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Ohsawa, Kazuhito  
九州大学応用力学研究所

Goto, Junya  
Interdisciplinary Graduate School of Engineering Science, Kyushu University

Yamakami, Masahiro  
Interdisciplinary Graduate School of Engineering Science, Kyushu University

Yamaguchi, Masatake  
Center for Computational Science and e-System , Japan Atomic Energy Agency

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<https://doi.org/10.15017/27087>

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出版情報：九州大学応用力学研究所所報. 139, pp.69-73, 2010-09. Research Institute for Applied Mechanics, Kyushu University

バージョン：

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# Trapping of multiple hydrogen atoms in a tungsten monovacancy

Kazuhiro OHSAWA\*<sup>1</sup>, Junya GOTO\*<sup>2</sup>, Masahiro YAMAKAMI\*<sup>2</sup>,

Masatake YAMAGUCHI\*<sup>3</sup> and Masatoshi YAGI\*<sup>1</sup>

E-mail of corresponding author: *ohsawa@riam.kyushu-u.ac.jp*

(Received July 30, 2010)

## Abstract

The configuration of multiple hydrogen atoms trapped in a tungsten monovacancy is investigated using first-principles calculations to determine trapping energy. Unlike previous computational studies, which have reported that hydrogen in BCC metal monovacancies occupies octahedral interstitial sites, it is found that the stable sites shift towards tetrahedral interstitial sites as the number of hydrogen atoms increases. As a result, a maximum of twelve hydrogen atoms can become trapped in a tungsten monovacancy.

**Key words :** *metal-hydrogen system, tungsten, fusion reactor, first-principles simulation, irradiation*

## 1. Introduction

The interaction between hydrogen (H) and metal is an important subject in the field of metallurgical science. For example, H absorption and diffusion mechanisms on and in iron (Fe) have been investigated in terms of chemical reactions<sup>1)</sup>. H retention assists superabundant vacancy formation in many metals<sup>2, 3)</sup> and degrades the mechanical properties of metals. H retention induces embrittlement of iron and steel<sup>4)</sup>. H bubble formation and blistering reduce the mechanical strength of metals<sup>5)</sup>. In order to examine the H retention mechanism, a stable configuration of H atoms trapped in a monovacancy in  $\alpha$ -Fe was analyzed using first-principles calculations<sup>6)</sup>.

The interaction between H-isotopes, deuterium and tritium, and plasma facing materials (PFMs) will have a strong impact on the success of the International Thermonuclear Experimental Reactor (ITER). The PFMs installed in future fusion reactors are expected to be exposed to high-flux and high-energy plasma particles for long time periods. As a result, many lattice defects will form in the PFMs due to plasma particle collisions. In addition to direct damage, H-isotopes will be

retained in vacancy-type lattice defects in the PFMs, a critical problem for fusion reactors. In particular, divertor armor tiles introduced to control the flow of recycling neutrals and impurities back into the core plasma are exposed to the most intense irradiation in magnetic confinement devices<sup>7)</sup>. In such extreme circumstances, tungsten (W) and its alloys show promise as PFMs due to their low H solubility and excellent thermal and low sputtering properties<sup>8, 9, 10)</sup>.

This paper elucidates the interaction between H and W to reveal fundamental properties of W that will affect its performance as a PFM. According to previous work<sup>11, 12, 13)</sup>, H is strongly attracted to vacancies in W, one of which can serve as a trapping center for multiple H atoms. Stable configurations of multiple H atoms trapped in a monovacancy are investigated using first-principles calculations of lattice relaxation. The trapping energy is calculated as a function of the number of H atoms, which permits estimation of the maximum number of H atoms that can occupy a W monovacancy.

The effect of the H zero-point oscillation is not necessarily negligible in metal-H systems. For example, the zero-point energy (ZPE) for a H atom in bulk W is estimated to be 0.271 eV according to our preliminary calculation<sup>14)</sup>. The ZPE is ignored in this paper for the sake of simplicity, but will be calculated in the near future using the H atom equilibrium positions presented herein.

\*1 Research Institute for Applied Mechanics, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

\*2 Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

\*3 Center for Computational Science and e-System, Japan Atomic Energy Agency, Tokai-mura, Ibaraki 319-1195, Japan

## 2. Simulation method

First-principles calculations based on the density functional theory<sup>15)</sup> are performed using the Vienna Ab-initio Simulation Package (VASP)<sup>16, 17)</sup> with the generalized gradient approximation<sup>18)</sup> and projected augment wave potentials<sup>19)</sup>. Usually, we employ a BCC supercell composed of 54 lattice points ( $3 \times 3 \times 3 \times 2$ ) containing a monovacancy and its Brillouin-zone with  $5 \times 5 \times 5$   $\mathbf{k}$  point sampling using the Monkhorst-Pack scheme<sup>20)</sup>. The plane-wave energy cutoff is 350 eV. Atomic positions and supercell size relaxations are iterated until the force acting on every atom is less than  $2 \times 10^{-3}$  eV/Å. Some cases are checked using a larger BCC supercell composed of 128 lattice points ( $4 \times 4 \times 4 \times 2$ ) containing a monovacancy with  $3 \times 3 \times 3$   $\mathbf{k}$  point sampling. The energy cutoff is 300 eV for these cases because of computer capacity limits.

Energetically favorable sites for H in the intrinsic bulk W are investigated by placing a H atom at tetrahedral and octahedral interstitial sites (T-site and O-site) in the BCC lattice, as shown in Fig. 1 (a) and (b). Based on the cohesive energy, T-sites are more favorable than O-sites by about  $-0.380$  eV for interstitial H in the intrinsic bulk W lattice, in accordance with the previous work<sup>13, 21)</sup>. Here, a negative sign indicates an exothermic reaction, while a positive one indicates an endothermic reaction.

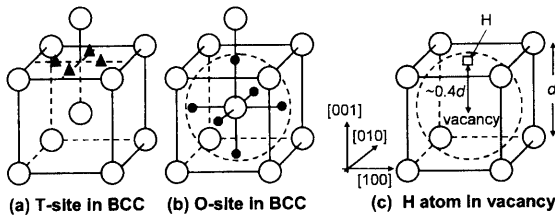


Fig. 1 (a) Tetrahedral and (b) octahedral interstitial sites in BCC lattice. Open circles indicate metal atoms. (c) Schematic view of a single H trapped in a monovacancy in BCC lattice.

Investigation of stable configurations of single and multiple H atoms show that H atoms migrate to the inner surface of a monovacancy in metals<sup>6, 11, 12, 22)</sup>. In previous work, the off-vacancy-center position close to the O-site was assumed to be the most favorable site for H, as shown in Fig. 1 (c). This analysis does not require such starting assumptions; the initial configurations for the H atoms in the vacancy are randomly generated. The H atoms are initially placed uniformly within one of multiple regions represented by gray squares in Fig. 2. For clarity, only the squares normal to the (001)

plane are shown, but there are equivalent ones normal to the {100} plane surrounding the monovacancy. The initial configuration has a maximum of one H atom in each square, leaving some unused when there are fewer H atoms than squares. The initial distribution is that shown in Fig. 2 (a) if  $m \leq 6$ , and that shown in Fig. 2 (b) otherwise, where  $m$  is the number of H atoms trapped in the monovacancy. The parameters  $s_1$ ,  $s_2$ , and  $s_3$  indicate the distance between the gray square and center of the vacancy, side length of each square, and distance between two squares, respectively. Usually, the values  $s_1 = 0.4d$ ,  $s_2 = 0.2d$ , and  $s_3 = 0.2d$  are chosen, where  $d$  ( $\sim 3.17$  Å) is the W lattice constant. However, these parameters may be adjusted to account for conditions such as convergence of the lattice relaxation. In our experience, a third of the relaxation processes arrive at a valid ground state, while the others arrive at a metastable state or do not finish within the expected number of relaxation steps.

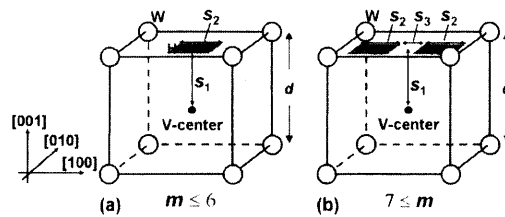


Fig. 2 Schematic view of initial distribution of  $m$  H atoms in a W monovacancy. Random placement of an H atom is uniformly distributed within each gray square. (a) Center of square is close to the O-site. (b) Center of square is shifted in the (100) direction.

The total trapping energy for single and multiple H atoms is defined as

$$E_{tot}(conf.) =$$

$$E[W_{n-1}VH_m] - E[W_{n-1}V] - m(E[W_nH^T] - E[W_n]), \quad (1)$$

where the function  $E$  is the cohesive energy of the supercell.  $W_{n-1}VH_m$  is a supercell composed of  $(n-1)$  W, a monovacancy, and  $m$  H;  $W_{n-1}V$  is that composed of  $(n-1)$  W and a monovacancy;  $W_nH^T$  is that composed of  $n$  W and one H embedded at a T-site; and  $W_n$  is perfect lattice composed of  $n$  W, respectively. The parameter *conf.* represents the H configuration in the monovacancy. Therefore, eq. (1) gives the total energy gain of  $m$  H atoms migrating from distant T-sites and becoming trapped in a monovacancy. The average trap-

ping energy is defined as

$$E_{ave}(conf.) = E_{tot}(conf.)/m, \quad (2)$$

which was used in this and other analyses<sup>11, 22)</sup>.

### 3. Inspection of previous work

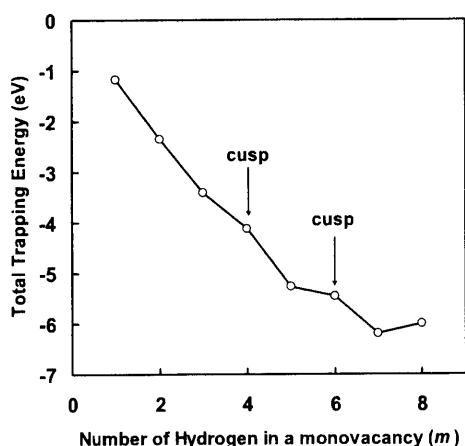


Fig. 3 Dependence of the total trapping energy ( $E_{tot}$ ) on the number of H atoms ( $m$ ) in a monovacancy by assuming that H atoms are located close to the O-sites. Two cusps are observed at  $m = 4$  and 6.

Position close to the O-site was assumed to be the most favorable site for H atoms in previous works<sup>11)</sup>. However, we are skeptical about the assumption. The dependence of the trapping energy on the number of H atoms has a strange profile, if every H atom is located close to the O-site. Two cusps are observed, as shown in Fig. 3. The cusps indicate that four and six H configurations in a monovacancy would be relatively unstable and adding a H atom induces stabilization. However, we can not find an appropriate reason why these configurations are unstable. In order to solve the question, initial positions of H atoms for lattice relaxation are given by random number.

### 4. Results

Stable positions for a single H in a monovacancy are calculated and shown in Fig. 4 projected onto the {001} plane. Single H occupies a location close to the O-site, which corresponds to the work of Liu *et al.* very well<sup>11)</sup>. However, the positions are slightly shifted in the  $\langle 100 \rangle$  or  $\langle 010 \rangle$  direction by about 0.05  $d$ .

Stable configurations of four and six H atoms trapped in a monovacancy are explained in detail and shown in Figs. 5 and 6, respectively. The planer configuration of four H atoms shown in Fig. 5 (a) is not

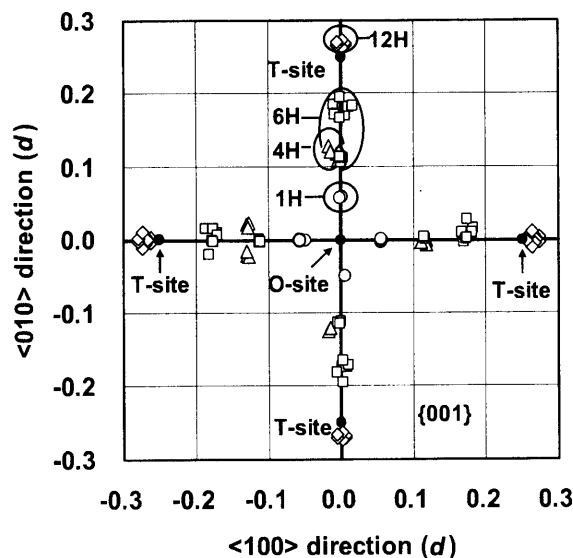


Fig. 4 Stable positions of H atoms projected onto the {001} plane. Circle, triangle, square, and diamond symbols correspond to the cases where one, four, six, and twelve H atoms are trapped in a monovacancy in a W lattice, respectively. O-site located at the center of figure.

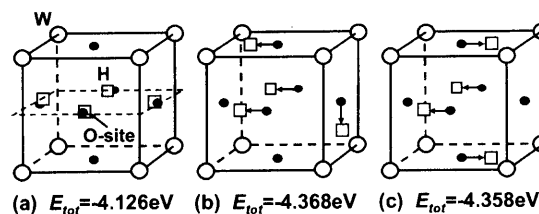


Fig. 5 Schematic view of configurations of four H atoms in a monovacancy. Open circles, open squares, and closed circles indicate W, H, and O-sites, respectively. (a) Metastable state; four H atoms are located close to O-sites on the (001) plane. (b) Ground state; tetrahedral configuration of four H atoms. (c) State that is nearly degenerate with the ground state.

a ground state structure. Instead, the tetrahedral configuration of H atoms in Fig. 5 (b) is a ground state and that in Fig. 5 (c) has a nearly degenerate trapping energy.

Many types of stable and metastable configurations can be found for the case of six H atoms. As in previous work, the total trapping energy is calculated by assuming that each H atom starts close to the O-site in

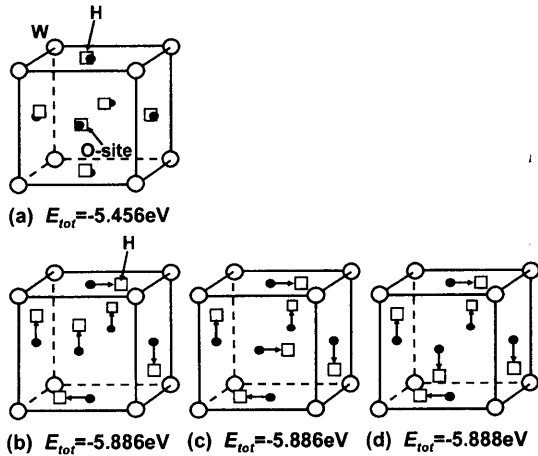


Fig. 6

Schematic view of configurations of six H atoms in a vacancy. Open circles, open squares, and closed circles indicate W, H, and O-sites, respectively. (a) Metastable state; six H atoms are located close to the O-sites. (b), (c) and (d) Degenerate ground states; H atoms are considerably shifted from the O-sites.

the vacancy, as shown in Fig 6 (a). In this case, the trapping energy is estimated to be  $E_{tot}(6\text{H}^0) = -5.456$  eV. However, the H configurations shown in Fig. 6 (b), (c), and (d) are found to be more stable, with trapping energy estimated to be  $E_{tot}(6\text{H}) = -5.886 \sim -5.888$  eV. By taking into account finite temperature, these energetically equivalent configurations can be regarded as degenerate ground states. The six H atoms in these configurations are not located close to the O-sites, but considerably shifted in the  $\langle 100 \rangle$  or  $\langle 010 \rangle$  direction by a large displacement of  $0.1 \sim 0.2d$ , as shown in Fig. 4. Four H atoms shift by about  $0.18d$  and the remaining two shift by about  $0.12d$  from the O-site.

As mentioned above and shown in Fig. 4, stable positions for the H atoms in the monovacancy gradually move away from the O-site in the  $\langle 100 \rangle$  or  $\langle 010 \rangle$  direction as the number of trapped H atoms increases. Here, we assume that the most favorable site for H is the T-site in the high H density limit. Thus, the stable configurations of more than six H atoms in a monovacancy are sought by assuming that H atoms are located close to the T-sites. So, the initial distribution of H atoms in Fig. 2 (b) is used.

Stable and metastable configurations for the case of twelve trapped H atoms are shown in Fig. 7. Two H atoms close to the T-sites are arranged in the  $\langle 100 \rangle$  direction on every  $\{100\}$  plane. The distance between the two H atoms is approximately  $d/2$  ( $\sim 1.6$  Å), much longer than an  $\text{H}_2$  molecule bond of length  $0.75$  Å. Therefore, these H pairs are not  $\text{H}_2$  molecules. The dis-

tance between H atoms is maximized because H atoms in a W lattice experience an effective mutual repulsion<sup>13, 21, 23</sup>. Thus, the configuration shown in Fig. 7 (a) is the lowest energy state.

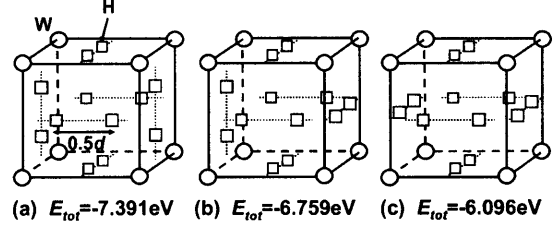


Fig. 7

Schematic view of configurations of twelve H atoms in a monovacancy. (a) Ground state. (b) and (c) Metastable states. Open circles and open squares indicate W and H, respectively. H atoms are located close to T-sites.

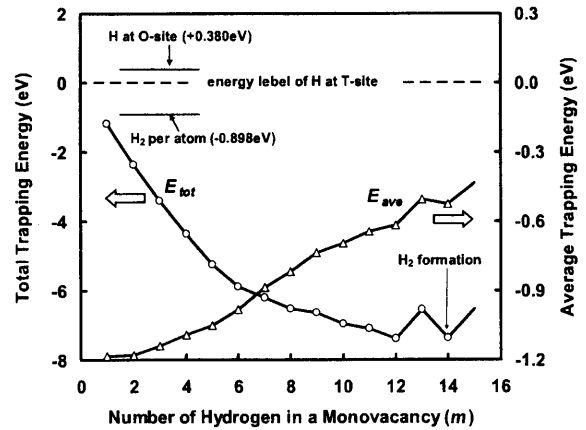


Fig. 8

Total (circles) and average (triangles) trapping energy as function of H atom number trapped in a monovacancy in a W lattice. Zero energy level corresponds to energy of H atom embedded at the T-site.

The number of H atoms that a W monovacancy can accommodate was expected to be quite large because there are twenty four T-sites on the inner surface of the vacancy in a BCC lattice. Figure 8 shows the dependence of total trapping energy on the H atom number. The ground state structures of the multiple H atoms are evaluated by comparing the energy of simulated stable and metastable configurations. The total trapping energy gradually increases as the number of H atoms increases to twelve, but ceases to increase once the number exceeds twelve. Additional H atoms move out of the vacancy and become trapped at T-sites outside the vacancy during the relaxation process.

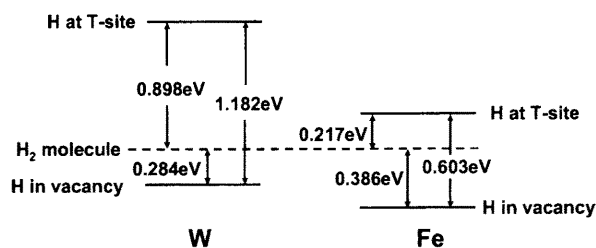


Fig. 9 Energy landscape of W and Fe lattice representing total energy gain of H trapping in a monovacancy.

Occasionally, the additional H atoms remain inside the vacancy as isolated H atoms, lowering the total trapping energy. As the H atom number increases above twelve, the trapping energy does not decrease monotonically; the formation of an H<sub>2</sub> molecule inside the vacancy contributes to an increase of the trapping energy. In particular, the total trapping energy for fourteen H atoms with the H<sub>2</sub> molecule formation is estimated to be -7.365 eV, which is almost the same as that for twelve H atoms of the ground state (-7.391 eV). No more than one H<sub>2</sub> molecule is observed inside the monovacancy at one time.

## 5. Discussion

To explain why a monovacancy in W can accommodate so many H atoms, we refer to the energy landscape of H in W and Fe shown in Fig. 9. One of the prominent properties of W is an extremely high chemical potential with H (0.898 eV). Thus, H is not usually retained in bulk W. However, there is a significant capacity for the H density to increase in an irradiation environment such as a fusion reactor. The energy gain is very large when a H embedded at a T-site migrates to a monovacancy in the W lattice (1.182 eV). This large energy gain, which traps a large number of H in the monovacancy, is not necessarily realized in other BCC metals; the energy gain of H migration in an Fe lattice is only 0.603 eV<sup>14)</sup>.

These simulations showed that H atoms move from the O-sites to more stable positions close to the T-sites as they increase in number, as shown in Fig. 4. This phenomenon may be related to the fact that a single H preferentially occupies a T-site in a perfect BCC lattice.

### Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (No. 20560616) from the Japan Society for the Promotion of Science. We would like to express to Dr. Aaron Froese our gratitude for his devoted support.

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