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Configuration and binding energy of multiple hydrogen atoms trapped in monovacancy in bcc transition metals

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We present a first-principles study of stable configurations of single and multiple H atoms in a monovacancy in bcc transition metals and binding energies of the H atoms to the monovacancy. Typical bcc transition metals are group-V elements (V, Nb, and Ta), group-VI elements (Cr, Mo, and W), and Fe. The most stable site for an interstitial H atom in the intrinsic bcc transition metals is a tetrahedral interstitial site (T site). On the other hand, a single or a few H atoms trapped in a monovacancy in bcc metals occupy close to octahedral interstitial sites (O sites) next to the monovacancy. However, stable configurations of four and more-than-four H atoms in the monovacancy are various and different depending on the host metals. Stable sites for H atoms are usually shifted toward the T site or diagonal interstitial site (D site) as the number of H atoms increases in the monovacancy. As a result, a maximum of six H atoms can be accommodated in a monovacancy in V, Nb, Ta, Cr, and Fe, which is in good agreement with previous computational studies, while 10 and 12 H atoms can be accommodated in a Mo and W monovacancy, respectively.

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I. INTRODUCTION

The study of vacancy-H interactions in metals is an important subject in the field of metallurgical science. For example, it will contribute to investigations of superabundant vacancy-H cluster creation.[1,2] The retention of H isotopes, namely, deuterium and tritium, in plasma facing materials (PFMs) is a critical problem for the success of future fusion reactors.[3–5] In particular, W and its alloys show promise as divertor armor tiles installed in the International Thermonuclear Experimental Reactor (ITER) due to the low H solubility and excellent thermal properties. One of the purposes of this paper is to elucidate a peculiar property of W associated with H trapping in a monovacancy compared with other bcc metals. In fact, simulations on H atoms trapped in a monovacancy have been intensively performed for a variety of metals.[6–11] However, the results obtained by first-principles calculations have to be inspected more inclusively because the configurations of multiple H atoms in a monovacancy are very complicated beyond expectation and incorrect configurations have been reported in some cases. For example, it has been reported that H atoms trapped in a monovacancy in bcc metals are energetically favorable sitting at slightly shifted O sites next to the monovacancy and a maximum of six H atoms can be accommodated in the monovacancy.[6,9,10] However, these results are not necessarily correct for all bcc metals. In fact, 12 H atoms can be accommodated in a W monovacancy and their stable positions are located at T sites.[11] Another purpose of this paper is the strict investigation of stable configurations of H atoms in a monovacancy in various bcc transition metals and an estimate of binding energies of H atoms to the monovacancy on the basis of first-principles calculations.

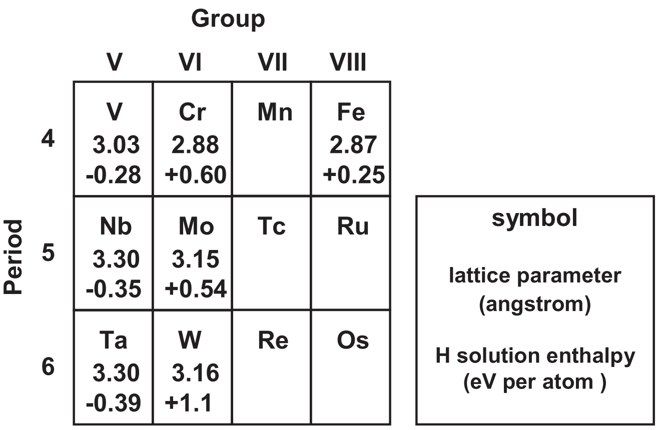
It is interesting that typical bcc transition metals gather in a part of the periodic table, as shown in Fig. 1,[12] i.e., group-V metals (V, Nb, and Ta), group-VI metals (Cr, Mo, and W), and Fe. Most of the alkali metals also have a bcc structure, but they are not dealt with in the present work. Group-V transition metals are hydrogen-storage materials.[13] Therefore, a large amount of H is absorbed in these metals and stable sites of H are experimentally examined by the channeling method.[14,15] On the other hand, Group-VI transition metals and Fe have low H solubility. In particular, Mo and W have been investigated as PFMs to be used in future fusion reactors due to the extremely low H solubility.[3–5,9,11,16]

It is possible that an unexpected ground-state or metastable configuration exists for multiple H atoms trapped in a monovacancy. Therefore, the atomic configurations should be inspected very carefully. A first-principles calculation is useful and is the sole method to inspect the valid H configurations. However, all H configurations in a monovacancy cannot be examined by a first-principles calculation. Then, an interpretation in terms of the effective medium theory helps us understand the stable atomic configurations.[17] In brief, H prefers to be located at a site of an optimal electron charge density.[9] The effective medium theory can explain the reasons why H atoms are located on the inner surface of a vacancy in metals and experience an effective mutual repulsion.[10,18] So, optimal atomic configurations of multiple H atoms in a monovacancy can be presupposed to some extent by the effective medium theory. In addition, a skillful simulation scheme was developed to find a valid atomic configuration.[11] The initial configurations for the H atoms in a monovacancy for lattice relaxation are randomly generated intentionally, as mentioned later.

Zero-point energy (ZPE) for H is not necessarily negligible in metal-H systems. So, two types of binding energies, including and not including the ZPE correction, are calculated for W-H (Ref. 11) and Fe-H (Ref. 19) systems. In the present work, the ZPE correction is estimated for the Mo-H system for comparison.

II. METHODOLOGY

Typical interstitial sites in a bcc lattice are the O site and T site. In addition, the D site is located between two neighboring



Period \ Group	V	VI	VII	VIII
4	V 3.03 -0.28	Cr 2.88 +0.60	Mn	Fe 2.87 +0.25
5	Nb 3.30 -0.35	Mo 3.15 +0.54	Tc	Ru
6	Ta 3.30 -0.39	W 3.16 +1.1	Re	Os

symbol

lattice parameter (angstrom)

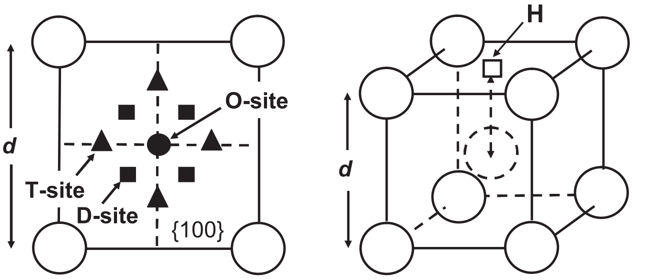
H solution enthalpy (eV per atom)

FIG. 1. Partial periodic table. Lattice parameters[12] and H solution enthalpy[13] are denoted for bcc transition metals, where positive and negative signs correspond to endothermic and exothermic solutions, respectively.

T sites, as shown in Fig. 2(a).[16] A single H atom trapped in a monovacancy is supposed to occupy a position close to an O site next to the monovacancy, as shown in Fig. 2(b).[6,9–11]

First-principles calculations based on the density functional theory[20] are performed using the VIENNA AB INITIO SIMULATION PACKAGE (VASP)[21,22] with the generalized gradient approximation[23] and projector augmented wave method.[24] All supercells used in the present simulations are composed of 54 lattice points ($3 \times 3 \times 3$ bcc lattice) containing a monovacancy. A cutoff energy is 350 eV for all metal-H systems. Usually, a Monkhorst-Pack scheme of $5 \times 5 \times 5$ k-point mesh is used within the Brillouin zone.[25] Atomic positions and supercell size relaxations are iterated until the force acting on every atom is less than 3×10^{-3}eV/Å. However, the calculation accuracy for the Fe-H system is lowered because of computer performance limits. In the case of the Fe-H system, $3 \times 3 \times 3$ k-point mesh is used and the convergence condition for lattice relaxation is 5×10^{-3}eV/Å. Nevertheless, the results of the present simulations for the Fe-H system are in agreement with those calculated in more accurate conditions.[19]

Most of the elements investigated in the present work, namely, V, Nb, Ta, Mo, and W, are paramagnetic (PM) bcc transition metals, while spin polarization has to be taken into account for the case of Cr and Fe. It has been reported that Cr is antiferromagnetic (AFM) below the Néel temperature, which ranges from room temperature to 600 K depending on impurities.[26] The AFM state of Cr is indeed more stable than the PM one, but the magnetism only slightly affects the properties of the Cr-H system. So, only the results in the AFM state are presented in this paper. The calculations associated with the Fe-H system are performed in the ferromagnetic (FM) state.



(a) **O-site, T-site, and D-site** (b) **monovacancy in bcc lattice**

FIG. 2. (a) Interstitial sites in a bcc lattice. Open circles are bcc metal atoms. Closed circle, triangle, and square symbols are the O site, T site, and D site, respectively. d is the lattice parameter. (b) Schematic view of a single H (open square) trapped in a monovacancy in a bcc lattice.

The binding energy for single and multiple H atoms to a monovacancy is defined in a total energy manner,

$$E_{\mathrm{tot}} = E[\mathrm{M}_{n-1}\mathrm{Vac}] - E[\mathrm{M}_{n-1}\mathrm{H}_m\mathrm{Vac}] + m(E[\mathrm{M}_n\mathrm{H}^{\mathrm{T}}] - E[\mathrm{M}_n]), \tag{1}$$

where the function E is the cohesive energy of the supercell. $\mathrm{M}_{n-1}\mathrm{Vac}$ is a supercell composed of $(n-1)$ metal atoms and a monovacancy; $\mathrm{M}_{n-1}\mathrm{H}_m\mathrm{Vac}$ is that composed of $(n-1)$ metal atoms, mH, and a monovacancy; $\mathrm{M}_n\mathrm{H}^{\mathrm{T}}$ is that composed of n metal atoms and one H embedded at a T site; and M_n is a perfect lattice composed of n metal atoms, where $n = 54$ in the present simulations. Therefore, Eq. (1) gives the total energy gain of mH atoms migrating from distant T sites and becoming trapped in a monovacancy.

The total binding energy including the ZPE correction is defined as

$$E_{zc} = E_{\mathrm{tot}} + m\mathrm{ZPE}(\mathrm{H}^{\mathrm{T}}) - \mathrm{ZPE}(\mathrm{H}_m^{\mathrm{V}}), \tag{2}$$

where $\mathrm{ZPE}(\mathrm{H}^{\mathrm{T}})$ is the ZPE for an interstitial H atom at a T site in an intrinsic bcc transition metal, and $\mathrm{ZPE}(\mathrm{H}_m^{\mathrm{V}})$ is the total ZPE for mH atoms trapped in a monovacancy. The ZPE for an interstitial H and mH in a monovacancy is calculated from the Hessian matrix, i.e., the matrix of the second derivatives of the energy with respect to the H positions at an equilibrium configuration.[27]

In order to find valid equilibrium configurations for H atoms in a monovacancy, an innovative simulation scheme is used.[11] Stable configurations of multiple H atoms are presupposed by the effective medium theory in advance.[17] Furthermore, the initial positions of the H atoms for lattice relaxation are intentionally distributed around the presupposed stable positions by using a random number. Relaxation processes starting from such randomly generated initial configurations do not always arrive at a valid ground state. Some of them do not finish within the expected number of relaxation steps. Of course, the relaxation processes that do not converge are excluded from samples used in the present analysis. However, such excluded relaxation processes are necessary to find unexpected equilibrium configurations of multiple H atoms. Proper ground-state and some metastable structures of the H atoms are selected among many equilibrium configurations obtained by the simulation scheme.

III. RESULTS

A. Outline

First of all, a broad outline revealed in the present simulations associated with H trapped in a monovacancy is described. The ZPE corrections of H atoms are calculated

TABLE I. E_d (eV): energy difference for an interstitial H at the T site and O site defined in Eq. (3). E_v (eV): vacancy formation energy defined in Eq. (4). E_{tot} (eV): total binding energy for ground-state structures of single and multiple H atoms to a monovacancy in each transition metal. m: the number of H atoms in a monovacancy.

		V	Nb	Ta	Cr	Mo	W	Fe
E_d		0.149	0.271	0.330	0.188	0.265	0.380	0.131
E_v		2.386	2.657	2.864	2.623	2.692	3.145	2.172
E_{tot}	m							
	1	0.328	0.317	0.284	1.015	0.971	1.182	0.575
	2	0.744	0.651	0.626	2.080	1.888	2.353	1.184
	3	1.032	0.919	0.912	2.846	2.785	3.423	1.584
	4	1.330	1.193	1.208	3.539	3.523	4.368	1.951
	5	1.497	1.357	1.452	4.124	4.197	5.256	2.272
	6	1.561	1.364	1.610	4.385	4.607	5.888	2.285
	7	0.970	0.925	1.260	4.086	4.673	6.173	−0.318
	8			0.994	3.935	4.817	6.532	
	9					4.883	6.770	
	10					4.984	6.979	
	11					4.926	7.101	
	12					5.182	7.391	
	13					3.200	6.541	
	14					4.667	7.365	

for some metal-H systems. However, it is found that the corrections do not essentially affect the subjects investigated in this paper, and thus the simulation results presented here do not include the ZPE corrections.

Energetically favorable sites for an interstitial H in an intrinsic bulk metal are investigated by placing an H atom at a T site and O site. The energy difference

$$E_d = E[\mathrm{M}_n\mathrm{H}^{\mathrm{O}}] - E[\mathrm{M}_n\mathrm{H}^{\mathrm{T}}] \tag{3}$$

is shown in Table I, where H^{O} and H^{T} indicate an interstitial H located at the O site and T site, respectively. The T site is more favorable than the O site for interstitial H, which is in accordance with previous works.[6,9–11]

Vacancy formation energy E_v in metals is defined as[28]

$$E_v = E[\mathrm{M}_{n-1}\mathrm{Vac}] - \frac{n-1}{n}E[\mathrm{M}_n]. \tag{4}$$

The vacancy formation energies estimated in the present simulations in Table I are in good agreement with the previous work on the basis of first-principles calculations.[28] However, the values of vacancy formation energies determined by various experiments are occasionally in disagreement with each other.[29]

Figure 3 shows typical equilibrium configurations of mH atoms in a monovacancy, where m is the number of H atoms trapped in the monovacancy. A single and a few H atoms trapped in a monovacancy are located on the inner surface of the vacancy close to the O sites and their configurations are simple, as shown in Fig. 3. However, equilibrium configurations of four and more-than-four H atoms are very complicated. Almost energetically degenerate ground-state and plural metastable configurations are found for the multiple H atoms. Besides, the ground-state configurations of the multiple H atoms are different depending on the host metals. Table I shows the total binding energy E_{tot} for ground-state structures of mH atoms in a monovacancy in each transition metal. Table II presents E_{tot} for ground-state and some metastable structures. Figure 4 shows the total binding energy E_{tot} for ground-state configurations as a function of the number of H atoms in a monovacancy in each transition metal.

As shown in Fig. 4 and Table I, the binding energy gradually increases and reaches a maximum as a function of the number of H atoms in a monovacancy. This analysis estimates the maximum number of H atoms trapped in the monovacancy at 0 K. As a result, a maximum of six H atoms can be accommodated in a monovacancy in V, Nb, Ta, Cr, and Fe. On the other hand, more than six H atoms can be accommodated in a Mo and W monovacancy.

As an example, stable positions for single and multiple H atoms in a monovacancy in Ta, Mo, and Fe projected onto the {001} plane are shown in Fig. 5. Single H occupies a location close to the O site, but stable positions for multiple H atoms are shifted toward the T site or D site as the number of H atoms increases in the monovacancy.

Seven bcc transition metals investigated in the present paper are classified into four categories by taking into account the characteristics of H trapped in a monovacancy, as follows. In addition, an effect of volume relaxation on cohesive energy is investigated for some supercells used in the present calculations.

B. V, Nb, and Ta

Group-V transition metals (V, Nb, and Ta) have a high hydrogen-storage capacity. It is emphasized that profiles of binding energy of H in Fig. 4 for these metals are very similar, which can be explained by the energy landscape in Fig. 6. The energy levels of an interstitial H at a T site in group-V metals are very close, ranging from −0.35 to −0.39 eV. Similarly, the energy levels of an H in a monovacancy are also very close, ranging from −0.66 to −0.71 eV. Therefore, group-V metals

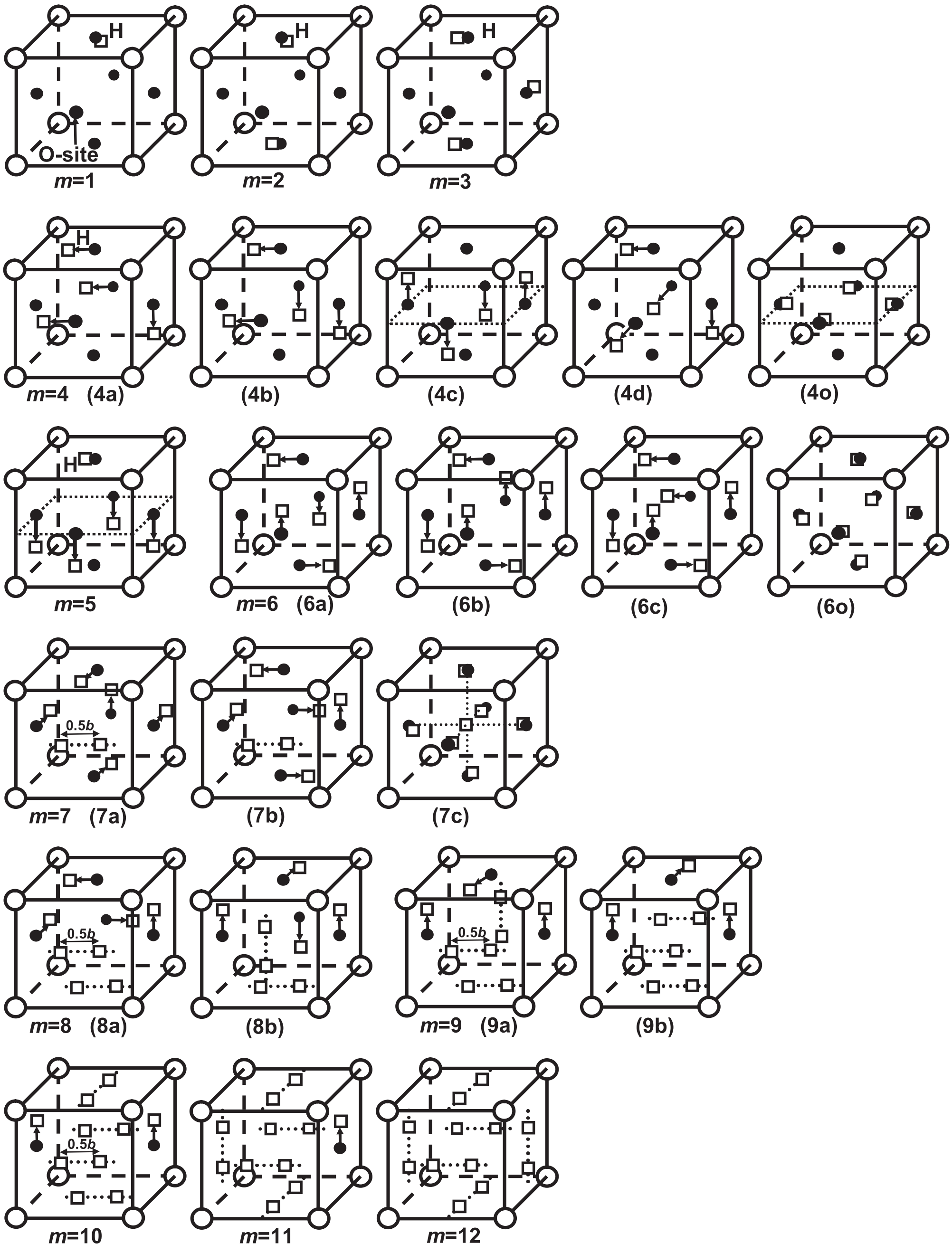


FIG. 3. Schematic view of single and multiple H atom configurations of ground and metastable states in a monovacancy in a bcc lattice. Open circle, open square, and small closed circle indicate the metal atom, H, and O site, respectively. m is the number of H atoms. ($4d$) Two H atoms shifting toward D sites. ($4o$) Planar structure of four H atoms. ($6o$) Regular octahedral configuration of six H atoms. ($7c$) Six H atoms close to O sites and an isolated H located at the center of the monovacancy.

are considered to have a very similar effect on H trapped in the monovacancy and thus the profiles of binding energy are also almost the same.

Ground-state structures of four H atoms in a monovacancy are the $4d$ type shown in Fig. 3, i.e., two H atoms are shifted from O sites to D sites. In addition, the $4b$ type of H configuration is also stable for Ta, according to Table II. Stable positions of H atoms are gradually shifted from O sites as the number of H atoms increases in a monovacancy, as shown in Fig. 5(a). However, an exceptional ground-state structure is found in the case of vanadium. The ground-state structure of six H atoms is a regular octahedral configuration of the $6o$ type shown in Fig. 3, according to Table II. Furthermore, other metastable structures of six H atoms are not found in a V monovacancy, which is confirmed repeatedly. Randomly generated initial configurations for six H atoms always become the regular octahedral ones during the relaxation process. An H_2 molecule formation is not observed inside a monovacancy in group-V transition metals, which corresponds to the work of Ouyang *et al.*[10]

TABLE II. Total binding energy E_{tot} (eV) for ground-state and metastable configurations of H atoms in a monovacancy in each transition metal. The first column represents equilibrium configuration types of H atoms exhibited in Fig. 3. Bold numbers indicate the ground state. Blanks mean that no equilibrium configuration is found there.

	V	Nb	Ta	Cr	Mo	W	Fe
4*a*					**3.523**	**4.368**	
4*b*			**1.208**		**3.523**	**4.367**	
4*c*		1.083	1.163	3.449	3.488	4.358	1.868
4*d*	**1.330**	**1.193**	**1.208**	**3.539**	3.517	4.354	**1.951**
4*o*	1.238	1.070	1.140	3.429	3.322	4.126	1.848
6*a*		**1.364**	**1.610**	**4.385**	**4.605**	**5.888**	**2.284**
6*b*		1.357	1.602	**4.385**	**4.607**	**5.886**	**2.285**
6*c*			1.606	**4.385**	**4.606**	**5.886**	**2.284**
6*o*	**1.561**	1.310	1.515	4.365	4.329	5.456	2.217
7*a*	0.907	0.925	1.249	**4.086**	**4.673**	**6.173**	
7*b*			**1.260**	4.069	4.663	6.161	
7*c*							−0.318
8*a*			0.994	3.935	**4.817**	**6.532**	
8*b*					4.801	6.514	
9*a*					**4.883**	**6.770**	
9*b*					4.794	6.638	

C. Cr

Cr belongs to group-VI transition metals and has very low H solubility. But the properties of H trapping are quite different from those of Mo and W. Only six H atoms can be accommodated in a Cr monovacancy, as shown in Fig. 4. The ground-state structure of four H atoms in the monovacancy is the 4*d* type shown in Fig. 3. On the other hand, ground-state structures for six H atoms in the monovacancy are the energetically degenerate 6*a*, 6*b*, and 6*c* types. As mentioned before, the AFM state is more stable than the PM one for intrinsic bulk Cr at a low temperature. In the present work, the properties of the Cr-H system are investigated in both states, but the magnetism does not essentially affect the simulation results.

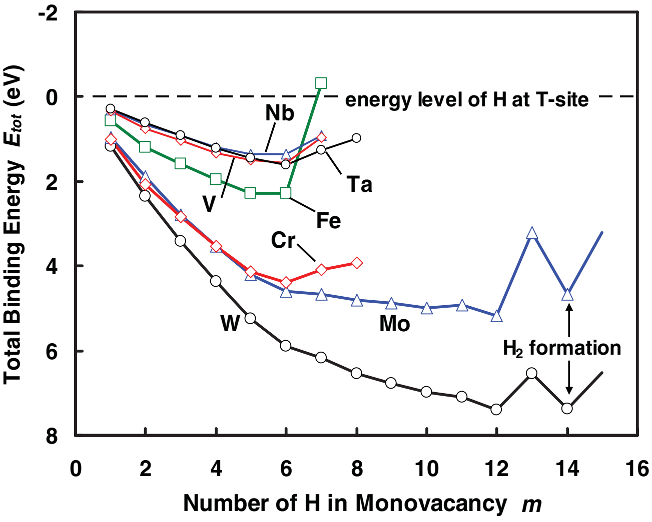


FIG. 4. (Color) Total binding energy E_{tot} as a function of H atom number m trapped in a monovacancy in each transition metal. Decrement of E_{tot} at $m = 13$ corresponds to the presence of an isolated H in the monovacancy. An H_2 molecule formation occurs at $m = 14$. Energy zero level corresponds to the energy of an interstitial H embedded at a T site far away from the monovacancy.

D. Mo and W

The properties of H atoms in a W monovacancy, e.g., stable and metastable configurations, were described in our previous work.[11] Therefore, the Mo-H system is investigated in detail in the present simulations. In summary, the properties of Mo-H and W-H systems are very similar.

Configurations of the 4*a* and 4*b* types shown in Fig. 3 are degenerate ground states for four H atoms in the monovacancy. Similarly, the 6*a*, 6*b*, and 6*c* types are degenerate ground states for six H atoms. Many equilibrium configurations, including ground-state and metastable structures, exist in the Mo and W monovacancy because more than six H atoms are trapped there. A new ground-state structure of nine H atoms of the 9*a* type shown in Fig. 3 is found in the present simulations. The configuration of the 9*b* type was presented as the ground-state structure of nine H atoms in our previous work,[11] but it must be corrected. The configuration of the 9*a* type is actually more stable than that of 9*b* by about 0.1 eV.

The solubility of H for group-VI transition metals is very low. However, many H atoms can be trapped in a monovacancy in Mo and W compared with other bcc transition metals, as shown in Fig. 4. A maximum of 12 H atoms can be accommodated in a W monovacancy clearly. However, it is troublesome to determine the maximum number of H atoms accommodated in a Mo monovacancy because the binding energies for 10 and 11 H atoms are almost equal. According to Table I, the binding energy monotonically increases as the number of H atoms increases to 10. Then, the binding energy only slightly decreases for 11 H atoms and reaches a maximum for 12 H atoms. Therefore, 10 H atoms can be accommodated in the Mo monovacancy if the analysis rule is strictly applied. However, the states of Mo monovacancy trapping 11 and 12 H

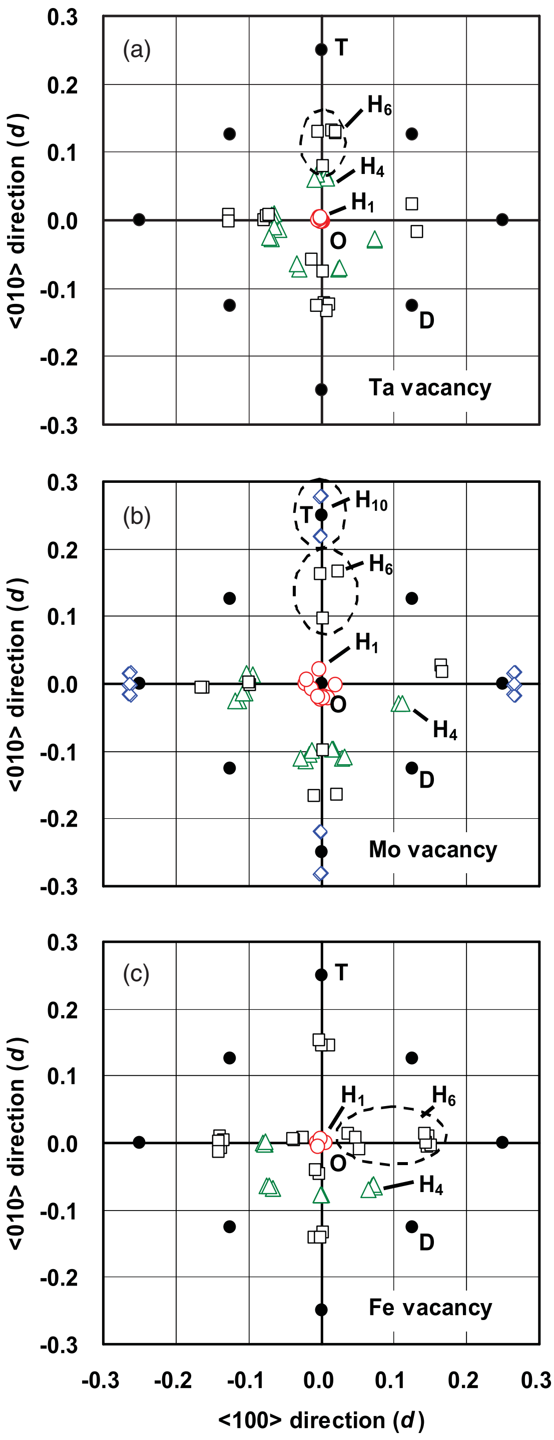


FIG. 5. (Color) Stable positions of H atoms projected onto the {001} plane in a monovacancy in (a) Ta, (b) Mo, and (c) Fe, respectively. Circle, triangle, square, and diamond symbols correspond to the case where one, four, six, and ten H atoms are trapped in a monovacancy, respectively. Symbols O, T, and D indicate O site, T site, and D site, respectively. The O site is located at the center of each figure. *d* is the lattice parameter.

atoms would be taken into account if the Mo-H system was investigated in a finite temperature. The formation of an H_2 molecule inside the vacancy is observed at $m = 14$ in Fig. 4.

The binding energy including the ZPE correction is calculated for the Mo-H system, as shown in Fig. 7. E_{tot} and E_{zc} are defined in Eqs. (1) and (2), respectively. Indeed, the values of the binding energy are changed by the ZPE correction but it is only slight. Besides, the binding energy profiles including and not including the ZPE correction are very similar. The ZPE correction is not essential for subjects dealt with in this paper, which agrees with previous works of the W-H (Ref. 11) and Fe-H (Ref. 19) systems.

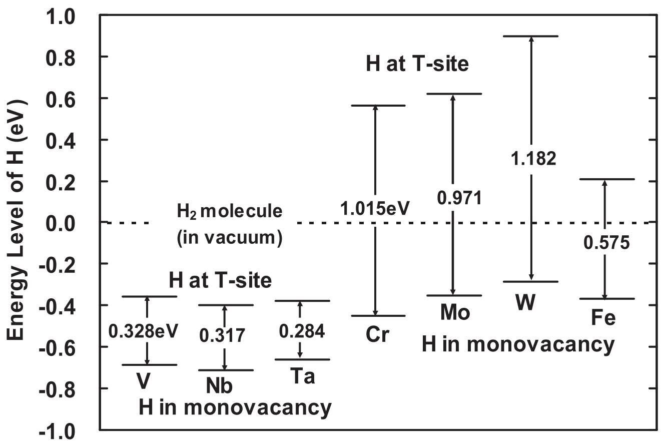


FIG. 6. Energy landscape of an interstitial H at the T site and a single H in a monovacancy in each transition metal. The energy zero level corresponds to an H_2 molecule in vacuum.

E. Fe

The properties of H in a Fe monovacancy are fundamentally similar to those of H in group-V metals and Cr. However, the profile of the binding energy of H atoms to the Fe monovacancy is intermediate between that of group-V metals and Cr, as shown in Fig. 4. The ground-state structure of four H atoms in a Fe monovacancy is the 4*d* type shown in Fig. 3. The configurations for six H atoms are the energetically degenerate 6*a*, 6*b*, and 6*c* types.

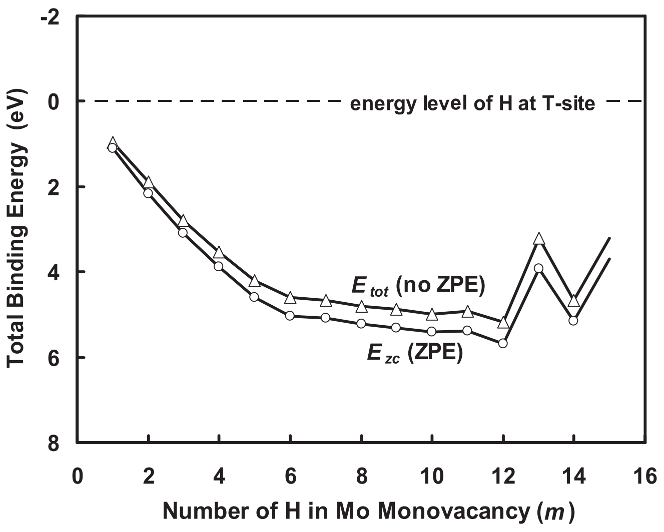


FIG. 7. Binding energy of H atoms to a Mo monovacancy including and not including the ZPE correction.

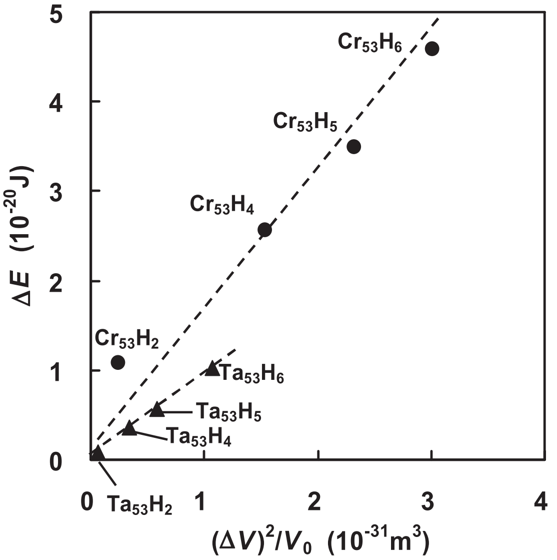


FIG. 8. Effect of volume relaxation on cohesive energy by mH atoms trapped in a Cr and Ta monovacancy, where $m = 2$, 4, 5, and 6.

F. Effect of volume relaxation

A monovacancy is expanded by H trapping, and then an optimal supercell size is calculated by volume relaxation using VASP. We investigate the effect of the volume relaxation on the cohesive energy of a supercell, $M_{53}H_m$Vac, where M is a metal atom, m is the number of H atoms, and Vac is a monovacancy. An analysis in terms of the elasticity theory is useful to deal with such a problem.[30,31] If H atoms trapped in a monovacancy were assumed to be the point source of expansion, a relation would be obtained,

$$\Delta E \sim C\frac{(\Delta V)^2}{V_0}, \tag{5}$$

where V_0 is the optimal volume of supercell M_{53}Vac composed of 53 metal atoms and a monovacancy. ΔV is the optimal volume expansion of supercell $M_{53}H_m$Vac by mH trapping. ΔE is the difference between cohesive energies of supercell $M_{53}H_m$Vac calculated in different supercell sizes; that is, cohesive energies are calculated in the fixed supercell size V_0 and in the optimal one $V_0 + \Delta V$ to examine the effect of volume relaxation. In fact, an explicit linear dependence is shown in Fig. 8. The order of magnitude of coefficient C is expected to be the bulk modulus.[32] However, the values of C estimated from Fig. 8 are smaller than their bulk modulus, i.e., C for Cr and Ta supercells is approximately estimated to be 160 and 100 GPa, respectively. Although an exact value of C has not been predicted yet, the relation expressed in Eq. (5) is generally observed for bcc metals.

IV. DISCUSSION

It has been reported that a maximum of six H atoms can be accommodated in a monovacancy in bcc transition metals. However, more than six H atoms can be accommodated in a monovacancy in Mo and W according to our previous[11] and present works. In order to explain why monovacancy in Mo and W can accommodate so many H atoms, the energy landscape of an H is referred to, as shown in Fig. 6. One of the remarkable properties of group-VI transition metals is the high heat of solution of H_2. In fact, the energy levels of an interstitial H atom at the T site are very high, as shown in Fig. 6. Thus, a large amount of H is not usually retained in group-VI transition metals. On the other hand, the difference between energy levels for an H at the T site and monovacancy associated with group-VI transition metals is also very large. Therefore, the energy gain is very large when an interstitial H embedded at a T site migrates to a monovacancy. So, H segregation to a monovacancy will be enhanced to reduce the high heat of solution if some sort of H is retained in group-VI transition metals. However, only six H atoms can be accommodated in a Cr monovacancy. The energy gain by the H migration to a vacancy in Cr is also very large (1.015 eV), which is the second largest after that of W (1.182 eV), as shown in Fig. 6. We have not found an appropriate answer to explain the H shortage in the Cr monovacancy yet. However, the result may be due to the small volume of the Cr monovacancy compared with Mo and W. The lattice parameter of Cr (2.88 Å) is smaller than that of Mo (3.15 Å) and W (3.16 Å), as shown in Fig. 1.

Stable positions of multiple H atoms in a monovacancy are usually shifted from O sites to T sites or D sites as the number of H atoms increases in the monovacancy, as shown in Fig. 5. We suppose that the H shift in the vacancy is induced by a mutual repulsive interaction between H atoms in metals.[18] However, an exceptional atomic configuration is revealed for six H atoms trapped in a V monovacancy. When less than six H atoms are trapped in the V monovacancy, they are slightly shifted from the O sites as well. However, the ground-state structure for six H atoms is the regular octahedral configuration of the 6o type shown in Fig. 3, that is, each H atom is located close to each O site. This is a unique configuration which is not observed in other bcc transition metals.

There are many metastable configurations whose energy levels are very close to those of the ground states. Therefore, we will have to consider not only ground states but also these metastable states in a finite temperature when behaviors of vacancy-H clusters are investigated.

V. SUMMARY AND CONCLUSIONS

Our summary and conclusions are as follows:

(1) Ground-state and metastable configurations of single and multiple H atoms in a monovacancy are investigated for bcc transition metals in terms of first-principles calculations. Initial configurations of H atoms in the monovacancy are randomly generated to some extent for lattice relaxation to find unexpected stable structures.

(2) Ground-state configurations of multiple H atoms in a monovacancy depend on the host metals. Energetically degenerate ground-state configurations are also obtained in some cases. In addition, energy levels of some metastable configurations are very close to those of the ground states.

(3) Stable positions of H atoms in a monovacancy are gradually shifted from O sites to T sites or D sites as the number of H atoms increases. However, stable positions of six H atoms in a V monovacancy are exceptionally located close to the O sites.

(4) A maximum of 12 and 10 H atoms can be accommodated in a W and Mo monovacancy, respectively. On the other hand, a maximum of six H atoms can be accommodated in a monovacancy in other bcc transition metals, namely, V, Nb, Ta, Cr, and Fe.

(5)The migration of an interstitial H to a monovacancy causes a large energy reduction for group-VI transition metals. The energy reduction enhances too many H segregation to a Mo and W monovacancy. However, only six H atoms can be accommodated in a Cr monovacancy due to its small vacancy size.

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