Towards understanding the carbon trapping mechanism in copper by investigating the carbon–vacancy interaction*

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We propose a vacancy trapping mechanism for carbon–vacancy (C–V) complex formation in copper (Cu) according to the first-principles calculations of the energetics and kinetics of C–V interaction. Vacancy reduces charge density in its vicinity to induce C nucleation. A monovacancy is capable of trapping as many as four C atoms to form C_nV ($n = 1, 2, 3, 4$) complexes. A single C atom prefers to interact with neighboring Cu at a vacancy with a trapping energy of -0.21 eV. With multiple C atoms added, they are preferred to bind with each other to form covalent-like bonds despite of the metallic Cu environment. For the C_nV complexes, C_2V is the major one due to its lowest average trapping energy (1.31 eV). Kinetically, the formation of the C_nV complexes can be ascribed to the vacancy mechanism due to the lower activation energy barrier and the larger diffusion coefficient of vacancy than those of the interstitial C.

Keywords: carbon, vacancy, copper, first-principles calculation

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1. Introduction

Nuclear fusion energy is considered to be a clean and infinite energy resource for future generations, which is being developed internationally via the International Thermonuclear Experimental Reactor (ITER) Project.[1] The final application of fusion energy is mainly dependent on the development of key materials in the tokamak fusion devices, such as the choice of the heat sink material (HSM). Due to their high thermal conductivity, high mechanical strength, and good radiation resistance,[2–6] copper (Cu) and Cu alloys are considered to be the most promising candidates for HSM, in which carbon (C) is commonly regarded as one of the most frequent impurity atoms. Consequently, exploring the interaction between C and Cu not only greatly helps us to understand the effects of C on the structure and properties of Cu, but also has a direct influence on the design and operation of a fusion reactor.[1]

The interaction of C with metal is of not only scientific interest but also of technological importance,[7–9] as it has a broad range of implications in the materials physics field. Although only a very small number of C atoms are present in Cu, it is expected to have a crucial influence on the energetics and kinetics of defects, and thus can have a large effect on the properties of Cu. The stability of the Cu matrix composites with C has been investigated in previous studies.[10–15] It was found that the substitutional impurities can significantly influence the diffusivity of C in the Cu matrix, and zirconium is predicted to be the best alloying element for preventing the diffusion of C in Cu–C alloy.[10] The deformational interaction in dilute Cu–C alloys has a long-range character.[12] A small amount of C in Cu will lead to strong deformation of the Cu host matrix in the vicinity of C.[13] High-resolution scanning electron microscopy results have demonstrated the existence of a solid zone at the Cu–C interface.[14] In Fe–Cu–C alloys, the Cu–C–vacancy clusters can prevent the formation of Cu precipitate crystalline structure under neutron irradiation.[16]

A vacancy, as a typical point defect in metal, plays a crucial role in the nucleation, evolution, and kinetics of large defects, which eventually governs the macroscopic deformation and failure mechanisms observed in a variety of metals.[17,18] Previous theoretical and experimental studies have shown that a strong affinity between the C atoms and vacancies exists.[7,19–23] Earlier experiments showed that C impurity atoms can be strongly trapped by a monovacancy in α-Fe, where asymmetric C–vacancy (C_1V) pairs can be easily formed by positron-lifetime measurements at the room temperature.[7,19] However, recent first-principles calculations[20,22] showed that C_2V complexes are energetically favorable in comparison to C_1V pairs in α-Fe. In the bulk Cu, it is found that a single C atom is energetically favorable sitting at the octahedral interstitial site (OIS).[11,15,24] However, the trapping mechanism of C in a vacancy has not been well understood. So far, few works have focused on this aspect. In order to understand the physical mechanism of C trapping, in this paper, we systematically investigate the dissolution, segregation, and accumulation behaviors of C in a vacancy using first-principles calculations. The temperature effects are also discussed according to the results from first-principles calculations.

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2. Computational method

Our first-principles calculations were performed using the pseudopotential plane-wave method implemented in the Vienna *ab-initio* simulation package (VASP) code[25,26] based on density functional theory (DFT). We used the generalized gradient approximation of Perdew and Wang[27] and projected augmented wave potentials,[28] with a plane wave energy cutoff of 400 eV. An fcc Cu supercell of 108 atoms without and with a monovacancy was used, and their Brillouin zones were sampled with $(3 \times 3 \times 3)$ k-points by the Monkhorst–Pack scheme.[29] The calculated equilibrium lattice constant is 3.63 Å for fcc Cu, in good agreement with the corresponding experimental value of 3.61 Å.[30] Both supercell size and atomic positions were relaxed to equilibrium, and energy minimization continued until the forces on all atoms were converged to less than 10^{-3} eV·Å^{-1}.

3. Results and discussion

3.1. Single C atom in a monovacancy

In our previous study,[24] we have examined the C behavior in intrinsic bulk Cu. We found that a single C is energetically favorable for sitting at the octahedral interstitial site (OIS)[11,15] with a solution energy of 1.57 eV in comparison to 2.73 eV at the tetrahedral interstitial site (TIS). Physically, the C solution behavior in a metal can be understood approximately in terms of the C solution energy in a homogeneous electron gas.[31] The C solution energy decreases monotonically with electron density decreasing until reaching the minimum at an optimal density of $n_0 \approx 0.024$ Å^{-3}.[31] However, if the charge density is lower than the optimal density, the solution energy increases. Since the electron density everywhere in the bulk Cu (as well as in most metals) is much higher than n_0, C generally has the lowest solution energy at the site where the electron density is the lowest. In the bulk Cu, the charge density of the OIS after the structure optimization is 0.13 Å^{-3}, which is 0.06 Å^{-3} lower than that of the TIS. The solution energy sequence of C is consistent with the charge density results, i.e., the lower the charge density is, the lower the solution energy is.

Apparently, the interstitial sites cannot effectively trap C atoms due to the larger solution energy. In order to further lower the C solution energy, it is desirable to create a structure that will further reduce the electron density. Vacancies or voids, as well as other regions with larger space, naturally can lower the electron density in its vicinity, providing an effective mechanism to meet this requirement. As a typical defect in metal, vacancies play a crucial role in trapping interstitial C atoms. Figure 1 shows seven high-symmetric sites for a single C atom at a monovacancy. Site 1 is the substitutional center. Sites 2 and 3 represent two different face OIS centers, and site 4 is the side OIS center. Site 5 is the midpoint between the substitutional center and its nearest neighbor Cu atom. Sites 6 and 7 are the TIS and OIS, respectively, and site 7 is outside of the vacancy. We calculate the values of solution energy ($E^{\rm sol}_{\rm V,C}$) of C at these highly-symmetric sites as well as other possible sites to find the energetically favorable sites. The solution energy $E^{\rm sol}_{\rm V,C}$ can be obtained by

$$E^{\rm sol}_{\rm V,C} = E_{(N-1)\rm Cu,V,C} - E_{(N-1)\rm Cu,V} - \mu(\rm C), \qquad (1)$$

where $E_{(N-1)\rm Cu,V,C}$ and $E_{(N-1)\rm Cu,V}$ are the total energies of the monovacancy system with and without C atoms. The third term $\mu(\rm C)$ on the right-hand side is the C chemical potential. The C chemical potential $\mu(\rm C)$ is the C energy per atom in the graphite structure. Here, we directly choose the value of -8.01 eV from Ref. [32] using first-principles calculations. It is well known that the DFT cannot efficiently describe the interaction between the planes in graphite due to the van der Waals forces. Therefore, we believe that it is basically consistent with the experimental value of -7.37 eV.[33]

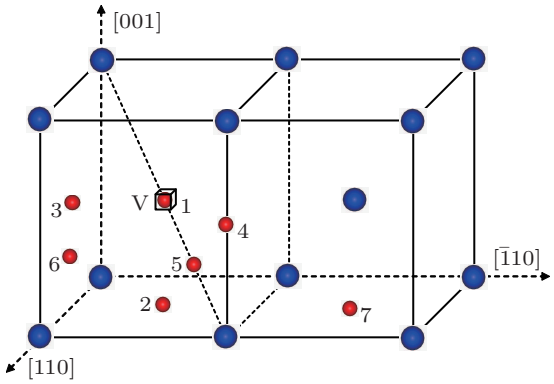


Fig. 1. (color online) Seven high-symmetric sites for a single C atom in the vicinity of a monovacancy. The larger (blue) and the smaller (red) balls represent Cu and C atoms, respectively.

The energy minimization finds the most stable site for C to be at an off-vacancy-center position ($\sim$1.64 Å from vacancy center) close to an OIS, i.e., site 2 or site 4 (the two sites are equivalent and correspond to the same atomic environment as shown in Fig. 1). The C solution energy at this site is 1.36 eV, which is 0.21 eV lower than that at the OIS in the intrinsic bulk Cu. This suggests that the trapping energy of a single C atom at the vacancy is -0.21 eV. The main reason that C has a lower trapping energy at the vacancy is because there exists a low electron density region in the vicinity of the vacancy. We find that C prefers to bind an isosurface of the same charge density of $\sim$0.09 Å^{-3} surrounding the vacancy, 0.04 Å^{-3} lower than that at the OIS in the intrinsic bulk Cu. The C solution energy is about the same on the isosurface with six minimum sites, very close to the six OIS's around the vacancy as indicated in Fig. 2(a). The solution energies at other sites with equivalent charge density at the octahedral-like surface (see

Fig. 2(a)), however, can be as large as ~ 0.78 eV higher than that at these six symmetrically equivalent sites. This reflects the additional atomic structural effect as C interacts with different sites around the vacancy.

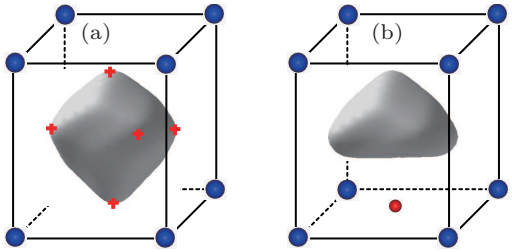


Fig. 2. (color online) (a) Isosurfaces of optimal charge density for C trapping at vacancy without C. The larger (blue) and the smaller (red) balls represent Cu and C atoms, respectively. (b) The crosses mark the six minimum-energy C trapping sites on the isosurface 1 C.

It is clear that a vacancy or vacancy-like defect can provide an optimal charge density for C to reduce the solution energy. Such an optimal charge density is shown to be an octahedral region around the vacancy internal "surface" as shown in Fig. 2. The most energetically favorable site is $\sim$1.64 Å off vacancy center close to an OIS. The vacancy center cannot effectively satisfy such a charge-density criterion, making C deviate from the vacancy center. Consequently, the C–V pair (complex) cannot be symmetric. Experimentally, it is still not available for providing the proof of a C–V asymmetric pair. However, the asymmetric C_1V pair has been found to be easily formed in bcc Fe according to the earlier experimental studies.[7,19] Similar to Cu's case, because a C atom prefers to bind onto the optimal spherical-like electron density region that the vacancy center cannot provide, it will deviate from the vacancy center to form the asymmetric C_1V pair in Fe and W.

3.2. Multiple C atoms at a monovacancy

The above results indicate that the C vacancy is strongly attractive in Cu, similar to the behavior of C in other bcc metals, such as Fe,[7,19] and W.[34] The extra trapping energy of C with vacancy suggests that the vacancy formation energy will be lowered by the presence of C in comparison to that in the intrinsic metal due to exothermic reactions. This is associated with C-assisted vacancy formation in Fe from a recent first-principles calculation.[21] The strong trapping of C by a vacancy implies that the vacancies can act as trapping centers, which drive a large number of C atoms to segregate towards the vacancies. Such a segregation of C atoms can further lead to the formation of C_nV complexes and influence the vacancy effective diffusivity in metals.[23] In the present work, we try to calculate the number of C atoms that one vacancy can trap. This depends on the way of calculating the C trapping energy at the vacancy. Generally, diffusion of C towards the vacancy in Cu should be associated with the C concentration. Qualitatively, at a low C concentration, C atoms can diffuse into the vacancy sequentially (the sequential way). At a high C concentration, multi-C atoms can diffuse into the vacancy at the same time (the simultaneous way).

For the sequential way, the sequential trapping energy ($E_{\rm seq}^{\rm trap}$) per C atom can be obtained by

$$E_{\rm seq}^{\rm trap} = E_{(N-1){\rm Cu,V,C}_n} - E_{(N-1){\rm Cu,V,C}_{n-1}} - E_{N{\rm Cu,C(OIS)}} + E_{N{\rm Cu}}, \quad (2)$$

where $E_{N{\rm Cu,C(OIS)}}$ and $E_{N{\rm Cu}}$ are the energies of the Cu supercell with and without C atoms, respectively. On the other hand, for the simultaneous way, the average trapping energy ($E_{\rm sim}^{\rm trap}$) per C atom is defined as

$$E_{\rm sim}^{\rm trap} = \frac{1}{n}[E_{(N-1){\rm Cu,V,C}_n} - E_{(N-1){\rm Cu,V}}] - [E_{N{\rm Cu,C(OIS)}} - E_{N{\rm Cu}}]. \quad (3)$$

A negative $E_{\rm sim}^{\rm trap}$ means energy gain when the C atoms are trapped by the vacancy with respect to dispersion into n different OIS's. The trapping energy as a function of the number of C trapped by the vacancy in Cu is shown in Fig. 3.

For the sequential method, according to Eq. (2), we calculate the sequential C trapping energy per C atom as a function of the number of C trapped by the vacancy as shown in Fig. 3. The first C atom attains a trapping energy of -0.21 eV. As more C atoms are added, they experience interactions among them. It is important to note that the trapping energy (-2.45 eV) becomes very low when the second C atom is added in comparison with the first one (-0.21 eV), suggesting that C_2V is more stable than C_1V in Cu. As shown in Fig. 3, after the second C atom is added, the trapping energy of C will increase with the increase of the number of C atoms trapped by the vacancy. The trapping energies of the third and the fourth C atom are -0.83 eV and -0.24 eV, respectively. Finally, the addition of the fifth C atom gives rise to a positive trapping energy of 0.31 eV. This suggests that the fifth C atom will prefer to occupy the OIS in bulk Cu rather than stay in the vacancy. Therefore, the maximal number of C atoms that can be trapped by the vacancy is 4 via the sequential way. The C_2V is found to be the major C–V complexes corresponding to the lowest trapping energy. Similar results can also be obtained for C in bcc Fe and W.[20,22,34]

On the other hand, the simultaneous method gives different results. The average trapping energy (-1.31 eV) becomes very low when the second C atom is embedded in comparison with that of the first one (-0.21 eV). With the increase of the number of C atoms, the trapping energy of each C atom increases again. When the number of C atoms increases up to 6, the average C trapping energy is still negative (-0.44 eV), which indicates that the number of C atoms trapped by the vacancy should be larger than 6. However, after carefully checking the atomic configurations of each C addition, we find that

a vacancy can only accommodate five C atoms. The sixth embedded C atom will fall into one of the OIS's out of the vacancy. Thus, it is energetically favorable for a monovacancy to trap as many as five C atoms via the simultaneous way, where the C_2V is still found to be the major complexes.

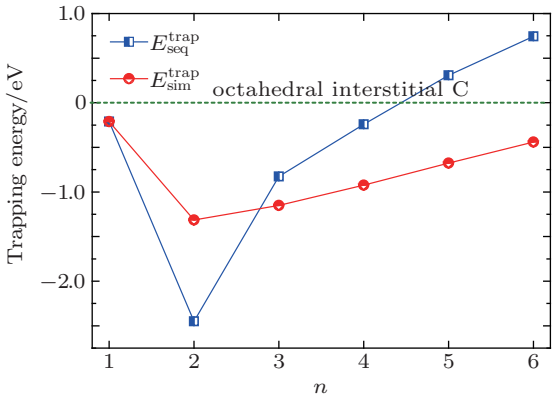


Fig. 3. (color online) Plots of trapping energy per C versus the number of C atoms trapped by the vacancy in Cu.

We show above two different ways to bring the C atoms into a monovacancy, leading to different numbers of C atoms that one monovacancy can accommodate. Via the sequential way, one monovacancy can hold four C atoms, less than five C atoms for the simultaneous way. As a matter of fact, the diffusion of C towards the vacancy should depend on the C concentration in Cu. Under low C concentration, the probability of the sequential way becomes much higher, while under high C concentration, the simultaneous way will be preferable. In the sequential way, averagely, one monovacancy will hold fewer C atoms than the maximum number (4 atoms) it can hold due to the lower C concentration in Cu. The monovacancy should contain two C atoms in most cases because the C_2V complex is most energetically favorable according to the present calculations.

We further investigate the atomic configurations and the charge density distributions for multiple C atoms trapped in the vacancy in order to explore the C–C interaction. The bond lengths between C atoms are calculated to be 1.36 Å, 1.33 Å, and 1.43 Å for C_2V, C_3V, and C_4V, respectively, as shown in Fig. 4. We see that the C–C bonds in the C–V complexes have the typical C covalent bond length for sp^2 bonds.[35] Figure 5 shows the charge density distributions of C atoms in the vacancy for C_2V, C_3V, and C_4V, respectively. Despite the metallic Cu environment, C–C covalent-like bonds are clearly formed (the high electronic concentration between the two C atoms). Such a strong covalent-like bond makes C atoms bond strongly at the vacancy, which further explains why the larger trapping energies are present for the 2C and 3C cases at the vacancy (Fig. 3). For the C_4V case, the bond length (1.43 Å) is little longer than those of other two cases. This might lead to the relatively weak C–C bonding at the vacancy, corresponding to the relatively low trapping energy (Fig. 3). In addition, we also find that C no longer prefers to occupy the optimal charge density region for the multiple C cases, because there is strong interaction between C atoms in the vacancy.

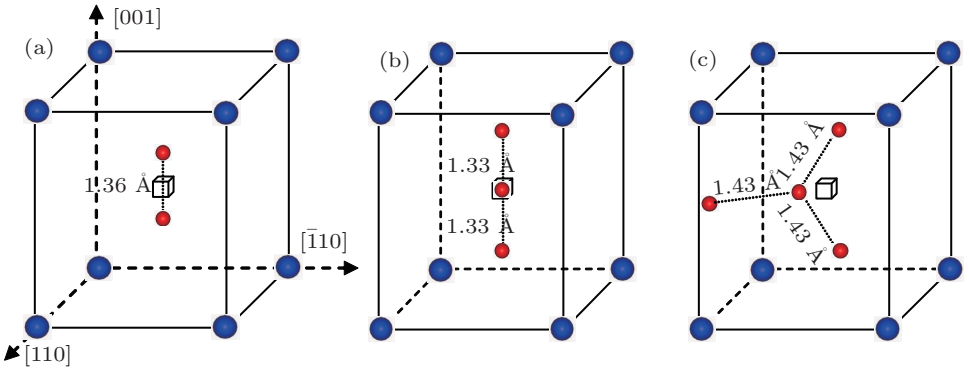


Fig. 4. (color online) The atomic configurations for multiple C atoms trapped in a monovacancy. (a) 2C, (b) 3C, and (C) 4C.

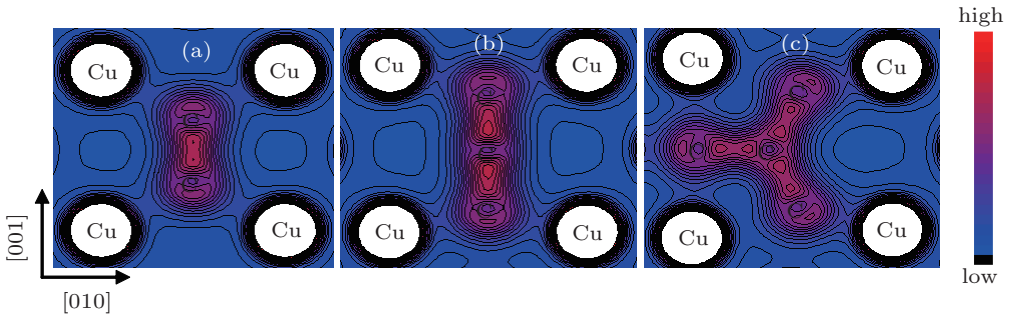


Fig. 5. (color online) Charge density distributions in the (100) plane for (a) C_2V, (b) C_3V, and (c) C_4V complexes, respectively.

3.3. Competition between C and vacancy diffusion in Cu

The above results clearly demonstrate the thermodynamic stability of C segregation towards a monovacancy. The next question is the formation mechanism of C_nV complexes, i.e., whether mobile interstitial C atoms can be trapped by a stable vacancy, or vice versa. We thus investigate the diffusion behaviors of a monovacancy and an interstitial C atom. We calculate the diffusion energy barriers for the monovacancy and the interstitial C atom in bulk Cu using a drag method relaxing the atomic positions constrained in a hyperplane perpendicular to the vector from the initial to the final position.[36–38]

As shown in Fig. 6(a), it is found that the monovacancy prefers to migrate towards the 1NN site along the ⟨110⟩ direction. The barrier of the monovacancy is calculated to be 0.76 eV in the intrinsic Cu, which is consistent with the previous studies.[39–41] There are two main mechanisms for impurity atoms diffusing into a solid, i.e., the interstitial and substitutional mechanisms, which depend on the occupation behavior of the impurity atoms. It has been demonstrated that C energetically prefers to occupy the interstitial sites in the bulk Cu. Therefore, C will diffuse into Cu via the interstitial mechanism. As mentioned above, the OIS is relatively stable in comparison to the TIS, and thus we consider the process that allows C to hop from an OIS to another nearest neighbor OIS. The OIS→OIS path (from an OIS to another nearest OIS directly) has been demonstrated to be the optimal diffusion path for a single interstitial C atom with an energy barrier of 0.93 eV (Fig. 6(b)), which is 22% larger than that of the monovacancy. This suggests that the monovacancy is much easier to diffuse than the interstitial C in Cu. However, such high energy barriers of the monovacancy (0.76 eV) and the interstitial C (0.93 eV) suggest the difficult diffusion for the monovacancy and the interstitial C at the lower temperature. Nevertheless, with the increase of temperature, they will become mobile.

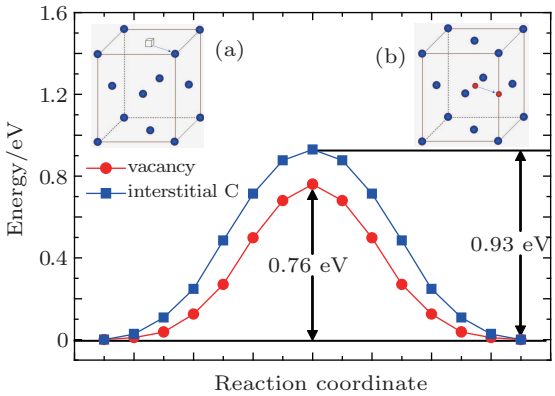


Fig. 6. (color online) Diffusion energy profiles for a monovacancy and an interstitial C atom in the intrinsic Cu. (a) Vacancy. (b) Interstitial C.

Next, we investigate the effects of temperature on the diffusion coefficient of vacancy and C at the typical experimental temperatures of 300–700 K for Cu.[2,4] It is well known that the diffusion coefficient of vacancy and impurity atom can be obtained by the Arrhenius diffusion equation $D = D_0 \exp(-E_a/kT)$, where D_0, E_a, k, and T are the pre-exponential factor, activation energy, the Boltzmann constant, and the absolute temperature, respectively. In terms of the diffusion theory presented by Wert and Zener,[42] D_0 can be expressed as $D_0 = (n_{ejp}\nu/6)(\sqrt{2}a/4)^2$ since Cu belongs to fcc structure metal, where n_{ejp}, a, and ν are a geometrical factor for the number of equivalent jump paths, the equivalent jump length, and the vibration frequency, respectively.

We calculate the vacancy diffusion energy barrier of 0.76 eV along the preferred path of the ⟨110⟩ direction in Cu. It is well known that the vacancy diffusion corresponds to the diffusion of the Cu atom. Thus, at the vibration frequency $\nu_V = \sqrt{2E_a/ma^2}$, m is also the mass of the Cu atom. Using the mass of the Cu atom of 1.05×10^{-25} kg and the Cu lattice constant of 3.63×10^{-10} m as well as the calculated vacancy diffusion energy barrier of 0.76 eV, we can thus obtain the vibration frequency $\nu_V = 4.19 \times 10^{12}$ Hz. Substituting this value into $D_0 = (n_{ejp}\nu/6)(\sqrt{2}a/4)^2$, we can further obtain the pre-exponential factor $D_0(V)$. After establishing the pre-exponential factor, the vacancy diffusion coefficient in Cu can be calculated according to the Arrhenius equation as explained above. As shown in Fig. 7, we depict the curve of the vacancy diffusion coefficient as a function of temperature, which is in good agreement with previous experimental values.[43–45]

A similar strategy can be applied to predict the C diffusion behavior with the confidence of vacancy in Cu and previous oxygen diffusion studies in W,[46] as well as an H diffusion study in Mo.[47] According to the Zener and Wert's theory,[42] the vibration frequency ν_C of the interstitial C atom can be approximately expressed as $\nu_V = \sqrt{2E_a/ma^2}$, where m is the mass of impurity atom. Similarly, substituting the mass of the C atom of 1.99×10^{-26} kg and the Cu lattice constant of 3.63×10^{-10} m, as well as the C diffusion energy barrier of 0.93 eV into the above formula, we can estimate the vibration frequency to be $\nu_C = 3.37 \times 10^{13}$ Hz, which is basically consistent with normal atom vibration frequency of 10^{12}–10^{13} Hz within an error range. Correspondingly, the C diffusion pre-exponential factor $D_0(C) = 5.55 \times 10^{-7}$ $m^2 \cdot s^{-1}$ can be obtained. We further depict the curve of the vacancy diffusion coefficient versus temperature in Fig. 7. Due to the few experimental or relevant calculated data, here we provide quite a useful reference to quantitatively understand the diffusion behaviors of C in Cu.

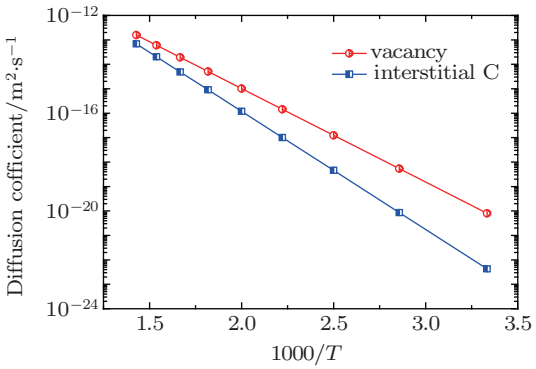


Fig. 7. (color online) Diffusion coefficients of vacancy and interstitial C in Cu versus reciprocal temperature.

As shown in Fig. 7, the diffusion coefficients of vacancy and C are obtained by the Arrhenius diffusion equation at different temperatures. It can be found that the diffusion coefficients of vacancy and C have strong temperature dependence, and thus the temperature plays a key role in determining the diffusion behaviors of vacancy and C. The diffusion coefficient will increase with increasing temperature, as shown in Fig. 7. One sees that the vacancy diffusion coefficients are larger than those of C in the typical temperature range, indicating that a monovacancy prefers to migrate into Cu in comparison to an interstitial C atom. Thus, we can give the formation mechanism of the C_nV complexes in Cu, i.e., the formation of the C_nV complexes can be ascribed to the trapping of migration vacancy by the relatively stable interstitial C in Cu.

4. Summary

In order to understand trapping mechanism of carbon (C) in copper (Cu), we have investigated structure, stability, and diffusion properties of C in Cu using a first-principles method. C atoms are easily trapped in the vicinity of vacancy. The most stable site for single C to be at a fixed position is ~ 1.64 Å away from the vacancy center close to an OIS. With multiple C atoms added, they prefer to bind with each other to form a covalent-like bond despite the metallic Cu environment. A monovacancy is shown to be capable of trapping as many as four C atoms to form C_nV ($n = 1, 2, 3, 4$) complexes. Among the C_nV complexes in Cu, C_2V is the major one due to its lowest average trapping energy (-1.31 eV), which corresponds to the lowest formation energy. Kinetically, the formation of the C_nV complexes can be ascribed to the interstitial mechanism due to a lower activation energy barrier (i.e., 0.76 eV) for the vacancy than that (i.e., 0.93 eV) for the interstitial C, and the larger diffusion coefficient of the vacancy than that of the interstitial C in the typical experimental temperature range for Cu.

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