

Interstitial Diffusion of C Interacting with Ambient H in Tungsten Crystals^{*})

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Negative binding energies between interstitial C (octahedral) and H (tetrahedral) in a bulk crystal of W (bcc) were obtained with the first-principle calculations, which indicate repulsive interaction in the interstitial C-H pair. The electron cloud associated to the each interstitial atom was analyzed with Bader's method. This analysis gives negative fractional charges of -0.35 and -0.37 for the interstitial C and H, respectively, supporting the repulsive interaction between them. Interstitial diffusion of C was studied including influences of ambient H atoms in the mean field approximation and the ergodic assumption. The calculated diffusion coefficients are significantly increased by the repulsive interaction with the H atoms.

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1. Introduction

The ground state ($X^2\Pi$) potential curve of an isolated C-H pair has a single-minimum at a certain (equilibrium) inter-nuclear distance ($\sim 1.1\text{\AA}$ [1]). This indicates that the isolated C-H interaction in the ground state is attractive. In a gas-phase at the room temperature, therefore, $C(g) + H(g) \rightarrow CH(g)$ is an exothermic reaction; the standard enthalpy of the reaction is -340.5 kJ/mol [2]. It is, however, obvious that, in a solid, the atomic interaction of the C-H pair would be influenced by surrounding matrix atoms. Concerning with C migration under influences of ambient H atoms, it is critical to understand the interaction of the C-H pair in the matrix.

Since W divertors were used in ASDEX-Upgrade [3] and planned for ITER hydrogen retention in the W divertors has been a key issue. Recently, influences on the hydrogen retention by material-mixing with plasma impurities are examined intensively. Strong correlations between levels of the hydrogen retention and C contamination in the W surface layers have been observed [4]. The W surface layers exposed to divertor plasmas may contain super-saturated H atoms. Thus, ambient H effects on the C migration are important subjects of study.

In this paper, the H effects on the migration of an interstitial C in a W crystal (bcc) are investigated theoretically. To this end, the interaction of an interstitial C-H pair in the W crystal is evaluated by means of the first-principle method (density functional theory). With the first-principle

method, the inter-atomic interactions in condensed matters are calculated without recourse to model (semi-empirical) interaction potentials. Then, interstitial diffusion of C interacting with ambient H atoms is studied by adopting the mean field approximation [5] and the ergodic assumption.

The present first-principle calculation of the interstitial C-H interaction in the W crystal is described in Sec. 2. Theoretical formulations and results for the interstitial diffusion coefficient of C including the ambient hydrogen effects are presented in Sec. 3. Sec. 4 is devoted to summary of the present study

2. First-Principle Calculation of Interstitial C-H Interaction in W Crystal

In the density functional theory, mutually interacting many-electron Schrödinger equations are approximated by a set of independent-particle equations (Kohn-Sham equation [6]) with energy functional of exchange and correlation among the electrons. For the exchange-correlation energy functional, Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) [7] was adopted in this study. Plane-wave basis was used to calculate wave-functions of valence electrons in a field of residual ions. Core electrons of the each ion, i.e. $[Xe]4f^{14}$ for W ion and $1s^2$ for C ion, were represented by a generalized pseudo-potential of the projector-augmented-wave (PAW) method [8]. For a given super-cell with the periodic boundary condition, ionic configurations and the cell shapes were relaxed at constant volumes until forces of every atom in the super-cell became smaller than 0.02 eV/\AA . The present

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calculations were implemented with VASP code [9]. Equilibrium volumes and bulk moduli as well as the total energy were determined by fitting computed energy-volume curves to Birch-Murnaghan's equation of state.

A binding energy of the interstitial C-H pair is given in terms of the standard formation energy E_F of the each interstitial particle,

$$\begin{aligned} E_B(\text{C-H}) &= E_F(\text{C}) + E_F(\text{H}) - E_F(\text{CH}) \\ &= E(\text{W}_n\text{C}) + E(\text{W}_n\text{H}) - E(\text{W}_n) \\ &\quad - E(\text{W}_n\text{CH}), \end{aligned} \quad (1)$$

where E in the second equation are equilibrium total energies of bcc super-cells containing n W atoms and the interstitial particles. In the equilibrium configuration, C sits at an octahedral-site (o-site), and H is at a tetrahedral-site (t-site). Fig. 1 shows the binding energies of three configurations of the interstitial C-H pairs. In this calculation, the reference super-cell containing 128 W atoms, $4 \times 4 \times 4$ shifted k-point grid of the Monkhorst-Pack scheme, and plane-wave cut-off energy of 350 eV were used. The present calculation gives negative binding energies for the all configurations, indicating inherently repulsive interaction in the interstitial pair. This contrasts to the attractive interaction in the isolated C-H pair in the gas-phase. Comparing with results of interstitial H-H pairs [10], the C-H repulsion appears much stronger. The nearest-neighbor interstitial pair of Fig. 1 (a) is not in equilibrium. The C-H pair repels each other, relaxing to the equilibrium (meta-stable) configurations of (b) and (c). The present result suggests that the interstitial C cannot be a trap of H in the bulk W crystal.

Since ionization energies of C and H (IP = 11.3 eV and 13.6 eV, respectively) are substantially larger than that of W (IP = 7.9 eV), appreciable electron transfer to the vicinity of the interstitial C and H from the neighboring W atoms may be possible. Bader's method [11] was used to evaluate fractional charges of the interstitial C and H.

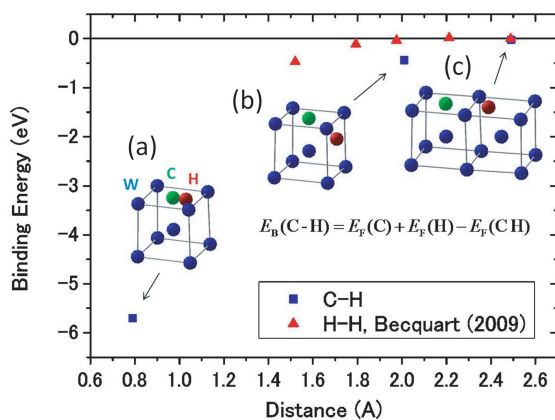


Fig. 1 Binding energies of interstitial C-H pairs in a W crystal (blue square). The binding energies of interstitial H-H pairs [10] are also plotted for comparison (red triangle).

This method analyzes directly electron density distribution without recourse to basis of the wave-function, whereas Mulliken's method [12] cannot be applied with the plane-wave basis. Negative fractional charges, -0.35 and -0.37 , were obtained for the interstitial C and H, respectively, that can explain the inherent repulsion of the interstitial C-H pair in the W crystal.

3. Ambient Hydrogen Effect on Interstitial Diffusion of C

In this study, the interstitial diffusion of C in a bcc W crystal was treated in the transition state theory. Fig. 2 illustrates transition between an initial and a final configuration of the interstitial C-H pair with C jumping into the adjacent o-site. Rate at which the transition between the initial and the final configuration takes place is given in terms of an activation free-energy and a hopping frequency (ν) to an intermediate (transition state) configuration,

$$\Gamma = \nu \exp[\Delta S_{\text{vib}}/k_B] \exp[-\Delta E/k_B T], \quad (2)$$

where k_B is Boltzmann constant and T temperature. For a given jumping rate, Γ , an interstitial diffusion coefficient in the bcc W crystal is [5],

$$D = \frac{2}{3} \left(\frac{a_W}{2} \right)^2 \Gamma, \quad (3)$$

where a_W is the lattice constant of the W crystal (~ 3.16 Å). The activation enthalpy, ΔE , was approximated with the formation energy difference between the initial and the transition state obtained by the present density functional calculation. The activation entropy of vibration, ΔS_{vib} , was obtained from normal mode frequencies of clusters including the interstitial C, H and the neighboring W atoms (linked with bonds in Fig. 2); other distant W atoms were assumed not to contribute to the entropy change apprecia-

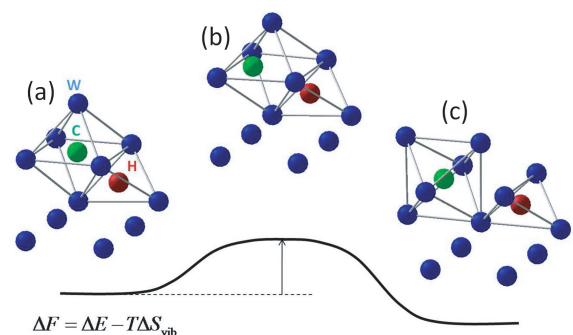


Fig. 2 Images of an elementary process in interstitial diffusion of C under influences of H. (a) Initial state (corresponding to Fig. 1 (b)), (b) transition state, and (c) final state configurations. The transition state configuration was determined by means of the nudged elastic band method [13] with three images. Free-energy curve associated with the transition is drawn in the figure.

Table 1 Activation enthalpy, entropy of vibration, and hopping frequency. o-C: an isolated interstitial C, o-C/t-H: an interstitial C-H pair (Fig. 2).

	ΔE (eV)	$\Delta S_{\text{vib}}/k_B$	ν (THz)
o-C	1.42	-0.03	16.3
o-C/t-H	0.97	-0.87	16.1

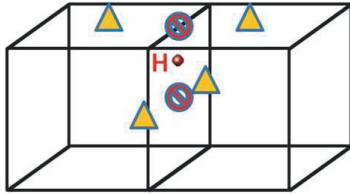


Fig. 3 Equivalent o-sites of interstitial C-H pairs. Four equivalent o-sites corresponding to Fig. 1 (b), and two corresponding to Fig. 1 (a).

bly. A normal mode frequency, whose principal component of the eigenvector of the Hessian matrix represented C oscillating in the direction to the adjacent o-site, was read as the hopping frequency. The present results of the activation enthalpy, the entropy of vibration and the hopping frequency are shown in Table 1, together with the results for an isolated interstitial C. The hopping frequency is affected little by including H. However, it appears that the activation enthalpy is reduced substantially due to the repulsive interaction of the C-H pair. The activation entropy of vibration is negative in both the cases. Including H gives a larger negative value for the activation entropy, which results in smaller values for the prefactors of the jumping rates, i.e. $\exp[\Delta S_{\text{vib}}/k_B]$. However, this effect would be negligible unless temperatures are extremely high. One can readily understand from these results that the presence of H increases the jumping rate of C, Eq. (2).

Four equivalent configurations of the interstitial C-H pair are possible per interstitial H as shown in Fig. 3. Since there are three o-sites per W in the bcc crystal, a statistical probability of the C-H pair formation is $4N_H/3N_W$, where N_H and N_W are the numbers of H and W in the crystal, respectively. Here, it is assumed that the interstitial H is, by time-averaged, distributed uniformly and distant from each other at low H concentrations, i.e. $N_H/N_W = x \ll 1$. In the ergodic assumption, therefore, a time-averaged jumping rate under the influence of the ambient H atoms is given by,

$$\langle \Gamma \rangle = \Gamma_0 \left(1 - \frac{4}{3}x \right) + \Gamma_H \frac{4}{3}x, \quad (4)$$

where Γ_0 and Γ_H are the jumping rates of the isolated C and the C-H pair, respectively.

On the other hand, there is another effect of the ambient H which interferes the interstitial diffusion of C. Since the C-H pair of Fig. 1 (a) is unstable due to the strong mu-

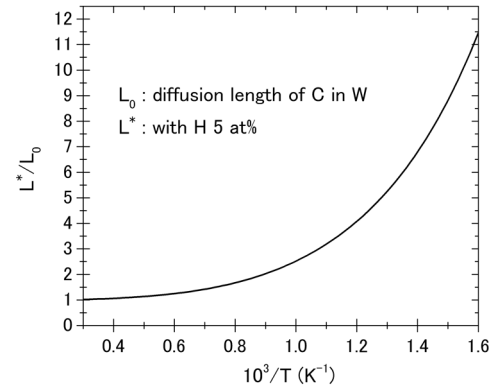


Fig. 4 Diffusion length ratio, $L^*/L_0 = (D^*/D_0)^{1/2}$, of an interstitial C in W crystal. L_0 is the diffusion length of an isolated C, L^* with 5 at% ambient H concentration.

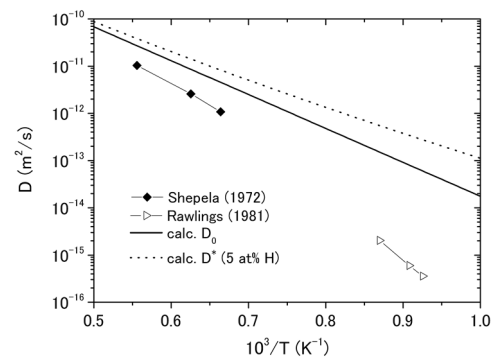


Fig. 5 Interstitial diffusion coefficients of C in the bulk W crystal. Two experimental values of volume diffusion coefficients, which were measured with single-crystal W samples, are also plotted for comparison.

tual repulsion, H at a t-site effectively blocks two nearest-neighbor o-sites from being occupied by C (see Fig. 3). The reduced interstitial diffusion coefficient is multiplied by a site-blocking factor in the mean field approximation,

$$D^* = D \left(1 - \frac{2}{3}x \right). \quad (5)$$

This approximation is proved to be valid if the diffusion coefficient of ambient H atoms is much larger than that of C [5].

For 5 at% concentration of H, i.e. $x = 0.05$, influences on the diffusion length are illustrated in Fig. 4. Except for extremely high temperatures, the diffusion length is increased under the influence of the ambient H. It contrasts to trapping effects, e.g. vacancy, which would impede the migration of C. The present results indicate that enhancement of the jumping rate due to the repulsive interaction with the ambient H, Eq. (4), dominates over interference due to the site-blocking, Eq. (5). At lower temperatures, increase of the diffusion length appears more significant. At 625 K, the diffusion length is increased by one order of magnitudes.

The present calculations of the interstitial diffusion coefficients are plotted in Fig. 5 together with two measurements of volume diffusion coefficients with single-crystal W samples. The calculated value should be read as an upper limit of the volume diffusion coefficient because the perfect crystal is assumed. Shepela's values [14] were deduced from measured concentration distributions of diffused radiotracer ^{14}C in the bulk, i.e. in-diffusion method. The activation enthalpy obtained in this measurement, 1.64 eV, is close to the present result of the isolated C (see Table 1). The present activation entropy and the hopping frequency of the isolated C give a pre-exponential factor of the diffusion coefficient of $2.6 \times 10^{-7} \text{ m}^2/\text{s}$ which is consistent with Shepela's value, $3.45 \times 10^{-7} \text{ m}^2/\text{s}$. In a lower temperature region, discrepancies between the present result and Rawlings's value [15] are very large. Rawlings's value of the activation enthalpy is $2.56 \pm 0.35 \text{ eV}$. This value was deduced from measured segregation rates of C from the bulk to a W (100) surface. Since a potential barrier at the seldge may be larger than that of volume diffusion due to reconstruction of the outer most surface layer, Rawlings's value should be read as an upper limit for the activation enthalpy of the volume diffusion.

As seen for the diffusion length, remarkable increase of the interstitial diffusion coefficient is illustrated in Fig. 5 (dotted curve), too. Contrary to it, some lattice defects may impede migration of C, which decrease apparent diffusion coefficients. Discrepancies between the present calculation and the measured values may be partially due to the defects. If such the defects in the samples were identified, its effects could be evaluated.

4. Summary

The repulsive interaction of the ground state interstitial C-H pair in the W crystal was obtained with the first-principle calculation. Bader's analysis was applied to evaluate fractional charges of the interstitial atoms. This analysis gives negative fractional charges for both the interstitial atoms, which is consistent with their mutual repulsive interaction.

Contrary to the C-H bonding in a gas-phase, they repel each other in the bulk W crystal. It enhances the time-averaged jumping rates of C under influence of the ambient H, which results in increase of the interstitial diffusion coefficient of C. Enhanced C diffusion into the bulk are observed in a low-energy D^+ ion-implantation experiment with a single crystal W sample [16]. The present

results appear to support the experimental observation. In the present study, the influence of the ambient H on the interstitial diffusion of C was evaluated theoretically by applying the ergodic assumption and the mean field approximation. More direct investigations may be feasible by means of kinetic Monte-Carlo methods using the present first-principle calculations of the jumping rates.

The volume diffusion coefficients of C measured with single-crystal W samples are compared with the present interstitial diffusion coefficients of the isolated C. The present calculation gives consistent results of the activation enthalpy and the pre-exponential factor of the diffusion coefficient with values measured by Shepela [14].

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