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Letter to the Editors

Hydrogen and vacancies in the tokamak plasma-facing material beryllium

H. Krimmel, M. Fähnle *

Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

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Abstract

Within the framework of the density functional electron theory in local-density approximation and the ab initio pseudopotential method the properties of vacancies and hydrogen atoms near vacancies in beryllium are calculated. The vacancy formation energy is 1.13 eV. The hydrogen atom is located off-centre, i.e., on a hexahedral interstitial site near the vacancy. © 1998 Elsevier Science B.V. All rights reserved.

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The properties of hydrogen isotopes in hexagonal beryllium (Be) play an important role in the context of the use of Be as plasma-facing material in a fusion reactor [1]. In a recent publication [2] it has been shown within the framework of the ab-initio density-functional electron theory in local-density approximation [3] that hydrogen isotopes occupy the hexahedral or the tetrahedral interstitial sites in Be, whereby the energetically most favourable position in the tetrahedron is not the geometrical centre, but a site close to the hexagonal basal plane. The calculated heat of solution for tritium on the hexahedral site is (0.8 ± 0.1) eV, in fair agreement with the experimental value (1 eV) of Swansiger [4].

For the diffusional properties of hydrogen isotopes in Be the interactions with impurities (especially oxygen [5]) and with vacancies generated by irradiation damage or by thermal excitations are relevant. No direct experimental information on the vacancy-formation energy is given in the literature. Assuming that the activation energy of self-diffusion (1.71 eV or 1.63 eV for diffusion parallel or perpendicular to the c-axis [6]) is determined by a vacancy mechanism and that a step according to an activation energy of 0.8 eV in the recovery behaviour of the electrical resistivity after irradiation is due to vacancy migration [7], a formation energy of 0.91 eV or 0.83 eV is obtained, which would yield a very high vacancy concentration of 0.003 or 0.006 at the melting point (inserting tentatively a vacancy formation entropy of 1 k_B). No experimental information is available on the interaction of hydrogen isotopes with vacancies in Be. In the present letter, therefore, the ab-initio calculations of Ref. [2] are extended to vacancies and vacancy-hydrogen interaction in Be.

The calculations were performed within the framework of the density-functional theory in local-density approximation [3] and the ab initio pseudopotential method, with a pseudopotential according to Vanderbilt [8] for Be and according to Kerker [9] for H. The errors for the vacancy formation energy arising from the use of a finite number of k-points for the sampling of the Brillouin zone and from the use of a finite number of plane waves were estimated to be smaller than 0.03 eV, respectively. The calculations were performed within the supercell formalism for supercells containing 36 regular sites and for the ab-initio calculated [10] lattice parameters of Be. The structural relaxation of the atoms surrounding the vacancy turned out to be smaller than 1% of the nearest-neighbour distance in the basal plane and hence considerably smaller than the

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* Corresponding author. Tel.: +49-711 689 1913; fax: +49-711 689 1932; e-mail; faehn@physix.mpi-stuttgart.mpg.de.

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relaxation of some percent of the atoms surrounding an interstitial hydrogen isotope. Because in simple metals the interactions of the defects in the supercell geometry are mainly due to elastic interactions [11] and because the results for hydrogen on interstitial sites were fairly well converged [2] for a supercell containing 36 sites, we assume that this holds also when introducing in addition the vacancy.

The calculated vacancy formation energy is 1.13 eV, with a gain of 0.035 eV due to structural relaxation. Assuming again a vacancy formation entropy of 1 k_B we arrive at a thermal vacancy concentration of $6 \cdot 10^{-4}$ at the melting point, which appears to be more realistic than the above estimated concentration from the activation energy of self-diffusion and from the recovery of the electrical resistivity.

To determine the position of the hydrogen atom close to a vacancy, we calculated in a first step the adiabatic potential [12] around the fully relaxed vacancy configuration (Fig. 1a, the meaning of the symbols is explained in Fig. 1b). Obviously, the location of H in the centre of the vacancy corresponds to a local maximum of the total energy, i.e., the equilibrium position is off-centre as in the case of Pd [13] and Cu [14]. The energetically most favourite position is at the hexahedral site (whereas the trigonal site corresponds to a saddle point of the energy surface). In a second step we started from the fully relaxed vacancy configuration, inserted the hydrogen atom at the hexahedral site and determined the structural relaxation of the surrounding atoms due to the additional forces exerted by the hydrogen atom. The corresponding energy gain of 0.038 eV is smaller than the difference in energies at the various interstitial sites of the adiabatic energy surface, so that the additional relaxation should not affect the energetical sequence of the metastable hydrogen positions. In a third step, we determined in isotropic and harmonic approximation a zero-point vibrational energy of 0.12 eV for hydrogen at the hexahedral position of the adiabatic energy surface which is again smaller than the difference in energies at the various interstitial sites. Altogether, we therefore can conclude that hydrogen at a vacancy in Be is located off-centre, namely at a hexahedral interstitial site in the basal plane. The attractive interaction energy between vacancy and hydrogen atom thereby is very large (1.62 eV), which is probably related to the fact that the free electron density at a regular interstitial site in Be is much larger than the density which is most favourable for the embedding of a hydrogen in a homogeneous electron gas (see, for instance Ref. [13]). Therefore the system may gain much energy by moving the hydrogen atom to a position close to a vacancy with smaller free electron density. The interaction energy is larger in magnitude than the vacancy formation energy. However, because the endothermic heat of solution of hydrogen in Be is very large [10] it nevertheless costs energy to create a vacancy and insert a hydrogen atom from a hydrogen molecule outside the crystal into the hexahedral interstitial site at a vacancy, i.e., there is no spontaneous formation of vacancy-hydrogen pairs.

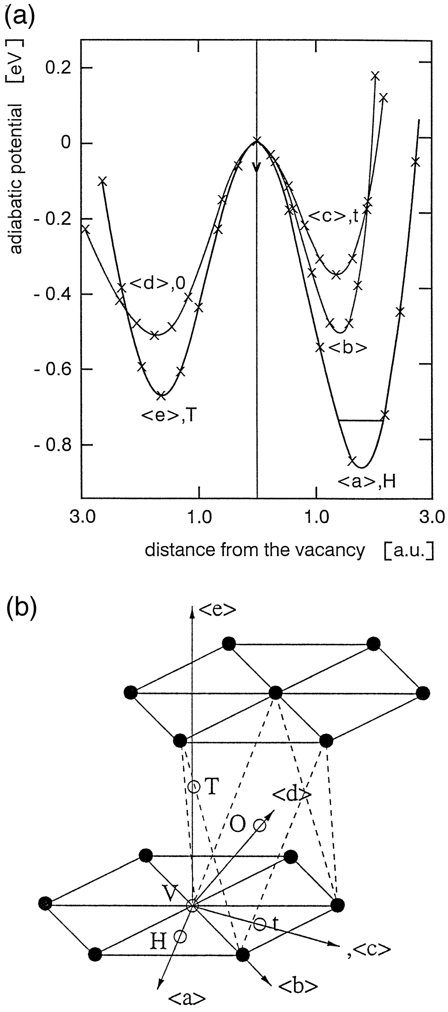

Fig. 1. The adiabatic potential (a), normalized to zero at the vacancy V, for hydrogen in the fully relaxed vacancy configuration in Be. V, t, O, T and H denote the vacancy position and the trigonal, octahedral, tetrahedral and hexahedral interstitial positions. The positions of the interstitial sites close to the vacancy are shifted towards the vacancy centre with respect to the positions in the ideal structure of Be (b) by 43%, 41%, 32% and 26% of the original distances from the vacancy centre. The horizontal line corresponds to the energy of the hydrogen atom at H including the zero-point vibrational energy (see text). The displacement paths $\langle i \rangle$ for the hydrogen atoms are depicted in (b) 1 a.u. $= 0.529 \cdot 10^{-10}$ m.

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