have been performed using SIESTA and a 54-atom cell.](image)
with Ref. [23], it is found that at 3000 K electronic entropy effects increase the formation energy by 0.2 eV. In a recent study in molybdenum, a metal analogous to tungsten, a similar result was found but first principles molecular dynamics simulations suggest that about two third of the temperature dependence of the vacancy formation energy comes from anharmonic lattice vibrations [15]. The exchange–correlation functional is also a source of discrepancy. Table 4 shows that the LDA value of the vacancy formation energy is very close to the GGA-PBE one, but that the new AM05 functional, that has been developed to improve vacancy properties, yields to a value larger by approximately 0.3 eV. Further investigations are therefore required to make a quantitative comparison between DFT and experiments at high temperature.

The interaction energies between two vacancies from first to fifth nearest-neighbor are represented in Fig. 3. The present SIESTA and PWSCF GGA-PBE results are in very good agreement with previous GGA PAW-VASP results [2]. At variance with the PLATO results of Ref. [3], di-vacancies are neither attractive at first and second nearest-neighbors nor until the fifth nearest-neighbor. The most striking feature is the strong repulsion at second nearest-neighbor, which is the most attractive configuration in iron [6]. The effect of exchange–correlation functional has been investigated on the binding energy of the di-vacancy (Table 4). The LDA functional as well as the AM05 functional yield to binding energies very similar to the GGA-PBE ones with a vanishing but slightly repulsive interaction at first nearest-neighbor and a strong repulsion at second nearest-neighbor. It can therefore be concluded that this result is quite independent on the exchange–correlation functional.

We have then investigated if the strong electronic entropy effect observed for the vacancy formation energy affects the di-vacancy properties. For an electronic temperature of 3000 K, the electronic free energy (or Mermin free energy) indicates that di-vacancies become attractive at nearest-neighbor, with a binding of 0.09 eV, and that they become less repulsive at second nearest-neighbor (see Table 4). This increase in binding free energy, i.e. decrease in di-vacancy formation free energy, is due to an increase of the density of states close to the Fermi level on sites around the defect (see Fig. 2).

The unexpected absence of binding between di-vacancies obtained in tungsten at 0 K led us to perform a systematic DFT study on bcc transition metals, namely Fe, V, Nb, Ta, Cr and Mo in addition to W. These calculations are performed using 54-atom cells since no significant cell-size effects are observed in W: the binding energies at first and second neighbors are $-0.03$ eV and $-0.48$ eV respectively using 54-atom cells against $-0.09$ eV and $-0.46$ eV

### Table 4
Comparison between DFT results of the formation energy of the mono-vacancy and the di-vacancy binding free energy at first (1nn) and second nearest-neighbor (2nn) positions in a 54-atom cell using different exchange–correlation functionals. Energies are expressed in eV.

<table>
<thead>
<tr>
<th></th>
<th>SIESTA GGA-PBE</th>
<th>PWSCF GGA-PBE</th>
<th>PWSCF LDA</th>
<th>ABINIT AM05</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f (V_1)$</td>
<td>$3.25$</td>
<td>$3.47$</td>
<td>$3.23$</td>
<td>$3.27$</td>
</tr>
<tr>
<td>$E_f (V_2 1nn)$</td>
<td>$-0.09$</td>
<td>$0.09$</td>
<td>$-0.03$</td>
<td>$-0.12$</td>
</tr>
<tr>
<td>$E_f (V_2 2nn)$</td>
<td>$-0.41$</td>
<td>$-0.27$</td>
<td>$-0.47$</td>
<td>$-0.50$</td>
</tr>
</tbody>
</table>

Fig. 3. Comparison between DFT results of the binding energy between two vacancies at first (1nn) to fifth nearest-neighbor (5nn) positions in a 128-atom cell.

Fig. 4. Binding energies between two vacancies in Fe at first and second nearest-neighbor positions: comparison between PWSCF results in a 54-atom cell and the Mendelev potential results [16]. The binding energy is defined as positive for an attractive interaction between the two vacancies.

Fig. 5. DFT di-vacancy binding energies at first and second nearest-neighbors: comparison between the results obtained for groups VB (V, Nb, Ta) and VIB (Cr, Mo, W) bcc transition metals using PWSCF and 54-atom cells.
respectively using 128-atom cells. The results obtained using the PWSCF code show that the binding energies between two vacancies at first and second nearest-neighbor, denoted respectively 1nn and 2nn hereafter, are strongly metal dependent (Figs. 4 and 5). The “standard” behavior in transition metals can be defined as the result given by empirical potentials of the EAM or second-moment approximation type. These potentials indeed account for the non pairwise interaction between atoms but they are representative of a featureless electronic density of states. In this respect, di-vacancy binding in Fe can be considered as standard, since DFT and empirical potentials, e.g. the Mendeleev EAM potential [16], give very similar results with an attractive interaction at 1nn and 2nn, the latter being the most attractive (see Fig. 4). A similar behavior is observed for Nb and Ta, although the amplitude of the binding is slightly larger for Nb and smaller for Ta. For all the other metals the relative stability between 1nn and 2nn is reversed. In V both configurations are still attractive, but in non magnetic Cr, 1nn is highly attractive whereas 2nn is slightly repulsive. And finally in Mo and W, 1nn is almost non-bonded and 2nn is largely repulsive. As a result, W appears to have the largest deviation from the standard behavior. The similarities between group VB metals Nb and Ta on the one hand and between group VIB metals Mo and W on the other hand as well as the striking contrast between these two groups of metals strongly call for a phenomenon governed by the filling of the d-band. The deviation observed for the 3d metals, V and Cr, suggests either that the underlying driving force is very sensitive to the d-band filling or that other contributions come into play.

In order to get more insight into the d-band filling effect at the origin of the atypical behavior of di-vacancies in W, we have performed a VCA study of the mono- and di-vacancies in W alloyed either with Ta or Re, i.e. with elements that have respectively less and more d-electrons. A full picture along the 5d series bcc metals is obtained by completing the calculations in Hf-Ta alloys. These VCA results cannot be directly transposed to real alloys since two relevant effects are neglected: the variations of the local chemical composition and the consequent non-uniform local lattice distortions due to atomic size effects. The results obtained with the PWSCF code are represented in Figs. 6 and 7. Strong deviations from a simple interpolation and extrapolation from the results in pure Ta and W are obtained. The vacancy formation energy is highest around Ta_{0.25}W_{0.75} VCA alloy. The relaxation energy is strongly composition dependent. It is minimal again around Ta_{0.25}W_{0.75} VCA alloy and it becomes quite large in Ta alloyed with Hf, before the bcc structure becomes mechanically unstable (Fig. 6). These results fully confirm predictions from tight-binding d-band calculations [27] and they show that indeed the behavior of the vacancy is governed by the position of the Fermi level with respect to the minimum of the pseudo-gap, which corresponds to Ta_{0.25}W_{0.75}.

Concerning di-vacancies, starting from W, it can be seen that the interactions between vacancies become even more repulsive upon Re alloying and that they start increasing upon Ta alloying. The 1nn di-vacancy in Ta_{x}W_{1-x} VCA alloys thus becomes rapidly attractive, with a maximum close to 0.6 eV around x = 0.25. This sharp variation of the binding energy suggests that the formation of di-vacancies in W under irradiation may be quite sensitive to impurity or alloying effects. The 2nn becomes attractive for x > 0.25. The di-vacancies in Ta become rapidly repulsive upon alloying with Hf. This is due to the fact that the important relaxation effects induce a larger decrease of the energy for two isolated vacancies than for a di-vacancy.

4. Conclusion

The results of DFT calculations of the formation, migration and binding energies of mono- and di-vacancies and of the stability of the SIA stability in pure tungsten are presented in this paper. Concerning the lowest energy structure of the SIA in W, we find that it is not tilted from the (111) direction when using pseudopotentials that include semi-core states, nor when using non-cubic supercells that reduce the interaction between periodic images of the (111) configuration. A thorough comparison between various exchange-correlation functionals, including the recent AM05 functional, confirms the strong repulsion between two vacancies at second nearest-neighbor positions of about −0.5 eV and the weak repulsion at nearest neighbor. The electronic entropy contribution to the free energy is also shown to yield an attraction between nearest-neighbor vacancies at high temperature in pure W. From a comparison with all the other bcc transition metals, it is concluded that tungsten exhibits the strongest deviation from empirical potential behavior. VCA calculations performed in the 5d series on binary alloys from Hf_{0.5}Ta_{0.5} to W_{0.5}Re_{0.5} confirm the strong variation with d-band filling of the mono- and di-vacancy properties, suggested by the group dependence observed in pure metals as well as by tight-binding d-band predictions. It is in particular shown that the nearest-neighbor di-vacancy in W becomes rapidly

![Fig. 6. Unrelaxed and relaxed formation energies of the mono-vacancy as a function of alloy composition ranging from Hf_{0.5}Ta_{0.5} to W_{0.5}Re_{0.5} using the VCA approximation and the PWSCF code with a 54-atom cell.](image)

![Fig. 7. Unrelaxed and relaxed binding energies of di-vacancies at first (1nn) and second nearest-neighbor (2nn) positions as a function of alloy composition using VCA and PWSCF with a 54-atom cell.](image)
attractive upon Ta alloying, with a maximum of the binding energy for $T_{a_{0.25}W_{0.75}}$.

Acknowledgments

This work was supported by the European Fusion Materials Modelling programme. It has been performed using HPC resources from GEnCI-CINES (Grant 2010-x201096020) and HPC for Fusion Facilities at Jülich. S.L. Dudarev (CCFE, UK) is acknowledged for pointing out the issue of interaction between images. F. Bruneval and B. Legrand (CEA/Saclay, France) are acknowledged respectively for their help with the Abinit code and for discussion on alloying effects.

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