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Physical properties of α-Fe upon the introduction of H, He, C, and N

Seiji Sakuraya[a], Keisuke Takahashi[a,*], Shaui Wang[b], Naoyuki Hashimoto[a], Somei Ohnuki[a]

[a] *Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8628, Japan*

[b] *International Institute for Carbon Neutral Energy Research, Kyushu University, 744 Motooka, Fukuoka, 819-0395, Japan*

Abstract

The effects of impurities of H, He, C, and N in α-Fe are investigated in terms of electronic structures using the density functional theory. Calculations reveal that H and He are stable at the T-site while C and N are stable at the O-site within α-Fe. The local strain field by H, He, C, and N in α-Fe cause structural elongation. Furthermore, the decrease of magnetic moment of Fe upon the introduction of C and N are found where the charge transfer is responsible. H, He, C, and N affect the electronic structure of α-Fe and change the fundamental physical properties of α-Fe.

Keywords: A. BCC Fe; B. Density functional theory; D. Magnetism; D. Hydrogen

1. Introduction

High strength α-Fe is a commonly-used material in automotive, construction, and nuclear reactor industries. However, impurities such as H, He, C, and N are commonly found in α-Fe and known to cause structural hardening or softening of α-Fe and eventually change the fundamental physical properties of α-Fe [1, 2, 3, 4, 5]. In particular, H causes structural embrittlement within α-Fe [6, 7, 8, 9]. He is introduced in α-Fe by the results of irradiation.

*The author to whom the correspondence should be addressed to; Email: keisuke.takahashi@eng.hokudai.ac.jp.

The presence of He is believed to cause void swelling and material embrittlement [10, 11]. C and N are frequent interstitial atoms in α-Fe. The effects of C and N in α-Fe are also known to affect the vacancy migration energy which potentially leads to dislocation behavior [12]. However, the electronic structures of such system and how impurities affect the physical properties of α-Fe have not been completely understood.

Fundamental understanding of impurities in α-Fe is a crucial step for understanding how such impurities affects the properties of α-Fe. In this work, the elementary phenomena of how H, He, C, and N affect the electronic structures of α-Fe are investigated within the density functional theory.

2. Computational methods

Density functional theory is implemented within the grid-based projector-augmented wave (GPAW) method [13]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is used for exchange-correlation [14]. Grid space and k-points are set to 0.18 Å and (4×4×4) within periodic boundary conditions, respectively [15, 16]. Lattice constant and magnetic moment of α-Fe are calculated to be 2.85 Å and 2.18 μ_B, respectively. (2×2×2) of BCC Fe cell is used in order to understand the primary interaction between impurities and neighboring iron atoms. The effect of H in BCC Fe is previously calculated with the (2×2×2) cell [8]. Furthermore, (3×3×3) BCC Fe cell is also performed by using linear combination of atomic orbitals (LCAO) method within GPAW where (2×2×2) k-points are applied. Lattice constant and magnetic momenet of BCC Fe with LCAO method are calculated to be 2.83 Å and 2.19 μ_B, respectively.

The dissolution energy of interstitial atoms were calculated based on Equation (1):

$$E_d = E(Fe_M) - E(Fe) - E_M \tag{1}$$

where M represents H, He, C, and N. Note that zero-point vibrational (ZPV) energy is considered in H cases. Positive signs indicate endothermic reactions.

The local strain field for xx, yy, and zz upon the introduction of impurities is calculated by Equation (2):

$$\epsilon_{xx} = \frac{(x - x_0)}{x_0}, \epsilon_{yy} = \frac{(y - y_0)}{y_0}, \epsilon_{zz} = \frac{(z - z_0)}{z_0} \tag{2}$$

where x, y, and z are the lattice lengths nearest to the impurities in BCC Fe and x_0, y_0, z_0 are corresponding lattice lengths without impurities.

The change of lattice constant is evaluated based on Equation (3).

$$a = \frac{V^{\frac{1}{3}}}{2} \tag{3}$$

where V is the volume of BCC Fe cell and a is the lattice constant.

Bader analysis is implemented in order to analyze the charge transfer between impurities and Fe[17, 18].

3. Results and Discussion

3.1. H, He, C, and N in α-Fe

Interstitial atoms (H, He, C, and N) were placed in bulk Fe. Each atom is stabilized at either the tetrahedral site (T-site) or the octahedral site (O-site) as seen in Figure 1. The change of physical properties in α-Fe upon dissolving impurities are collected in Table 1. Calculations demonstrate that H and He are stable at the T-site while C and N are stable at the O-site. Note that the dissolution energies in Table 1 indicate that H, He, C and N in α-Fe are endothermic reactions.

The dissolution energy of H at T-site is calculated to be 0.27 eV which has good agreement with experimental and theoretical value of 0.29 eV and 0.30 eV, respectively [6, 19, 20]. It must be noted that the effect of the ZPV energy is relatively large where the H dissolution energy is calculated to be 0.19 eV without ZPV energy. He in the T-site of α-Fe particularly has a high dissolution energy of 4.91 eV which is slightly larger than previous theoretical work [21]. He ($1s^2$) has a closed-shell electronic structure making it is reasonable to assume that He does not interact with Fe as indicated by low charge transfers of 0.18 electrons from Fe. Dissolution energy of C at the O-site is calculated to be 1.17 eV which has good agreement with molecular dynamic results of 1.22 eV [22]. N is stabilized at the O-site having 0.89 eV of dissolution energy which is not previously reported.

One possible explanation of the stability of the impurities site in α-Fe can be found by electron negativity and the distance between impurities and neighbor Fe atoms. The distance between the nearest Fe atom and O-site(T-site) is calculated to be 1.42 Å (1.59Å). Electrons are concentrated on the O-site while there are less electrons around the T-site. C and N have higher

electron negativity than H. Therefore, C and N prefer to interact with more electrons than H and He cases.

3.2. Strain field

The local strain field and the change of lattice constant upon introduction to the impurities are collected in Table 1. The local strain field and the change of lattice constant are calculated by using Equations (2) and (3), respectively. The induced strain field upon the introduction of impurities is larger than the change of lattice constant because the local strain field near impurities are considered while the change of lattice constant is calculated based on volume of the cell.

The lattice constant is slightly elongated by 0.04 Å upon H in the T-site of α-Fe. The local strains of α-Fe with He at T and O sites have positive signs, demonstrating elongation in all directions. As He has a closed shell structure, He repulses with the surrounding Fe atoms, resulting in elongation.

It is interesting to see that strain of α-Fe with C and N at the O-site indicates negative signs, demonstrating shrinkage, in x and y directions. However, large strain field is seen in the z-direction. This indicates that four surrounding Fe atoms shown in Figure 1 in the x- and y-directions are attracted by C and Z while two Fe atoms in z-directions are repulsed. Although the local strain of Fe with C and N shows shrinkage in the x and y directions, large expansion is seen in the z-direction, resulting in the expansion of the lattice constant.

3.3. Magnetic properties

The change of magnetic moment upon the impurities is explored. The magnetic moments of the nearest Fe atom to impurities are collected in Table 2. The magnetic moment of Fe remains unchanged with the introduction of H at the T-site The magnetic moment of Fe slightly increases when He is introduced at the T-site. As He has a closed-shell electronic structure, one can consider that He physically blocks the metallic bonding of Fe atoms. Therefore, Fe gains more unpaired spins, resulting in an increase of the magnetic moment.

It is interesting to see the dramatic change of magnetic moment of Fe as seen in the cases of C and N. Table 1 shows that significant charge transfer can be seen in C and N compared to H and He. For that reason, it can be considered that unpaired spins of Fe interact with C and N, resulting in a decrease of the magnetic moment.

3.4. Electronic structures

The electronic structures of BCC Fe with the stable site of H, He, C, and N are investigated by analyzing the projected density of states (PDOS) shown in Figure 2. PDOS shows that the peak of the d-state of Fe is decreased and broaden upon the introduction of C and N. The change of the d-state of Fe is supported by the Bader analysis where C and N are negatively charged by 1.04 and 1.17 electrons, respectively. Thus, C and N interact with Fe through charge transfer.

PDOS shows that He is not interacting with Fe as He has a closed shell structure. This is also supported by the Bader analysis where He is negatively charged by only 0.18 electrons, resulting in low dissolution energy. In the case of H in Fe, the s-state of H slightly affect the Fe as the s-state of H is broaden. Bader analysis also indicate the slight charge transfer of -0.42 electrons from Fe to H co.

4. Conclusion

The effects of impurities (H, He, C and N) in α-Fe were investigated by using the density functional theory. In particular, dissolution energy, strain field, magnetism, and electronic structures are discussed. H and He are stabilized at the T-site while C and N prefers the O-site. The local strain field and the change of lattice constant indicate that α-Fe elongated upon the introduction of H, He, C, and N. Furthermore, decrease of magnetic moment of Fe are seen by C and N which is due to the charge transfers from Fe to C and N, resulting in the change of electronic structure of Fe. Thus, physical properties of α-Fe are affected by the introduction of impurities.

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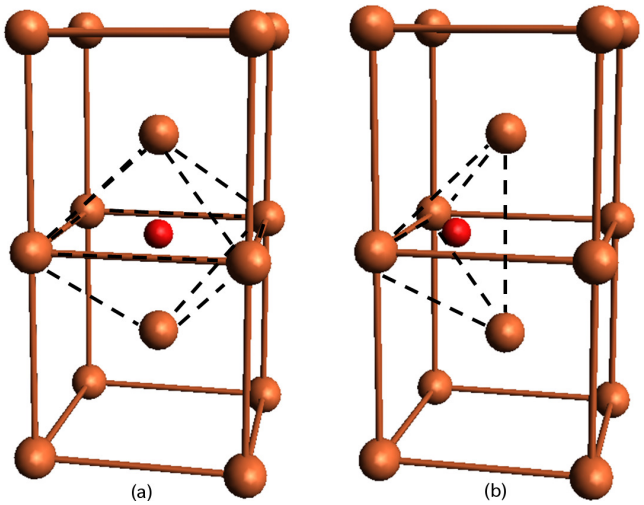


Figure 1: Position of interstitial atoms: (a)Octahedral site and (b)Tetrahedral site. Atomic code: Fe; orange, Interstitial atom; red.

Table 1: E_d:Dissolution energy (eV), ϵ: strain field, A:lattice constant ($\AA$), and q:charge transfer from Fe of impurities (H, He, C, and N) in α-Fe. Bold refers to stable site. The values in brackets are calculated results in (3×3×3) using LCAO method.

	E_d	ϵ			A	q
		ϵ_{xx}	ϵ_{yy}	ϵ_{zz}		
Fe					2.85(2.84)	
H_T	**0.27(0.20)**	0.013(0.015)	0.043(0.050)	0.043(0.050)	2.87(2.85)	-0.42(-0.38)
H_O	0.45(0.31)	-0.005(-0.007)	-0.005(-0.007)	0.104(0.123)	2.87(2.85)	-0.46(-0.40)
He_T	**4.91(4.93)**	0.036(0.036)	0.093(0.114)	0.093(0.114)	2.90(2.85)	-0.18(-0.14)
He_O	5.11(5.12)	0.035(0.042)	0.035(0.042)	0.155(0.177)	2.90(2.85)	-0.19(-0.15)
C_T	1.93(1.36)	-0.001(-0.007)	0.151(0.174)	0.151(0.173)	2.90(2.85)	-1.00(-0.93)
C_O	**1.17(0.64)**	-0.016(-0.011)	-0.016(-0.011)	0.212(0.249)	2.91(2.86)	-1.04(-0.87)
N_T	1.37(1.48)	0.013(0.011)	0.127(0.158)	0.127(0.144)	2.90(2.86)	-1.12(-1.01)
N_O	**0.89(0.64)**	-0.018(-0.011)	-0.018(-0.011)	0.208(0.246)	2.91(2.86)	-1.17(-1.01)

Table 2: Magnetic moment of the nearest Fe atom from interstitial atoms. Bold refers to stable site.

	Magnetic moment (μ_B)
Fe	2.18(2.19)
H_T	**2.17(2.23)**
H_O	2.04(2.07)
He_T	**2.29(2.28)**
He_O	1.99(2.14)
C_T	1.66(1.67)
C_O	**1.63(1.64)**
N_T	1.56(1.53)
N_O	**1.70(1.62)**

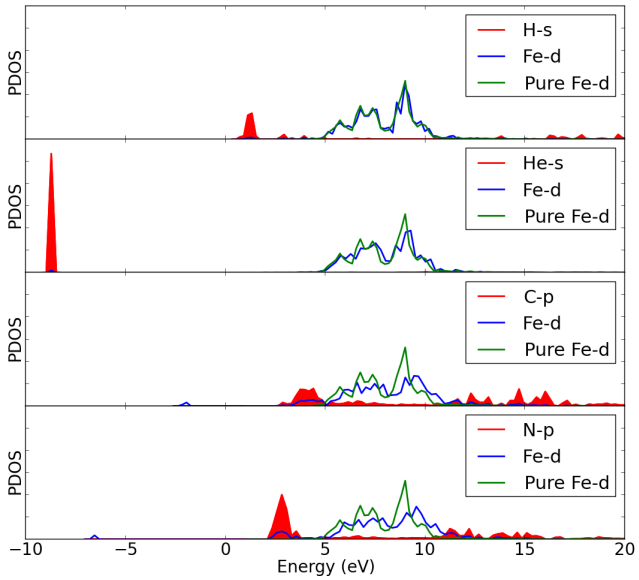


Figure 2: Projected density of states of the s-state of H, the s-state of He, the p-state of C, and the p-state N and the nearest Fe atom of the d-state to impurities. Corresponding the d-state of Fe without impurities is plot as Pure Fe-d.