Energetics of carbon and nitrogen impurities and their interactions with vacancy in vanadium*

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We studied the energetic behaviors of interstitial and substitution carbon (C)/nitrogen (N) impurities as well as their interactions with the vacancy in vanadium by first-principles simulations. Both C and N impurities prefer the octahedral site (O-site). N exhibits a lower formation energy than C. Due to the hybridization between vanadium-d and N/C-p, the N-p states are located at the energy from −6.00 eV to −5.00 eV, which is much deeper than that from −5.00 eV to −3.00 eV for the C-p states. Two impurities in bulk vanadium, C–C, C–N, and N–N can be paired up at the two neighboring O-sites along the ⟨111⟩ direction and the binding energies of the pairs are 0.227 eV, 0.162 eV, and 0.201 eV, respectively. Further, we find that both C and N do not prefer to stay at the vacancy center and its vicinity, but occupy the O-site off the vacancy in the interstitial lattice in vanadium. The possible physical mechanism is that C/N in the O-site tends to form a carbide/nitride-like structure with its neighboring vanadium atoms, leading to the formation of the strong C/N–vanadium bonding containing a covalent component.

Keywords: vanadium, carbon/nitrogen, vacancy, first-principles

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1. Introduction

In the fusion reactor, some components, such as the first wall, the divertor, and the structural materials exposed to plasma particles and electromagnetic radiation, will be irradiated by high energy neutrons,[1–6] which induces the degradation of the series properties and the residual radioactivity of the exposed materials. In order to efficiently utilize the fusion power, tremendous efforts have been devoted to searching for the suitable structural materials in the last few decades.[7–15]

In many experimental studies, vanadium and vanadium-based alloys have been attested to be promising structural materials owing to their excellent performances at high temperatures,[16–19] such as the intrinsic low-activation characteristics, high-temperature strength, and high thermal stress factor,[17] all of which can satisfy the requirements of safety operation in the extreme conditions. However, some small atomic-radius elements such as carbon (C) and nitrogen (N) are always present in vanadium-based materials, either as alloying elements in vanadium or as impurities in pure vanadium solid. We already knew that once beyond their solubility limit, C and N impurities tend to precipitate as carbides and nitrides, further leading to a notable change of the mechanical properties such as hardening and embrittlement. Moreover, even the high-purity vanadium can also contain a few atomic parts per million (appm) of these impurities. Several experimental and theoretical studies have demonstrated that C and N are the most frequent foreign interstitial atoms in the realistic vanadium and vanadium-based alloy materials.[20–26] Experimentally, some basic behaviors of C and N in vanadium-based alloys have been investigated. For example, in Ref. [22], Diercks *et al.* investigated the correlation between the mechanical properties of vanadium-based alloys and the impurity levels of C and N. Through the thermal desorption spectroscopy experiments,[23,24] it was found that C and N impurities in the He_nV_nX-type defects (X = C/N), namely, carbides and nitrides, could influence He dissociation from the He_nV_nX-type complexes remarkably. It was also pointed out in Ref. [25] that the reduction of C in the grain boundaries can affect the ductility of vanadium alloys. Recently, Li *et al.* investigated the stability and diffusion behaviors of a C or N impurity in vanadium solid using first-principles simulation method.[26]

Although many studies have investigated the behaviors of C or N impurity in vanadium or vanadium alloys as mentioned above, to the best of our knowledge, the C–N interaction and the interplay of C or N impurity atoms with the vacancy in vanadium have not yet been explored on the theoretical side till now, especially the binding properties between C or N impurity and vacancy. Several experiments have shown that at concentrations as low as a few appm, C and N might already have significant influences on the structural defects, such as vacancies in other metals.[27–30] The observed effects gener-

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ally originate from an attractive interaction between the impurity atoms and the vacancies. Even though the solubility limits are low, the interactions of C/N impurities with the vacancies are strong enough according to the previous theoretical predictions.[31–33] Motivated by this, here we employ first-principles simulations to investigate the C–N interaction and their interactions with a single vacancy in the vanadium solid in detail. Our results indicate that, differing from the previous results,[31–33] both C and N impurities in vanadium do not like to stay at the vacancy vicinity but at an octahedral interstitial site outside of the vacancy. This kind of interesting phenomenon mainly stems from that C and N impurities prefer to form the covalent-like bonding with the two first nearest-neighbor (1nn) vanadium atoms.

2. Methodology

The first-principles calculations were performed using the Vienna *ab-initio* simulation package (VASP) code,[34,35] which is based on the density functional theory. The Perdew and Wang (PW91) functional[36] within the generalized gradient approximation for the exchange–correlation interaction and the projector augmented wave potentials[37,38] were adopted. In the current work, a supercell composed of 128 atoms (4×4×4) was used to model the vanadium solid, and the plane wave energy cutoff was set to be 350 eV, which is sufficient for the calculations of the total energy and the geometry of the supercell. The Brillouin zone was sampled with a 3×3×3 k-point mesh generated by the Monkhorst–Pack scheme.[39] All of the atomic coordinates and volumes were relaxed with the conjugate gradient method until the forces on all the atoms in our calculations were less than 10^{-3} eV·Å^{-1}. The Methfessel–Paxton smearing method[40] was employed to integrate the Brillouin zone and account for the partial occupancy of the metals near the Fermi level with a smearing width of 0.1 eV, which keeps the convergence error of the total energy below 1 MeV. The equilibrium lattice constant of the bcc vanadium obtained from the present calculations is 2.98 Å, which is in excellent agreement with various experimental data ranging from 2.99 Å to 3.00 Å.[41–44]

3. Results and discussion

3.1. Single C and N impurities in bcc vanadium

In bcc metal, there are two kinds of typical point defects, namely, the substitution defects and the interstitial ones. For simplicity, we here only consider two typical high symmetrical interstitial sites, i.e., tetrahedral and octahedral sites, and set all substitution sites to be equivalent, as illustrated in Fig. 1. For these two cases, the formation energy of an interstitial or a substitution impurity X (X = C, N) can be defined by

$$E^{\mathrm{f}}_{\mathrm{int}} = E_{\mathrm{vanadium},X} - E_{\mathrm{vanadium}} - E_{\mathrm{ref},X}, \quad (1)$$

$$E^{\mathrm{f}}_{\mathrm{sub}} = E_{(n-1)\mathrm{vanadium},X} - \frac{n-1}{n}E_{\mathrm{vanadium}} - E_{\mathrm{ref},X}, \quad (2)$$

where $E_{\mathrm{vanadium},X}$ stands for the total energy of the vanadium supercell containing n vanadium atoms and one interstitial X atom, E_{vanadium} is the total energy of the perfect vanadium supercell, and $E_{\mathrm{ref},X}$ is the reference energy of the X atom. For the N atom, $E_{\mathrm{ref,N}} = E_{\mathrm{N_2}}/2$, where $E_{\mathrm{N_2}}$ is the energy of an isolated N_2 molecule in a vacuum ($E_{\mathrm{ref,N}} = -8.30$ eV in our calculation). For the C atom, $E_{\mathrm{ref,C}}$ is the energy per C atom in the graphite solid. After calculation, we obtain $E_{\mathrm{ref,C}} = -8.06$ eV, which is almost identical to the previous DFT value of 8.01 eV[45] and comparable to the experimental value of 7.37 eV within the error range.[42]

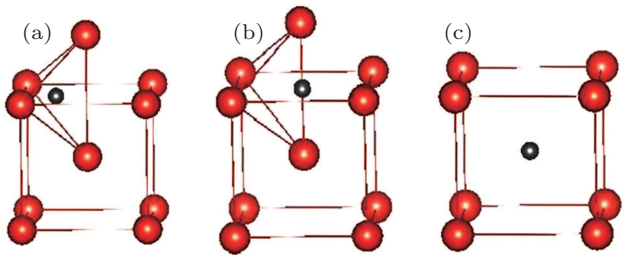


Fig. 1. (color online) Three possible positions for an impurity atom in vanadium: (a) tetrahedral site (T-site), (b) octahedral site (O-site), and (c) substitution site (S-site). Small (gray) and large (red) balls represent impurity atom (C or N) and vanadium atom, respectively.

In Table 1, we summarize the formation energies of C and N in the S-site, O-site, and T-site of the vanadium solid. It is obvious that for both C and N atoms, the most favorable positions are the O-site with the corresponding formation energies of −2.11 eV and −2.92 eV, respectively, which are in good agreement with the previous results.[26] The negative formation energies denote exothermic processes for both impurities in vanadium. We also note that the formation energy (−2.11 eV) of impurity C in vanadium is significantly higher than that (−2.92 eV) of impurity N. This indicates that (i) the solution of impurity C is more difficult than that of impurity N in vanadium; (ii) impurity N at this position is inclined to have a higher affinity than impurity C.

Table 1. Formation energy (in eV) of impurity (C or N) at different possible position in bulk vanadium.

Configuration	C		N	
S-site	0.61	0.59[a)]	1.32	1.23[a)]
T-site	–1.03	–1.10[a)]	–1.52	–1.60[a)]
O-site	–2.11	–2.10[a)]	–2.92	–2.97[a)]

[a)] Ref. [26].

In Fig. 2, we plot the total density of states (TDOS) of vanadium with and without an impurity atom at the interstitial sites. In contrast to the pure vanadium, it is important to note that an additional peak is present in the low-energy part (i.e., −11.0 eV) with impurity C occupying either the T-site or the O-site. Therefore, it is expected that the presence of the small peak should be straightforwardly related to impurity C. On the

other hand, the main peaks near the Fermi energy should be the vanadium–vanadium bondings as they remain almost unchanged with impurity C embedding. Similar to the C case, we note that the TDOS also has an additional small peak in the low-energy part (i.e., −15.50 eV) when the N atom occupies the two interstitial sites. So, the appearance of such a small peak should be from the C/N-s orbital. Also, it should be expected that C/N-p and vanadium-d orbitals around the Fermi energy exhibit hybridization. This hybridization should dominate the C/N–vanadium bonding with the covalent character, while the C/N-s orbital contributes little to the C/N–vanadium covalent bonding.

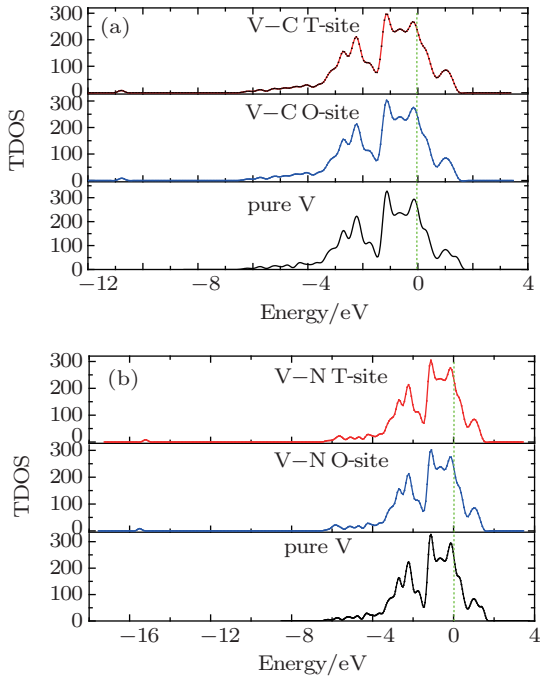


Fig. 2. (color online) The total DOS of vanadium without and with the impurity atom at the T-site and the O-site: (a) impurity C case, (b) impurity N case. The Fermi energy is set to be zero in all cases.

In order to attest the formation of covalent bonding between C/N and vanadium atoms, we further calculated the local density of states (LDOS) of C/N for impurity C/N at the O-site because the O-site is lower in formation energy of C/N than the T-site. As seen from Fig. 3(a), the interstitial C in vanadium exhibits the strong characteristic peak in the low-energy region from −5.00 eV to −3.00 eV, which corresponds to the p orbital of the interstitial C. For the interstitial N case (Fig. 3(b)), one strong characteristic peak also appears in the low-energy part from −6.00 eV to −5.00 eV, corresponding to the contribution of the p electrons from N. Figure 3 also shows the LDOS of the 1nn vanadium atom of impurity C/N in a vanadium solid. It is found that the LDOS of the 1nn vanadium atom in the low-energy region becomes dispersive and is similar to that of C/N. This demonstrates that the hybridization of C/N-p and vanadium-d is present when impurity C/N is introduced; the hybridization means the formation of a possible bonding between C/N and vanadium containing the covalent character. At the same time, we can also explain the formation energy difference between C and N at the O-site according to the covalent bonding character. As shown in Fig. 3, both C–vanadium bonding and N–vanadium bonding exhibit a strong covalent character due to the hybridization between the vanadium-d and C/N-p orbitals. However, it is obvious that the vanadium–N covalent bonding should be much stronger than the vanadium–C covalent bonding. This is because the C-p states are shifted to energy from −5.00 eV to −3.00 eV (Fig. 3(a)) due to the hybridization between vanadium-d and C-p, whereas the N-p states are located much deeper in energy from −6.00 eV to −5.00 eV (Fig. 3(b)) in comparison with the C-p states. This indicates that the N–vanadium covalent bonding is stronger than the C–vanadium one, as a result of the lower formation energy of N at the O-site than that of C.

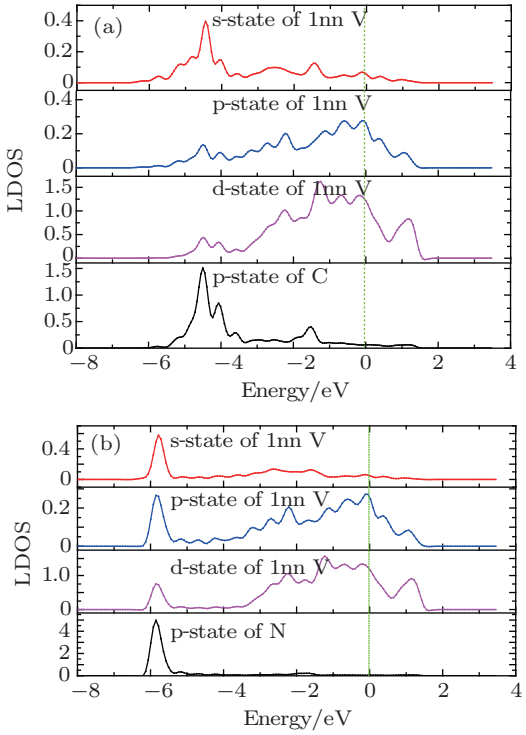


Fig. 3. (color online) The LDOS of 1nn vanadium atom of impurity C/N atom after the C/N occupying the O-site in vanadium solid: (a) impurity C case, (b) impurity N case.

To obtain further insight into the interaction between an interstitial impurity and its neighboring vanadium atoms, we display the charge density distribution for an individual C or N atom placed in the O-site of the vanadium solid in Fig. 4. Indeed, as expected above, the C/N–vanadium interaction leads to clear charge transfer from vanadium atoms to the impurity atom. Both C and N have high tendencies to form strong covalent-like bonding with the neighboring vanadium atoms including the 1nn and 2nn (the next nearest neighbor) cases, especially with the two 1nn vanadium atoms (Figs. 4(a) and 4(b)). Moreover, such a tendency slightly decreases from C to N, similar to the behaviors of C and N in

other bcc metals.[31,46] The C/N–vanadium bonding characteristics should be directly originated from the hybridization between C/N-p and vanadium-d as shown above. As illustrated in Figs. 4(a) and 4(b), local lattice distortions of two 1nn and four 2nn vanadium atoms caused by the addition of C or N are clearly present. The equilibrium geometry shows an outward relaxation for the 1nn vanadium atoms (see Figs. 4(a) and 4(b)). This phenomenon should be attributed to the large atomic radius of C/N. The covalent radii of C and N atoms are ~ 0.77 Å and $\sim$0.71 Å, respectively. It is generally believed that the interstitial position, i.e., the O-site in bcc vanadium (as well as most bcc metals), should be too small to accommodate the impurity atoms with larger atomic radius.[47–49] Thus, the additions of both C and N can cause the distortion of the local host atoms, particularly the two 1nn vanadium atoms.

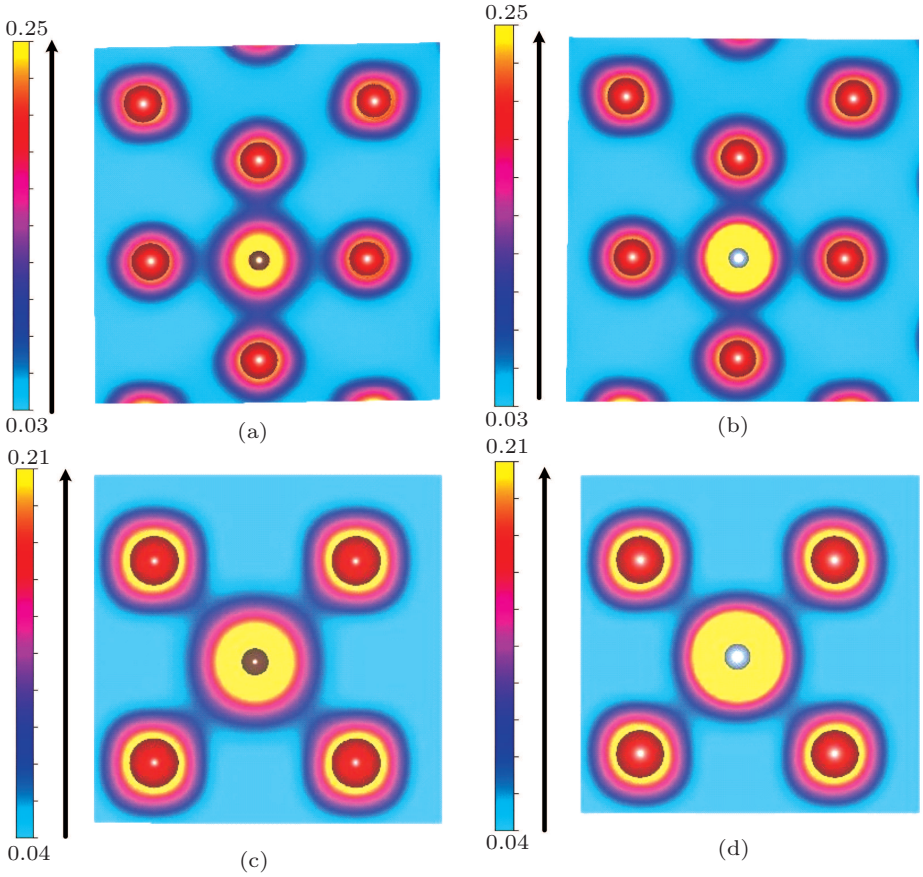


Fig. 4. (color online) The charge density distributions of impurity at an octahedral position in the (010) plane: (a) C with 1nn vanadium atoms, (b) N with 1nn vanadium atoms, (c) C with 2nn vanadium atoms, (d) N with 2nn vanadium atoms.

3.2. Interaction between two impurities in vanadium

Our theoretical results show that the O-site is the most stable position for single C or N atom in bcc vanadium solid. As is well known, in a real material, there is a high possibility for the co-existence of impurities in the nearby interstitial positions. Thus, we turn to address the impurity–impurity interactions. According to the impurity formation energies in vanadium (Table 1), the stabilization is much more significant for the octahedral lattice than for the tetrahedral geometry when the impurity C or N occupies the interstitial sites. In this section, only the O-site is considered for the interaction between impurities.

We construct seven possible configurations containing two impurities including C–C, C–N, and N–N pairs in bcc vanadium. As presented in Fig. 5, one impurity (i.e., A_1) occupies one O-site, and the second interstitial impurity atom (i.e., A_2) is located at a different O-site according to the different distance. The binding energy between two impurities (A_1–A_2) is given as

$$E^{\mathrm{b}}_{A_1-A_2,\mathrm{vanadium}} = E_{A_1,\mathrm{vanadium}} + E_{A_2,\mathrm{vanadium}} - E_{A_1-A_2,\mathrm{vanadium}} - E_{\mathrm{vanadium}}, \quad (3)$$

where $E_{A_1,\mathrm{vanadium}}$ and $E_{A_2,\mathrm{vanadium}}$ are the total energies of the vanadium supercell with A_1 and A_2, respectively, and $E_{A_1-A_2,\mathrm{vanadium}}$ denotes the total energy of the vanadium supercell simultaneously containing A_1 and A_2. The positive/negative binding energy means attraction/repulsion between the two impurities. Table 2 lists the binding energies of A_1–A_2 pairs with the change of distance between the two impurities. As shown in Table 2, the A_1–A_2 interaction exhibits

a strongly repulsive nature between the two impurities when they are too close or too far from each other. Interestingly, the cfg^2 is the most stable configuration for all the C–C, C–N, and N–N pairs in bulk vanadium, as the binding energies are positive with this configuration. Thus, we can conclude that two impurity atoms can be paired up at the two neighboring O-sites along the ⟨111⟩ direction. According to Table 2, the binding energies of C–C, C–N, and N–N pairs are 0.227 eV, 0.162 eV, and 0.201 eV, respectively, and the corresponding optimal distance is 0.866 Å. At the same time, the positive binding energies between A_1–A_2 pairs mean that C or N atoms are able to agglomerate even without defects such as vacancies. Such behavior may result in a high C or N concentration at some local position and further lead to the formation of carbide or nitride in bulk vanadium.

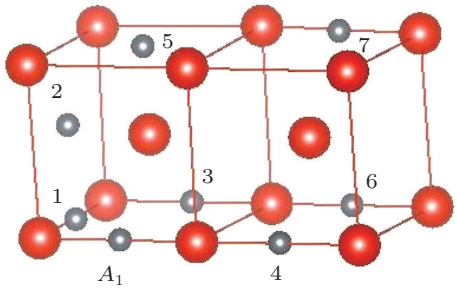


Fig. 5. (color online) Seven possible configurations for two impurities in bcc vanadium. A_1 is one O-site occupied by the first impurity. The second impurity atom will be located at different O-sites labeled by i ($i = 1, 2, \ldots, 7$).

Table 2. Binding energies (in eV) of A_1–A_2 pairs in bulk vanadium with different configurations as shown in Fig. 5. The $d_{A_1-A_2}$ (in Å) represents the distance between the two impurities.

Configuration	C–C	C–N	N–N	$d_{A_1-A_2}$
cfg^1	–0.713	–0.837	–0.964	0.707
cfg^2	0.227	0.162	0.201	0.866
cfg^3	0.011	–0.022	–0.071	1.000
cfg^4	–1.710	–1.670	–1.670	1.000
cfg^5	–0.063	–0.08	–0.078	1.118
cfg^6	–0.194	–0.196	–0.198	1.414
cfg^7	–0.104	–0.097	–0.087	1.732

We further observe that the C–C pair is significantly less repulsive than the N–N pair at the shorter distances, i.e., from cfg^1 to cfg^4. At the larger distance, i.e., from cfg^5 to cfg^7, the C–C interaction is either less or more repulsive than the N–N pair. It is also worth mentioning that the C–C pair can also be formed when two C atoms are located at the two respective O-sites along the ⟨010⟩ direction with the distance of 1.000 Å (cfg^3 in Fig. 5). This case corresponds to a metastable configuration of C–C pair in comparison with that of cfg^2, but the binding energy is still positive (0.011 eV), suggesting that it is energetically possible for the formation of the C–C pair in bulk vanadium.

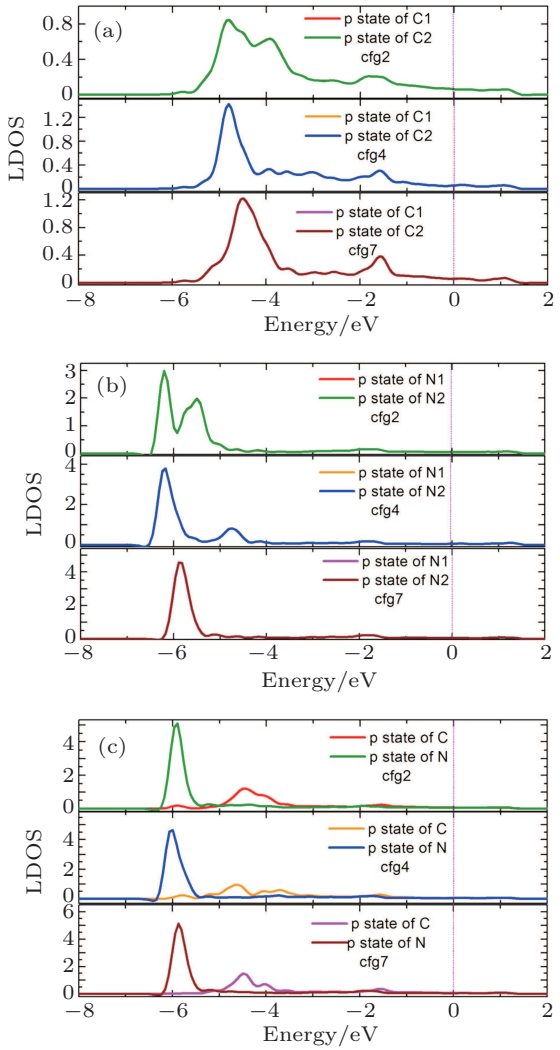


Fig. 6. (color online) Comparison of LDOSs of the C–C, N–N, and C–N pairs in the cfg^2, cfg^4, and cfg^7 configurations (see these configurations in Fig. 5) in vanadium: (a) p states of C–C pair, (b) p states of N–N pair, (c) p states of C–N pair.

In order to gain further insight into the stability of C–C, N–N, and C–N pairs, we then compare the LDOSs of these pairs with different atom–atom distances in vanadium. As shown in Figs. 6(a) and 6(b), when the distance between two C/N atoms is larger (cfg^7 in Fig. 5) in the vanadium system, there appears a low energy state in the LDOS, which is the result of the hybridization between the vanadium-d and C/N-p states and is a common feature of the system of a C/N atom with the nearest neighboring vanadium atoms. Note that the LDOSs of the two C/N atoms in a pair are in coincidence (Fig. 5). With the decrease of the distance between two C/N atoms, however, another smaller peak appears in cfg^4 in the low energy state (~ -4.00 eV for C–C pair in Fig. 6(a) and ~ -4.80 eV for the N–N pair in Fig. 6(b)) in addition to the original bigger peak. In other words, the low energy state splits into two states. More obviously, with the further decrease of the distance between two C/N atoms, the low energy state in cfg^2 (the most stable pair in the vanadium system) clearly splits into two states, which are ~ -4.80 eV/-6.20 eV

(Fig. 6(a)) and ~ -4.00 eV/-5.30 eV (Fig. 6(b)) for the C–C pair and N–N pair, respectively. This phenomenon could be understood according to the formation of bonding and anti-bonding states between the low energy states of the two C/N atoms. When the two C/N atoms are far from each other and have no interaction in vanadium, each of the C/N atoms has a low energy state as if they were in two separate vanadium solids. As the two C/N atoms are close to each other, the valence electrons hybridize in the two low energy states and form both bonding and anti-bonding states, leading to the positive binding energy between two C/N atoms in vanadium. However, due to the fact that both the bonding and the anti-bonding states are below the Fermi energy and are thus occupied by valence electrons, the binding between the two 1nn C/N atoms (cfg^1 in Fig. 5) is not stable with the larger negative binding energy (Table 2). This may indicate that the two 1nn C/N atoms are repulsive to each other. Such electronic mechanism of the same kind of C–C or N–N pair interaction in vanadium is similar to that of solute–solute atoms interaction in α-Ti as studied by Hu *et al.*[50,51] Their investigations demonstrated that, when two of the same kind of solute atoms meet each other in the α-Ti system, the valence electrons of the two solute atoms fill the bonding and the anti-bonding states, both the bonding and the anti-bonding states are below the Fermi energy and are filled by the valence electrons. Furthermore, we find that the above features in the heterogeneous C–N atomic pair do not appear, as seen from Fig. 6(c). This might be because the valence electrons of the C and N atoms are very difficult to fill the bonding state when they meet each other in free space or metals.

4. The property of C/N–vacancy interaction

Generally, when an impurity is dissolved in a solid metal, it can be easily captured by vacancies. Further, with the increase of impurity atoms, they tend to accumulate to form the impurity–vacancy clusters. According to the current calculations, however, we discover that both C and N impurities do not prefer to stay at the vacancy center and its vicinity, but occupy the O-site that is out of the vacancy. Such anomalous behavior is because the C/N impurity occupies the O-site outside the vacancy to form a vanadium–carbide/vanadium–nitride structure. Below, we will present the detailed discussion.

Figure 7 gives the possible configurations of a vacancy and an impurity C/N in vanadium. The formation energy ($E^{\rm f}_{\rm C(N),vac}$) of one C/N atom around a vacancy is given as

$$E^{\rm f}_{\rm C(N)} = E_{(n-1)\text{vanadium},X} - \frac{n-1}{n}E_{\text{vanadium}} - E_{\text{ref},X}. \quad (4)$$

This formula is similar to Eq. (2), i.e., the lower the formation energy, the more stable the C/N position around the vacancy.

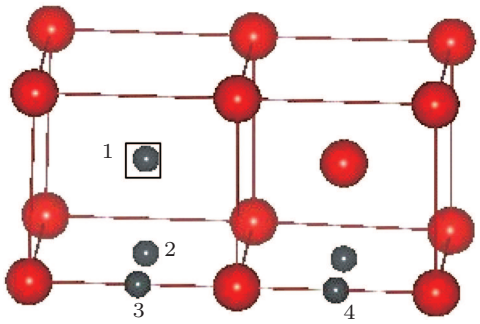


Fig. 7. (color online) Four possible sites for one C/N atom in the vicinity of one vacancy in vanadium. The larger red balls, the smaller gray balls, and the open square represent vanadium atoms, C/N atoms, and vacancy center, respectively.

Table 3. Formation energy (in eV) of one impurity (C/N) atom around a vacancy in vanadium with a different configuration given in Fig. 7.

Configuration	C–vac	N–vac
cfg^1	0.656	1.322
cfg^2	0.368	–0.643
cfg^3	–0.480	–0.893
cfg^4	–1.265	–1.904

Table 3 lists the formation energies of one C/N around the vacancy with four different configurations. We note in Table 3 that the off-center position (cfg^2 or cfg^3) for both C and N is always energetically more favorable than the substitution site (cfg^1), similar to the behaviors of C/N in other bcc metals.[27–33,46] Indeed, the off-center position can make the C/N keep as many interactions as possible with the vanadium neighbors, for example, the C/N at site 2 (the 1nn O-site of the vacancy center) interacts with four 1nn vanadium atoms, while the C/N at site 3 only binds two 1nn vanadium atoms. This is especially right for the C or N impurity, displaying strong C–vanadium or N–vanadium covalent-like bonding. A substitution C/N (cfg^1) is not stable, and will spontaneously shift to the off-center position finally after the structure optimization. Such a finding is fully consistent with the previous experimental measurements[27–29] and theoretical simulations[31,46] of metal-C/N systems. However, the formation energies of the two impurities at site 4 (i.e., cfg^4) are significantly lower than those at sites 2 and 3 (i.e., cfg^2 or cfg^3), in other words, both C and N do not prefer to stay at the vacancy center and its vicinity, but occupy the O-site off the vacancy in the interstitial lattice in vanadium. This obviously differs from the behavior of C/N in other bcc transition metals,[27–33,40,46,52,53] C/N impurities in those transition metals (e.g. α-iron and tungsten) can be easily captured by the vacancy with a large binding energy (low formation energy). Such a difference with the C/N–vacancy behaviors reported in α-iron[31,46] and tungsten[52,53] is puzzling to us because the only difference is the choices of metals. Apparently, a more detailed investigation on the interactions of C and N with the vacancy in vanadium is desirable.

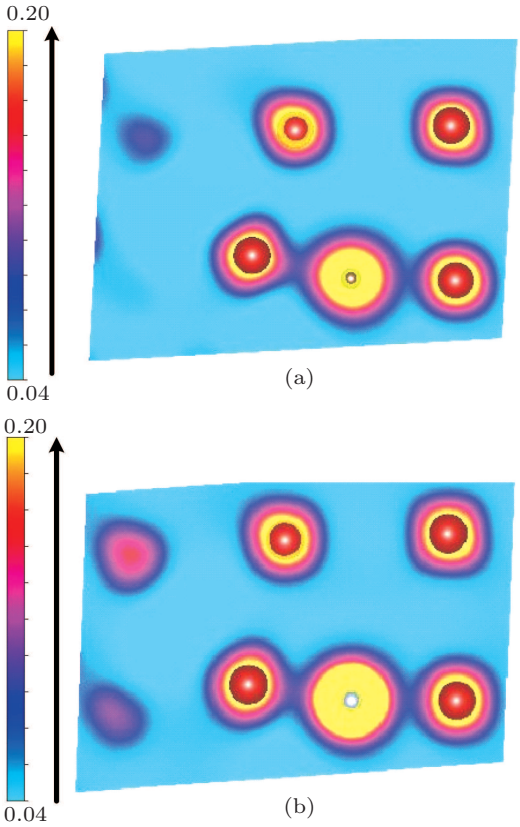


Fig. 8. (color online) The charge density distributions in the (110) plane for (a) C and (b) N at the O-site, which is out of the vacancy. The larger red balls, the middle gray ball, and the smaller white ball denote vanadium atoms, C atom, and N atom, respectively.

Now, we discuss the possible physical origin underlying the behavior of the C/N–vacancy interaction in bcc vanadium. It is important to realize that, according to the normal understanding, a vacancy in most metals can open up more space (i.e., free volume) to bind any given solute such as hydrogen,[54–56] helium,[57–59] oxygen,[60–62] carbon,[63] and so on. Whereas in vanadium, the energy minimization finds the most stable position for the C/N solute to be at an O-site, which is off vacancy-center/vicinity (site 4 presented in Fig. 7). The electronic structure analysis might support the higher stability of the off vacancy-center/vicinity position. Figure 8 shows the charge density distribution in the (110) plane for C/N solute, which is at the O-site out of the vacancy. Clearly, a significant charge accumulation between C/N and its two 1nn vanadium atoms along the $\langle 100 \rangle$ direction is found, indicating the strong covalent interaction of C/N–vanadium, i.e., the formation of C/N–vanadium covalent bonding. This finding is also consistent with that the C/N solute prefers to occupy the O-site in the interstitial lattice in vanadium, as shown above. Such behavior of C/N occupying the interstitial position in vanadium tends to form vanadium carbide or vanadium nitride. The electronic structure properties of covalent and metallic bonding in carbides have been studied in the previous experiments.[64,65] The results showed that C solutes prefer to be embedded between two vanadium atoms to form a nominal NaCl-like structure. Toth[66] and Storms[67] investigated the transition metal carbides and nitrides, such as VC_{1-x}, and VN_{1-x}. They were found to exhibit strong covalent bondings between C/N and vanadium atoms. Froidevaux and co-worker studied the C–vacancy interaction in vanadium carbide[68] and found that the C atoms and vacancies are not randomly arranged on the lattice sites; moreover, the C atoms easily deviate from the vacancies. Thus, the good agreement with experiments can fully demonstrate the validity of current theoretical predictions. Such behavior of C/N off the vacancy center as well as its vicinity in vanadium is also similar to that of C/N in other metals, which has been investigated in the previous studies.[69]

5. Conclusion

We have investigated the atomic geometry, formation energies, and electronic structure of interstitial and substitution carbon (C)/nitrogen (N) impurities as well as interactions of the two impurities with the vacancy in vanadium solid, employing the first-principles calculations. The results show that the octahedral site (O-site) for both C and N impurities is the lowest energy geometry structure in vanadium. In comparison with C, N exhibits the lower formation energy. Due to the hybridization between vanadium-d and N/C-p, the N-p states are located at the energy from -6.00 eV to -5.00 eV, which is much deeper than that from -5.00 eV to -3.00 eV for the C-p states. Regarding the interaction between two impurities in bulk vanadium, C–C, C–N, and N–N can be paired up at the two neighboring O-sites along the $\langle 111 \rangle$ direction and the binding energies of pairs are 0.227 eV, 0.162 eV, and 0.201 eV, respectively. Further, we find that both C and N do not prefer to stay at the vacancy center and its vicinity, but occupy the O-site off the vacancy in the interstitial lattice in vanadium. The possible physical mechanism is that C/N in the O-site tends to form a carbide/nitride-like structure with its neighboring vanadium atoms, leading to the formation of the strong C/N–vanadium bonding containing covalent component.

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