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Strong hydrogen trapping at helium in tungsten: Density functional theory calculations

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Using first-principles density functional theory calculations, we have investigated the interaction of H and He in W, a potential plasma-facing material in fusion reactors. Strong attraction is found between He and H due to a decreased electron density around He. In the vicinity of a substitutional He atom, the H choose to stay in the tetrahedral-, rather than octahedral-interstitial sites. The maximum number of H atoms that one substitutional He can trap is 12, despite a much smaller local open volume than a vacancy offers. The trapping energy to He for the first H is as large as −0.96 eV. Such a strong attraction well explains the observed enhanced retention of H and He near the surface of W under both sequential and simultaneous bombardments. At ideal He/H ratio, He might suppress to a considerable extent the H blistering at the W surface. In a semiquantitative analysis, we decompose the strong He-H interaction into three parts, namely, an attractive force induced by valence electron depletion around He, repulsive forces contributed by elastic compression of the He-H separation and a H-H repelling in high-density electron gas.

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I. INTRODUCTION

Tungsten is considered to be a promising candidate for the first wall and divertor plate in fusion reactors because of its high melting point, high thermal conductivity as well as low sputtering yield for light elements.[1] As a plasma facing material, tungsten is subject to irradiation of H isotopes, He, and neutron, which leads to bubble formation, surface blistering, and hence embrittlement. Therefore, the mechanical behavior of H and He in W is one of the prime concerns in fusion materials research and has been under intensive investigations since the beginning of the new century. Understanding of He-induced embrittlement of W requires good knowledge of all basic processes controlling microstructural evolution, including diffusion and accumulation of He atoms in the host.[2–4] By comparison, behaviors of H in both structural and functional materials have been under analysis for a much longer time.[5] Regarding He- and H-materials interactions, the well-established essential qualitative insight deduced from the effective-medium theory[6] is that, in most metals, the He-He and He-metal interactions are almost purely elastic and similarly, H is attracted to anywhere that has a small electron density. Detailed descriptions of an individual He (Ref. 7) or H atom[8] in W have become attainable thanks to the recent advances in first-principles theory and computing power. A quantitative predictive understanding of He (or H) accumulation (bubble evolution), especially its dependence on temperature and He (or H) concentration, nonetheless, is far from sufficient and still presents a challenge. Important directions for future research on this issue probably involves more precise treatment of the van der Waals forces for He with the density functional theory (DFT) (Ref. 9) and the non-Born-Oppenheimer quantum mechanics for H,[10] which will provide accurate inputs for the rate theory,[2,3,11] molecular dynamics,[8] or kinetic Monte Carlo method[8,12,13] depicting structure evolution of reactor materials.

Since in the future deuterium-tritium reactors, He and H will coexist in the plasma-facing materials, the interaction between H, He, and He irradiation-induced defects is of great importance for it can affect the transport of H, the fuel recycling, and the tritium inventory. Tremendous efforts have been devoted to clarifying the interplay of H and He in W. Hino *et al.*[14] were the first to examine the effect of preirradiated He on the retention of H in W. Nagata and Takahiro[15] studied the effect of He irradiation on trapping and thermal release of deuterium (D) implanted in W using ion-beam analysis. It was found that the retention of D ions was significantly enhanced by He preirradiation. Similar conclusion was reached by Iwakiri *et al.*[16] who employ the thermal desorption spectrometry (TDS) technique. Their transmission-electron micrograph of He-irradiated W at room temperature strongly suggests that the strong trapping of H is associated with the high density of small He bubbles. Unfortunately, the atomic structure of the bubble-matrix interface where H atoms are assumed to accumulate, i.e., information of the strain field and distribution of atomic species, remains largely unknown due to the limitation in experimental resolution. More recently, Lee *et al.* measured the retention of both H and He under sequential[17] and simultaneous[18] irradiations using TDS. Again, the appearance of He enhances H trapping near the surface of W. Interestingly, under both 300 and 700 K conditions, He retention was found to be influenced very little by the presence of H. The reason, speculated by the authors, might be that the low-energy He implanted into W diffuse rapidly through interstitial sites until get trapped by vacancies, impurities, or grain boundaries to form He clusters, the mobility of which is rather low if the temperature is not high enough (e.g., 1000 K), due to the strong He-vacancy binding, and the stress field and secondary defects associated with them. The rapidity of He diffusion can be well understood from the very small diffusion barrier (0.06 eV) demonstrated by first-principles DFT calculations.[19] Experimentalists are now paying attention to the blistering[20] and modification[21] of W surface subjecting to mixture beam (including H and He) irradiation, trying to elucidate how retention and trapping influence the diffusion of He and H and, in turn, the mechanical properties of the plasma-facing materials.

On the theory side, an electronic level understanding of the interaction of He and H in W demands a first-principles quantum-mechanical treatment. There are only a very limited number of works reporting first-principles calculations on the energetics of He and H which form clusters in W.[22,23] As expected from the qualitative insight based on the effective-medium theory, both studies indicate attraction between He and H. The largest cluster treated by Lee *et al.* consists of six vacancies, four He, and four H, but only *one* assumed atomic configuration was calculated. By comparison, Becquart and Domain searched the stable atomic alignments for He_mH_nV ($m+n \leq 6$, V stands for vacancy) clusters in W, using the same approach. It was found that removing a He atom from this mixed cluster is more energy consuming (3–4 eV) than removing a H atom (~ 1 eV), suggesting that the incoming H cannot destroy the He-vacancy combination. At this stage, complete first-principles investigations on sizable $He_mH_nV_q$ (m, n, $q \geqslant 1$) clusters embedded in metals are still unaffordable due to both the size of the basis sets and the extreme complexity in atomic configurations. Since the He/H ratio in the mixed ion flux is one of the key factors for the damage it incurs to the plasma-facing materials in a fusion reactor, the stability of $He_mH_nV_q$ clusters or bubbles with respect to this proportion has to be elucidated. A good starting point for attacking such a complicated problem, in our view, is to scrutinize $He_1H_nV_1$ or $He_nH_1V_n$. Since first-principles computations[7] have already made it clear that the most stable position for an individual He atom in W is the substitutional site, it is advisable, for simplicity, to deal first with clusters in which each He is combined with a distinct vacancy. In varying the parameter n in clusters $He_1H_nV_1$ and $He_nH_1V_n$, we can answer these questions: (i) how many H can one individual, substitutional He attract (or trap) and (ii) how many He can one individual, interstitial H attract? The first question is relevant to the situation where H is much more abundant than He and the flux of He is very low such that the chance for He to cluster is small. If the He/H ratio is ideal, we might even hope for He to suppress to a considerable extent the H blistering at the W surface if they are trapped at disconnected He atoms. On the contrary, the second question is pertinent to the situation that H is less abundant than He. In fact, since, as mentioned above, the binding of He with other He atoms are much stronger than H does, there will be no limitation on the size of He cluster which is neighboring a H atom and hence the second question does not make sense.

To answer the first question, we have carried out detailed first-principles density functional theory calculations on the energetics of cluster $He_1H_nV_1$ in W, using supercells with periodic boundary conditions. Similar to the H_nV_1 case,[24] H is found to bind with He strongly due to a decreased electron density around He. Unlike the vacancy case, however, the H chooses to stay in the tetrahedral interstitial site (TIS) rather than octahedral interstitial site (OIS) when He present nearby. One substitutional He can, at most, trap (attract) 12 H atoms, despite a much smaller local open volume than a vacancy offers. Such a high efficiency could explain the observed enhanced retention of H and He near the surface of W under both sequential and simultaneous bombardments. By varying the lattice constant of W from 3.17 Å down to 2.83 Å, we find that the OIS get less and less unfavorable and finally overtake the TIS as the ground-state positions for H when the lattice constant comes down to 2.87 Å or smaller. Since there is no real chemical bonding between He and H, it is the lattice constant and crystal symmetry of W that determines how many H atoms an individual He can trap. We emphasize the fundamental difference between a substitutional He and a vacancy with respect to H trapping is that H_2 have no chance to form as there is no enough open space associated with the former.

II. METHODOLOGY

Our first-principles DFT calculations were carried out using Vienna *ab initio* simulation package (VASP).[25] The electron-ion interaction was described using projector augmented wave[26,27] potentials, the exchange-correlation between electrons using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof[28] form. We expanded the one-electron wave functions in a plane-wave basis with an energy cutoff of 480 eV. Systematic calculations presented here have been performed on 54-atom supercells modeling He and H doped bcc W. Such a size of supercell was shown to yield reliable formation energy for impurities.[7] The Brillouin-zone integration was performed within Monkhorst-Pack scheme using a $(3\times3\times3)$ mesh and the Methfessel-Paxton smearing with a width of 0.20 eV. To obtain the total binding energy for each system, the atomic positions were fully optimized with the volume of the supercell being fixed. The lattice constant of the bulk bcc W was calculated to be 3.17 Å, in good agreement with both the experimental value (3.16 Å) (Ref. 29) and previous DFT results. The stable position for a single H or He atom in W was determined by its solution energy in W, in reference to an isolated He atom or H_2 molecule.

$$E^{f}_{defect} = E^{tot}_{system} - \frac{N}{54}E^{54}_{\mathrm{W}} - E_{defect}, \tag{1}$$

where E^{tot}_{system} is the total (binding) energy of the system with defect, N is the number of W, E^{54}_{W} is the total energy of a perfect $3\times3\times3$ supercell of bcc W, and E_{defect} is the total energy of an isolated He atom which is zero by definition, or half of the energy for an isolated H_2 molecule. We considered three possible positions for He or H, namely, the substitutional sites, the TISs, and the OISs. The calculated formation energies of defect for each case, together with the results reported in literature, are summarized in Table I. Notice that in Ref. 22, Lee *et al.* took the free H atom as the reference state for H rather than an isolated H_2 molecule. Thus, we subtract one half of the energy for H_2, -3.39 eV, to their values for H_{sub}, H_{octa}, and H_{tetra}. It is surprising to see that our calculated H_{sub} is very different from that given in Ref. 22, we believe this huge discrepancy is due to their putting H at the center of the vacancy. For hydrogen at the substitutional site, calculation shows that if we deflect H from the exact center of the vacancy, it will be relaxed to an off-vacancy-center position (by ~ 1.26 Å) which is close to an OIS, and the energy lowering associated with this relaxation is over 1.3 eV. Otherwise, the agreement with the pre-

TABLE I. The calculated formation energies (eV) of an isolated He or H atom doped in W. Note that the energy cutoff used in Refs. 22 and 23 was 350 and 400 eV, respectively, and ours was 480 eV. Reference 23 employed a GGA functional of Perdew and Wang (Ref. 30) different from this work.

Configuration	H_{sub}	H_{octa}	H_{tetra}	He_{sub}	He_{octa}	He_{tetra}
This work	2.65	1.28	0.90	4.52	6.34	6.07
Reference 23				4.70	6.38	6.16
Reference 22	4.31	1.32	0.92	5.00	6.48	6.23

vious results is acceptable. We note that the energy cutoff used in Refs. 22 and 23 was 350 and 400 eV, respectively, and ours was 480 eV. Also, Becquart and Domain[23] employed a GGA functional of Perdew and Wang,[30] different from this work.

It has to be pointed out that none of the computed results presented in Table I considered zero-point motion energy. This is no problem for He because the substitutional site is over one eV more stable than the interstitial sites and the zero-point effect has no chance to overturn its site preference, but for H, zero-point energy has to be taken into account because (i) H has a much smaller mass, (ii) the energy difference related to its site preference is only a few tenth of eV, and (iii) we here examine the energy state of H at very different environment in a crystal, i.e., we are comparing the stability of H at positions far away or near the He atom. Our computation shows that in the absence of He, the zero-point energy for H is about 0.263 and 0.256 eV at the TIS and OIS, respectively, much more significant than in the case of H in Fe;[31] and with a substitutional He as the nearest neighbor, it reduces, respectively, to 0.197 and 0.169 eV.

To determine whether the cluster HeH_nV is saturated with H, we calculated the formation energy for the $(n+1)$th H and compared it with that for an isolated (one H in a 54-atom cell) in the TIS in bulk W ($E^{\mathrm{tetra}}_{W_{54}H} - E_W = -2.488$ eV).

$$\Delta E(n) = (E_{W_{53}HeH_n} - E_{W_{53}HeH_{n-1}}) + 2.488. \tag{2}$$

III. RESULTS AND DISCUSSION

A. A single H near He

It is known from early calculations (Refs. 22 and 23) that H will occupy the TIS in W when there is a substitutional He nearby but the particular energy related to this site preference was not reported. Our calculations demonstrate that in the immediate neighborhood of the He, the TIS is 0.04 eV is more stable than the OIS for H. And when zero-point effect is taken into account, the site preference of TIS over OIS is only 0.01 eV, on the same order of the numerical error. Notice that (see Table I) this preference energy is 0.38 eV in the absence of He. To understand this dramatic decrease, we turn to the electronic-structure analysis. In Fig. 1, we plot the valence electron density on the (100) plane containing a TIS H in W, with (right panel) and without (left panel) the doped He atom. It is clearly seen that the substitution of W for He reduces the charge density around the interstitial sites nearby. When one W atom is replaced by He, the H bonds more strongly with the other W. We also find He pulls the TIS H toward the OIS (0.38 Å), thereby diminishing the difference in bonding environment for these two interstitial sites. Additionally, the He experiences a downward shift (about 0.15 Å) pushed by H due to the weakness of the He-W interaction. This will further reduce the valence-electron distribution around H, leading to an extra drop of the site preference for H.

To search the maximum number of H atoms that one He can attract in W, we added H atoms one by one into the supercell near the He and minimize the energy to find the optimal structures. For the first H, our calculation gives a trapping energy of −0.96 eV, i.e., there will be an energy lowering of 0.96 eV when a H atom is attracted from far away to the vicinity of the He. This attraction is comparable to the vacancy case, where it is −1.18 eV (Ref. 24). The distance between He and H is 1.62 Å after relaxation, about 9% smaller than the ideal separation, 1.77 Å. We emphasize that there is no chemical bonding between He and H. The driving forces acting on H in these two cases have the same physical origin. The He atom (right panel of Fig. 1), just like a vacancy, provides a charge-depletion region on one side of the H atom, thereby reduces the coordination number for chemical bonding. For the same reason, H has a tendency to segregate to the surface in most metals.

B. Sequential trapping of H near He

Since the energy difference between TIS and OIS is very small (0.04 eV) for H, we ought to consider both of them when adding more H atoms to the neighborhood of He. That is, four TIS and one OIS in each face of the primary cubic ($a=3.17$ Å) centered at the He atom. So, to introduce the

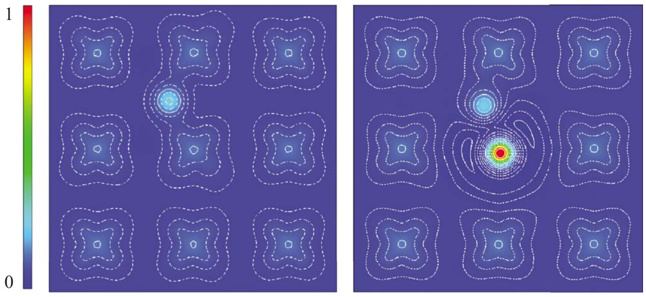

FIG. 1. (Color online) The calculated valence-electron density on the (100) plane in W with (right) and without (left) the doped He atom. Contours start from 0.044 $e/\mathrm{a.u.}^3$ and increase successively by a factor of 1.414.

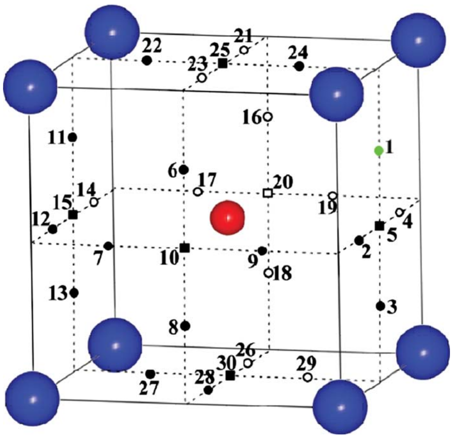

FIG. 2. (Color online) Schematic view of the all the tetrahedral (circle) and octahedral (square) interstitial sites around the substitutional He in bcc W. The first H atom is put at Site 1. Solid symbols denote inequivalent sites.

second H, we have in principle 29 (=5×6−1) sites to try. In Fig, 2, we show schematically a whole set of the 30 interstitial sites (24 TIS and six OIS) in the six faces of that primary cubic. The first H is put at Site 1 (denoted as S1). It immediately follows that the S16-S20 are equivalent to S6-S10 so the former five sites will not be considered in trying to find the best position for the second H. Moreover, S4, S14, S21, and S26 are equivalent to S2, S12, S23, and S28, respectively; S29 and S23 are equivalent to S22 and S9. So, lattice symmetry helps to reduce the number of sites we need to try to 18, still a daunting task.

Obviously, knowledge about the H-H interaction in W can help us to narrow the search of the stable position for the incoming H. According to Henriksson *et al.*'s (Ref. 8) DFT calculations, the equilibrium H-H distance in W is about 2.2 Å. Since the He-H interaction is attractive, the H-H separation near the He is presumably no larger than 2.2 Å. If we leave a margin of 0.2 Å for relaxation, then we need consider only the sites within 2.4 Å from the first H (located at S1) for the second H. They are S5, S2, S3, S25, S9, and S6, away from S1 by $\frac{a}{4}$(=0.79 Å), $\frac{\sqrt{2}}{4}a$(=1.12 Å), $\frac{a}{2}$(=1.58 Å), $\frac{\sqrt{5}}{4}a$(=1.77 Å), $\frac{\sqrt{6}}{4}a$(=1.94 Å), and $\frac{\sqrt{8}}{4}a$(=2.24 Å). Since S2 and S5 are too close to S1, there must be a strong repulsion if another H is put in those positions. Finally, we have four sites to check, namely, S3, S25, S9, and S6. Our total energy calculations demonstrate that S6 is the most stable site for the second H if there is already a H located at S1. The trapping energy is −0.91 eV, slightly weaker than that for the first H. These two H, paired up along ⟨110⟩ direction, are attracted to He and slightly away from the (100) or (010) plane. The optimized H-H distance is 2.01 Å, about 10% smaller than the ideal value, 2.24 Å.

With this knowledge of H-H interaction in the vicinity of He and the equality of S11 and S16, we are sure that the optimal position for the third H should be either one of the two. The trapping energy further decreased very slightly to −0.89 eV. With much confidence, we put the fourth H at the other of the two, which has a trapping energy of −0.88 eV. Figure 3 is a schematic view of the sequential trapping of H atom to the vicinity of a substitutional He in W. Positioning of the fifth H is not straight forward. There are three sets of candidates. S3, S8, S13, and S18 all have a distance of 1.58 Å to the nearest H and are equivalent for the fifth H; S26, S27, S28, and S29 all have a distance of 2.51 Å to the nearest H and also are equivalent for the fifth H. Our calculations prove that the fifth H at S3 will experience repulsion and S29 is energetically a better choice. Since there is no optimal site for H5, this trapping is further weakened to −0.75 eV.

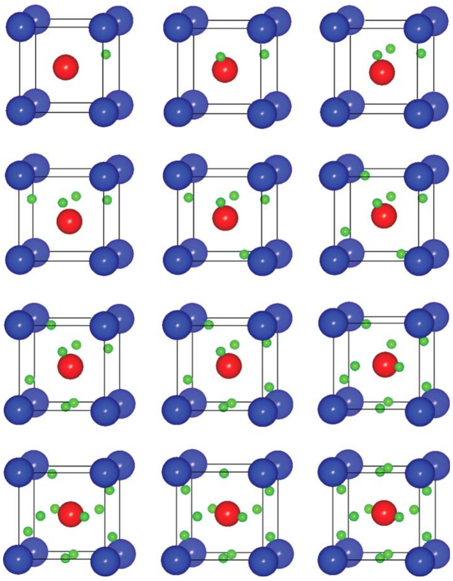

FIG. 3. (Color online) Atomic configurations for H atoms trapped one by one to a substitutional He in W. Large, mediate, and small spheres represent the W, He, and H atoms. Note that the small cubic is not the unit cell used in calculation; rather, it displays the local structure of around the defect.

The candidates for the fifth H are also reasonable guess for the sixth H, except for S3, S26, and S28 which are too close to S29 designated for H5. Now we have S8 (distance from S29, $d=\frac{\sqrt{6}}{4}a=1.94$ Å, equivalent to S18), S13 ($d=\frac{\sqrt{10}}{4}a=2.51$ Å), and S27 ($d=\frac{a}{2}=1.58$ Å) for H6. Note that all of the three have one of the pre-existing H atoms as their nearest neighbor at a distance of 1.58 Å, which is noticeably shorter than the optimal value, 2.0–2.2 Å. Of these three sites, S13 has the lowest energy for H6. Since all the three have neither optimal separation with H1-H4, nor with H5, we were forced to explore the possibility to break up the optimal H1-H4 group in order to find the most stable for H6. Note that the seemingly only repulsion inside the H1-H6 cluster comes from S11-S13 pair, which has a separation of 1.58 Å. To reduce this repulsion, our approach is to shift the H at S11 to S22, in view of the fact that the distance between S6 to S22 is $\frac{\sqrt{6}}{4}a=1.94$ Å, quite close to the optimal H-H separation. It turned out such a perturbation results in a much reduced S11-S13 repulsion, whereas not introducing repulsion between S22 and S6. As a consequence, the total energy is further lowered. Finally, the trapping energy for H6 is evaluated to be −0.59 eV.

Having decorated the He with six H atoms one by one, let us have an overview of the $\mathrm{He_1H_6}V$ cluster (second row,

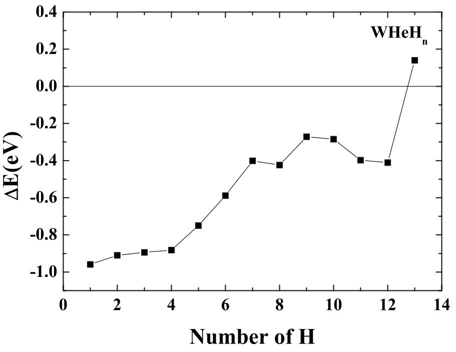

FIG. 4. The calculated trapping energy when one H atom is attracted from a perfect W bulk environment to the vicinity of a substitutional He. The trapping process is in a sequential manner. One He is capable of trapping 12 H in total. All the H atoms are in the first shell of interstitial sites centered by the He.

third column, Fig. 3). Exactly, there is one H in each face of the small cubic centered at He. To locate H7, at least one face will have to accommodate two H. We now have two options. One is to put H7 at S8 (or, equivalently S18); the other is shift the H at S29 to S26 and put H7 at S28. It turns out that these two configurations give nearly the same trapping energy for H7, i.e., −0.40 eV. It is more or less straight forward to add more H atoms to this cluster until the number of H raises to 12 (Fig. 3). Each time the new H-H pair ($d=1.58$ Å) formed in one face try to stay further away other pairs. In cases of adding H9 and H10, one other unpaired H shift to the neighboring TIS upon structural optimization. A further addition of H13 to one of the faces from far way will cost 0.14 eV, as a result of strong repelling between the three H in that face. Thus it is conclusive that He can attract 12 H in the first shell of interstitial sites.

In Fig. 4, we display the calculated trapping energy for each H introduced sequentially to the vicinity of the substitutional He in W. Note that all the H atoms, including H13, are in the first shell of interstitial sites centered by the He. Apparently, H13 did not find its stable position at this distance from He.

To make a thorough search for the H-trapping capability of He, we have also investigated the energy state of H in the second ($d_{\text{He-H}}=\frac{\sqrt{13}}{4}a=2.86$ Å) and third ($d_{\text{He-H}}=\frac{\sqrt{21}}{4}a=3.63$ Å) shell of interstitial sites, with the first shell full with 12 H atoms. The calculated trapping energy for the 13th H is 0.14 and 0.02 eV, respectively. This means that the $\text{He}_1\text{H}_{12}V_1$ is indeed saturated in the sense of trapping H.

C. Electronic structure around H and He

To give a physical picture to understand the trapping of H by He, we now turn to the electronic-structure analyses of this serial of system. In Fig. 5, we draw the calculated isosurfaces of charge density at the He_1H_nV_1 cluster with various number H atoms. The atomic structures are replots of part of Fig. 2. Again, the large, medium, and small spheres represent the W, He, and H atoms. Yellow curved isosurfaces stand for the charge density of 0.02 a.u.$^{-3}$. We note again that the small cubic is not the unit cell used in calculations, rather, it displays the local structure of around the defect. The vivid three-dimensional isosurfaces show that when a He atom is put into a W vacancy, it cannot fill up the electron density hole in the interstitial region. There is an electron-depleted region around He, which is favorable for the H by reducing its bonding coordination number. As more H atoms were introduced, the surface of optimal electron-density shrunk and finally reduced to a small chicken wire frame surrounding the He atom.

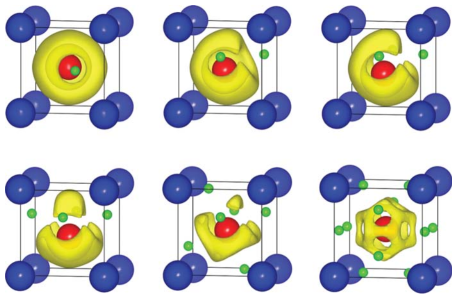

FIG. 5. (Color online) The calculated isosurfaces of charge density at the He_1H_nV_1 cluster with various number H atoms. Large, medium, and small spheres represent the W, He and H atoms. Yellow curved isosurfaces stand for the charge density of 0.02 a.u.$^{-3}$. Note that the small cubic is not the unit cell used in calculations, rather, it displays the local structure of around the defect.

D. Quantification of the H-trapping mechanism

Having done the first-principles calculations and obtained the numerical data on this specific system, we now want to quantify the H-trapping mechanism for He in W. The underlying motivation is that a quantitative understanding of H interactions at an individual He should provide a solid starting point for the treatment of He-vacancy complexes and even He bubbles which is more relevant from a technological perspective. Further more, such an understanding, if attainable, would also shed much light on other point defects, dislocations, grain boundaries, and solute clusters.

The interaction of H with He in W can be generally decomposed into two parts for convenience of analyses. One contribution comes from the distortion of the lattice structure induced by He; the other comes from the chemical bonding. Our density functional theory calculations demonstrate that the lattice distortion caused by substitution of He for W is negligible. Compared with the perfect W crystal, the side length of the primary cubic (shown in Fig. 2) shrinks 0.001 Å when the center W is replaced by He, in a ($3\times3\times3$) 54-atom supercell. Such a small contraction will exert no noticeable effect on the energetics of incoming H atoms.

Regarding H-He interaction, we still have two parts to consider. The major part, which accounts for the strong attraction, comes from the reduced valence-electron density induced by the substitution of He. A minor contribution, which is always repulsive, however, should also be taken into account. As a first-order approximation, we assume the H-He (as nearest-neighbors) repulsion in W is the same as in the vacuum. In Fig. 6, we display the calculated binding energy of a H-He pair in vacuum as a function of their in-

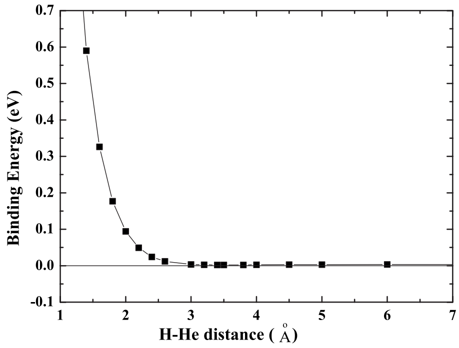

FIG. 6. The calculated binding energy (eV) of a H-He pair in vacuum as a function of their special separation (Å). Positive values mean repulsion.

teratomic distance. As expected from the fact that He has a close shell of electrons, the H-He interaction is monotonously repulsive, up to the limitation inherent in the density functional theory.[32] With this curve, the repulsion between H and He can be readily estimated once the H-He distance is determined. It must be pointed out that when the first H is attracted to the neighborhood of He, the repulsive part of the H-He interaction should be neglected, because He, which is *soft* compared with the W atoms sitting around, has the freedom to adjust itself. This is the case for the first four H, as all of them choose a position on the same side (upper side in Fig. 3) of the He. And we think it is for this reason, H1-H4 all have similar trapping energies. But the situation changes for H5. Upon arrival of H5, He experiences a compression for it can no longer adjust itself downward. It is seen in Fig. 6 that when separated by 1.7 Å H-He, the repulsion energy is about 0.17 eV. This value agrees very well with the trapping energy decrease from H5 to H4 (Fig. 4). The same argument applies for H6.

Since one of our main interests in the present work is figuring out how many H atoms one substitutional He can trap, we have to deal with the H-H interaction as well. The equilibrium H-H distance in W is 2.01 Å, as reported above. However, the binding energy for such a H-H pair is only as small as −0.02 eV, demonstrated by early *ab initio* calculations.[8,24] As a consequence, only at distances smaller than 2 Å, does H-H repulsion appear. Our calculations show that when 12 H are trapped around the He, two in each faces of the primary cubic (see Figs. 2 and 3), the distance between neighboring H atoms reduces to 1.74 Å.

The interaction between H atoms embedded in metals has long been a subject under extensive studies. Advances in a predictive theory are mainly focused on the electron gas approximation[33] because the H-metal bonding presents a challenge to formulation. Fortunately, electrons in the interstitial region of a metal can be more or less adequately approximated by a jellium of electron gas. Both nonself-consistent[34] and self-consistent[35] first-principles investigations have been devoted to the formulation to this interaction. It is conclusive that at an electron density of $r_s = 2.07$ a.u. (Corresponding to valence electron density in Al. r_s is defined as $\frac{4\pi}{3} r_s^3 = n$ with n denoting the electron density), the H-H interaction is monotonously repulsive.[33,34] Our density functional theory calculations show that the valence electron densities at the TIS and OIS in W are 0.041 and 0.038 $e/\text{a.u.}^3$. The corresponding r_s in this region is about 1.82 a.u. Thus it is safe to predict that if there are two or more H atoms in the same face of the primary cubic centered at the He (see Fig. 2 and 3), the interaction between one another must be repulsive. This theoretical rationale is in exact qualitative accordance with our DFT results that when two H are trapped, the S1-S6 configuration is 0.42 eV more stable than the S1-S3 alignment. If the accumulation of H at the He does not lead to lattice expansion around He, one would expect each time one more H (from H7 to H12) is positioned in one face of the primary cubic, there arises a repulsive energy of about 0.42 eV. They are additive because the repulsion between H atoms in different faces are negligible. But in fact, however, there is a remarkable expansion of the W lattice around He upon arrival of multiple H atoms. Our calculations demonstrate that after trapping 12 H, the side length of the primary W cubic enlarged from 3.17 Å (without defect or with only substitutional He) to 3.35 Å. Such a volume expansion accounts mainly for the variation in the trapping energy for H7-H12.

E. Comparison of He and vacancy

Finally, we want to compare the He atom with a monovacancy for their capability in trapping H in W. As mentioned above, Liu *et al.*[24] have investigated the interaction of H with an individual vacancy, using the same method and nearly the same parameters as in the present work. Their calculations showed that the trapping energy for the first H was −1.18 eV, 0.20 eV larger than what we obtained in the He case; if attracts all at once, a vacancy can trap at least ten H, until a H_2 molecule is formed inside the vacancy given that the H concentration is high enough. The fundamental difference between He and vacancy is that the H may reside at the center of the vacancy, providing the flexibility to form H_2; whereas, they can only surround the He as nearest neighbors, thereby hindering the formation of hydrogen molecules. Since, according to our results, the $\text{He}_1\text{H}_n V_1$ clusters are quite stable for n up to 12, we are very curious to inspect the stability of clusters $\text{H}_n V_1$, simply by removing the He atom and reoptimize the atomic structure of the computation cell. Our calculations demonstrate that for both $n = 11$ and 12, the energy state of H is lower than in a TIS site in perfect W, indicating that a vacancy, like a substitutional He, probably can also trap 12 H. Such a discrepancy with the results reported in Ref. 24 is puzzling to us because the only difference in computation methods is that they used a generalized gradient approximation in Perdew and Wang form Ref. 30 and we employed the Perdew-Burke-Ernzerhof form.[28] Apparently, a more complete scrutiny of the effect of exchange-correlation functional on the calculated activity of He and H is desirable.

IV. SUMMARY

To summarize, we have performed density functional theory computations to examine the He-H interaction in the form of $He_1H_nV_1$ ($n=1,12$) cluster in tungsten. It is found that a substitutional He behaves like a strong trap for the interstitial H due to a decreased electron density around it. Near the He, H will stay in the tetrahedral interstitial site as in the perfect bulk W. In total, one He can attract as many as 12 H atoms. The trapping energy for the first H is −0.96 eV, only slightly weaker than in the vacancy case, and that for the 12th H is −0.4 eV. To make the search complete, we have also studied the energy state of H in the second ($d_{\text{He-H}}=a\sqrt{13}/4=2.86$ Å) and third ($d_{\text{He-H}}=a\sqrt{21}/4=3.63$ Å) shell of interstitial sites with the first shell fully filled. The calculated trapping energy for the 13th H is 0.14 and 0.02 eV, respectively. This means that the $He_1H_{12}V_1$ is saturated in the sense of trapping H. The strong He-H interaction are analyzed by a decomposition into three parts, namely, attractive force induced by valence-electron depletion around He, repulsive forces contributed by elastic compression of the He-H separation and H-H repelling in high-density electron gas. This predicted high trapping capability of He offers an explanation of the observations that a small quantity of He ions make a great impact on H irradiation behavior.[7]

The numerical study presented here make a good starting point to elucidate the stability of $He_mH_nV_q$ clusters or bubbles with respect to the He/H ratio in the mixed ion flux, which is one of the key factors for the damage it incurs to the plasma-facing materials in a fusion reactor. For instance, if a He bubble has a sharp (100) interface with the W matrix, we would expect, based on Fig. 3, that each He at the interface will trap three H on average. And if the size of the bubble can be determined then the H-retention capability of such a He bubble can be readily estimated. First-principles calculations on this subject are underway.

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[1] G. Janeschitz, J. Nucl. Mater. **290-293**, 1 (2001); W. M. Shu, M. Nakamichi, V. Kh. Alimov, G.-N. Luo, K. Isobe, and T. Yamanishi, *ibid.* **390-391**, 1017 (2009).

[2] W. D. Wilson, C. L. Bisson, and M. I. Baskes, Phys. Rev. B **24**, 5616 (1981).

[3] N. M. Ghoniem and M. L. Takata, J. Nucl. Mater. **105**, 276 (1982).

[4] For a recent review, see H. Trinkaus and B. N. Singh, J. Nucl. Mater. **323**, 229 (2003).

[5] For a review, see S. M. Myers, M. I. Baskes, H. K. Bimbaum, J. W. Corbett, G. G. DeLeo, S. K. Estreicher, E. E. Haller, P. Jena, N. M. Johnson, R. Kirchheim, S. J. Pearton, and M. J. Stavola, Rev. Mod. Phys. **64**, 559 (1992).

[6] J. K. Nørskov and N. D. Lang, Phys. Rev. B **21**, 2131 (1980).

[7] C. S. Becquart and C. Domain, Phys. Rev. Lett. **97**, 196402 (2006).

[8] K. O. E. Henriksson, K. Nordlund, A. Krasheninnikov, and J. Keinonen, Appl. Phys. Lett. **87**, 163113 (2005).

[9] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).

[10] M. Cafiero and L. Adamowicz, Phys. Rev. Lett. **89**, 073001 (2002).

[11] Q. Xu, N. Yoshida, and T. Yoshiie, J. Nucl. Mater. **367-370**, 806 (2007).

[12] C. C. Fu, J. D. Torre, F. Willaime, J. L. Bocquet, and A. Barbu, Nature Mater. **4**, 68 (2004).

[13] S. Sharafat, A. Takahashi, Q. Hu, and N. M. Ghoniem, J. Nucl. Mater. **386-388**, 900 (2009).

[14] T. Hino, K. Koyama, Y. Yamaguchi, and Y. Hirohata, Fusion Eng. Des. **39-40**, 227 (1998).

[15] S. Nagata and K. Takahiro, J. Nucl. Mater. **290-293**, 135 (2001).

[16] H. Iwakiri, K. Morishita, and N. Yoshida, J. Nucl. Mater. **307-311**, 135 (2002).

[17] H. T. Lee, A. A. Haasz, J. W. Dawis, and R. G. Macaulay-Newcombe, J. Nucl. Mater. **360**, 196 (2007).

[18] H. T. Lee, A. A. Haasz, J. W. Davis, R. G. Macaulay-Newcombe, D. G. Whyte, and G. M. Wright, J. Nucl. Mater. **363-365**, 898 (2007).

[19] C. S. Becquart and C. Domain, J. Nucl. Mater. **385**, 223 (2009).

[20] Y. Ueda, M. Fukumoto, J. Yoshida, Y. Ohtsuka, R. Akiyoshi, H. Iwakiri, and N. Yoshida, J. Nucl. Mater. **386-388**, 725 (2009).

[21] K. Tokunaga, T. Fujiwara, K. Ezato, S. Suzuki, M. Akiba, H. Kurishita, S. Nagata, B. Tsuchiya, A. Tonegawa, and N. Yoshida, J. Nucl. Mater. **390-391**, 916 (2009).

[22] S. C. Lee, J. H. Choi, and J. G. Lee, J. Nucl. Mater. **383**, 244 (2009).

[23] C. S. Becquart and C. Domain, J. Nucl. Mater. **386-388**, 109 (2009).

[24] Y. L. Liu, Y. Zhang, H. B. Zhou, G. H. Lu, F. Liu, and G. N. Luo, Phys. Rev. B **79**, 172103 (2009).

[25] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996).

[26] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[27] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[28] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[29] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 2005).

[30] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992); J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *ibid.* **46**, 6671 (1992).

[31] Y. Tateyama and T. Ohno, Phys. Rev. B **67**, 174105 (2003).
[32] Richard Martin, *Electronic Structure of Solids* (Cambridge University Press, Cambridge, England, 2005).
[33] F. Perrot, J. Phys.: Condens. Matter **6**, 431 (1994).
[34] J. K. Nørskov, Phys. Rev. B **20**, 446 (1979) and references therein.
[35] For a recent advance, see S. A. Bonev and N. W. Ashcroft, Phys. Rev. B **64**, 224112 (2001) and references therein.