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Stability of vacancy-type defect clusters in Ni based on first-principles and molecular dynamics simulations☆

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ABSTRACT

Using first-principles calculations based on density-functional theory, the energetics of different vacancy-type defects, including voids, stacking fault tetrahedra (SFT) and vacancy loops, in Ni are investigated. It is found that voids are more stable than SFT at 0 K, which is also the case after taking into account the volumetric strains. By carrying out *ab initio* molecular dynamics simulations at temperatures up to 1000 K, direct transformations from vacancy loops and voids into SFT are observed. Our results suggest the importance of temperature effects in determining thermodynamic stability of vacancy clusters in face-centered cubic metals.

In face-centered cubic (*fcc*) metals, agglomeration of vacancies usually leads to the formation of voids, vacancy-type dislocation loops and stacking fault tetrahedra (SFT). It is generally regarded that SFT are the dominant type of vacancy clusters in low stacking fault energy (SFE) materials, such as Ni [1–3]. Different formation mechanisms of SFT have been proposed previously, including dissociation of [111] Frank vacancy loops [4], collapse of vacancy clusters [5], aggregation of vacancies [6], and directly within collision cascades [7]. However, these proposed mechanisms are mostly inferred from molecular dynamics simulations whose fidelity relies on the reliability of empirical interatomic potentials. Another concern is that different potentials yield distinct, but often different, conclusions as to the equilibrium structures of vacancy clusters. A typical example is the stable form of vacancy clusters predicted by different embedded atom method (EAM) potentials. While the Bonny2013 potential [8] predicts SFT are the most stable forms of vacancy type defects in Ni, the Bonny2011 potential [9] suggests that [111] Frank vacancy loops are more preferred [10]. The potential-dependent properties of vacancy clusters are also found in a previous study for Cu [11]. These observations point to the need for accurate calculations, independent of any specific potential models. As a cross-check, first-principles calculations can be employed to study the stability of different vacancy-type defects and provide accurate results compared to those from empirical potentials. Nevertheless, this approach is restricted by the system size required for the study of vacancy clusters.

Experimentally, the properties of vacancy clusters in materials are of great interest for material performance in a radiation environment, since the formation and growth of vacancy clusters may lead to significant volumetric swelling [12]. For Ni, both SFT and vacancy loops are observed after ion irradiation at room temperature. For example, it is reported that the majority (90%) of vacancy clusters are SFT in Ar irradiated Ni [13]. However, other studies show that the majority of vacancy clusters (61.8%) are in the form of loops in Kr^+ irradiated Ni [14]. Besides SFT and vacancy loops, the clustering of vacancies can lead to the creation of voids (three-dimensional empty spaces in the crystal structure), which is also an important vacancy-type defect.

In this work, the energetics of various vacancy clusters in Ni is investigated using *ab initio* calculations in relatively large supercells. The configurations considered are SFT, voids and vacancy platelets of hexagonal and triangular shapes on the [111] plane. Our calculations indicate that voids are more stable than the corresponding SFT configurations with the same number of vacancies. This relative stability is not influenced even by taking into account of volumetric strain (lattice expansion or compression). Through *ab initio* molecular dynamics (AIMD) simulations, direct transformations of voids or vacancy loops to SFT are observed, suggesting that SFT are more stable thermodynamically.

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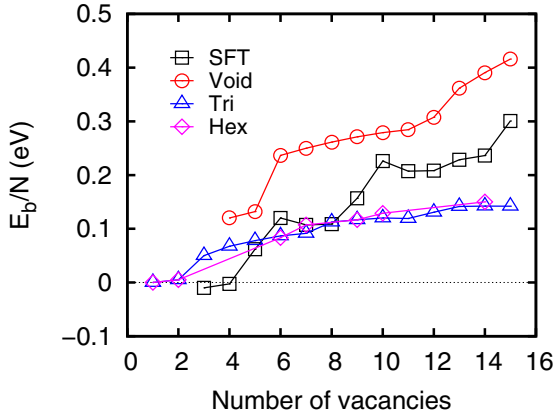

Fig. 1. Binding energies per vacancy for different vacancy clusters in pure Ni: SFT, voids and vacancy platelets of triangular (Tri) and hexagonal (Hex) shapes on the [111] plane.

Ab initio calculations were carried out based on density-functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [15]. A gradient corrected functional in the Perdew-Burke-Ernzerhof (PBE) form was used to describe the exchange and correlation interactions [16]. Electron-ion interactions were treated within the projector-augmented-wave (PAW) method [17]. The energy cutoff for the plane-wave basis set was set to be 270 eV. All calculations were performed with spin-polarization to account for magnetic properties. For structural optimizations, the energy convergence was set to be 10^{-4} eV and the atomic positions were relaxed by minimizing the Hellmann-Feynman forces on each atom to less than 10^{-2} eV/Å. Periodic boundary conditions were employed. The calculation of defect clusters requires large supercells to reduce the interactions among the defects and their periodic images. In this work, a $5 \times 5 \times 5$ supercell containing 500 atoms was used, and the energetics of vacancy clusters with 1 to 15 vacancies were studied. Owing to the large supercell, only Γ point was included in the calculations. The formation energy, E_f^{Nv}, of a vacancy cluster with N vacancies in a N_p-atom perfect supercell was calculated by $E_f^{Nv} = E - E_0 + \frac{N}{N_p} E_0$, where E and E_0 are the total energy of defective and perfect supercells, respectively. The binding energy, E_b^N, was then obtained by $E_b = NE_f^v - E_f^{Nv}$.

The used energy cutoff and kpoint are first tested to ensure the convergence regarding the reported energetics of vacancies. The calculated formation energy of a single vacancy in a 500-atoms supercell is 1.47 eV with our calculation parameters, in good agreement with a previous result of 1.47 eV [18]. Increasing energy cutoff to 400 eV leads to 1.48 eV, while increasing kpoint to $2 \times 2 \times 2$ also results in 1.48 eV. For vacancy clusters, a difference of 0.03 eV in calculated binding energy of a 15*v*-SFT is observed when increasing to $2 \times 2 \times 2$ kpoints. The results suggest that our calculations are reliable to give accurate energetics for vacancies in Ni. Previous studies suggest that the PBE functional is better to describe the properties of Ni [19]. This functional form is, therefore, used in this study.

Four different types of vacancy clusters are considered, namely, triangular loops, hexagonal loops, SFT and voids. When vacancy number N is a magic number, the structure of corresponding vacancy cluster is definitive. However, those non-magic vacancy number clusters may take many different shapes. In this case, several competitive structures are studied and only those structures with the lowest energy are reported. The methodology to construct different vacancy clusters is given as follows. For [111] triangular vacancy loops, their structures from 1*v*–3*v* are unambiguous. For 4*v*, there are two configurations, in which the difference resides in the location of the fourth vacancy. Our calculations show that a rhombus-shaped structure is more energetically favorable. Therefore, we take this rule as a principle to construct other imperfect vacancy loops by adding additional vacancies starting from the edge center outside the magic number vacancy loops. Similar methodology is used to construct hexagonal vacancy loops. In this case, $N = 7$ corresponds to a perfect hexagonal vacancy loop. Larger loops are created by placing additional vacancies at the edge center. Imperfect SFT structures are constructed with the help of classical molecular dynamics (LAMMPS code [20]) based on the Mishin potential [21]. By taking the constructed vacancy loop as input, a short MD simulation at 600 K was carried out followed by an energy minimization. The obtained structure is then fed into *ab initio* calculations to further calculate the energy. We have compared energies of different SFT structures obtained from different initial loop configurations as described above and reported the lowest energy ones. To construct void structures with n vacancies, we delete an atom in the center together with its $(n - 1)$ nearest neighbors, as did in a previous study [5]. However, other configurations in tetrahedral and octahedral shapes are also considered. It should be pointed out that, in the calculation process, we also made a literature survey on vacancy clusters in *fcc* metals to cross-check our results [22,23]. A complete list of stable configurations identified in our calculations is provided in Supplementary materials. The calculated binding energies of different vacancy clusters considered are provided in Fig. 1.

The results in Fig. 1 indicate that [111] vacancy loops in either triangular or hexagonal shape have similar binding energies. The binding energies of the corresponding SFT are higher than those of vacancy loops when the vacancy number is larger than 6. Besides, there are local maximums in the binding energies of SFT, such as 6, 10 and 15, suggesting that these perfect SFT are rather stable. Surprisingly, it is observed that the binding energies of voids are always larger than those of SFT containing the same number of vacancies, despite the fact that vacancy clusters in Ni are often found in the form of SFT instead of voids in experiments [24]. This discrepancy does not necessarily indicate the failure of DFT, since these energies are calculated at 0 K without consideration of thermal effects. Note that energy differences between

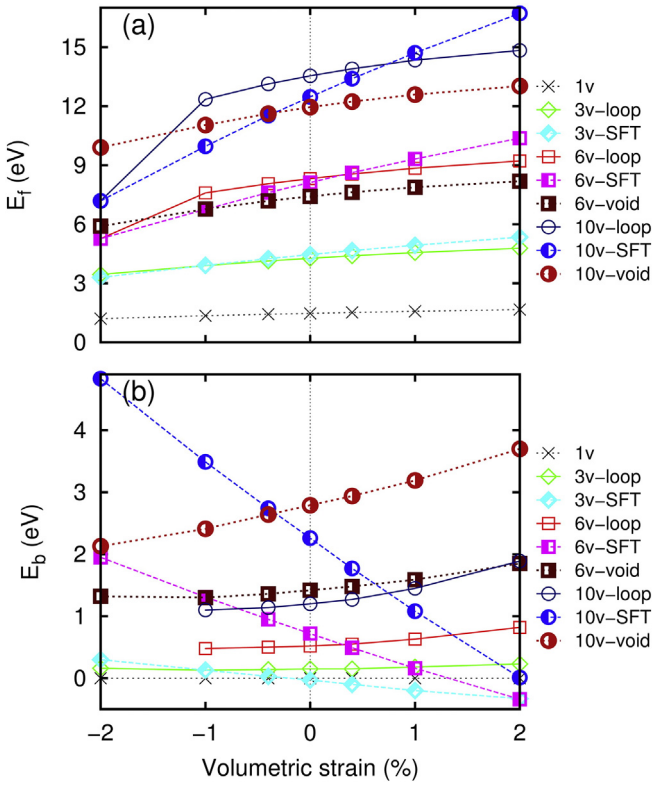

Fig. 2. Formation and binding energies of different vacancy clusters as a function of volumetric strain. Because of the similar binding energies between triangular and hexagonal vacancy loops, only the triangular vacancy loops are considered.