

Ab-initio Modelling of Point Defect-Impurity Interaction in Tungsten and other Bcc Transition Metals

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Abstract. Ab-initio calculations have been performed to investigate systematically defect-impurity interaction in Tungsten and other bcc transition metals. It is found that the most stable configuration of C and N atoms is the octahedral interstitial site whereas O and H atoms are located in the tetrahedral configuration. For the particular case of bcc-W, the binding energies formed by the carbon and nitrogen atoms located at octahedral sites, and mono-vacancy on a nearest neighbor site are very large, 1.39 eV and 1.91 eV, respectively. Implication of these results of diffusion of point defects in tungsten is discussed and compared with the case of bcc-Fe.

Introduction

Tungsten is one of the main candidate plasma facing material for the divertor and other components of future fusion power plants, where it will be exposed to charged particles and neutron bombardments. It has high melting temperature, relatively high thermal conductivity, and high resistance to sputtering. There is ample evidence that impurity atoms play a significant part in micro-structural evolution under neutron irradiation. For example, impurities have a strong degrading effect on mechanical properties due to strong interaction with radiation point defects, the so-called trapping effect in metals. In addition, ferritic steels based on bcc Fe-Cr alloys are the advanced first-wall structural materials in fusion reactors [1].

Very recently, we have carried a systematic study of the database of point defect formation and migration energies in all bcc transition metals using density functional theory (DFT) formalism [2-5]. Screw dislocation behaviour in bcc-W has also been investigated by atomistic modelling in [6]. The benefits of using accurate DFT descriptions of defects in bcc transition metals have now become clear. Our recent systematic studies of self-interstitial atom (SIA) defects in all bcc transition metals show that in all the non-magnetic bcc transition metals, including bcc-W, the most stable defect configuration has the $\langle 111 \rangle$ (crowdion) orientation, in contradiction with earlier empirical potential results suggesting that the $\langle 110 \rangle$ orientation [2-3]. Our benchmark DFT calculation of the migration energy of a mono-vacancy (1.78 eV) and the prediction of positive binding energy between two vacancies in the first-nearest neighbor of bcc-W are also in excellent agreement with the available experimental observations [4]. We now apply density functional theory (DFT) to the investigation of the interaction between impurity atoms and mono-vacancies in bcc-W and other bcc transition metals.

Ab-initio calculations

DFT calculations were performed within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional for the exchange and correlation energies. We used the ab-initio package PLATO based on linear combination of atomic-like orbitals [2-5] and relativistic semi-core pseudo-potentials, and cross-checked the results with VASP code that combines the

plane-wave based basis set with projected augmented wave (PAW) pseudo-potentials [7-9]. A reference bcc super-cell containing 128 atoms and a 3x3x3 shifted k-point grid was used in all the calculations of defect structures with energy cut-off of 400 eV. The equilibrium lattice parameters calculated in previous studies [2-4] were used. All calculations were performed at constant pressures fully relaxing the atomic positions in the supercells.

A systematic DFT study of impurities (C, N, O and H) in all the bcc transition metals (W, Ta, Mo, Nb, Cr, V and Fe) has been carried out in order to find which interstitial configuration is the most stable one in the bcc lattice sites.

Table 1.

Energy difference for an impurity atom positioned in the tetrahedral interstitial site with respect to the octahedral site in all bcc transition metals

ΔE (eV)	V	Nb	Ta	Cr	Mo	W	Fe
C	1.037 PLATO	1.048 PLATO	1.067 PLATO	1.118 PLATO	1.261 PLATO	1.239 PLATO	0.902 VASP
N	0.803 PLATO	0.732 PLATO	0.698 PLATO	0.866 VASP	0.763 PLATO	0.722 PLATO	0.765 VASP
O	-0.255 PLATO	-0.267 PLATO	-0.275 PLATO	-0.251 PLATO	-0.284 PLATO	-0.315 PLATO	-0.360 VASP
H	-0.116 PLATO	-0.120 PLATO	-0.122 PLATO	-0.177 VASP	-0.249 PLATO	-0.361 PLATO	-0.220 VASP

Table 1 summarizes the calculated formation energy difference of C, N, O and H between the tetrahedral and octahedral configurations in the seven bcc transition metals: V, Nb and Ta in group 5B, Cr, Mo and W in group 6B and Fe in group 8 of periodic table. The calculations were performed either by PLATO or VASP codes as it is indicated in the Table 1. It is found that for C and N, the most stable interstitial configuration is the octahedral one. On another hand, both O and H prefer to occupy the tetrahedral configuration. The energy difference between these two configurations is quite similar in all bcc transition metals ranging from 0.902 to 1.261 eV for C, 0.698 to 0.866 eV for N, -0.255 to -0.360 eV for O and -0.116 to -0.361 eV for H.

Table 2. Comparison of calculated elastic constants (in GPa), elastic compliance matrix elements (in 1000/GPa) and Debye temperature (in K) in bcc-W with the elastic constants predicted in presence of N positioned at octahedral site

Bcc-W	C_{11}	C_{12}	C_{44}	S_{11}	S_{12}	S_{44}	T_D
DFT	518	199	147	2.453	6.803	-0.682	376
EXP.	501	198	151	2.570	6.600	-0.730	400
N in W	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	T_D
DFT	493	219	230	516	130	142	357

In order to see the effect of these impurities on mechanical properties, we have performed DFT elastic constant calculations without and with the presence of impurity in bcc transition metals. Table 2 shows the elastic properties and Debye temperature calculated in bcc-W and compared with experimental values. We see that the DFT prediction of elastic properties is in an excellent agreement with experimental data for bcc tungsten. The presence of N at the octahedral site changes the symmetry of bcc-W from cubic to the tetragonal one and the calculated elastic constants of tungsten with nitrogen impurity are also shown in the Table 2. No negative eigenvalues were found from the calculated elastic matrix indicating that tungsten in presence of nitrogen atom at the octahedral site is still mechanically stable. The predicted Debye temperature of 357K is however

lower than 376 K predicted in bcc-W indicating that the acoustic modes in the presence of nitrogen are softer.

Binding energy between vacancy and impurity

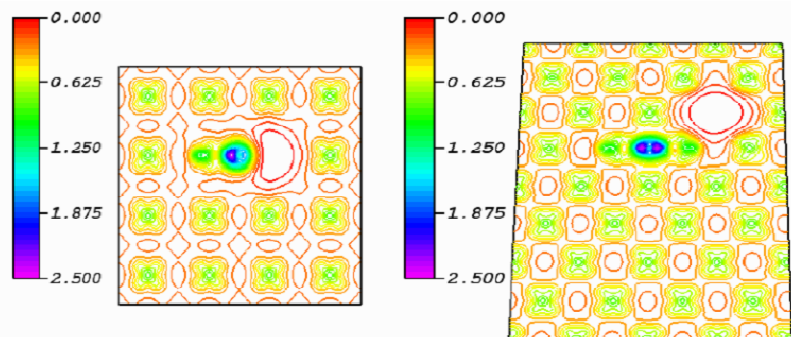
We have further investigated the binding energies between point defects and impurity atoms in bcc transition metals. Table 3 summarizes the binding energies of a C or a N atom situated close to a vacancy in bcc-W. Here we considered four configurations: 1NN, 2NN, 3NN and 4 NN corresponding to the distance of $0.125a$, $0.125\sqrt{2}a$, $0.125\sqrt{5}a$ and $0.125\sqrt{6}a$, respectively. The formation energies of the mono-vacancy were taken from previous calculations [2-4] whereas reference energies of the isolated foreign atom were obtained from single atom calculations in a large supercell. The result indicates that a stable vacancy-impurity pair is formed in tungsten for all four configurations. These data show that the situation in bcc-W is different to bcc-Fe where the DFT calculations predicted that the 3NN vacancy-impurity pair is not a stable configuration [10]. Therefore the vacancy is strongly bonded in tungsten up to the 4NN distance for both carbon and nitrogen as the foreign atom.

Table 3. Binding energy between an impurity atom located at octahedral interstitial site and a vacancy positioned at different nearest neighbours to O site in bcc-W

$E_b(\text{vac_impurity})$ (eV)	1NN	2NN	3NN	4NN
CARBON (O site) in bcc-W	1.384	0.781	0.461	0.274
NITROGEN (O site) in bcc-W	1.914	0.885	0.539	0.383

Fig. 1 shows the self-consistent electronic charge density maps calculated for one carbon atom interacting with a vacancy positioned at the 1NN and the 4NN distance from the impurity. The left figure is the electronic map projected on the (100) plane whereas the right one, (111) plane. We see that the charge densities are strongly deformed around the vacancy position close to the impurity atom position. For the 1NN vacancy-impurity pair the interaction is directional along the line linking between them whereas for the 4NN vacancy-impurity pair the charge density contours around the vacancy is rather isotropic.

Figure 1. Electronic charge density maps for C impurity atom interacting with a vacancy located at the 1NN (left) and 4 NN (right) to the O site in bcc-W.



Discussion

We are now able to discuss the role of strongly binding energies between a mono-vacancy and an impurity atom on the diffusion of defects in bcc-W. The interaction between carbon and nitrogen atoms and a mono-vacancy positioned in the first and fourth nearest neighbor to the impurity in bcc-

W is illustrated in Fig. 2. Taking into account that the migration energy of a vacancy in bcc-W is 1.78 eV (compared to 0.64 eV in bcc-Fe) [2-4], a large interaction between a vacancy with C (1.39 eV compared 0.47 eV in Fe [10]) and with a N atom (1.91 eV compared to 0.71 eV in Fe [10]) means that they can act as pinning centres in materials. This strongly affects on mobility of defects (in this case the mono-vacancies).

Further investigations will be performed to understand the mechanism of interaction between the crowdion which is the most stable SIA configuration in non-magnetic bcc transition metals, and the four impurity atoms studied in the present work.

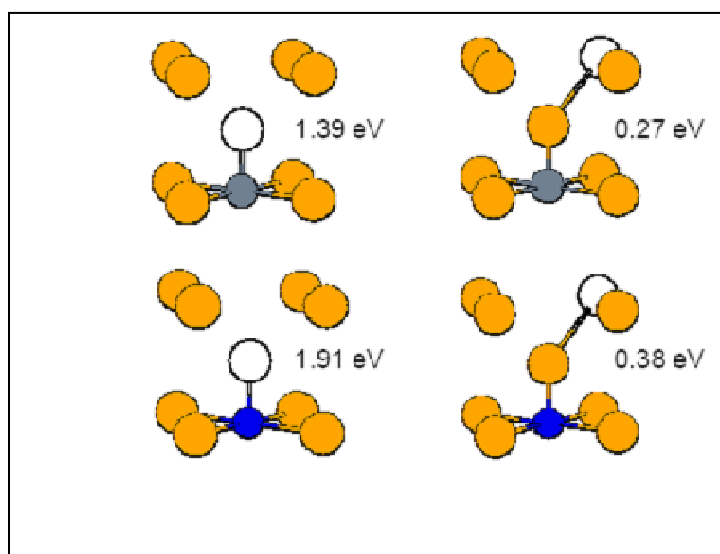


Figure 2. Binding energies between C (top) and N (bottom) impurity and vacancy positioned in 1NN and 4NN in bcc-W

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