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# First-principles study of interaction between vacancies and nitrogen atoms in fcc iron

Fei Ye[a,*], Ke Tong[a], Ya Kun Wang[a], Zitian Li[a], Feng Zhou[b]

[a] Key Laboratory of Materials Modification by Laser, Ion, and Electron Beams (Ministry of Education), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

[b] Key Laboratory of Ship-Machinery Maintenance and Manufacture for Ministry of Transportation, Dalian Maritime University, Dalian 116026, China

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ABSTRACT

The interaction between vacancies and nitrogen atoms in fcc iron has been systematically studied by first-principles calculations. The interstitial N atoms bind strongly with vacancies into $V_nN_m$ clusters, and each vacancy prefers only two N atoms that locate at the first nearest neighboring octahedral interstitial sites to the vacancy and align along the ⟨1 0 0⟩ directions. The number of N atoms is determined by the local lattice distortion evaluated by the expansion of atomic coordination polyhedrons with respect to the vacancy at the center. The most stable $V_1N_2$ cluster can be considered as a structural unit for the cluster development. Moreover, in larger $V_nN_m$ clusters with relatively high stability, the vacancies aggregate at the center and the N atoms are around the vacancies. Then, the effect of N solute on radiation swelling depending on the N concentration is discussed from a perspective of the cluster formation. The radiation swelling increases with the N concentration because the existence of N atoms can promote the vacancy aggregation and, hence, the nucleation and growth of voids. However, as the concentration further increases, N atoms will saturate the surfaces of vacancy clusters to form barrier layers, which can hinder the combination of the $V_nN_m$ clusters and the void formation.

## 1. Introduction

Austenitic iron alloy is one of the primary structural materials in current nuclear equipment. It is well known that the microstructure features, the mechanical properties and the radiation resistance of the alloy are influenced by the interaction of point defects with solute atoms [1–4]. It has been reported that the light impurities, such as nitrogen, significantly affect the swelling of stainless steel under electron or neutron radiation [5–12]. When N concentration varies from 0.002 to 0.083 wt%, the radiation swelling increases with the concentration, then decreases as the concentration further increases at electron radiation dose of 5 dpa [8–10]. These results were explained by a model based on two competitive factors: the influence of absorbed impurities in the voids caused by the production of an additional gas pressure in voids for their stabilization, and the effect of impurities segregated around the surface of voids by the lowering of surface tension [10]. In the study of Tavassoli et al., it has been observed that the 316L(N) steel with N concentration about 0.06–0.08 wt% in fusion system shows obvious radiation swelling under high neutron radiation dose (greater than 70 dpa) [11,12].

Since the nucleation and growth of voids are attributed to the aggregation of vacancies, the study of interactions of vacancies and/or nitrogen atoms may contribute to further understand the effect of nitrogen on the radiation swelling at atomic scale. The interactions in body-centered cubic (bcc) iron have been widely studied by both first-principles calculations [13–15] and the calculations based on empirical potentials [16–20]. It has been confirmed that the second-nearest-neighbor (2nn) vacancies have strong attractive interaction and then the vacancies aggregate into compact clusters, linear chains, single or double layered structure [16–19,21]. For nitrogen atoms, the octahedral site is the most stable location and two nitrogen atoms have repulsive interaction [22] or weak attractive interaction along ⟨1 2 0⟩ and ⟨1 1 1⟩ directions [20]. In the case of the interaction between vacancies and nitrogen atoms, the nitrogen atoms bind strongly with the vacancies into vacancy-nitrogen clusters $V_nN_m$, where $n$ and $m$ are the numbers of the vacancies and nitrogen atoms, respectively [4,20,22,23]. The nitrogen atoms prefer to occupy the first-nearest-neighbor (1nn) octahedral sites to the vacancies, and the most stable configuration of $V_1N_2$ cluster is that two N atoms locate at the first nearest neighboring octahedral interstitial sites to the vacancy and align along the ⟨1 0 0⟩ directions [4,20,22,23]. Moreover, this $V_1N_2$ cluster often appears in the corresponding larger $V_nN_m$ clusters [23].

* Corresponding author.
*E-mail address:* yefei@dlut.edu.cn (F. Ye).

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The calculations for the face-centered cubic (fcc) iron are relatively limited partly due to the difficulty in the choice of relevant reference state for modeling the paramagnetic state. It has been found that the vacancies in fcc iron can also aggregate into cluster [24], and N atoms also locate in octahedral interstitial sites [20,25]. Hepburn et al. have simulated the interaction between vacancies and N atoms using first-principles calculations based on collinear magnetic structures as reference states [25]. The calculation results were the same as those in bcc iron that the nitrogen atoms prefer to occupy the 1nn sites to the vacancies, and the two N atoms in the most stable $V_1N_2$ cluster align along the ⟨1 0 0⟩ directions. Moreover, it was found out that a vacancy can bind up to six N atoms, while the additional binding energy reduces significantly above two. The N atoms show a preference for the sites near the surface of vacancy clusters suggesting that they will decorate the surface of voids. However, the mechanism for the formation of the certain cluster structure and the study of the interaction between the clusters are still lack so that the effect of nitrogen solute on the radiation swelling at atomic scale remains unclear.

In this work, a detailed study of the energetics and interaction between vacancies and N atoms in fcc Fe using first-principles calculations is present. The local lattice distortion, charge density and magnetic moments around $V_1N_m$ cluster are first studied to understand the interaction between a vacancy and N atoms. Then, the $V_nN_m$ clusters with up to 3 vacancies and 6 N atoms are examined to illustrate the structural evolution of the clusters. Finally, the effect of nitrogen solute on the radiation swelling is discussed from a perspective of the cluster formation.

## 2. Computational details

The first-principles calculations were performed using the plane wave pseudo-potential code, Vienna *ab initio* simulation package (VASP) [26,27]. It performs fully self-consistent density functional theory (DFT) calculations to solve the Kohn–Sham equations. The electron-ion interaction was described with the projector augmented wave (PAW) method [28,29]. The generalized gradient approximation (GGA) with the Perdew and Wang functional for the exchange correlation interaction was adopted [30]. The Vosko-Wilk-Nusair interpolation was applied for the correlation part of the exchange-correlation functional [31].

A full treatment of fcc Fe is required to take the paramagnetism into account. Experiments have shown that the fcc Fe ground state most likely consists of a noncollinear spiral magnetic structure [32,33]. This has been confirmed by computer simulation using the linear muffin tin orbital in the atomic sphere approximation [34,35], while the VASP code cannot explore such configuration. In recent simulations of Fe-Cr-Ni alloy [24,25,36], the paramagnetism has been successfully modeled through localized moments by using a set of stable, ordered collinear magnetic structures. As shown in these studies, this method is sufficient for an at least qualitative, and in many cases even a quantitative understanding of specific features in the physical properties of fcc Fe. The advantage is that a more detailed study of defect cluster structures and the effect of defects on local magnetic moment is possible, although the level of approximation involved is certainly not ideal and the results should be used carefully. The same approach was adopted here, and the calculations were performed in the most stable ordered magnetic state of fcc Fe suggested in the previous study [24], as shown in Fig. 1. It has a magnetic (0 0 1) layered structure in which the local magnetic moments of Fe atoms on every two layers are in the same direction, and thus was named antiferromagnetic double layer collinear magnetic state (denoted as afmD in Ref. [24]).

To examine the influence of the magnetic state, another stable magnetic state of fcc Fe named antiferromagnetic single layer state (afmI) was considered for the $V_1N_m$ clusters. This state also consists of magnetic (0 0 1) planes but with opposite magnetic moments on adjacent planes [24,25]. The calculation results are given in the supplement material after the corresponding results of the afmD state. It can be seen that the relative stability of the clusters is not influenced by the magnetic states, though the different magnetic states give several tenth of eV of difference in the calculated energies. Therefore, we believe that general conclusions for the $V_nN_m$ cluster structures can be made from the calculation performed in the afmD state.

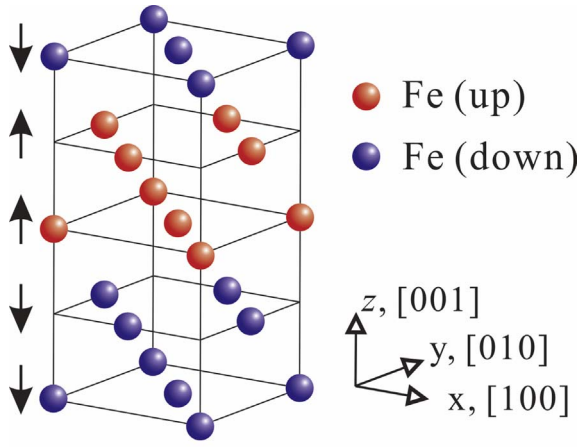


**Fig. 1.** The afmD structure model in which the Fe atoms in two fcc unit cells have up, up, down, down ordering of magnetic moments in adjacent magnetic planes. Arrows indicate local moments of Fe atoms on these magnetic planes.

The local magnetic moments on atoms were initialized to impose the magnetic ordering and were then allowed to relax during the calculation. The relaxed local magnetic moments were determined by integrating the spin density within spheres centered on the atoms. Sphere radii of 1.302 and 0.741 Å were used for Fe and N, respectively.

All calculations used 4 × 4 × 4 supercells of 256 atoms with supercell dimensions held fixed at their equilibrium values and ionic positions free to relax. A 2 × 2 × 2 *k*-point Monkhorst-Pack grid was used to sample the Brillouin zone. The plane-wave cutoff energy was taken to be 450 eV. The structures were deemed relaxed once the forces on all atoms had fallen below 0.03 eV/Å. The calculated equilibrium lattice constants are $a = 3.446$ Å and $c = 3.737$ Å, which is in good agreement with the previous calculation [24]. The local magnetic moment for each Fe atom is 1.95 $\mu_B$.

It is noted that the relaxed unit cell is actually a face-centered-tetragonal (fct) structure, i.e. $c \neq a = b$, due to the magnetically ordered state, while the ideal fcc structure was found to be structurally unstable. This indicates that the approximation involved in this model is not ideal. In spite of this, it was demonstrated that the calculations based on this state are consistent with, and extend, previous works [24,25,36].

Various arrangements of the vacancies and N atoms in $V_nN_m$ clusters have been examined to find out the most stable configurations. In the following sections, the clusters with the most stable structure are mainly discussed unless otherwise stated. To compare the stability of the clusters, the formation energy and binding energy of the clusters are calculated. The formation energy $E_f$ of a $V_nN_m$ cluster is defined as

$$E_f = E_{total} - jE^{ref}(Fe) - mE^{ref}(N), \quad (1)$$

where $E_{total}$ is the total energy of the system with defects, $E^{ref}$(Fe) and $E^{ref}$(N) are the energies of Fe and N atom in their reference states, $m$ and $j$ are the numbers of N atoms and Fe atoms in the system, respectively. The Fe atom in the reference state is the average of the total energy in the fct-afmD state without defects. The reference energy for N atom in the reference state is obtained by calculating the isolated $N$ atom in vacuum. Obviously, the formation energy of isolated vacancy and N atom in fcc Fe can also be calculated by the equation.

The binding energy $E_b$ of a $V_nN_m$ cluster is defined as the energy difference of the formation energies of isolated defects and the defect cluster, i.e.