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Vacancies, interstitials and gas atoms in beryllium

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ABSTRACT

Here we present the results of first-principles quantum mechanical calculations of energetic parameters of vacancies, interstitials, gas atoms (H, He) and some small point defect complexes in beryllium. It is found that the most energetically favorable position for self-interstitial is the basal octahedral one, for hydrogen atoms is the basal tetrahedral, while He atoms can be located with equal probability in basal octahedral and basal tetrahedral interstitial positions. The formation of divacancies and tri-vacancies from individual vacancies is shown to be energetically unfavorable, which implies high stability of beryllium against vacancy clustering. The preliminary estimates of diffusion pathways for H and He interstitials indicate essential differences: while hydrogen diffusion is nearly isotropic, that of He occurs preferentially in basal planes with the migration energy of only 0.1 eV.

1. Introduction

Irradiation of fusion reactor structural and functional materials with fast particles from reactor plasma will result in the production of point defects. This will be accompanied by accumulation of gaseous impurities (helium and tritium), both implanted from hot plasma and produced in nuclear reactions induced by fusion neutrons. At the elevated temperatures typical for the reactor operation point defects tend to agglomerate into defect clusters (voids, dislocation loops). The vacancy-based defects in metals are known to be efficient traps for gas atoms, which, in turn, stabilize vacancy clusters against thermal dissociation (see e.g. [1]). The synergetic result is the promotion of gas bubble formation and the enhanced retention of gas atoms. The first effect causes such deleterious macroscopic effects, as swelling, embrittlement and surface erosion. The second effect is sometimes also undesirable, in particular – for beryllium, which is a candidate functional material for fusion reactor blanket and the plasma facing first wall. In order to find a way for suppression of fusion material degradation, one should understand the physical mechanisms of radiation point defect clustering in the presence of helium and tritium. This would be impossible without a reliable database on properties of self point defects and gas impurities (formation and migration energies, energies of defect interaction, etc.).

Unfortunately, for beryllium this database is incredibly poor. Here we present a summary of systematic first-principles calculations for vacancies, small vacancy complexes, interstitials, and gas atoms (H, He) in beryllium. A detailed discussion of the implications of the obtained results for the simulation of damage evolution in irradiated beryllium will be given elsewhere.

2. Calculational details

Our calculations have been performed using VASP code [2] with the generalized gradient approximation (GGA) as proposed in [3]. The effect of core electrons was represented by using both ultrasoft Vanderbilt pseudopotentials and PAW method implemented in VASP. A comparison of these methods has demonstrated practically no difference in the predicted defect energies. In all calculations the constant volume supercells with hcp crystalline structure (as appropriate for Be) and the optimized lattice parameter values $a = 2.259$ Å and $c/a = 1.572$ [4] were used. Supercell sizes were varied from 36 to 200 atoms in order to eliminate the interaction of defects with their images emerging due to the periodic boundary conditions.

Brillouin zone sampling of the wave-functions and charge density was done using the gamma-centered Monkhorst-Pack k-point grid [5]. A detailed earlier study [4] has demonstrated that the energy cutoff of at least 450 eV and a high number of k-points (at least (12,12,12) sampling mesh) are necessary to guaranty the defect energy convergence. In some of the most resource consuming calculations we used, however, somewhat weaker restrictions (300 eV cutoff or (9,9,9) sampling mesh), which might result in a slight (~0.05 eV in the worst case) underestimation of the defect energy (cf. [4]).

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3. Simulation results

3.1. Self point defects

The calculated energy parameters of vacancy and several small vacancy complexes in Be are summarized in Table 1. The vacancy formation energy was found to be close to 0.8 eV, which is less than predicted by the earlier simulations [6–10], but consistent with the available experimental data. Indeed, using the known values of self-diffusion activation energies (1.6–1.7 eV [11]) and the vacancy migration energy of 0.7–0.8 eV [12], the vacancy formation energy can be estimated to fall within 0.8–1.0 eV.

In order to clarify the kinetics of vacancy clustering, one needs the binding energies of vacancies in small clusters. Hence, we have studied three divacancy configurations: two pairs at the first nearest neighbor (1NN) separation, oriented in basal plane ($2V_{aa}$) and along pyramidal direction ($2V_{ac}$), and one pair at the 2NN separation along the *c*-axis ($2V_{cc}$). The divacancy binding energy was defined as, $E^b_{2V} = 2E^f_V - E^f_{2V}$, where E^f are the divacancy and vacancy formation energies. The data for beryllium collected in Table 1 suggest that, in contrast to many other metals, the formation of divacancies from individual vacancies is energetically unfavorable. Moreover, the formation of a tri-vacancy ($3V_{cac}$) by addition of one more vacancy to $2V_{ac}$ divacancy is as energetically unfavorable, as the formation of the divacancy itself (note that the formation energy of $3V_{cac}$, as indicated in Table 1, differs from that published earlier in [4], which was a misprint). The energy penalty associated with the formation of small vacancy complexes implies high swelling resistance of Be in the absence of possible void stabilizers (gas atoms), that was confirmed by beryllium foil irradiation in high voltage electron microscope at 570 K up to dose of 15 dpa [14].

The situation with a self-interstitial is more complicated than for vacancies, because its possible configurations in Be are not a priori clear. We have studied eight interstitial configurations, six of which are shown in Fig. 1 and the remaining two are dumbbells oriented either normally to the basal plane (S), or along direction $\langle 11\bar{2}0\rangle$ in the basal plane (BS). Information about the stability of different configurations against small shifts from the equilibrium positions and the formation energies for stable ones is summarized in Table 2. As can be seen, six interstitial configurations are stable and their formation energies are generally quite high, while two configurations undergo spontaneous transition to some another configurations. The stable configurations can be divided into two sets. The first one includes the most energetically favorable basal octahedral (BO) configuration, which is closely followed by the crowdion and basal split ones; the energies scatter in this group is within 0.2 eV. Configurations in the second group (O, T, S) are nearly 1 eV less energetically favorable, differing in energy from each other by less than 0.1 eV.

Table 1
The calculated formation and binding energies for a vacancy and small vacancy clusters.

Configuration	Sites in supercell	E^f (eV)	E^b (eV)
V	200	0.81	
V	96	0.85	
$2V_{aa}$	96	1.96	−0.26
$2V_{ac}$	96	2.07	−0.37
$2V_{cc}$	96	1.97	−0.27
$3V_{cac}$	96	3.27	−0.35

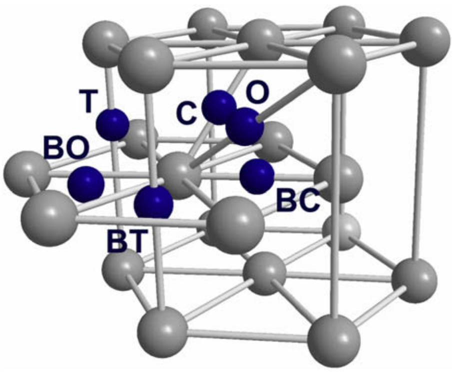

Fig. 1. The possible interstitials positions in beryllium: octahedral (O), tetrahedral (T), crowdion (C), basal octahedral (BO), basal tetrahedral (BT), and basal crowdion (BC).

3.2. Gas impurities

In addition to self point defects, we have studied the energetics of interstitial hydrogen and helium atoms. Four high-symmetry interstitial positions (T, O, BT, and BO) were considered as potential candidates for gas atom locations. The heat of solution of gas atoms, which for impurities is the experimentally measurable parameter analogous to the formation energy for self point defects, was estimated as

$$U_s = E^{\mathrm{Be+G}}_{tot} - E^{\mathrm{Be}}_{tot} - E^{\mathrm{G}}_{ref} = E^{\mathrm{G}}_{c} - E^{\mathrm{G}}_{ref},$$

where $E^{\mathrm{Be+G}}_{tot}$ and E^{Be}_{tot} are the total energies of relaxed simulation cells with and without a gas atom, and E^{G}_{ref} is the energy of a gas atom outside the crystal.

3.2.1. Hydrogen

Among four considered initial positions of hydrogen atoms, only two turned out to be stable, namely BT and O. As can be seen in Table 2, BT configuration is approximately 0.2 eV more favorable than O. The absolute values of hydrogen heat of solution depend on the reference hydrogen energy E^{G}_{ref}, which depends on hydrogen loading conditions. For typical experiments, where hydrogen solubility in Be is measured in equilibrium with the high-pressure molecular hydrogen environment, the appropriate reference energy is half of the energy of hydrogen molecule. In this case the heat of hydrogen solution is quite high, ~1.6 eV. On the other hand, for atomic hydrogen environment E^{G}_{ref} is lower by half the dissociation energy of H_2 molecule (~2.3 eV, as estimated with VASP code). Correspondingly, the endothermic hydrogen solubility in Be from molecular environment becomes exothermic for the atomic environment (see Table 2). The latter conclusion is in agreement with the experimental observations. Indeed, molecular hydrogen has very low solubility in beryllium (typically 1–10 appm [13]), while charging of Be samples with atomic deuterium from a plasma source resulted in deuterium concentrations of 5–7 at% [15].

The insertion of a hydrogen atom into a basal tetrahedral (BT) position results in noticeably stronger outward relaxation of neighboring Be atoms than into O position, and one might assume that the energy of elastic lattice distortion should be higher for BT than for O. The fact that BT configuration is more energetically favorable than O can be related to the noticeably higher electron density in BT positions, which simplifies the screening of a proton charge by surrounding electrons. Thus, the energetic proficiency of locating hydrogen atom in that or other high-symmetry positions is determined by a competition between the repulsion from the nearby Be atoms and the electron density localization.

Because the local electron density increase promotes the capture of hydrogen ions, one could speculate that positioning of two hydrogen atoms on neighboring BT positions in the same basal plane would result in additional energy gain. However, the energy

Table 2
The calculated formation energies for self-interstitials and heats of solution of hydrogen and helium atoms in Be (in eV).

	Sites in supercell	Configuration							
		O	T	S	C	BO	BT	BS	BC
Self-interstitial	150	5.24	5.22	5.29	4.39	4.20	unst.	4.30	unst.
Hydrogen[a]	96	−0.51	unst.	unst.	–	unst.	−0.72	–	–
		1.71					1.58		
Helium	96	unst.	unst.	–	–	5.81	5.82	–	–

[a] The energy values in the upper row correspond to the atomic hydrogen environment and those in the lower row – to the molecular environment.

of such hydrogen pair is 0.17 eV higher than the sum of energies of two isolated hydrogen atoms. In other words, hydrogen atoms in the same basal plane tend to avoid each other. For comparison, a pair of hydrogen atoms in neighboring O and BT positions practically does not interact.

The principal migration pathway found for hydrogen atom includes jumps between BT and O positions with the apparent migration barrier of $\sim$0.38 eV. This value nicely correlates with the available experimental data [16,17]. Other possible jumps, O → BO → O and BT → BO → BT, have noticeably higher barriers (0.6 and 0.8 eV, respectively).

3.2.2. Helium

For helium atoms also only two interstitial configurations were found to be stable, namely BO and BT, with practically the same heats of solution (see Table 2). Note that both stable configurations are in the basal plane. According to preliminary estimates, the transition of He atom along the pathway BO → BT requires the effective barrier of only 0.1 eV, whereas the transition BO → O → BO along *c*-axis involves migration barrier of 0.36 eV. This indicates that interstitial helium diffusion in beryllium is strongly anisotropic, occurring preferentially along basal planes.

The poor solubility and fast diffusion of interstitial helium as found here for beryllium, is typical for other metals as well. Normally, this results in the very quick and efficient capture of interstitially dissolved He atoms by vacancies, voids and extended defects (dislocations, grain boundaries). Correspondingly, one should expect very strong promotion of gas bubble formation in the presence of helium in beryllium, which was confirmed by many experiments (see e.g. [18]).

4. Summary

In this paper we summarize the data for point defects in beryllium obtained by now in the framework of our first-principles calculations. Considered are both self point defects (vacancies and interstitials) and such practically important gases as hydrogen and helium. The obtained values of self defect formation energies and gas atom heats of solution, migration barriers and interaction energies provide a sound basis for predictions of the kinetic behavior trends for the defect structure in irradiated Be. Among the most interesting predictions are the repulsive vacancy–vacancy interaction, the three-dimensional character of self-interstitial and H migration, as opposed to the preferentially planar migration of He atoms.

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