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# Thermodynamics of hydrogen-induced superabundant vacancy in tungsten

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ABSTRACT

We investigate superabundant vacancy formation induced by hydrogen in tungsten in terms of an equilibrium thermodynamic model to estimate hydrogen isotope retention in plasma facing materials. Vacancy-hydrogen cluster concentrations in the bulk tungsten are calculated as a function of the H concentration at finite temperature. A monovacancy in usual bcc transition metals is capable of accommodating six H atoms, while a maximum of 12 H atoms can be accommodated in a tungsten monovacancy, according to first-principle calculations. The present results provide thermodynamic profiles of vacancy-hydrogen clusters trapping more than six H atoms for the first time. In present work, configurational transitions of H atoms trapped in the monovacancy and activation energies for them are investigated by examining the transition paths in order to calculate configurational entropy. Vacancy-hydrogen clusters trapping more than six H atoms exist in thermodynamic equilibrium. However, the major vacancy-hydrogen clusters are composed of six H atoms in a wide range of temperature and H concentration.



## 1. Introduction

Investigations of interaction between tungsten (W) and hydrogen (H) isotopes, deuterium (D) and tritium (T), are important subjects in the field of fusion reactor because W and its alloys show promise as divertor armor tiles installed in the International Thermonuclear Experimental Reactor (ITER) due to the very low natural H solubility of W and large H diffusivity in a bulk W [1,2]. Besides, W and its alloys have some excellent properties as plasma facing materials (PFMs), e.g., high melting point and high thermal conductivity [3]. However, the divertor armor tiles are exposed to the most intense plasma particle irradiation in fusion reactors for a long time period. One of the purposes of the present work is to contribute to the study of H isotopes absorbed in the PFMs in fusion reactors. In particular, T retention and desorption of the PFMs are very important safety concerns in future fusion reactors because T is a radioisotope whose physical half-life is about 12 years. In order to examine the H-isotope effects, two types of simulations are performed in the present work, i.e., including and not including zero-point energy (ZPE) corrections of H atoms. Superabundant vacancy (SAV) formation induced by hydrogen is observed in a variety of metals when the metal specimens are held at high temperatures and high hydrogen pressures [4–6]. In the present paper, concentrations of the vacancy-hydrogen (Vac-H) clusters are calculated as a function of local H concentration at finite temperature for the H retention analysis. High hydrogen pressure causing the SAV formation is not achieved by plasma in fusion reactors. However, sufficiently high local H concentration is expected to be realized in W specimens by such intense irradiation. Actually, a large amount of H or H isotopes retention, about 0.1 atomic percent, has been reported in the vicinity of the surface of W specimens by irradiation experiments [7].

Although H does not dissolve in a bulk W because of the low H solubility, it is supposed to be trapped in vacancy-type lattice defects. In order to elucidate atomistic mechanism about the H trapping, some previous works are performed in terms of first-principle calculations [8,9]. It has been reported that stable structures of H atoms trapped in a W monovacancy are anomalous compared with those in usual bcc transition metals [10]. An H prefers to be located close to an octahedral interstitial site (O site) next to a monovacancy in bcc transition metals by first-principle calculations. As a result, a maximum of six H atoms can be accommodated in the vacancy because there are six O sites next to the monovacancy in bcc lattice [11]. However, ground-state structures of multiple H atoms trapped in a tungsten and molybdenum (Mo)

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monovacancy are exceptionally complicated compared with those in usual bcc transition metals [10]. The H atoms in the W and Mo monovacancy are gradually shifted from O sites to more stable positions close to tetrahedral interstitial sites (T sites) as they increase in number. In particular, a maximum of 12 H atoms can be accommodated in the W monovacancy. Some distinct and unknown phenomena are expected to be found associated with the SAV formation in the intrinsic bulk W because of the anomalous H configurations in the vacancy. Another purpose of the present work is to elucidate thermodynamic properties of the SAV formation in a bulk W. The reliability of Vac-H clusters trapping more than six H atoms will be discussed in the present paper.

Vac-H cluster concentrations in a bulk W are calculated as a function of the bulk H concentration for different temperature in an equilibrium thermodynamic model in which free energy of the system is assumed to be composed of internal energy, configurational and vibrational entropy. Free energy in this work does not include the effects of partial pressure and chemical potential of H gas because H atoms are assumed to be introduced in the W specimens by irradiation [12]. The internal energy, e.g., formation energy for an empty monovacancy and binding energy of H atoms to the monovacancy, are estimated in terms of first-principle calculations. The configurational entropy is derived from the total number of distinguishable microstates by Boltzmann's relation. However, too many degenerate ground states exist for H atoms trapped in a W monovacancy because of the complicated H structures. So, a practical criterion is introduced to determine distinguishable and independent microstates associated with the H atoms in the vacancy, as mentioned later.

This paper is organized as follows: Section 2 presents the technical aspects of first-principle calculations, thermodynamic equilibrium model in the present paper, and method of energy barrier calculation associated with configurational transitions of H atoms. Section 3 gives internal energy of the W–H system, e.g., binding energy of H atoms to a W monovacancy associated with distinct ground-state structures. In Section 4, the configurational and vibrational entropy introduced in the present paper are described. Particular attention is paid to the practical criterion introduced in the present work, i.e., how distinguishable microstates are determined for the multifold degenerate configurations of H atoms in the W monovacancy. In Section 5, we describe thermodynamic profiles of Vac-H cluster concentrations and the dependence on temperature and H concentration. In Section 6, we discuss the present work and assignment left for future work.

## 2. Methodology

### 2.1. First-principle calculation

First-principle calculations based on density functional theory [13] are performed to investigate the W–H system using the Vienna ab initio simulation package (VASP) with the projector augmented wave method [14–16]. The generalized gradient approximation by Perdew et al. is used [17]. Large supercells composed of 432 lattice points ($6 \times 6 \times 6$ bcc lattice) are used in the present simulations in order to examine vibrational entropy. The cutoff energy for plane wave is 350 eV. The Monkhorst–Pack k-point mesh is $2 \times 2 \times 2$ for the unit cell [18]. Atomic positions and supercell volume relaxations are iterated until the force acting on each atom is less than $2 \times 10^{-3}$ eV/Å.

Vacancy formation energy $e_v$ in an intrinsic bulk W is defined as

$$e_v = E[W_{n-1}V] - \frac{n-1}{n}E[W_n], \quad (1)$$

where the function $E$ is the cohesive energy of the supercell. $W_{n-1}V$ indicates a supercell composed of $(n-1)$ W atoms and a monovacancy V; and $W_n$ is a perfect lattice composed of $n$ W atoms, where $n = 432$ in the present paper. The binding energies for single and multiple H atoms to a W monovacancy are defined in a total energy manner,

$$e_k = E[W_{n-1}V] - E[W_{n-1}VH_k] + k(E[W_nH^T] - E[W_n]), \quad (2)$$

where $W_{n-1}VH_k$ is a supercell composed of $(n-1)$ W, a monovacancy V, and $k$ H trapped in the vacancy; and $W_nH^T$ is that composed of $n$ W and an interstitial H atom embedded at a T site because H prefers to be located at T site in an intrinsic bulk W [8–10]. Positive sign of $e_k$ indicates an attractive interaction between H and W monovacancy. The total binding energy including ZPE corrections is

$$e_k^z = e_k + kZ(H^T) - Z(H_k^V), \quad (3)$$

where $Z(H^T)$ is the total ZPE for an interstitial H atom located at a T site in the bulk W and $Z(H_k^V)$ is the total ZPE for $k$ H atoms of stable configuration trapped in a W monovacancy. The ZPEs are calculated by means of harmonic approximation assuming that the force acting on an H atom is proportional to the displacement from the equilibrium position. Then, the ZPEs are derived from eigenvalues of Hessian matrix which is second derivatives of energy with respect to the H positions of the stable configuration [19]. To calculate the Hessian matrix, the H atoms are displaced in the direction of each Cartesian coordinate from the stable positions by 0.02 Å in the present work. The values obtained from the harmonic approximation are agreement with those from non-linear adiabatic potential and experiments. For example, stretching vibration of $H_2$ molecule is estimated to be 4275 $cm^{-1}$ (128 THz) by the harmonic approximation in the present simulation. The value calculated on the basis of adiabatic theory is 4162.06 $cm^{-1}$ [20]. The results obtained from molecular spectroscopy are 4161.18 and 4159.2 $cm^{-1}$ [21,22]. The ZPE derived from the harmonic approximation is about 2 or 3 percent larger than those from other methods. Lattice vibrations are also calculated by the harmonic approximation.

### 2.2. Equilibrium thermodynamic model

The SAV formation induced by H is investigated in an equilibrium thermodynamic model, as shown in Fig. 1. The present model is composed of $N_0$ W and $N_H$ H atoms, where $N_0$ and $N_H$ indicate the total number of W and H atoms in the model, respectively. We apply here the independent point defect approximation, that

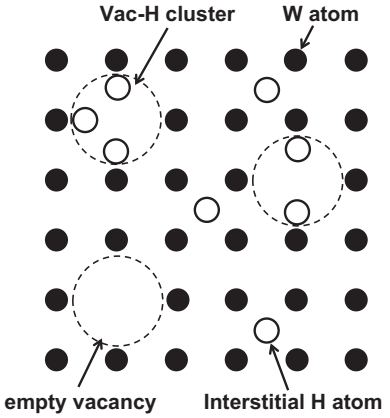


**Fig. 1.** Schematic view of equilibrium thermodynamic model containing Vac-H clusters and interstitial H atoms. Open circles and closed ones indicate H and W, respectively.