Stability of carbon-vacancy complexes in α-Fe

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Abstract. We investigated the stability and structure of CnV and NnV complexes in α-Fe using first-principles calculations. In the case of CnV complexes, C2V is most stable due to the energy gain by forming the C-C bonding. However, N2V is less stable than N1V. This is due to the repulsive interaction between N atoms in NnV complex. The overlap population analysis reveals that the C 2s – C 2p antibinding interaction is reduced by the C 2s – C 2p bonding interaction. The interaction between the N 2s and N 2p orbitals is not strong enough to cancel the N 2s – N 2s antibonding interaction because the energy difference between the N 2s and N 2p orbitals is larger than that between the C 2s and C 2p orbitals.

1. Introduction
Carbon is the most important element in steel. In α-Fe, which crystallizes in BCC structure, carbon atoms occupy octahedral sites (O sites). The O site in BCC structure is distorted along the <100> directions. Therefore, a carbon atom strongly binds to a vacancy because of the energy gain associated with the release of distortion. Recently, theoretical studies suggest that C2V complex, in which strong C-C bond is formed, is stable in α-Fe [1, 2]. However, the origin of C-C bond is still unclear. In this work, we have evaluated the stability and structure of CnV complex in α-Fe using first-principles calculations. In addition, to clarify the origin of the C-C bond, we have analyzed the chemical bonding using first-principles molecular orbital calculations. For comparison NnV complexes have been also calculated.

2. Computational Method
In order to obtain the energies and stable structures of CnV and NnV complexes, we employed the Vienna ab initio simulation package (VASP) [3, 4] with the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [5]. Potential based upon the all-electron projector augmented wave (PAW) method were used [6, 7]. We employed a supercell composed of 54 lattice sites with a BCC structure (3 × 3 × 3 unit cell). All calculations were spin-polarized. Structural relaxation of the atoms was continued until the forces on all atoms became less than 0.01 eV/Å. The stability of CnV and NnV complexes was evaluated by the formation energy $E_{X_n V}^f$ with reference to the energy of an isolated C or N atom $E(X, 0)$ and an isolated vacancy $E(0, V)$ in α-Fe matrix as follows:

$$E_{X_n V}^f = [E(X_n, V) + nE(0, 0)] - [nE(X, 0) + E(0, V)].$$

C and N atoms occupy O sites in α-Fe matrix. Around a vacancy in α-Fe matrix, there are six first nearest-neighbor (NN) and twelve second NN O sites. The formation energy of second NN C1V, –0.046 eV, is 0.65 eV larger than that of first NN C1V, –0.696 eV. Although the second NN O site is
less stable than the first NN O site, the second NN sites were also considered as initial sites of C and N atoms for searching stable structures of $C_nV$ and $N_nV$ complexes. We performed first-principles calculations for all the possible structures of $C_nV$ and $N_nV$ complexes up to $n = 6$. In order to analyze the chemical bonding, the discrete-variational (DV) Xα cluster method using a program code SCAT [8, 9] is employed with a cluster model composed of 59 lattice sites.

3. Results and discussion

The formation energy of $C_nV$ and $N_nV$ complexes are shown in Figure 1. The $C_nV$ complex shows the minimum value at $C_2V$ while the formation energy of $N_nV$ complexes increases with increasing number of N atom. The formation energy of $C_nV$ complex is still negative up to $C_4V$ and steeply increases at $C_5V$ and $C_6V$. The most stable structures of $C_nV$ and $N_nV$ complexes are shown in Figure 2. In $C_2V$, $C_3V$ and $C_4V$ complexes, C atoms occupy the first NN O sites and move inwards by structural relaxation to form C-C bonds. On the other hand, N atoms occupy the separated first NN O sites not to form the N-N bond in $N_2V$. In $N_3V$, two N atoms occupy the unstable second NN O sites to avoid the formation of N-N bonds. In $N_4V$, all of four N atoms occupy the unstable second NN O sites and the N-N bonds are not formed. These stable structures clearly indicate that the C-C bonds are stable in $C_nV$ complex while strong repulsive forces occur between N atoms in $N_nV$ complex.

![Figure 1](image1.png)

**Figure 1.** Formation energies of $C_nV$ and $N_nV$ complexes as a function of carbon or nitrogen atoms.

![Figure 2](image2.png)

**Figure 2.** Stable structures of $C_nV$ and $N_nV$ complexes. (a) $C_2V$, (b) $C_3V$, (c) $C_4V$, (d) $N_2V$, (e) $N_3V$, and (f) $N_4V$.

Figure 3 shows the partial density of states (DOS) of $C_2V$ and $N_2V$ complexes. The most pronounced
The difference between $C_2V$ and $N_2V$ complexes is the position of 2s orbitals. Therefore, contour plots of 2s orbitals are drawn in Figure 4. Regarding 2s component, there are two 2s orbitals in the valence band: one is a bonding and the other is an antibonding orbital. In $N_2V$, two N 2s orbitals appear at around -16 eV and the energy separation between the bonding and antibonding orbitals is very small. This is because two N atoms are well separated and the antibonding interaction between N 2s orbitals is not significant. On the other hand, the 2s antibonding orbital in $C_2V$ is located just below the C 2p band because of the antibonding interaction between C 2s orbitals. As a result, C 2p component appears in the C 2s antibonding orbital.

![Figure 3. Partial DOS of $C_2V$ and $N_2V$ complexes.](image)

![Figure 4. Contour plots of 2s-2s bonding and antibonding orbitals in $C_2V$ and $N_2V$ complexes.](image)

(a) C 2s-C 2s antibonding in $C_2V$, (b) C 2s-C 2s bonding in $C_2V$, (c) N 2s-N 2s antibonding in $N_2V$, and (d) N 2s-N 2s bonding in $N_2V$.

In order to quantitatively evaluate the effect of 2p orbital, overlap populations at each molecular orbital for the C-C bond were calculated. Figure 5 shows the overlap population diagram for the C-C bond in $C_2V$. Regarding the C 2s antibonding orbital, a large negative component arises from the antibonding interaction between C 2s components and almost cancel the bonding component of the C 2s bonding orbital. The interaction between C 2s and C 2p components at the C 2s antibonding orbital is bonding and reduces the antibonding interaction between C 2s components. Therefore, the interaction between C 2s and C 2p orbitals play an important role to form the C-C bond.

In Figure 3, the DOS of $C_2V$ and $N_2V$ complexes with different structures were compared. In order to clarify the origin of the difference, the energy differences between 2s and 2p orbitals with the same bond length of C-C and N-N bonds are shown in Figure 6. The energy difference between the 2s bonding and 2s antibonding orbitals increases with decreasing bond length both in $C_2V$ and $N_2V$ complexes. This is because the antibonding interaction becomes stronger with decreasing bond length. The energy difference at the same bond length is almost comparable between $C_2V$ and $N_2V$ complexes. On the other hand, the energy difference between the 2s antibonding and the bottom of 2p band in $N_2V$ is still more than 4 eV even if two N atoms become closer to each other. The energy difference
between N 2s and N 2p orbitals is too large to interact with each other.

![Figure 5](image5.png)

**Figure 5.** Overlap population diagram of C-C bond in C$_2$V complex.

![Figure 6](image6.png)

**Figure 6.** Energy differences between the 2s antibonding orbital and the bottom of 2p band, and the 2s bonding and antibonding orbitals in (a) C$_2$V and (b) N$_2$V complexes.

4. Conclusion
First-principles calculations were performed to investigate the stability and structure of C$_n$V and N$_n$V complexes in α-Fe. The antibonding interaction between C 2s orbitals in C$_n$V complex is reduced by the bonding interaction between C 2s and C 2p orbitals, which leads to the formation of C-C bonds in C$_2$V, C$_3$V and C$_4$V complexes. In N$_n$V complex, the interaction between N atoms is quite repulsive because of the antibonding interaction between N 2s orbitals. The energy difference between N 2s and N 2p orbitals is too large to reduce the antibonding interaction.

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