

# Stability and structures of the $\epsilon$ -phases of iron nitrides and iron carbides from first principles

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First-principles calculations were performed for the  $\epsilon$ -phases and other iron carbides/nitrides with hexagonal close-packed Fe sublattices. Although these nitrides/carbides have similar crystal structures, they exhibit different chemical and physical properties. Relative to  $\alpha$ -Fe, graphite and  $N_2$ , all the  $\epsilon$ -type nitrides are stable, while all the carbides are metastable. The lattice parameters of the  $\epsilon$ -iron nitrides vary differently from those of the  $\epsilon$ -carbides, as a function of the concentration of X (X=N, C). The structural relationships of  $\epsilon$ -Fe<sub>2</sub>X with  $\eta$ -Fe<sub>2</sub>X and  $\zeta$ -Fe<sub>2</sub>X are discussed.

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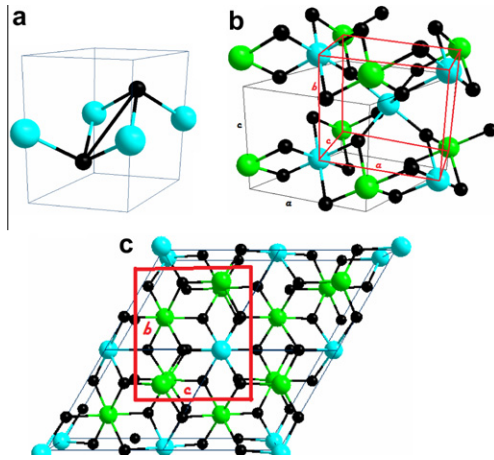
Iron nitrides and carbides play an important role in iron alloys and steels [1–3]. Nitrogen has been introduced into stainless steels to reduce the Ni content for application in both humans and animals [1,3,4]. Tanelke and co-workers [5] reported improvement in creep resistance through boundary pinning effects of carbonitride precipitates. In transformation-induced plasticity (TRIP) aided steels, fine, hard particles, such as iron nitride and carbide precipitates, are crucial to increase their hardness [6–8]. Therefore, knowledge about the formation and stability of iron nitride and -carbide precipitates is useful for the further development of stronger and tougher steels [1,2,5,9,10].

Around 1950, Jack reported his study of the crystal structures of  $\epsilon$ -iron nitrides and proposed models of phase transitions from  $\epsilon$ -phases to  $\eta$ -Fe<sub>2</sub>C and  $\zeta$ -Fe<sub>2</sub>N [11,12]. Since then, many experimental and theoretical studies have been made on the crystal structures, and the electronic and magnetic properties, of the carbides and nitrides of the  $\epsilon$ -phases [13–22]. Liapina and co-workers [13] investigated the structural properties of the  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub> phases. Nagakuri and Tanehashi [14]

studied the  $\epsilon$ -Fe<sub>2</sub>N and  $\zeta$ -Fe<sub>2</sub>N phases and proposed different ionic models for  $\zeta$ -Fe<sub>2</sub>N and  $\epsilon$ -Fe<sub>2</sub>N. On the other hand, there is little information about the crystal structures of the  $\epsilon$ -phase iron carbides. Using first-principles methods, Eck and co-workers [17] investigated structures and electronic properties of binary 3d transition metal nitrides, while Shang et al. [18,19] studied the structural behavior of the  $\epsilon$ -nitrides using first-principles techniques. Recently, we performed first-principles calculations for the Fe<sub>2</sub>C phases and showed how  $\epsilon$ -Fe<sub>2</sub>C transforms into  $\eta$ -Fe<sub>2</sub>C, and addressed their structural relationships with the  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>,  $\theta$ -Fe<sub>3</sub>C and Fe<sub>7</sub>X<sub>3</sub> phases [22]. In the present letter we report our systematic study on the stability and structural properties of the  $\epsilon$ -Fe<sub>2</sub>X<sub>1+x</sub>, and related  $\eta$ - and  $\zeta$ -Fe<sub>2</sub>X phases, as well as  $\chi$ -Fe<sub>5</sub>X<sub>2</sub>,  $\theta$ -Fe<sub>3</sub>X and Fe<sub>7</sub>X<sub>3</sub> phases. Their relative stability and mutual structural relationships are addressed.

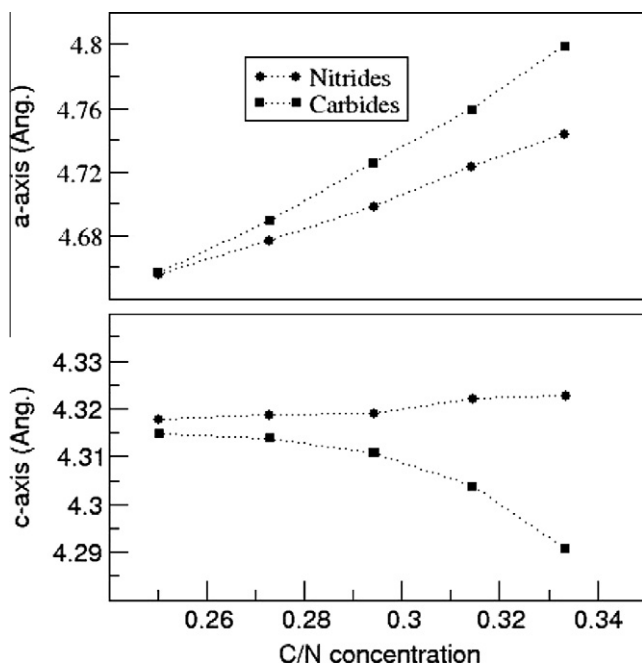
A small hexagonal unit cell was first used by Jack and co-workers to describe the structure of the  $\epsilon$ -phases (Fig. 1a) [2,11,12,14]. We refer to this model here as Jack-1. Its space group is  $P\bar{3}m1$  (nr. 164), with lattice parameters  $a_0 \approx 2.75$  Å and  $c_0 \approx 4.35$  Å [1,2,22,23]. In that unit cell, there are two Fe atoms and interstitial (octahedral) sites partially occupied by X atoms (see Fig. 1a). Jack also used a supercell model (Jack-2) with  $a_h = \sqrt{3} a_0$ ,  $c_h = c_0$  (where  $a_0$  and  $c_0$  are the lattice parameters of Jack-1), which contains six Fe atoms [12,18,19,23]. In this model there are several possible

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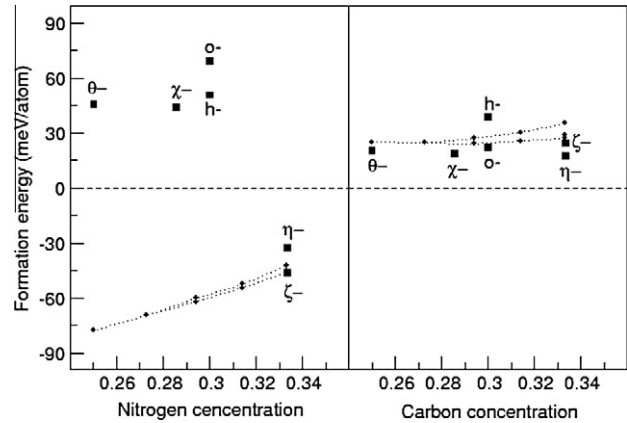


**Figure 1.** Structural models for  $\epsilon\text{-Fe}_3\text{X}_{1+x}$  ( $X = \text{N}$  or  $\text{C}$ ). The black spheres represent iron atoms and the blue (or red or green) spheres represent X atoms. (a) Jack-1 model. (b) Jack-2 model and  $\eta\text{-Fe}_2\text{X}$  with red lines for the unit cell. (c) (0 0 1) projection of Jack-3 and (1 0 0) projection of  $\zeta\text{-Fe}_2\text{X}$  phase. The blue spheres are the 4 X atoms at the b-sites and the green spheres are the 8 X atoms at the c-sites.

ways in which the carbon atoms can be arranged in the interstitial sites (Wyckoff sites: 2b, 2c, 2d) in the hexagonal close-packed (hcp) Fe sublattice. Note that the 2c- and 2d-sites are structurally equivalent (Fig. 1b). Jack-2 is generally used to describe the structure of  $\epsilon$ -phases [12,17–23]. Furthermore, Jack proposed another supercell (Jack-3) with lattice parameters  $a_h = 2\sqrt{3} a_0$ ,  $c_h = c_0$  (again,  $a_0$  and  $c_0$  are the lattice parameters of Jack-1) in order to account for the weak diffraction lines, which could not be indexed within the Jack-2 model [11,12,22,23]. Jack-3 contains 24 Fe atoms with X atoms at the 8c-sites and the 8b-sites (Fig. 1c). Note that, different from the averaged occupation model used before, the arrangements of the X atoms in Jack-3 may



**Figure 2.** The calculated lattice parameters of the  $\epsilon$ -phases for nitrides and carbides. The dotted lines are for guidance of eyes.



**Figure 3.** The calculated formation energies of the  $\epsilon$ -phases (connected with the dotted lines), and other members of the hcp family for nitrides (left) and carbides (right). Two extreme cases of distributions of X at the b-sites are connected with the dotted lines in order to guide the eye.

in some cases break the symmetry of the Jack-2 model; however, we still employ the same symbols of the Wyckoff sites to describe the Fe hcp sheets and interstitial sites for carbon and nitrogen atoms because the Fe sublattice is almost unchanged.

The formation energy ( $\Delta E_f$ ) per atom of an iron nitride or carbide ( $\text{Fe}_n\text{X}_m$ ) from the elements ( $\alpha\text{-Fe}$ , graphite and  $\text{N}_2$ ) can be described as [20–23,24]:

$$\Delta E_f = \{E(\text{Fe}_n\text{X}_m) - [nE(\text{Fe}) + mE(\text{X})]\} / (n + m) \quad (1)$$

At  $T = 0 \text{ K}$  and  $p = 0 \text{ Pa}$ , the formation enthalpy equals the calculated formation energy, i.e.  $\Delta H(\text{Fe}_n\text{X}_m) = \Delta E(\text{Fe}_n\text{X}_m)$ , when the zero-vibration contribution is ignored, since it is much smaller than the formation energies [24]. The formation enthalpy/energy defined in this way can be used to measure the stability of the iron nitrides and carbides with respect to the  $\alpha\text{-Fe}$  phase, graphite and molecular  $\text{N}_2$ .

First-principles calculations were performed for the  $\epsilon$ -phases using the density functional theory method<sup>1</sup> within the generalized gradient approximation (DFT-GGA) [25]. The computational details used here, together with the results of  $\alpha\text{-Fe}$  and graphite, have been described in earlier publications [22,24,27]. Calculations for the  $\text{N}_2$  molecule were performed in a cube with an axis length  $a = 12 \text{ \AA}$ . A cut-off energy of the wave functions of 1000.0 eV was employed to describe the strongly localized 2p bonds of the  $\text{N}_2$  molecule. The bond length calculated in this way is 1.11  $\text{\AA}$ , which is close to the experimental value of 1.10  $\text{\AA}$ .

Our calculated results are shown in Figures 2 and 3. Figure 2 shows the calculated lattice parameters of the

<sup>1</sup>We use the VASP code, employing the density functional theory within the projector-augmented wave method. The generalized gradient approximation was employed for the exchange and correlation energy terms [24]. The cut-off energy of the wave functions was 550/500 eV for nitrides/carbides. Reciprocal space integrations were carried out using dense  $k$ -meshes, e.g. a  $12 \times 12 \times 12$  grid with 84  $k$ -points in the irreducible Brillouin zone of  $\theta\text{-Fe}_3\text{X}$  using the Monkhorst and Pack method [26]. Details of the settings are described in Refs. [22,24,27].

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