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Interaction between helium and self-defects in α-iron from first principles

Chu-Chun Fu *, F. Willaime

Service de Recherches de Métallurgie Physique, CEA/Saclay, 91191 Gif-sur-Yvette, France

Abstract

The interaction between helium and self-defects in α-iron has been studied by means of density functional theory calculations. We show that the fast migrating interstitial helium atoms, which are known to strongly interact with vacancies, can also be weakly trapped by self-interstitial atoms, with a binding energy of about 0.3 eV. The small He_n clusters, which can form as a result of the attractive interaction between interstitial helium atoms, induce strong lattice distortions and we predict that the emission of a self-interstitial atom is energetically favorable for $n > 4$. We also report on the structural and energetic properties of small helium–vacancy clusters (He_nV_m) with n/m ratio around the optimal value with respect to the emission of vacancy or helium ($n/m \simeq 1.3$). We suggest that helium dissociation from these clusters can be responsible for stages above 700 K (II and IV) observed in thermal helium desorption spectra.

1. Introduction

It is well established that the introduction of helium in metals either by implantation or by (n, α) transmutation reactions during high energy neutron irradiation can induce bubble formation [1], void swelling [2], and consequent changes in the microstructure [1,3]. Ferritic steels are proposed as structural materials in fusion reactors. In the fusion environment, large amounts of insoluble helium can be produced in addition to radiation damage (vacancies and self-interstitial atoms). Therefore, understanding the behavior of helium in iron is a crucial issue in the research on fusion reactor materials. Previous atomistic simulations performed using empirical potentials (EP) have provided information on solution and migration properties of He in α-iron, and their interaction with vacancies, self-interstitial atoms, and interstitial clusters [1,4–8]. However, the accuracy of these predictions may depend on the empirical potential used, and it has been questioned by recent *ab initio* calculations which show that the relative stabilities of the various He solution sites are not correctly reproduced by existing EP [9,10]. In the absence of experimental validation, predictive *ab initio* data on the behavior of He in iron are therefore needed. In a previous work, we have investigated the solution and migration properties of He atoms in α-iron, their strong interaction with vacancies, and the energetics of small helium–vacancy clusters [10]. Here, we focus on the study of interaction between interstitial or

* Corresponding author. Tel.: +33 1 69 08 29 32; fax: +33 1 69 08 68 67.
E-mail address: chuchun.fu@cea.fr (C.-C. Fu).

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substitutional helium and self-interstitial atoms, the possibility of self-defect creation (e.g. loop punching) caused by the clustering of interstitial helium, and the structures and dissociation energies of the most stable small helium–vacancy clusters.

2. Method of calculation

The present calculations have been performed within the density functional theory (DFT) as implemented in the SIESTA code [11]. The calculations are spin polarized and use the generalized gradient approximation (GGA). Core electrons are replaced by nonlocal norm-conserving pseudopotentials. Valence electrons are described by linear combinations of numerical pseudo-atomic orbitals. The pseudo-potential and the basis set used for Fe and He atoms are the same as in Refs. [10,12]. The charge density is represented on a regular real space grid of 0.078 Å. The present method was shown to successfully account for the properties of self-defects in iron and of He in a bcc iron matrix [10,12]. Supercell calculations are performed to study the defect properties. All the results reported here have been obtained on 128 atom cells using a $3\times3\times3$ k-point grid and the Methfessel–Paxton broadening scheme with a 0.3 eV width. The structures are fully optimized by relaxing both the atomic positions and the shape and volume of the supercell.

The calculated binding energies of a vacancy, a self-interstitial atoms or an interstitial He atom to a He_nV_m cluster are defined as the energy differences between the configuration where the defect is infinitely separated from the cluster and where it is added to the cluster, making a He_nV_{m+1}, a He_nV_{m-1}, or a $He_{n+1}V_m$ cluster, respectively. The dissociation energy of a defect from a cluster is assumed to be the sum of the corresponding binding energy and the migration energy of the isolated defect [5,10].

In order to evaluate the effect of the supercell size in the reported defect energies, we have compared the results obtained using 250 atom cells instead of 128 for the defects which induce the largest lattice distortions. We find that the discrepancies in both formation and binding energies are about 0.1 eV for He_4, and less than 0.05 eV for He_3. The corresponding differences for other He_nV_m clusters (n, $m = 0,1, 2, 3$ or 4) are expected to be smaller than 0.1 eV, since lattice distortions induced by interstitial and vacancy type defects tend to cancel out. These error bars are significantly smaller than the binding energies determined in this work.

3. Results

3.1. Interaction between interstitial He and self-interstitial atoms

Helium atoms produced by irradiation are likely to initially occupy interstitial sites in the iron matrix. According to *ab initio* results an interstitial helium (He_{int}) prefers to be in the tetrahedral rather than the octahedral site and it migrates almost athermally with an activation energy of 0.06 eV [10]. It can be deeply trapped by a vacancy, gaining 2.3 eV in energy and become a substitutional impurity. However, we have considered here the alternative when the interstitial helium atom finds a self-interstitial atom before it is trapped by a vacancy. We have therefore calculated the interaction energies between a tetrahedral interstitial He and a $\langle1\,1\,0\rangle$ dumbbell – the most stable mono-interstitial configuration – for various relative positions of the two defects. We find that several of them are attractive, three of them are shown in Fig. 1. The most favorable situation found is when the He atom resides in a third nearest tetrahedral site to the dumbbell (see Fig. 1(a)). The corresponding binding energy is 0.26 eV and the dissociation energy – obtained by adding the migration energy of interstitial He – is 0.32 eV. However, self-interstitial atoms can act as efficient traps only at temperatures where they are weakly mobile; since their migration energy is $\simeq$0.3 eV [12] this will be the case only at relatively low temperatures. It is worth mentioning that recent empirical potential simulations [8] also show a positive binding energy (attraction) of 0.34–0.37 eV between a $\langle1\,1\,0\rangle$ dumbbell and a neighboring octahedral He (the octahedral site being the most stable interstitial site for the potentials used). In addition, those simulations evidenced attractive interactions between an interstitial He and $\langle1\,1\,1\rangle$ oriented self-interstitial clusters, suggesting that the interstitial He atoms may trap $\langle1\,1\,1\rangle$ loops and slow their fast migration.

3.2. Interaction between substitutional He and self-interstitial atoms

When a self-interstitial atom (I) approaches a substitutional He (He_{sub}) a spontaneous recombination–replacement (kick-out) reaction is expected to

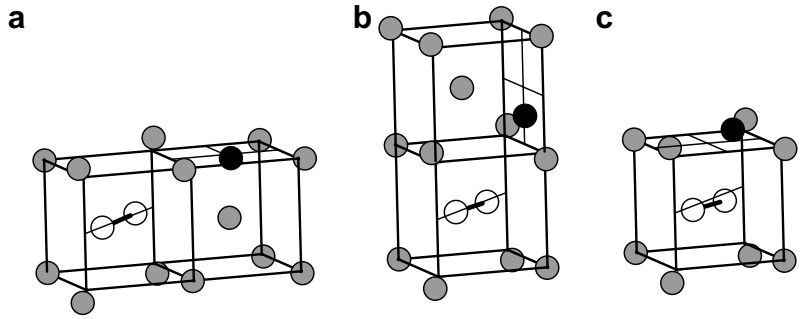

Fig. 1. Schematic representations of stable configurations containing a $\langle 1\,1\,0\rangle$ dumbbell and an interstitial He at various tetrahedral positions. The black, gray and white spheres symbolize the He, the Fe lattice atoms, and the $\langle 1\,1\,0\rangle$ dumbbell, respectively. The atoms are at their relaxed positions.

occur. We confirm here that the $He_{sub} + I \rightarrow He_{int}$ reaction implies a large energy gain, namely 3.6 eV. In other words the energy gained by recombining a Frenkel pair (5.9 eV) largely overcomes the energy lost by moving a helium atom from a substitutional to a tetrahedral site leaving an empty vacancy behind (2.30 eV). What happens before this reaction actually occurs – i.e. when the two defects are close to each other without the self-interstitial atom spontaneously kicking the helium atom out of the vacancy – may also be important. We have therefore investigated such configurations by considering first the interaction between a He_{sub} and a $\langle 1\,1\,0\rangle$ dumbbell. The kick-out reaction occurs spontaneously when a He_{sub} is at the nearest neighbor site within a (1 1 0) plane containing the dumbbell (Fig. 2(a)), but when the He_{sub} is out of the plane (Fig. 2(d)) a finite energy barrier prevents spontaneous recombination. In the latter configuration a binding energy of 0.24 eV is found. From such a metastable configuration the $\langle 1\,1\,0\rangle$ dumbbell may perform usual translation–rotation jumps [12]. We have investigated one of them by considering the final configuration where the He_{sub} and the dumbbell are third neighbors (Fig. 2(e)) which has a binding energy of 0.16 eV. The corresponding migration energy is 0.4 eV, i.e., slightly larger than the migration energy of an isolated $\langle 1\,1\,0\rangle$ dumbbell (0.34 eV). Jumps similar to this one, i.e. between these types of metastable configurations, are likely to occur only if none of the migration barriers leading to kick-out processes are significantly lower. This possibility remains to be investigated. These preliminary results show that one cannot exclude the possibility that a $\langle 1\,1\,0\rangle$ dumbbell will be temporally trapped by a substitutional He before the kick-out reaction

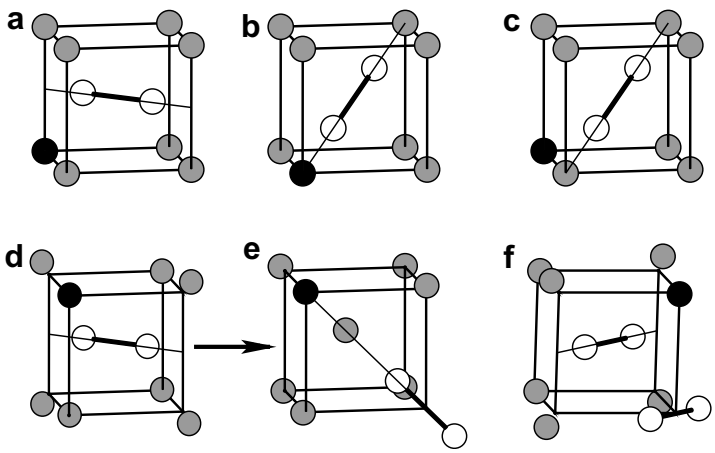

Fig. 2. Schematic representations of systems containing a substitutional He and a mono- or a di-interstitial: configurations (a), (b), and (c) are unstable against a kick-out reaction, while (d), (e) and (f) are local minima. (d) and (e) represent the initial and final positions of a $\langle 1\,1\,0\rangle$ dumbbell performing a translation–rotation jump in the neighborhood of a substitutional He.

occurs. The situation may be similar in the di-interstitial case (two parallel ⟨1 1 0⟩ dumbbells). The most stable complex formed by the reaction of a di-interstitial with a substitutional He has an energy lower by 3.1 eV than that of the two isolated defects. As in the single interstitial case, we have found a metastable configuration with the two defects close to each other but without spontaneous recombination (Fig. 2(f)), the corresponding binding energy is 0.52 eV. Further calculations are needed to complete these energy landscapes.

The formation energy of a ⟨1 1 1⟩ dumbbell is 0.7 eV higher than the ⟨1 1 0⟩ dumbbell according to *ab initio* calculations [12]. In order to see whether this relative stability may change in presence of helium, we have performed calculations with a ⟨1 1 1⟩ dumbbell close to a He_{sub}. We find that a recombination–replacement reaction occurs spontaneously and the ⟨1 1 1⟩ dumbbell is unstable for the both closest configurations (Fig. 2(b) and (c)).

3.3. Stability of small He_nV_m clusters

In agreement with previous results [5,6], we have shown by means of *ab initio* calculations that there are strong attractive interactions between interstitial He atoms and vacancies and that interstitial He atoms also attract each other. The binding energies of He_{int} to He_nV_m clusters are found to be positive in all cases, and the clustering of interstitial He atoms is energetically favorable even in absence of vacancies [10]. Fig. 3 shows the energetically most favorable configurations containing 2, 3, 4, and 5 interstitial He atoms. The following properties of these clusters are summarized in Table 1: the binding energies of the last He_{int} to the He_{n-1} clusters, the relaxation volumes i.e. the volume increase in the fully relaxed system containing defects with respect to bulk bcc iron, and the relaxation amplitude from their original positions of the most perturbed atoms (the atoms at the center of the cubes in Fig. 3). It is clear that the lattice distortion increases rapidly with the number of He_{int}. Concerning the structures of these clusters some characteristics are interesting to point out. Compact structures with He atoms occupying closest interstitial sites are preferred in order to minimize Fe–He repulsive interactions, and extended two-dimensional platelet-like structures are not favored. The He_2 cluster with two tetrahedral He atoms residing on opposite faces of the conventional cubic cell and the He_4 cluster with four tetrahedral He in the same plane are 0.32 eV and 0.42 eV higher in energy than their respective ground state configurations shown in Fig. 3.

Table 1
Properties of He_n clusters with $n = 2$–5: $He_{int} + He_{n-1} \rightarrow He_n$ binding energies E^b in electron volts (eV); the relaxation volumes ΔV in units of Fe atomic volume (V_0); and the relaxation amplitude from its original position of the most perturbed atom d in units of the bcc iron lattice parameter (a_0)

	He_2	He_3	He_4	He_5
E^b (eV)	0.43	0.95	0.99	1.22
ΔV (V_0)	1.99	3.12	4.28	5.42
d (a_0)	0.13	0.23	0.33	0.37

The binding energies of a self-interstitial atom (I) and a He_{int} to small helium–vacancy clusters are compared in Fig. 4. These values represent the gain in energy when a defect is added to a given cluster according to the following reactions: $He_nV_m + He_{int} \rightarrow He_{n+1}V_m$ and $He_nV_m + I \rightarrow He_nV_{m-1}$. The I to cluster binding energies decrease linearly with n. In almost all the cases considered here, the I to cluster binding energy is larger than the He_{int} to cluster binding energy, which means that the absorption of a self-interstitial atom is more favorable than that of an interstitial helium. The only exceptions are when the initial cluster contains only one vacancy (He_nV) and $n \geqslant 3$; the energy gain of the $He_nV + He_{int} \rightarrow He_{n+1}V$ reaction is then indeed larger than that of the $He_nV + I \rightarrow He_n$ reaction. We may expect other exceptions when extrapolating our results to larger values of n. For instance in the He_nV_4 case the addition of an interstitial He is predicted to be energetically more favorable than the addition of a self-interstitial atom for $n > 7$.

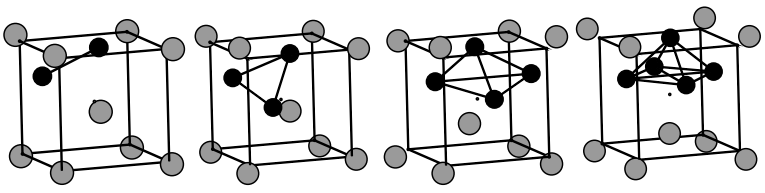

Fig. 3. Schematic representations of He_n clusters containing 2, 3, 4 and 5 He_{int} atoms. All atoms are at their relaxed positions.

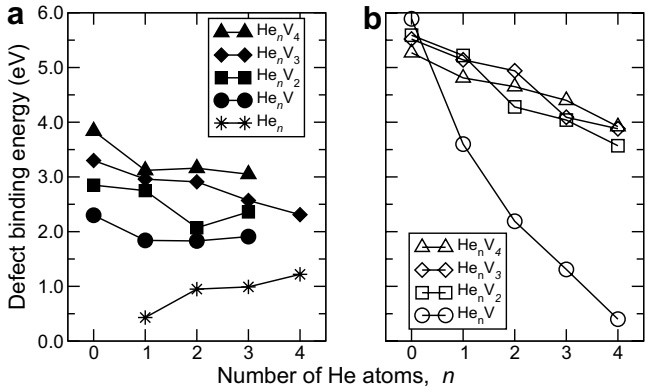

Fig. 4. Binding energies of: (a) a He_{int} atom and (b) a $\langle 1\,1\,0\rangle$ dumbbell to a He_nV_m cluster. The abscisa refers to the number of He atoms in the initial cluster.

Concerning He_n clusters, it is interesting to study from the energetic point of view the emission – or dissociation – of various defects from them. The defects we consider are He_{int}, and the mono-, di- and tri-$\langle 1\,1\,0\rangle$ interstitials (I, I_2 and I_3). The values taken for the migration energies to calculate the dissociation energies are 0.06, 0.34, 0.42 and 0.42 eV, respectively [10,12]. The results are plotted in Fig. 5. We see that all the I_m ($m = 1$, 2 and 3) dissociation energies decrease linearly with n and that the emission of a mono-interstitial is energetically more favorable than that of an interstitial He from a He_n cluster for $n > 3$. We also predict that the emission of I, I_2, and I_3 may occur spontaneously from a He_n cluster for $n > 4$, $n > 6$ and $n > 7$, respectively. Therefore, a He_n cluster with $n > 4$ may decrease its local pressure and decay to He_nV by releasing a self-interstitial atom. A similar result has been reported by Wilson et al. [13] by investigating the behavior of He in Ni. They found that a spontaneous emission of I, I_2 and I_5 from a He_n cluster is possible for $n > 4$, $n > 7$, and $n > 15$, respectively. Morishita et al. have suggested, after examining He_nV_m clusters in Fe for n, $m = 1$–20 using empirical potential simulations [6], that the emission of small $\langle 1\,1\,1\rangle$ interstitial loops from a He_n cluster (loop punching) may be even more favorable than the emission of a mono-interstitial for $n \gtrsim 8$.

3.4. Properties of the most stable He_nV_m clusters

Previous studies [5,10] have revealed that the stability of small He_nV_m clusters against the thermal emission of vacancies or interstitial He atoms depends mainly on the relative concentrations of He and vacancies in the cluster, i.e., the n/m ratio. In post-irradiation annealing conditions e.g. in a

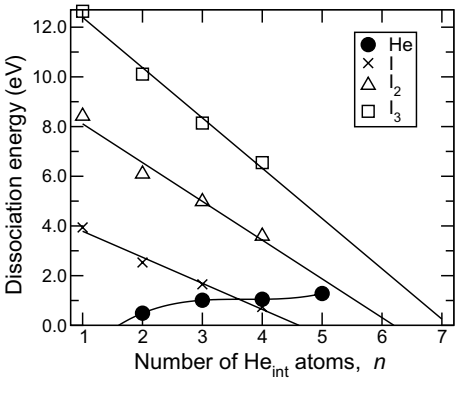

Fig. 5. Dissociation energies of a He atom, a mono-, di-, or a tri-$\langle 1\,1\,0\rangle$ interstitial from small interstitial He_n clusters.

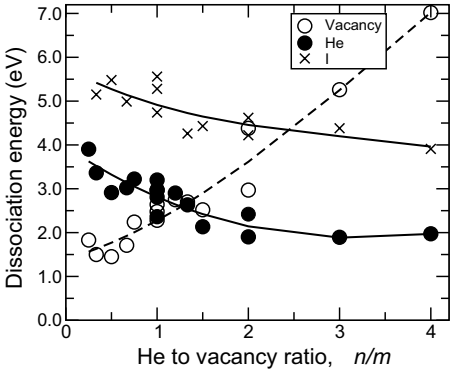

Fig. 6. Dissociation energies of a vacancy, a He atom or a self-interstitial atom (I) from a He_nV_m cluster as function of He to vacancy ratio.

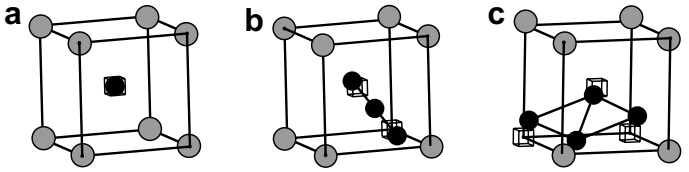

Fig. 7. Lowest energy configurations of: (a) the substitutional He, (b) the He_3V_2, and (c) the He_4V_3. The atoms are at their relaxed positions.

thermal He desorption experiment [14], defect dissociation processes with increasing activation energies will take place as temperature increases. The present dissociation energies suggest that clusters with large n/m ratios tend to emit He_{int} and clusters with low n/m ratios tend to emit vacancies. At variance with previous empirical potential results [5], the emission of self-interstitial atoms from clusters containing at least one vacancy always requires higher activation energies than the emission of interstitial He atoms (Fig. 6). We have found that the small He_nV_m clusters that can survive at high temperatures have a n/m ratio around 1.3 [10]. The lowest energy configurations found for some of them: the HeV (substitutional He), the He_3V_2, and He_4V_3 are shown in Fig. 7. Helium atoms prefer substitutional rather than interstitial sites. In the case of He_{sub} (HeV), the lattice distortion induced by the insertion of He is very small, the nearest neighbor Fe atoms only present an inward relaxation of 1.2% with respect to their positions in the bcc iron matrix. This is also the case for small He_nV_n clusters, where all He atoms are substitutional and reside in nearest neighbor sites. The respective He dissociation energies for $n = 1$, 2, 3 and 4 are 2.36, 2.81, 2.97 and 3.22 eV. We note that they increase with the number of He atoms in the cluster n. The He_3V_2 cluster contains two He in near substitutional sites and a third He in the midway position between them. The energetically most favorable configuration of the He_4V_3 cluster consists of three He atoms in near substitutional sites and a fourth He atom in an octahedral site. The four He atoms remain in the same plane. The calculated dissociation energies of He from He_3V_2 and He_4V_3 clusters are 2.13 eV and 2.63 eV, respectively. From the energetic point of view the present results suggest a possible interpretation of some high temperature stages (II and IV) in the thermal He desorption spectra [14]. Experimental results show that stage II can be observed even at very low He irradiation dose at temperatures around 750 K with an activation energy of 2.4 ± 0.4 eV. We have proposed that the dissociation of He from HeV is a good candidate for this stage [10]. Here, we suggest that He desorption from the high stability clusters containing more He atoms, such as He_nV_n with $n > 1$ and He_4V_3 may be responsible for stage IV, which has been observed at 800–1000 K at higher He irradiation doses with an estimated activation energy around 2.9 eV.

4. Conclusions

First principles calculations have been performed to study the interaction between helium and self-interstitial atoms and the stability of small He_nV_m clusters in α-iron. Interstitial He atoms are found to have attractive interactions with self-interstitial atoms, these interactions being much weaker than those with vacancy type defects. At low temperatures a fast migrating interstitial He can be trapped by a $\langle 1\,1\,0\rangle$ dumbbell with a detrapping energy of 0.32 eV. Interstitial helium clusters He_n with $n > 4$ are suggested to be unstable against the spontaneous emission of a self-interstitial atom. The dissociation of small helium–vacancy clusters with $n/m \simeq 1.3$ such as He_nV_n with $n > 1$ and the He_4V_3 are suggested to be responsible for stage IV in the thermal helium desorption spectra.

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