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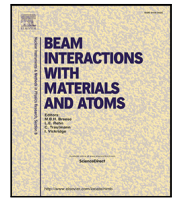
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Energy landscape of hydrogen in the vicinity of monovacancy in beryllium

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ABSTRACT

The present work is devoted to fill the lack of data related to the hydrogen behavior in the vicinity of monovacancy in the hexagonal compact structure of beryllium. These data are of importance to feed coupled reaction–diffusion models dedicated to the simulation of hydrogen behavior in beryllium in order to analyze its thermal release as function of concentration and temperature. This work aims to evaluate the trapping and detrapping energies for several pathways surrounding a vacancy as well as the impact of multiple trapping of hydrogen on these data. In addition, the data to compute the detrapping rates for a single hydrogen are given. The determination of the energy landscape in the vicinity of the monovacancy has shown that the trapping energy varies from 0.39 eV (equal to the activation energy for diffusion in non-defective bulk) down to 0.12 eV while the activation energy for detrapping mechanism rises to 1.08 eV up to 1.48 eV. The lowest detrapping energy, 0.86 eV, is obtained from hydrogen filled vacancy whereas the multi-trapping does not significantly affect the trapping energy.

Beryllium has been chosen as one of the plasma-facing materials for the ITER's first wall. Due to the low burning efficiency of the deuterium–tritium fusion reaction, significant amounts of hydrogen isotopes could be implanted and finally trapped in walls. For safety reasons, the allowed tritium inventory to be present at any time in the vacuum vessel must be limited to 700 g. Consequently, the development of an operational technique to remove tritium from the first wall is essential. Baking of the in-vessel components could be efficient for this purpose [1,2] but the heating temperatures should be assessed in respect to the temperatures required for achieving a full tritium detrapping. The temperature impact of the hydrogen release is not only important to limit the tritium inventory in the vessel during the normal operations, but also to evaluate the tritium behavior in case of loss of confinement. Thermal Desorption Spectroscopy (TDS) is an experimental technique allowing to get these information. As mentioned by Oberkofler et al. [3], although much experimental data have been acquired in the past on hydrogen retention and its transport in beryllium, the details of the elementary processes are still not completely clear. In parallel, codes solving reaction–diffusion systems of equations [4,5] have been developed from the modeling of the atomic-scale mechanisms to tentatively simulate TDS experiments. A good agreement between experiment and simulations has been reported in Ref. [6] but obtained at the price of some empirical adjustment due to an insufficient description of the atomic elementary processes as hydrogen trapping or detrapping from beryllium defects. These related

data are not easily accessible from experiment, but many of them can be obtained from Density Functional Theory (DFT) calculations.

The insertion energies of hydrogen in interstitial sites [7–11] as well as in monovacancy (V_1) [8,12] have been computed. In addition, several migration pathways have been investigated for the diffusion of hydrogen in non-defective bulk, empty V_1 , and also for the trapping of a single hydrogen in V_1 [8,9,11]. Despite these numerous studies, the description of the energy landscape of hydrogen in beryllium bulk is still incomplete. In particular the activation energies for the multi-trapping of hydrogen in V_1 as well as a detailed analysis of trapping and detrapping pathways of hydrogen in monovacancy are lacking. These data are of importance since vacancies are known to be the dominant defects in beryllium [9]. Therefore, the present communication is devoted to determine these data.

DFT calculations are performed with the Quantum Espresso code [13] using the PBE exchange and correlation functional. The simulation details as well as the computational optimization are the same as those reported in a publication by our group (see Ref. [14]). The saddle points of pathways as well as the associated activated energies (trapping and de-trapping mechanisms) are determined using the Nudged Elastic Band (NEB) method [15] incorporating the climbing image scheme [16]. The correction of activation energies with the elastic effect [17] has not been considered. It was shown to have a weak impact (few meV) on the insertion energies of hydrogen in

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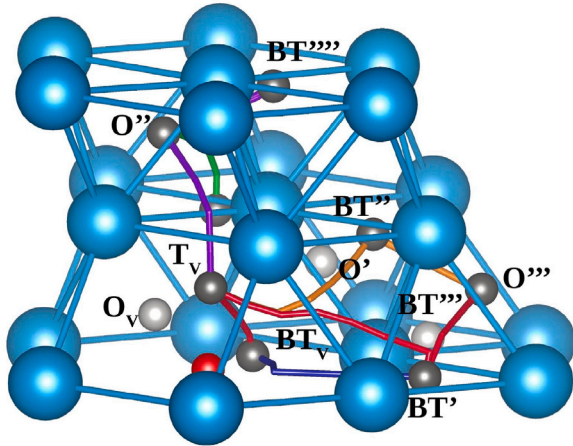


Fig. 1. Schematic view of the insertion sites and identified migration paths (colored lines) in the vicinity of vacancy (red sphere). Blue spheres correspond to beryllium atoms, small dark ones are the stable insertion site whereas the lightest ones become unstable in presence of vacancy. The V subscript is used for sites inside the vacancy and notation ', ', etc. are referred to first, second, etc., neighborhood of the monovacancy.

beryllium bulk. The vibrational frequencies are computed at the center Brillouin zone by DFPT implemented in Quantum Espresso to assess the stability of each insertion sites and to compute the vibrational Helmholtz energy [18]. The discussion related to the accuracy of the latter are reported in Ref. [11].

In the hexagonal compact structure, there are six insertion sites for hydrogen. Previous works [7,10,11] have stated that hydrogen is stable in the basal tetrahedral (BT) and octahedral (O) sites where the former being the ground state. Our investigation of site stability in the vicinity of vacancy shows that hydrogen is only stable in T-like (above and below vacancy position) and BT-like sites called T_V and BT_V (Fig. 1); the latter is the most favorable trapping configuration with an energy 0.14 eV lower than T_V . Unlike Zhang et al. [12], the O_V and BO_V sites are found unstable: hydrogen in O_V relaxes toward T_V , while the phonons calculations lead to imaginary frequencies when hydrogen is inserted in BO_V . Therefore, inside the vacancy cavity, only five trapping sites exist (2 T_V and 3 BT_V) in agreement with the previous Ganchenkova's study [7]. The notation of insertion sites around the monovacancy is the following: ', ', etc. are referred to first, second, etc., neighborhood of the monovacancy. Regarding the hydrogen insertion next to the vacancy, O' is not stable whereas the relaxation of hydrogen in BT''' is accompanied by a spontaneous migration of vacancy leading to a trapping in BT_V . All the other sites shown in Fig. 1 are stable. BT' , BT'' or BT'''' , which are not strictly in the basal plane, does not significantly differ BT sites from an energetic viewpoint since the energy only decreases by a few dozen of meV between BT' and BT'''' . As a consequence, the impact on the energies of vacancy vanishes rapidly with the distance.

From the stable insertion sites, the activation energy for the trapping and detrapping processes are thereafter computed. According to the large number of distinct sites around the vacancy, the energetic landscape can be processed by five elementary migration paths as shown in Fig. 1.

Starting from the most stable site BT_V , the direct path to leave the vacancy (blue data in Fig. 2) has the highest activation energy, 1.48 eV; consequently, the trapping energy is also the highest (0.39 eV). The latter value is similar to the activation energy of diffusion process for the hydrogen in non-defective beryllium bulk [9,11]. In addition,

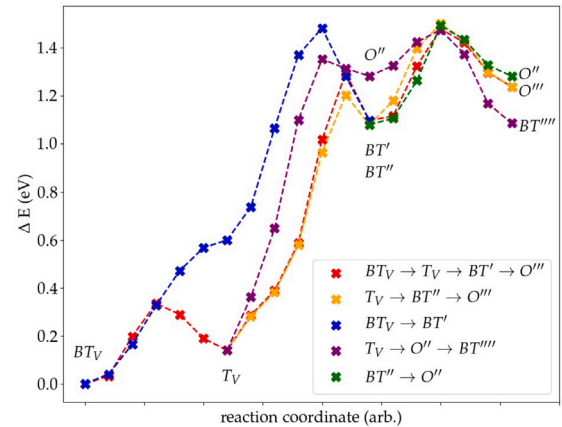


Fig. 2. Migration pathways of the hydrogen migration in the vicinity of monovacancy in beryllium computed with NEB method.

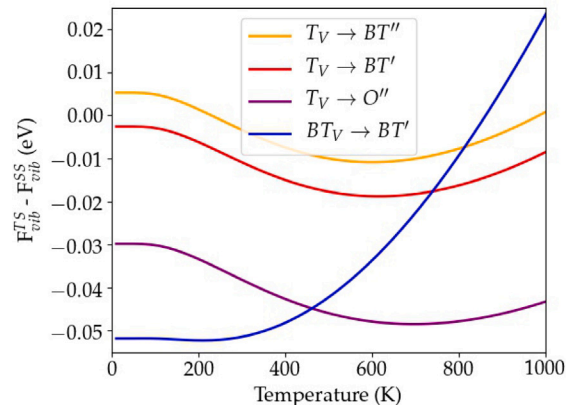


Fig. 3. Vibrational Helmholtz energies required to compute the attempt frequencies for the detrapping processes of single hydrogen. The notations TS and SS refer to transition state and stable site, respectively.

the involved saddle point is a second-order transition state. In the vacancy neighborhood, the activation energies to displace a hydrogen from a site to another one are low. It means these barriers should not have a significant impact on (de)trapping processes. Other exit paths involve T_V site. The detrapping energy to leave perpendicularly to the basal plane ($T_V \rightarrow O''$) is equal to 1.21 eV while energies are slightly lower in the basal plane with 1.15 eV and 1.08 eV, toward BT' and BT'' , respectively. Reasonably, the most efficient way for the trapping mechanism involve BT' and BT'' with an activation energy equals to 0.2 and 0.12 eV. The hydrogen diffusion path ($E_{\text{trap}} = 0.24$ eV and $E_{\text{detrap}} \approx 1.3$ eV) reported by Zhang et al. [12] is in agreement with our results. Nevertheless the comparison is not straightforward because the O_V site is considered as stable while we have shown this present study shows that it relaxes to T_V . This ascertainment is supported by the fact that the $T_V \rightarrow BT'$ path (red data in Fig. 2) includes, at halfway, the O_V site. Regarding the other sites, the migration energies of $BT'' \rightarrow O'$, $BT'' \rightarrow O'''$, $O'' \rightarrow BT''''$ and $BT' \rightarrow O'''$ are close to one in non-defective beryllium bulk, *i.e.*, ≈ 0.2 eV and ≈ 0.4 eV for $O \rightarrow BT$ and $BT \rightarrow O$, respectively. That confirms that the vacancy influence tends to be localized in its neighborhood.

Table 1

Activation energies associated to (initial state) \rightarrow (final state) in eV in the case of multiple trapping phenomena. E_{trap} is the activation energy of the trapping and E_{detrap} the activation energy to de-trapping (bold number).

Number of H	$E_{\text{trap}}/E_{\text{detrap}}$ (eV)	
	$BT' \rightleftharpoons T_V$	$T_V \rightleftharpoons BT_V$
2	0.18/ 1.07	0.18/ 0.36
3	0.18/ 0.99	0.23/ 0.43
4	0.13/ 0.99	–
5	0.20/ 0.86	–

These results, summarized in Fig. 2, do not highlight a significant anisotropic behavior for the elementary process of hydrogen (de)trapping, moreover the temperature effect tends to reduce it for the detrapping mechanisms (Fig. 3). Due to low trapping energies, the trapping rate should be kinetically controlled by diffusion in beryllium (the jump rates are available in Ref. [11]). In regards of aforementioned statements only the vibrational Helmholtz energies for the detrapping pathways are herein computed (Fig. 3). According to the Eyring's theory, the detrapping probabilities could be therefore computed with those data.

Regarding to the multiple trapping phenomena, previous studies have shown that a monovacancy could favorably accommodate the insertion of five hydrogen atoms [7,12] with an energy varying at each insertion step. Consequently, it is expected that hydrogen migration in the vacancy vicinity is also function of number of trapped atoms. Migration pathways toward hydrogen–vacancy complex have been investigated by considering a favorable mechanism obtained for single hydrogen, *i.e.*, a path through BT' . Our results show that the activation energy of trapping mechanism varies very slightly in comparison to single trapping but the overall impact would remains negligible. Nonetheless, about the detrapping mechanisms, the activation energy decreases as far as the number of trapped atoms increases. A drop is highlight for the detrapping of the fifth hydrogen atom for which the lowest activation energy (0.86 eV) is obtained. Complete data are reported in Table 1.

In summary, stable hydrogen positions in the vicinity of monovacancy have been determined, and the energy landscapes of both single and multiple trapping phenomena have been computed. The activation energy for the trapping mechanism varies between 0.39 and 0.12 eV while the multi-trapping phenomena do not affect this data. In contrast, the lowest detrapping energy is obtained from the filled vacancy configuration whereas, in case of single hydrogen, it includes in the following interval: 1.08 eV up to 1.48 eV. The necessary data to compute the attempt frequencies and therefore the jump probabilities are given for the detrapping pathways of the single hydrogen. These data are planned to be integrated in the next future in reaction–diffusion codes like CRDS [4], FESTIM [19] or MHIMS [20] currently developed to predict the retention and release of hydrogen isotopes in metallic materials in function of fluence and temperature for ITER applications. Additionally, these data could be used in the next future to develop a hydrogen–beryllium potential in the framework of the molecular dynamics.

CRediT authorship contribution statement

L. Ferry: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **F. Viot:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Y. Ferro:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **M. Barrachin:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Viot reports financial support was provided by European Consortium for the Development of Fusion Energy.

Data availability

Data will be made available on request.

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