

## Positron trapping at the effective open volume in FeCr alloy containing hydrogen/helium atoms

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Positron annihilation spectroscopy (PAS) is a sensitive probe of the shallow traps of light charged particles such as He/H embedded in solids. The nature of the shallow traps that attract positrons—i.e., whether the properties of the light charged particles or the number of particles contained in the traps affects the probability of positron capture—has so far remained unresolved. Here, the shallow traps of positron in FeCr alloy, namely (H, He)–V nano-clusters with open volume, have been investigated by first-principles calculations and a multi-grid based program package for electronic structure calculations. Various defect structures were modeled, including vacancies, interstitial helium atoms, and helium or hydrogen atoms occupying Fe vacancy sites. We calculated the charge density distribution at the (H, He)–V nano-clusters, and the results show that the charge density at the He/H–V clusters is significantly lower than around the neighboring Fe/Cr sites. The calculated lifetimes of positrons confined in the shallow traps are consistent with the effective open volume of the (H, He)–V complexes. These results suggest that a helium atom forms a more repulsive ion core than a hydrogen atom when it occupies the vacancy, resulting in a decrease in positron lifetime.

### 1. Introduction

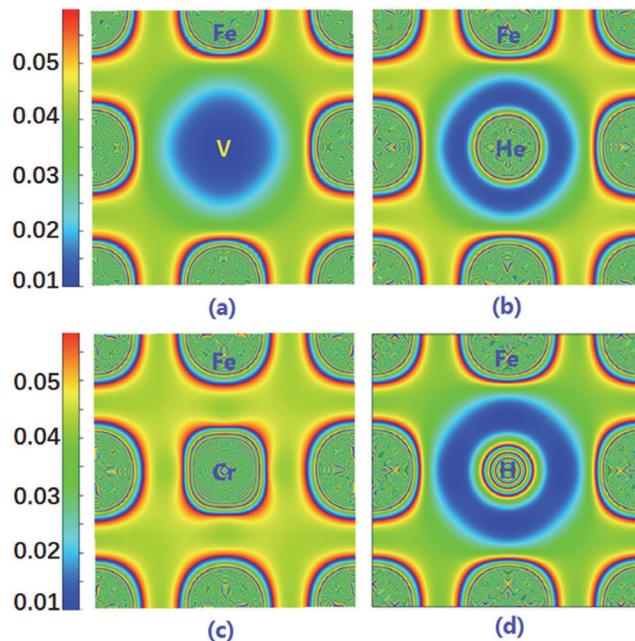
Positron annihilation spectroscopy (PAS) has been proved to be sensitive to open-volume defects, and could characterize the evolution of the size and concentration of the open-volume defects. This is because open-volume defects, in neutral or negative charge states, act as efficient positron traps because of the reduced repulsion of positive ions. However, the positron trapping at hydrogen/helium-vacancy complexes is not very easy because hydrogen and helium affects the electron density and distribution of defects in metals and alloys [1]. In our previous research, coincidence Doppler broadening of positron annihilation was used to identify gaseous atoms in Fe9wt%Cr alloy [2]. It is assumed that this identification is not entirely dependent on the concentration of the gaseous atoms in the specimens, but is related to the electronic structure and microscopic arrangement of atoms surrounding the positron annihilation site. Frequently, we shall be concerned with the annihilation of positrons for which the initial state will depend not only on the background potential system, but also on the Coulomb force of the positron that sometimes may considerably perturb the original electronic system by the light charged particles. A particular benefit gained from the many-electron theories is our increased understanding of the relevance of positron studies to the electronic structure of the unperturbed system. Positron studies of electronic structure have provided a valuable confirmation of many of the established concepts of solid-state physics and, in some cases, have provided information not obtainable from other characterization techniques.



Shallow traps formed by light charged particles and vacancies are common in various alloys, and nuclear energy structural materials are a good example [3–6]. Our work focused on model calculations of the positron annihilation parameters for the effective open volume in a Fe9wt%Cr alloy containing hydrogen/helium, and on the distribution of hydrogen and helium in nano-clusters. Furthermore, our study also investigated whether the positron attraction is affected only by the properties of light charged particles or if the number of particles contained in the vacancies also plays a role.

## 2. Experiments

The present first-principles calculations were performed within density-functional theory as implemented in the Vienna ab initio simulation package (VASP) [7–9] with the plane wave basis and projector-augmented wave (PAW) method [10, 11]. Exchange and correlation functions were taken in a form proposed by Perdew, et al. [12] within the generalized gradient approximation (GGA), and the cutoff energy was 300 eV for the plane wave basis. A  $4 \times 4 \times 4$  body centered cubic (bcc) supercell that correspond to the Fe9wt%Cr alloy was built. The supercell approach with periodic boundary conditions was used to study hydrogen/helium-defect properties, and the energy criterion for relaxation was 0.01 meV. Theoretical positron lifetime calculations for bcc FeCr lattice containing vacancies and nano-clusters consisting of  $m$  ( $m = 1, 2$  and  $6$ ) vacancies with  $n$  ( $n = 1$  to  $11$ ) hydrogen/helium atoms related to the present study were carried out using the atomic superposition method, as implemented in MIKA-Doppler code [13]. In our model, a cell with 1458 atoms was typically sufficient to obtain accurate results for positron lifetime for large nano-clusters. For the enhancement factor of the electron density at the positron, the relation proposed by Boronski and Nieminen based on the local density approximation (LDA) was used [14].



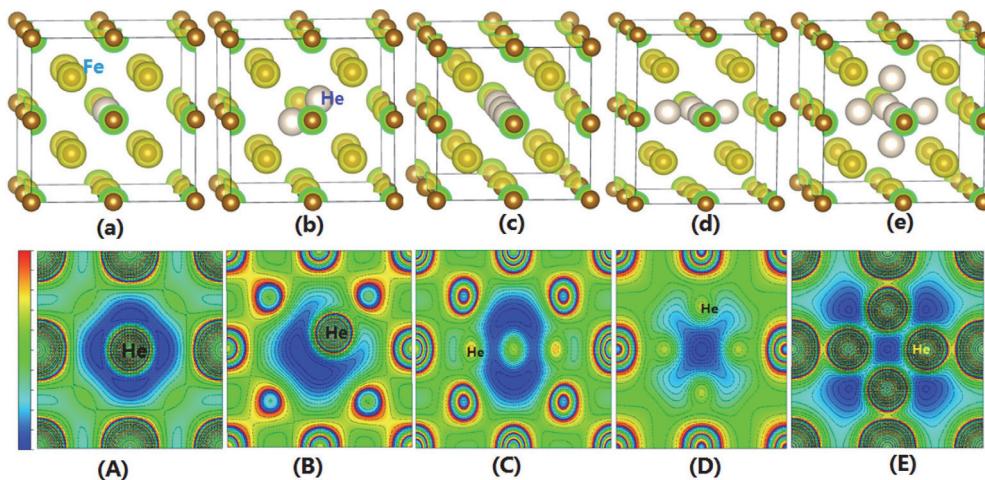
**Fig. 1** Charge density contours in a Fe vacancy and around a helium or hydrogen atom occupying a Fe vacancy site. The units are  $e/\text{Bohr}^3$ ; and the red and blue colors correspond to high and low charge densities, respectively.

### 3. Results and discussion

#### 3.1 Defect structure construction

The positron is delocalized in perfect crystal materials. According to the principles of quantum mechanics, a delocalized positron is randomly distributed in each position of the crystal materials. In the crystal, the positively charged ions core produces a strong repulsive force on the positron, which limits the positron wave function so that it is mainly distributed in the low-electron-density region. The vacancy-like defects in the solid without helium or hydrogen are active positron traps; however, once they are bound with He or H, they become less effective in the trapping of positrons. In order to understand the characteristics of positron trapping sites, the electronic structure of defect systems have been investigated using the charge density. Fig. 1 shows that various defect structures were modeled, including a Fe vacancy [Fig. 1(a)] and a helium [Fig. 1(b)] or hydrogen [Fig. 1(d)] atom occupying a Fe vacancy site (i.e., substitutional He or H). The energy cutoff was set at 300 eV for helium and hydrogen, and a  $6 \times 6 \times 6$  Monkhorste-Pack k-mesh was used for FeCr in its  $4 \times 4 \times 4$  bcc supercells. Fig. 1 shows the charge density contours of a helium/hydrogen atom occupying an Fe vacancy site. To display all the typical surrounding Fe and Cr cations around helium and hydrogen, the contour plane was positioned on the (110) plane of FeCr supercells. The units in Fig. 1 are  $e/\text{Bohr}^3$ ; and the red and blue colors correspond to high and low charge densities, respectively. Fig. 1 demonstrates that the charge density around a vacancy is much lower than around the neighboring He/H sites; moreover, the charge density at He/H sites is significantly lower than at the neighboring Fe/Cr sites. The differential charge density contours indicate that there are obvious differences between the different defect types in terms of their ability to attract positrons. While  $\text{He}^{2+}$  is believed to be positively charged because of the difficulty of obtaining electrons in the crystal,  $\text{H}^+$  can be either neutral or positively charged after entering the material. Hence, positrons are repelled by He-V clusters while H-V clusters can sometimes represent trapping sites for positrons. Although the doped helium/hydrogen atoms increasing the charge density in Fe/Cr sites, these sites still have a strong attraction to positrons when the V-to-H/He ratio is large.

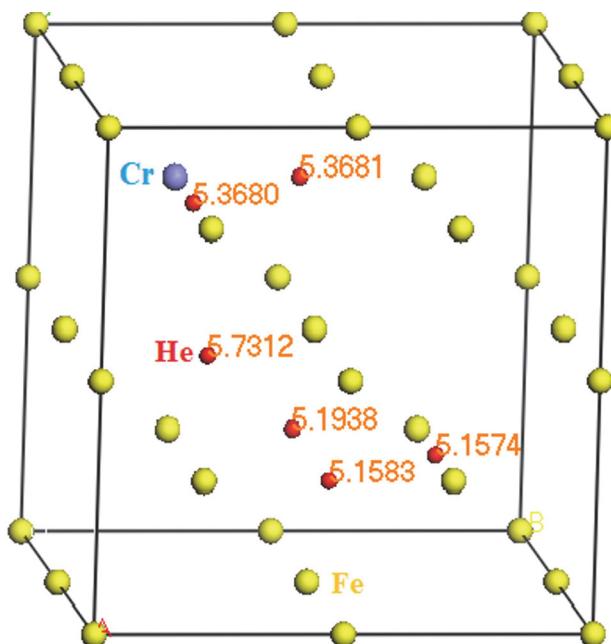
To elucidate the electronic structure of helium-vacancy clusters, we computed the changes in the charge density of various  $\text{He}_n\text{V}_1$  clusters due to a helium interstitial based on the symmetric arrangements; some of them are displayed in Fig. 2 for  $n = 1 - 4$  and 6. During calculation, the



**Fig. 2** He-induced charge density redistribution in the (110) plane for  $\text{He}_n\text{V}_1$  clusters. The units are  $e/\text{Bohr}^3$ ; and the red and blue colors correspond to high and low charge densities, respectively.

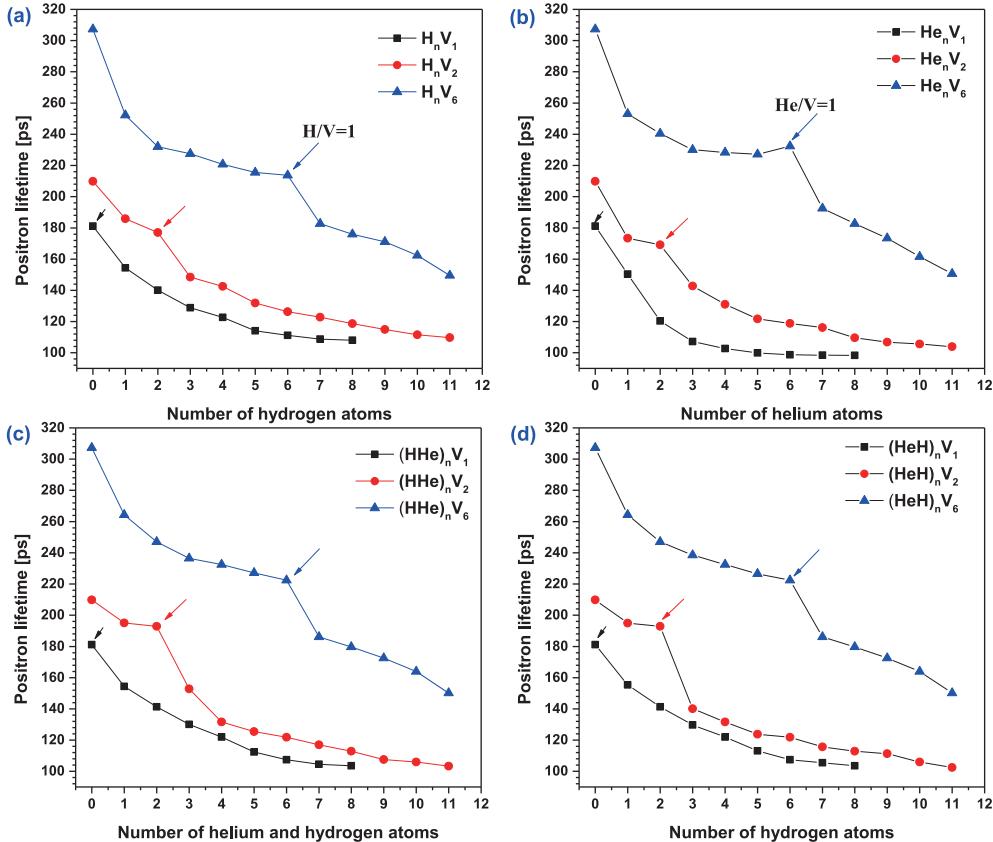
**Table I** Structural parameters for bulk Fe–He–V in angstrom.

	He <sub>1</sub> V <sub>1</sub>	He <sub>2</sub> V <sub>1</sub>	He <sub>3</sub> V <sub>1</sub>	He <sub>4</sub> V <sub>1</sub>	He <sub>5</sub> V <sub>1</sub>	He <sub>6</sub> V <sub>1</sub>
x	5.462	5.558	6.674	6.613	5.985	5.769
y	5.462	5.558	5.033	5.146	5.634	5.769
z	5.462	5.558	5.033	5.146	5.634	5.769

**Fig. 3** Calculated formation energies for helium atom at tetrahedral interstitial sites in FeCr model.

helium atom is unrelaxed, otherwise it will move to other sites because of the low migration energy of helium in Fe (0.06 eV) [15]. Instead, all other atoms are allowed to fully relax until the force acting on each atom reaches  $10^{-3}$  eV/Å. With a continuous accumulation of helium atoms at the vacancy, we find that the helium atoms repel the surrounding charge cloud, resulting in charge density redistribution around the neighboring Fe atoms in Figs. 2(A)–(E). Helium is confined to the vacancy, and as the number increases, it not only increases the repulsive force on the positron, but also reduces the effective open volume of the vacancy, which reduces the lifetime of positron in the He<sub>n</sub>V<sub>1</sub> cluster. Table I shows the change of structural parameters for various He<sub>n</sub>V<sub>1</sub> clusters that occurs because a significant pressure builds up on the surrounding Fe lattice. It can be seen that the lattice volume increases with the increase in the number of helium atoms.

To estimate the relative stability of helium in FeCr, the calculated formation energies of helium atom at tetrahedral interstitial sites in FeCr are shown in Fig. 3. Helium atoms were placed in the tetrahedral interstitial sites around Fe and Cr atoms respectively, and the formation energies of helium atoms at corresponding positions were calculated. In the FeCr model, we find that the interstitial He atoms tend to be far away from the Cr atom, which is more likely to occur in the tetrahedral position of the Fe atoms.

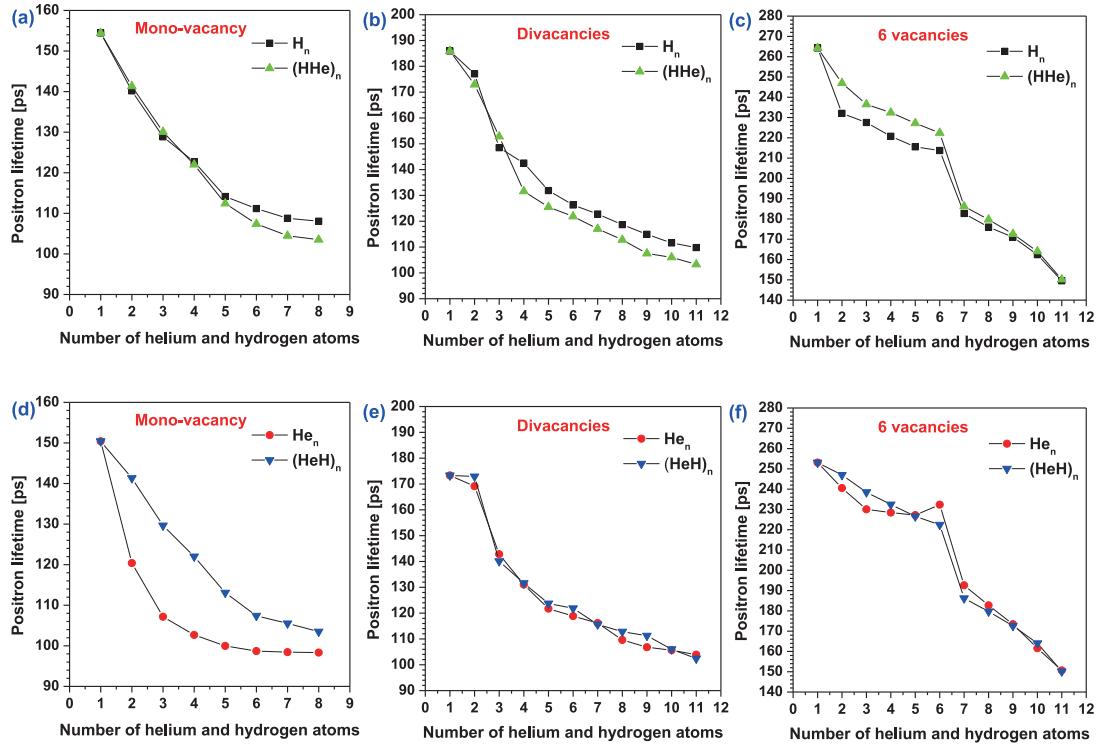


**Fig. 4** Calculated positron lifetime in nano-clusters consisting of  $m$  ( $m = 1, 2$  and  $6$ ) vacancies with  $n$  ( $n = 1$  to  $11$ ) hydrogen/helium atoms.

### 3.2 Theoretical positron lifetime calculations

In order to understand the sensitivity of positrons trapped by  $(H/He)_n V_m$ , the calculations of positron lifetime by density-functional theory have been carried out as a function of the size of the vacancy-clusters in FeCr containing hydrogen/helium. The ratio of hydrogen and helium atoms versus vacancies in the nano-clusters has been varied.

The present calculation gives a value of positron lifetime as 113 ps for a perfect FeCr bcc lattice. Positron lifetime in Fe9wt%Cr has been determined experimentally by positron spectroscopy. Therefore, it is suitable for testing the computational method. The computed positron lifetime for a monovacancy in FeCr is 179 ps, 154 ps for 1H–1V, 150 ps for 1He–1V and 141 ps for 1H–1He–1V. This clearly indicates that the lifetime of a trapped positron is larger than that of a positron in the free state because the electron density inside a nano-cluster is less than that in the interstitial area. The lifetime for a trapped positron is sensitive to the vacancy-clusters size as well as the ratio of hydrogen and helium atoms in the vacancy-clusters. Fig. 4 shows the computed positron lifetimes for 1, 2 and 6 vacancies containing  $n$  ( $n = 1$  to  $11$ ) hydrogen/helium atoms.  $(HHe)_n$  refers to the first one in the model with H atom and then He atom alternately, then calculate the positron lifetime value and  $(HeH)_n$  is the opposite. The longer lifetime corresponds to an increased vacancy-clusters size in the bcc FeCr lattice, similar to the results for nickel and iron [16]. The computed positron lifetimes for increasing numbers of H/He atoms in the nano-clusters ( $1V + nH/He$ ,  $2V + nH/He$  and  $6V + nH/He$ ), show a monotonic decrease in Fig. 4. It can be seen that the positron lifetime decreases slowly with the growth of hydrogen and helium atoms in the nano-clusters when the number of hydrogen/helium atoms is less than



**Fig. 5** Calculated positron lifetime for a monovacancy, divacancies, and 6 vacancies containing hydrogen/helium in the FeCr model.

the number of vacancies in the nano-clusters i.e., when the ratio  $n(\text{He/H atoms})/m(\text{Vacancies}) < 1$ . When the ratio  $n(\text{He/H atoms})/m(\text{Vacancies}) > 1$ , there is a sharp decrease of positron lifetimes for the nanoclusters containing hydrogen/helium. This indicates that the effective open volume of a nanocluster changes when hydrogen/helium atoms are trapped by vacancies.

The computed positron lifetimes for a monovacancy, divacancies, and 6 vacancies containing hydrogen/helium in FeCr are shown in Fig. 5, which presents the evolution of vacancy-clusters bound with different number of hydrogen/helium atoms. It is interesting to note that the positron lifetime is sensitive to the relative amount and variety of the atoms decorating the vacancies. The computed lifetimes from induced hydrogen/helium atoms in a monovacancy show constant decrease and saturation around 100 ps for He, 108 ps for H, and 103 ps for HHe or HeH, as shown in Fig. 5(a) and Fig. 5(d). We found that the positron lifetimes for  $(HHe)_n$  or  $(HeH)_n$  are between that of  $H_n$  and  $He_n$  in a monovacancy and in divacancies. This is obviously due to the minimum effective open volume of  $\text{He}_n\text{V}$ ; i.e., the helium atom forms a more repulsive ion core than the hydrogen atom when it occupies the vacancy, resulting in a decrease in positron lifetime. The repulsive force between the He ions and the charged positron will cause a greater possibility for annihilation of the positron in the interstitial regions where the free-electron density is higher. For 6 vacancies containing hydrogen/helium, the longer lifetime for  $(HHe)_n$  or  $(HeH)_n$  than that of  $H_n$  and  $He_n$  when  $n < 6$ . However, once  $n$  is greater than 6, similar to the situation in a monovacancy and in divacancies, the effective volume effect dominates.

## 4. Conclusion

(H, He)–V complexes with open volume in FeCr alloys have been studied by first-principles calculations and by Doppler code. The results show that the positron is sensitive to the relative position of the gas atoms decorating the open volume; i.e., to the configuration of the (H, He)–V complexes. The main conclusions are:

- (1) In order to understand the characteristics of positron trapping sites, the electronic structure of defects have been investigated using the charge density. It was found that the charge density at He/H–V clusters is significantly lower than that around the neighboring Fe/Cr sites.
- (2) To estimate the relative stability of helium in FeCr, the formation energy of helium-vacancy at tetrahedral interstitial sites was calculated. We found that the interstitial He atoms tend to be far away from the Cr atom, which is more likely to occur in the tetrahedral position of the Fe atom.
- (3) The positron lifetimes for 1, 2, and 6 vacancies containing  $n$  ( $n = 1$  to 11) hydrogen/helium atoms were calculated by MIKA–Doppler code. Positrons confined in the shallow traps exhibit lifetimes that are consistent with the effective open volume of the (H, He)–V complexes. It is interesting that a helium atom forms a more repulsive ion core than a hydrogen atom when it occupies the vacancy, resulting in a decrease in positron lifetime.

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## References

- [1] T. Troev, N. Nancov, L. Petrov, and E. Popov, Rep. Lett. Phys. **1**, 746892 (2008).
- [2] X.-Z. Cao, T. Zhu, S.-X. Jin, P. Kuang, P. Zhang, E.-Y. Lu, Y.-H. Gong, L.-P. Guo, and B.-Y. Wang, Appl. Phys. A, **123**, 177 (2017).
- [3] T. Zhu, S.-X. Jin, P. Zhang, L.-G. Song, X.-Z. Cao, and B.-Y. Wang, J. Nucl. Mater. **505**, 69 (2018).
- [4] Q. Xu, T. Ishizaki, K. Sato, T. Yoshiie, and S. Nagata, Mater. Trans. **47**, 2885 (2006).
- [5] T. Zhu, S.-X. Jin, L.-P. Guo, Y.-C. Hu, E.-Y. Lu, J.-P. Wu, B.-Y. Wang, L. Wei, and X.-Z. Cao, Philos. Mag. **96**(3), 253 (2016).
- [6] T. Zhu, X. Z. Cao, S. X. Jin, J. P. Wu, Y. H. Gong, E. Y. Lu, B. Y. Wang, R. S. Yu, and L. Wei, J. Nucl. Mater. **466**, 522 (2015).
- [7] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- [8] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [9] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- [10] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- [11] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- [12] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- [13] T. Torsti, M. Heiskanen, M. J. Puska, and R. M. Nieminen, Int. J. Quantum Chem. **91**, 171 (2003).
- [14] E. Boronski and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).
- [15] C. C. Fu and F. Willaime, Phys. Rev. B **72**(6), 064117 (2005).
- [16] T. Ishizaki, Q. Xu, T. Yoshiie, S. Nagata, and T. Troev, J. Nucl. Mater. **307–311**, 961 (2002).