Interaction between impurity nitrogen and tungsten: a first-principles investigation*

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We investigate the stability, diffusion, and impurity concentration of nitrogen in intrinsic tungsten single crystal employing a first-principles method, and find that a single nitrogen atom is energetically favourable for sitting at the octahedral interstitial site. A nitrogen atom prefers to diffuse between the two nearest neighboring octahedral interstitial sites with a diffusion barrier of 0.72 eV. The diffusion coefficient is determined as a function of temperature and expressed as $D(\mathrm{N}) = 1.66 \times 10^{-7} \exp(-0.72/kT)$. The solubility of nitrogen is estimated in intrinsic tungsten in terms of Sieverts' law. The concentration of the nitrogen impurity is found to be 4.82×10^{-16} Å^{-3} at a temperature of 600 K and a pressure of 1 Pa. A single nitrogen atom can easily sit in an off-vacancy-centre position close to the octahedral interstitial site. There exists a strong attraction between nitrogen and a vacancy with a large binding energy of 1.40 eV. We believe that these results can provide a good reference for the understanding of the behaviour of nitrogen in intrinsic tungsten.

Keywords: tungsten, nitrogen, diffusion, first-principles

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1. Introduction

The interaction of impurity atoms with metal is of great scientific and technological interest, which has a broad range of applications in the material physics field. For example, nitrogen (N) is generally the most common foreign interstitial atom in a metal matrix. Above the N solubility limit, it is easy to form the nitrides, which are useful to improve the strength and the hardness of metals such as steels. Below the solubility limit, even a very small number of N impurity atoms in the interstitial site can change the thermal and the mechanical properties significantly[1,2] due to the strong interaction between N and metal. In addition, interstitial N atoms can also trap migrating vacancies so as to reduce the vacancy diffusion coefficient, as well as easily interacting with extended defects such as dislocations and grain boundaries.

Metals are used as the plasma facing material (PFM) in a fusion reactor, in which N is regarded as one of the most common impurities.[3] Consequently, exploring the interaction between N and a metal PFM not only greatly helps us to understand the effects of N on the structure and properties of metals, but also provides a direct reference for the design and the operation of a fusion reactor.[4] Tungsten (W) and W alloys are considered to be the most promising PFMs because of their low sputtering erosions and good thermal properties, such as high thermal conductivity and high melting temperature.[5,6] Although N is present only in a very small quantity, it is expected to have a crucial influence on the energetics and kinetics of defects and thus can have a large effect on the properties of W. Under irradiation conditions, there is some evidence that impurity atoms play a major role in the damage process in metals such as ferritic steels, owing to the strong interactions between impurities and point defects.[7] It was observed that radiation hardening can be enhanced due to the presence of interstitial N impurities either via increasing the defect loop density or by stabilizing small dislocation loops.[2]

N-metal systems[1,2,7–17] have been studied extensively and used widely in a variety of industrial fields due to their well-known properties and fundamental importance. N impurities have been found to interact strongly with metals such as ferritic steels,[1,2,7] Mo,[12,14] V,[11,13] Ti, and Zr.[8] Among

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the nitrides, recently, W nitrides (WN_x) have been extensively researched and have received a lot of attention.[18] Generally, the WN is considered to have a ground-state structure with a cubic cell where half of the octahedral site is occupied by W atoms and the other half by N atoms.[15] Wang *et al.*[19] have also found that there exists another stable WN_2 phase for WN_x at the pressure above 30 GPa, where the phase structure is a staking of N–W–N "sandwich" layers linked with strong covalent N–N single bonding. However, these studies mentioned above are considered to be only for the higher N concentration case.

Up to now, we see that less work has been done on the investigation of N as a solid solution in W, especially for the low N concentration case. Correspondingly, many fundamental aspects underlying the interaction of a N impurity with a W matrix remain not well understood. In this study, we investigate the interaction structure, energetics and kinetics between N and W using state-of-the-art first-principles calculations. We believe that these results can provide a useful reference for W as a promising PFM in fusion tokamaks.

2. Computational method

Our first-principles calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code[20,21] based on the density functional theory (DFT). We used the generalized gradient approximation of Perdew and Wang[22] and projector augmented wave potentials[23] with a plane wave energy cutoff of 350 eV. The bcc W supercells of 128 atoms were used, and the Brillouin zones were sampled with (3×3×3) $\boldsymbol{k}$-points by the Monkhorst–Pack scheme.[24] The equilibrium lattice constant was calculated to be 3.17 Å for bcc W, in good agreement with the corresponding experimental value of 3.16 Å.[25] Both the supercell size and the atomic positions were relaxed to equilibrium, and energy minimization was converged until the forces on all the atoms were less than 10^{-3} eV·Å^{-1}.

The solution energy for N atom at interstitial sites in the intrinsic W is defined as

$$E^{\mathrm{s}} = E_{n\mathrm{W,N}} - nE_{\mathrm{W}} - \mu_{\mathrm{N}}, \tag{1}$$

where the $E_{n\mathrm{W,N}}$ is the total energy of the supercell containing n W atoms and one N atom, E_{W} and μ_{N} are the energy of an ideal bulk W atom and the N chemical potential, respectively.

As to the N chemical potential, it is one half of the energy of an N_2 molecule due to its stable configuration in an atmospheric environment and can be written as

$$\mu_{\mathrm{N}} = \frac{1}{2}E_{\mathrm{N_2}}(T = 0\ \mathrm{K}) + E_{\mathrm{N_2}}(T, p), \tag{2}$$

where the $E_{\mathrm{N_2}}$ ($T = 0$ K) is the energy of an N_2 molecule at $T = 0$ K and can be obtained to be −8.31 eV in value according to the present first-principles calculation, and the corresponding N–N bond length is 1.11 Å. The term $E_{\mathrm{N_2}}(T, p)$ is the energy of N_2 molecule, dependent on temperature and pressure In the following analysis, we will neglect this term, because the temperature is zero in the present study.

The binding energy between the N atom and the vacancy in W is defined as

$$\begin{aligned} E^{\mathrm{b}}_{\mathrm{NV}} = &\left[E_{(n-1)\mathrm{W,NV}} - E_{(n-1)\mathrm{W,V}}\right] \\ &- \left[E_{n\mathrm{W,N(O\text{-}site)}} - nE_{\mathrm{W}}\right], \end{aligned} \tag{3}$$

where $E_{(n-1)\mathrm{W,NV}}$ and $E_{(n-1)\mathrm{W,V}}$ are the energies of the supercell with one N atom at the vacancy and of the supercell with only one vacancy, respectively, $E_{n\mathrm{W,N(O-site)}}$ is the energy of the supercell with an octahedral interstitial site (O-site) N atom. Here, a negative binding energy indicates repulsion between the N atom and the vacancy, while a positive value represents attraction.

3. Results and discussion

3.1. Solution properties of single N atom in intrinsic bulk W

There are several possible sites involved in tetrahedral interstitial site (T-site) and O-site occupation by a single N atom. As to N interstitial sites, here we first consider the high symmetry cases for both T-site and O-site, i.e., N atom stays in the centre of interstitial sites. We find that a single N atom energetically prefers to sit at the O-site with a solution energy of +138 eV lower than +210 eV at the T-site. This is consistent with the most common explanations of the experimental observations[26] and theoretical simulations.[27] Interestingly if the N atom is slightly off-centre of the T-site, it always shifts towards the O-site after the optimization of the structure. This suggests that the T-site is not a local energy minimum site for N but a saddle point, similar to the behaviours of N in other bcc metals such as α-Fe.[1]

The covalent radius of N atom is close to 0.74 Å. Thus, we believe that both the T-site and the O-site might be considered to be too small. It is well known that the atom distribution at O-site in the bcc metal is asymmetric, where there exist two first nearest neighbour host atoms and four second nearest neighbour host atoms. Such an asymmetric structure will result in local distortions and a rather strong deformation interaction when the impurity atom occupies the other site. According to the present calculations, the N atom is found to prefer to sit at the asymmetric O-site rather than occupy the symmetric T-site in W, although the general "effective space" of the T-site of the bcc metal lattice is larger than that of the O-site.

We believe that there are two possible pathways leading to a very low solution energy at the O-site in comparison with that at the T-site: one is through a low electron density mechanism in the O-site and the other is through an N-W bonding mechanism. First, the N solution behaviour in a metal can be understood in terms of the N solution energy (immersion energy) in a homogeneous electron gas model.[28,29] The N solution energy decreases monotonically with electron density decreasing down to an optimal electron density of $d_0 = 0.031$ Å^{-3}.[28,29] Since the electron density everywhere in the intrinsic bulk W is much higher than d_0, the N generally has a lowest solution energy at the place where the electron density is the lowest. In the intrinsic bulk W, the present calculations show that the O-site has a density of 0.25 Å^{-3} that is lower than 0.27 Å^{-3} of T-site and is the lowest as well. Thus, N prefers to occupy the O-site with a lower electron density rather than stay at the T-site. Here, we need point out that it is still much higher than the optimal electron density of 0.031 Å^{-3} from the homogeneous electron gas model, although the electron density of 0.25 Å^{-3} at the O site is the lowest in the intrinsic bulk W The reason is that the present environment is not the homogeneous electron gas, but a periodic lattice structure containing ionic W and electrons, i.e., a mixed system with high density. Next, there also exists a N–W bonding mechanism for N solution at the interstitial site. The covalent-like bond is shown to form between the N atom and the first nearest-neighbour W atoms, as shown in Fig. 1, and the N–W bond length is close to be 1.93 Å. We can see that the present calculated bond length is slightly lower than the experimental value of 2.07 Å.[13]

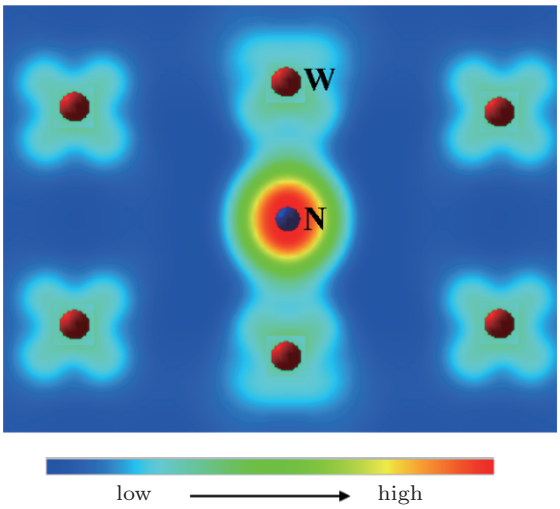


Fig. 1. (colour online) Charge density distribution for N at the O-site in the (001) plane. The smaller and the larger balls represent N and W atoms, respectively.

3.2. Diffusion of interstitial N atoms in intrinsic bulk W

The diffusion properties are quite important for us to understand the behaviour of N atoms in intrinsic bulk W. On the one hand, the diffusion coefficient, as one of the most fundamental properties in a metal, will in turn affect the retention and the migration of N atoms in intrinsic bulk W. On the other hand, the diffusion coefficient is also an important index to determine the diffusion rate of N atoms, which can help us to further understand the diffusion properties quantitatively. Therefore, we can obtain the diffusion activation energy from the first-principles calculation, which helps us to further determine the diffusion coefficient of N atoms in the bulk W.

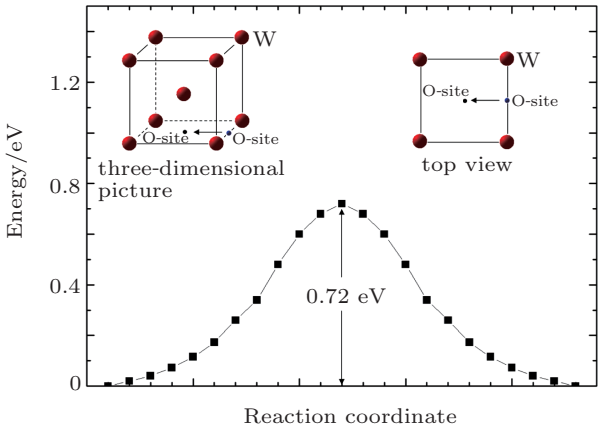


Fig. 2. (colour online) Diffusion energy barrier for an interstitial N atom in intrinsic bulk W.

First, we calculate the diffusion energy barrier for a single N atom at an O-site which jumps to another

O-site via a mediate transition state T-site (O→T→O path) in bcc W using a drag method similar to that in the previous studies.[30] The energy barrier for this path is calculated to be 0.72 eV, which is shown in Fig. 2. Recently, Domain *et al.*[1] have calculated the energy barrier of N atom in bcc Fe using a first-principles method. They obtained an energy barrier of 0.77 eV which is a little higher than that of 0.72 eV of N atom in intrinsic bulk W. The underlying physical mechanism might be that the lattice constant for W (3.17 Å) is larger than that of Fe (2.87 Å), so that N atom can migrate easily in intrinsic bulk W.

Next, we estimate the N diffusion coefficient in the intrinsic bulk W. The diffusion rate of an interstitial impurity atom in metal is generally expressed as

$$D = D_0 \exp(-E_{\rm m}/kT), \tag{4}$$

where D_0 and $E_{\rm m}$ are the temperature independent pre-exponential factor and migration energy, respectively, with k and T being the Boltzmann constant and the absolute temperature, respectively. In terms of the diffusion theory presented by Wert and Zener,[31] D_0 can be expressed as $D_0 = \frac{1}{6}a^2\nu$ for a cubic structure metal, where a and ν are the lattice constant and the vibration frequency, respectively. ν can be approximately written as $\nu = \sqrt{2E_{\rm m}/ma^2}$, where m is the mass of impurity N atom. Using the mass of N atom of 2.32×10^{-26} kg and the W lattice constant of 3.17 Å as well as the calculated N diffusion energy barrier of 0.72 eV, we can thus obtain the vibration frequency $\nu = 0.99 \times 10^{13}$ Hz. Substituting this value into $D_0({\rm N}) = \frac{1}{6}a^2\nu$, the pre-exponential factor $D_0({\rm N})$ can be obtained to be a value of 1.66×10^{-7} m^2/s.

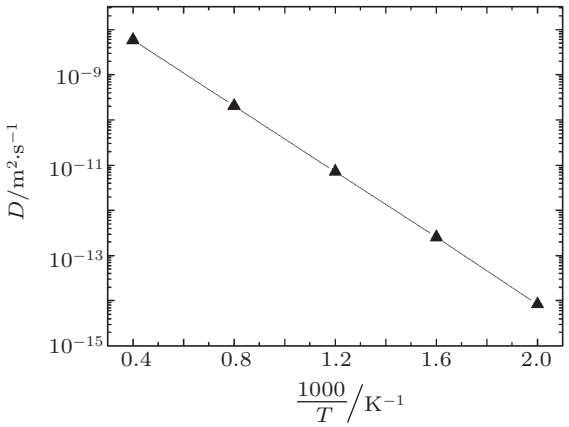


Fig. 3. N diffusion coefficient via interstitial mechanism versus reciprocal temperature in the intrinsic bulk W.

Next, according to the diffusion rate equation (the Arrhenius diffusion equation), as explained above, the N diffusion coefficient in the intrinsic bulk W is calculated to be $D({\rm N}) = 1.66 \times 10^{-7} \exp(-0.72/kT)$. Figure 3 plots the curve of N diffusion coefficient as a function of temperature. For example, $D({\rm N})$ is 2.53×10^{-13} m^2/s at a temperature of 625 K. Due to few experimental or the relevant calculated data, here we provide a quite useful reference for quantitatively understanding the diffusion behaviours of N atoms in the intrinsic bulk W.

3.3. Concentration of interstitial N atoms in intrinsic bulk W

After establishing the solution and diffusion behaviours of N atoms, we now turn our attention to the estimation of interstitial N atom concentration in the intrinsic bulk W. Figure 4 shows the potential energy diagram for the solution of N atoms in the intrinsic bulk W. It is found that there exists an endothermic reaction if N atoms enter into the intrinsic bulk W. Here, we can roughly quantify the role that interstital sites play in the trapping process by estimating the N solution concentration distribution in the intrinsic bulk W. In the low concentration limit, the interstitial impurity concentration at a given temperture is determined by Sieverts' law. The equilibrium concentration of N in a metal is defined as

$$C_{\rm N} = \sqrt{p/p_0}\exp(-E^{\rm s}/kT), \tag{5}$$

where p and p_0 are the pressure of N_2 gas around W and the standard atmospheric pressure (here p_0 is a constant reference pressure), respectively. $E^{\rm s}$ is the solution energy of N atom at the O-site in the intrinsic bulk W. Using the calculated N solution energy of 1.38 eV, we can give a solution concentration of N

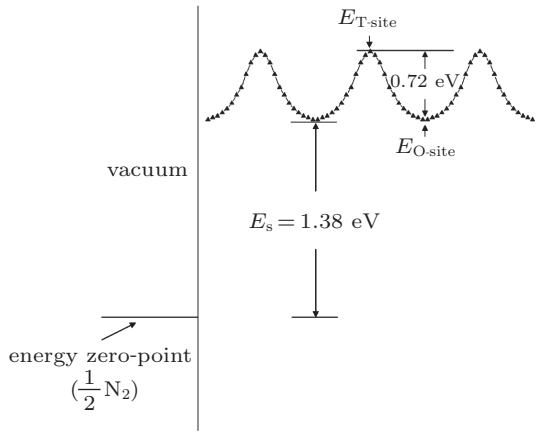


Fig. 4. Potential energy diagram for N atom in intrinsic bulk W.

in the intrinsic bulk W. For example, the N solution concentration is 6.04×10^{-25} Å^{-3} at 300 K. Because few experimental or relevant calculation data are available, we thus provide a quite useful reference.

Figure 5 shows the concentration of N atoms in the intrinsic bulk W as a function of temperature at the pressure of 1 Pa. We can see that the solution concentration is 4.82×10^{-16} Å^{-3} at 600 K and 3.09×10^{-10} Å^{-3} at 1200 K, respectively. There exists a relatively low N interstitial concentration in intrinsic bulk W when the temperature is under 1200 K. In addition, it is important to note that the solubility of N atoms in intrinsic bulk W strongly depends on the temperature and increases notably with increasing temperature. The concrete concentration values of N at the interstital site in the intrinsic bulk W can be increased by 6 orders of magnitude from 600 K to 1200 K. This implies that there exists a strong endothermic reaction for the N solution in the intrinsic bulk W. Here we again provide a quite useful reference for quantitatively understanding the solution properties of N atoms in intrinsic bulk W.

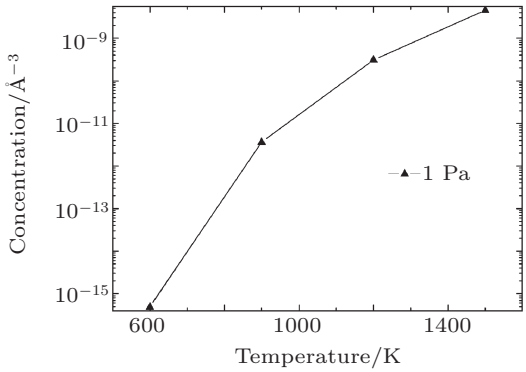


Fig. 5. Solution concentration of N atoms in intrinsic bulk W as a function of temperature at the pressure of 1 Pa.

3.4. Interaction between the N atom and the vacancy in intrinsic bulk W

Now, we turn our attention to the interaction between N atoms and other possible defects. As a typical defect in metal, vacancies enter into the picture here because they are one of the most common defects under radioactive circumstances and are generally considered to be trapping sites in their vicinity. Next, we will calculate the N binding energy in the vicinity of a monovacancy.

Figure 6 shows six possible sites for a single N atom at a monovacancy. Site 1 is the substitutional centre. Sites 2 and 5 are the face O-site centre and the side O-site centre, respectively. Sites 3 and 4 are the T-site and O-site, respectively, and site 4 is outside the vacancy. Site 6 is the midpoint between the substitutional centre and its nearest neighbour W atom. We calculate the binding energies of N atom at these sites as well as other possible sites to find the energetically favourable sites. The energy minimization shows that there exists a strong attraction between the N atom and the vacancy with a large binding energy of 1.40 eV lower than that at the O-site in intrinsic W. We further find that the most stable site for the N atom cannot sit in the centre of the vacancy, but at an off-vacancy-centre position ($\sim$ 1.37 Å from the vacancy center) close to an O-site (Fig. 7). Moreover, there are the same 6 most stable sites close to the O-sites next to the vacancy centre in the vicinity of the vacancy, which is indicated in Fig. 7.

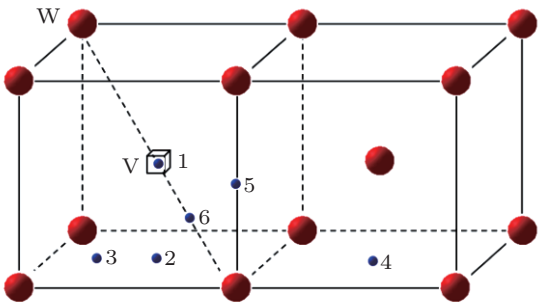


Fig. 6. (colour online) Six possible sites for a single N atom in the vicinity of a monovacancy. The larger and the smaller balls represent W and N atoms, respectively.

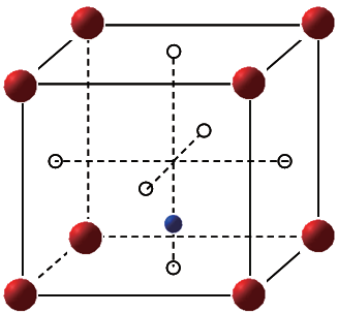


Fig. 7. (colour online) Optimal site for N binding at a monovacancy. The circles mark the 6 O-sites. The larger and the smaller balls represent W and N atoms, respectively.

The main reason for N to have a much large binding energy at the vacancy site is that N will be off the vacancy centre to bond with the neighbour W atom in the vicinity of the vacancy, i.e., through an N–W bonding mechanism. The N atom can be found to form a covalent-like bond with the first nearest-neighbour W atom. The corresponding bond length is close to be 2.05 Å, in good agreement with the experimental value of 2.07 Å.[13] The underlying physical

mechanism might be that vacancy can provide a large space for the interaction between N and the neighbour W atom in comparison with the case of intrinsic bulk W.

4. Conclusion

Using the first-principles method, we investigate the stability, the diffusion, and the concentration of nitrogen (N) impurity in an intrinsic tungsten (W) single crystal. A single N atom is shown to energetically prefer to sit at the octahedral interstitial site (O-site). Kinetically, a N atom prefers to diffuse between the two nearest-neighbour O-sites with a diffusion barrier of 0.72 eV. By estimating the pre-exponential factor, we determine the diffusion coefficient as a function of temperature according to the Zener and Wert's theory, which is expressed as $D(\mathrm{N}) = 1.66 \times 10^{-7} \exp(-0.72/kT)$. The solubility of N atoms is estimated in the intrinsic bulk W in terms of Sieverts' law. We find that the concentration of impurity N atoms is 4.82×10^{-16} Å^{-3} at a temperatures of 600 K and a pressure of 1 Pa. We further find that there exists a strong attraction between N and the vacancy with a large binding energy (1.40 eV). The most stable site for N is not in the centre of the vacancy, but at an off-vacancy-centre position close to an O-site.

References

[1] Domain C, Becquart C S and Foct J 2004 *Phys. Rev.* B **69** 144112

[2] Little E A and Harries D R 1970 *Met. Sci. J.* **4** 188

[3] Rubel M, Philipps V, Marot L, Petersson P, Pospieszczyk A and Schweer B 2010 *J. Nucl. Mater.* **415** 5225

[4] Liu Y L, Zhou H B, Jin S, Zhang Y and Lu G H 2010 *Chin. Phys. Lett.* **27** 127101

[5] Wang X L, Xu Y and Zeng Z 2009 *Acta Phys. Sin.* **58** 72 (in Chinese)

[6] Li X C, Shu X, Liu Y N, Gao F and Lu G H 2011 *J. Nucl. Mater.* **408** 12

[7] Little E A 1976 *Int. Met. Rev.* **204** 25

[8] Ruban A V, Baykov V I, Johansson B, Dmitriev V V and Blanter M S 2010 *Phys. Rev.* B **82** 134110

[9] Felton S, Cann B L, Edmonds A M, Liggins S, Cruddace R J, Newton M E, Fisher D and Baker J M 2009 *J. Phys.: Condens. Matter* **21** 364212

[10] Cruz M M, Silva R C, Franco N and Godinho M 2009 *J. Phys.: Condens. Matter* **21** 206002

[11] Yamanaka S, Kashiwara Y, Sugiyama H and Katsura M 1997 *J. Nucl. Mater.* **247** 244

[12] Hautala M, Anttila A and Hirvonen J 1982 *J. Nucl. Mater.* **105** 172

[13] Kainuma T, Iwao N, Suzuki T and Watanabe R 1979 *J. Nucl. Mater.* **80** 339

[14] Filius H A and van Veen A 1987 *J. Nucl. Mater.* **144** 1

[15] Choi D and Kumta P N 2007 *J. Am. Ceram. Soc.* **90** 3113

[16] Toth L E 1971 *Transition Metal Carbides and Nitrides* (New York: Academic Press) Vol. 7

[17] Jhi S H, Ihm J, Louie S G and Cohen M L 1999 *Nature* **399** 132

[18] Liu F, Qin Z X, Xu F J, Zhao S, Kang X N, Shen B and Zhang G Y 2011 *Chin. Phys.* B **20** 67303

[19] Wang H, Li Q, Li Y, Xu Y, Cui T, Oganov A R and Ma Y 2009 *Phys. Rev.* B **79** 132109

[20] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558

[21] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169

[22] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244

[23] Blochl P E 1994 *Phys. Rev.* B **50** 17953

[24] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[25] Kittel C 1996 *Introduction to Solid State Physics* (New York: Wiley) 7th ed.

[26] Rosato V 1989 *Acta Metall.* **37** 2759

[27] Williamson G K and Smallmann R E 1953 *Acta Crystallogr.* **6** 361

[28] Puska M J, Nieminen R M and Manninen M 1981 *Phys. Rev.* B **24** 3037

[29] Norskov J K 1982 *Phys. Rev.* B **26** 2875

[30] Liu Y L, Zhang Y, Zhou H B, Liu F, Luo G N and Lu G H 2009 *Phys. Rev.* B **79** 172103

[31] Wert C and Zener C 1949 *Phys. Rev.* **76** 1169