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# Electronic structure and magnetic properties of Fe<sub>3</sub>C with 2p and 3p impurities

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*Ab initio* calculations were performed to determine the effect of 2p and 3p impurities on the structural, electronic, and magnetic properties of cementite. We predict that phosphorus, sulfur, and all 2p impurities replace carbon, while aluminum and silicon substitute for iron. The magnetization and magnetic moments on iron atoms in the special and general positions only slightly change for impurities in the

carbon sites, but they essentially decrease for impurities that substitute for iron (Al, Si). We find that boron and nitrogen (to a lesser degree) promote the stabilization of cementite and may be dissolved with the formation of ternary Fe<sub>3</sub>(C, B) and Fe<sub>3</sub>(C, N) cementites. Aluminum and especially silicon sharply suppress the formation of cementite.

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**1 Introduction** Industrial iron materials such as steel and cast iron always contain some light impurities (carbon, nitrogen, oxygen, hydrogen, boron) and 3p elements (silicon, phosphorus, sulfur), which either are added intentionally or appear during manufacture. Even at a very small concentration, these impurities can essentially change the properties of materials and the kinetics of phase transformation [1–4]. Carbon is the most important impurity, which modifies the properties of steels because it increases durability and also raises the threshold of cold brittleness. Boron increases durability and hardening capacity and suppresses the appearance of ferrite in austenite steels during heat treatment. Boron has high neutron-absorbing ability and steels with boron additions are used in nuclear industry. Nitrogen is used to increase hardness, wear, and corrosion resistance, but nitrogen and oxygen can form fragile nonmetallic inclusions that degrade the properties. Silicon is always present in steel, because it is added during melting to remove FeO and increases the durability, especially the limit of fluidity. Silicon at high concentrations improves the elastic properties, corrosion resistance and also increases electrical resistivity. Aluminum raises heat and oxidation resistance. Sulfur and phosphorus are harmful impurities in steel since they lead to brittleness at high and low temperatures, respectively.

The properties of carbon steel are substantially determined by the formation of iron carbide, cementite Fe<sub>3</sub>C, which plays an important role in improving the hardness and durability. The impurities may have different solubilities in ferrite, austenite, and cementite. They may be dissolved in cementite and change its properties. It is known that this iron carbide is metastable and easily dissociates with the formation of bcc Fe and graphite [1–4]. This graphitization process strongly depends on impurities, which can favor the dissociation or, *vice versa*, stabilize cementite. The impurities can form compounds, which are more stable than cementite, and such impurities as nitrogen and boron are used in a small content, because they form binary nitrides, borides, and ternary carbonitrides and carboborides. For example, boron is well dissolved in cementite and forms a continuous family of ternary carboborides Fe<sub>3</sub>(C, B) [5, 6]. The orthorhombic boride Fe<sub>3</sub>B with cementite structure is a stable compound as distinct from metastable Fe<sub>3</sub>C [5–7].

The properties of carbon steel depend strongly on the concentration of impurities and the character of their interaction with iron, carbon, and cementite [1–4]. However, despite the technological importance and intensive experimental studies, the mechanism of the influence of accompanying impurities and alloying additions on the structure and microscopic characteristics of cementite

remains unclear. Qualitative correlations between the bond strength and experimental hardness of Fe<sub>3</sub>C were established in Ref. [8], where the effect of 3d impurities (Ti, V, Cr, Mn, Co, and Ni) on the chemical bonding was studied within the cluster spin-restricted approach. *Ab initio* calculations gave information on the electronic structure and stability of undoped Fe<sub>3</sub>C [9–12] and Fe<sub>3</sub>C alloyed with 3d and 4d transition metals [13–16]. The magnetic properties of impurities were found to depend on their atomic numbers and the trends to ferromagnetic or antiferromagnetic coupling of impurities in Fe<sub>3</sub>C coincide with their magnetic behavior in Fe due to the similarity of their electronic structures.

Here we present the results of first-principles calculations for Fe<sub>3</sub>C with 2p and 3p impurities, which were performed by using the projector-augmented waves (PAW) method as implemented in the Vienna *ab initio* simulation package VASP [17, 18] with the generalized gradient approximation (GGA) for the exchange-correlation energy [19]. The calculations of Fe<sub>3</sub>C–X, (X = B, N, O, Al, Si, P, S) were carried out using a 6 × 6 × 6 *k*-points sampling grid and a kinetic energy cut-off of 350 eV for the expansion of valence orbitals. Local magnetic moments were determined by the integration over the atom-centered spheres with the appropriate radii.

## 2 Results and discussion

**2.1 Crystal structure and preferable sites for 2p, 3p impurities** Cementite has the orthorhombic crystal structure (space group Pnma), where eight Fe atoms (Fe<sub>g</sub>) are in “general” positions (8d), four Fe atoms (Fe<sub>s</sub>) are in “special” positions (4c), while four carbon atoms are eight-coordinated and are located in triangular prisms [20–22]. The calculations were performed for the Fe<sub>12</sub>C<sub>4</sub> cell (four formula units), where the impurity (B, N, O, Al, Si, P, or S) occupies Fe<sub>g</sub>, Fe<sub>s</sub>, or C positions. For Fe<sub>3</sub>C, we obtained the optimized lattice parameters and internal atomic positions to be in good agreement with the experimental data [20–22] and other theoretical estimations [9–13][15, 23].

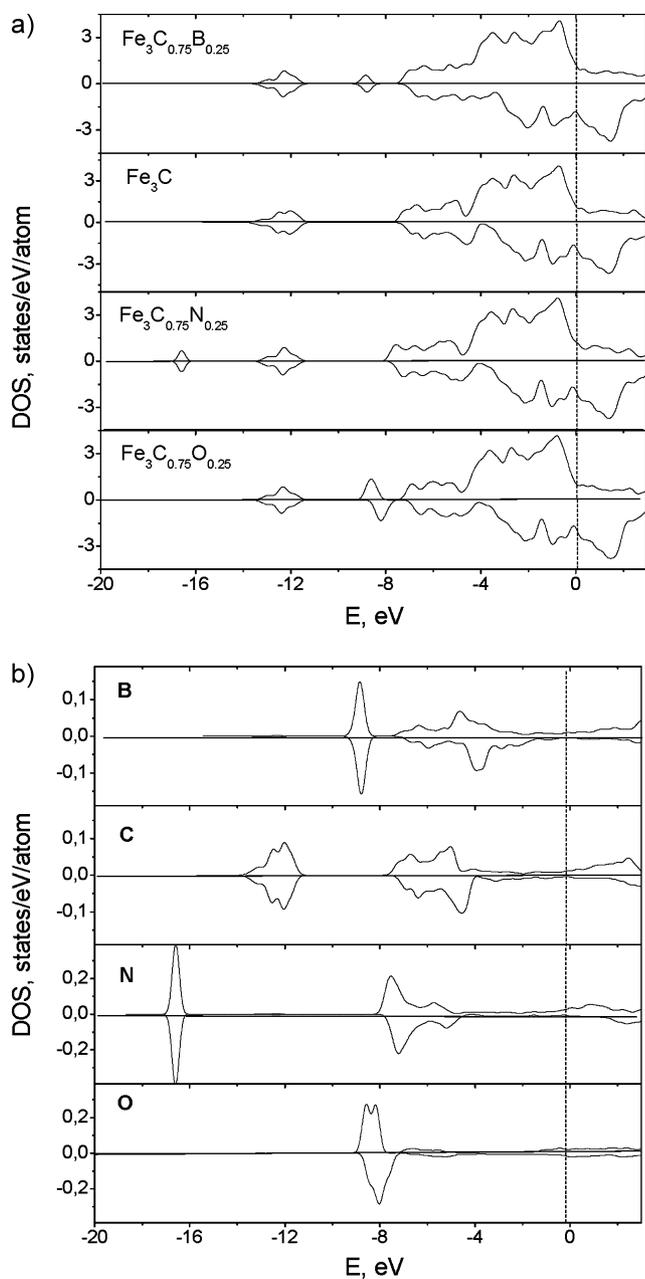
To find the effect of impurities on the stability and their energetically preferable sites, we estimated the variation in enthalpy of formation  $\Delta H$ , which was calculated with the total energies of cementite, iron, carbon, and impurities in their equilibrium states (the crystal parameters of bcc, graphite,  $\alpha$ -B<sub>12</sub>, fcc, diamond, rhombic  $A_{cam}$ , and  $F_{add}$  structures were optimized for iron, carbon, boron, aluminum, silicon, phosphorus, and sulfur, respectively). Oxygen and nitrogen were modeled by the two-atomic molecules located in the cube with the lattice parameter of 10 Å. The calculated interatomic distances 1.224 and 1.114 Å in O<sub>2</sub> and N<sub>2</sub>, respectively, are in agreement with the experimental bond lengths (1.207 and 1.098 Å) in these molecules.

To predict the preferred sites for impurities, we considered the substitutional Fe<sub>g</sub>, Fe<sub>s</sub>, and C sites for the 3p impurities (Al, Si, P, S), while for the light impurities (B, N, O) we took into account the possibility of occupation of both the regular (prismatic) carbon site and the interstitial

octahedral position. It should be noted that the carbon octa-sites in cementite were suggested in the experimental investigations [24]. The distortions induced by an impurity were taken into account based on the forces calculations, while preserving the lattice symmetry (a similar approach was employed for the study of 3d impurities in Fe<sub>3</sub>C [15]). Our calculations show that boron, nitrogen, oxygen, phosphorus, and sulfur substitute for carbon in its regular position. However, only boron has a very strong preference to occupy the carbon prismatic site, while there is a small energy difference (0.05 eV) between the interstitial and prismatic positions for the oxygen and nitrogen impurities. It should be noted that *ab initio* modeling has demonstrated also that the occupation of prismatic and octahedral positions in Fe<sub>3</sub>C by carbon differs by a very small energy and results in a similar electronic structure [10]. In the pure Fe<sub>3</sub>C, the short Fe–C distance is 1.99 Å, while the shortest distance between the iron atom and the impurity in the carbon prismatic position is equal to 2.06, 1.96, and 1.94 Å for B, N, and O, respectively, which correlates with the decrease of their atomic radii. Aluminum and silicon substitute for iron in the particular site with preferred energy (the total energy difference between occupations of the Fe<sub>s</sub> and Fe<sub>g</sub> positions) of 0.07 and 0.01 eV/atom, respectively. Note that the energy difference for silicon is very small and the preferred site may change from Fe<sub>s</sub> to Fe<sub>g</sub> with more accurate relaxation for the larger supercell, because the relaxation effect is much stronger for the impurity in the Fe<sub>g</sub> site.

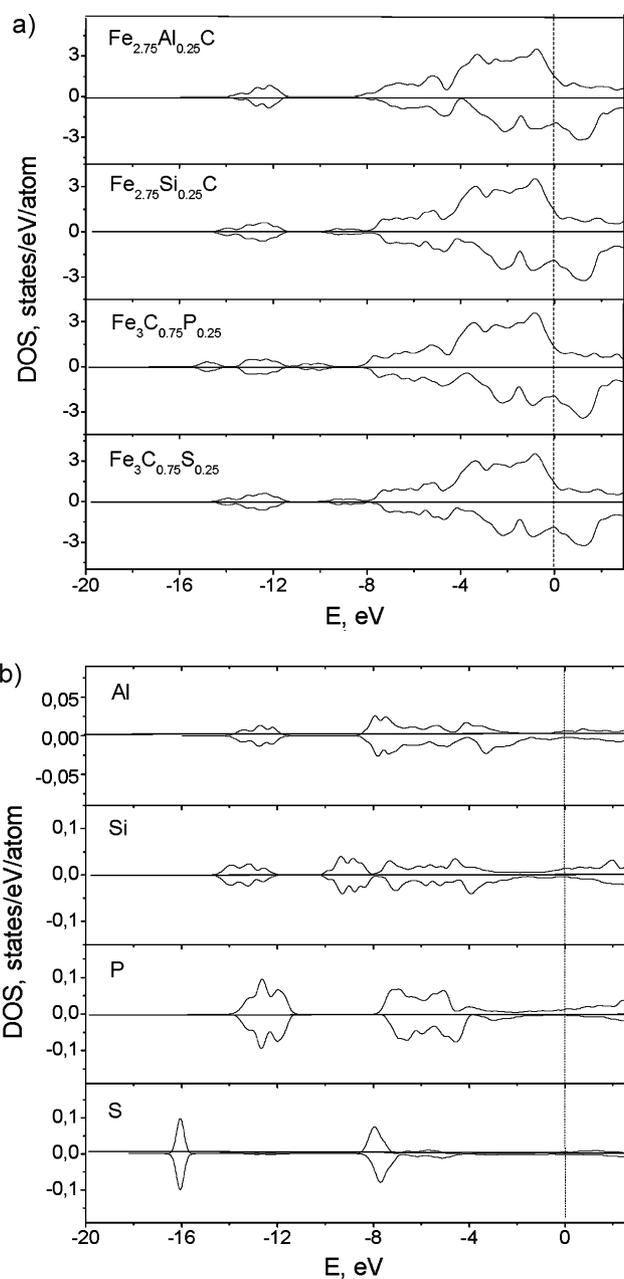
**2.2 Density of states and local magnetic moments** Total densities of states (DOS) for Fe<sub>3</sub>C and Fe<sub>3</sub>C<sub>0.75</sub>X<sub>0.25</sub> (X = B, N, O) are shown in Fig. 1. The Fermi level,  $E_F$ , in Fe<sub>3</sub>C falls in the region of almost completely filled Fe3d spin-up states (3d<sup>↑</sup>) and partially empty Fe3d spin-down states (3d<sup>↓</sup>), and the density of states at the Fermi level for the spin-up ( $N^{\uparrow}(E_F)$ ) is higher than for the spin-down ( $N^{\downarrow}(E_F)$ ) states. The density of states for energies from –4 eV to  $E_F$  is determined by the Fe3d states and the C2p states give a small contribution to DOS near  $E_F$ . The C2p states are mainly located within the energy interval from –8 to –4 eV, where the density of the Fe3d states is small, that testifies weak Fe3d–C2p hybridization. Indeed, the Fe–Fe bonding was calculated to give the main contribution to cohesive energy, while the Fe–C and C–C contributions are much smaller [10]. Note that these results are in agreement with previous theoretical data for Fe<sub>3</sub>C [9–15].

The replacement of carbon by a 2p impurity (Fe<sub>3</sub>C<sub>0.75</sub>X<sub>0.25</sub>) results in the appearance of an additional X2s band, which is gradually shifted to low energy with the atomic number of the impurity (B2s, N2s and O2s states are at –8, –16, and –21 eV (omitted in Fig. 1b), respectively). We find that only the B2p states give contributions to DOS from –4 eV to  $E_F$ , whereas the 3d–2p hybridization is small for other 2p impurities. The main changes in the total density of states take place only for energies below –4 eV, where the



**Figure 1** Total (a) and impurity (b) density of states (DOS) for  $\text{Fe}_3\text{C}-\text{X}$ , where X is a 2p element. Positive and negative values are for spin-up and spin-down states.

Fe3d-states give an insignificant contribution. The oxygen 2p states are separated by a pseudogap from the p-d band, while for other impurities they are located within the C2p band (2p states of impurities are also shifted to low energies with atomic number). The increase of electron concentration for nitrogen and oxygen impurities leads to the filling of antibonding p states, which show the spin splitting near the Fermi level and give a small contribution (mainly due to spin-up states) in  $N(E_F)$ , while this contribution for boron and carbon is also small (Fig. 1b).



**Figure 2** Total (a) and impurity (b) density of states (DOS) for  $\text{Fe}_3\text{C}-\text{X}$ , where X is a 3p element. Positive and negative values are for spin-up and spin-down states.

For the Al and Si impurities, the 3s and 3p states are mainly in the region of C2s states and in the hybrid Fe3d-C2p band, respectively (Fig. 2). Only these impurities give a contribution to DOS above -4 eV, that shows the formation of direct Al,Si3p-Fe3d bonds (Fig. 2b). The P3s and S3s states are below the C2s band, while their 3p states are located near the bottom of the C2p band. Thus, we found that for cementite with 2p and 3p impurities, the Fermi level is also located at the almost filled Fe3d $\uparrow$  states and the local minimum of partly occupied Fe3d $\downarrow$  states (Figs. 1a and

**Table 1** Local magnetic moment ( $m$ ,  $\mu_B$ ), total magnetization ( $M$ ,  $\mu_B$ ), and formation energy  $\Delta H$  (eV/f.u.) for cementite with 2p and 3p impurities.

	Fe <sub>3</sub> C <sub>0.75</sub> B <sub>0.25</sub>	Fe <sub>3</sub> C	Fe <sub>3</sub> C <sub>0.75</sub> N <sub>0.25</sub>	Fe <sub>3</sub> C <sub>0.75</sub> O <sub>0.25</sub>	Fe <sub>2.75</sub> Al <sub>0.25</sub> C	Fe <sub>2.75</sub> Si <sub>0.25</sub> C	Fe <sub>3</sub> C <sub>0.75</sub> P <sub>0.25</sub>	Fe <sub>3</sub> C <sub>0.75</sub> S <sub>0.25</sub>
$m(\text{Fe}_s)$	2.10	1.96 (1.99 [14])	1.98	2.19	1.34	1.33	2.02	2.08
$m(\text{Fe}_g)$	1.89	1.86 (1.95 [14])	1.88	2.09	1.70	1.48	1.87	1.89
$m(\text{X})$	-0.14	-0.12 (-0.16 [14])	-0.06	0.14	-0.04	-0.04	-0.08	-0.03
$M$	1.84	1.85	1.89	2.05	1.55	1.54	1.88	1.90
$\Delta H$	-0.06	0.22	0.18	0.33	0.65	1.29	0.23	0.29

2a). For all 2p and 3p elements the Fermi level falls in the pseudogap between the bonding and antibonding impurity states and the impurity contribution in  $N(E_F)$  is small (Figs. 1b and 2b). The variation in the number of valence electrons does not lead to any essential shift of  $E_F$  in cementite and the main changes in DOS occur near the bottom of the valence band.

**2.3 Magnetic properties** The local magnetic moments on atoms ( $m$ ) and total magnetization ( $M$ ) obtained for cementite with 2p and 3p impurities are shown in Table 1. We find the magnetic moments on iron atoms in special ( $1.96\mu_B$ ) and general positions ( $1.86\mu_B$ ) to be in a good agreement with previous calculations [10–15] and experimental data [25]. All 2p and 3p impurities (except for oxygen) substituting for carbon have a small negative magnetic moment and slightly change the magnetic moments on the nearest iron atoms and the total magnetization. Oxygen has a positive induced magnetic moment, and the magnetization and local magnetic moments increase for the nearest iron atoms both in special and general positions in Fe<sub>3</sub>C<sub>0.75</sub>O<sub>0.25</sub>. Magnetization also increases in cementite with boron, but in this case the local moments increase only on the iron atoms in special positions. As we found [26], magnetization linearly increases with the boron concentration (Fe<sub>3</sub>C → Fe<sub>3</sub>C<sub>1-x</sub>B<sub>x</sub> → Fe<sub>3</sub>B) mainly due to the volume expansion and the decrease of the Fe3d<sup>↓</sup> occupation. The 3p impurities located in iron sites (Al, Si) also have small induced magnetic moments like the 2p and 3p impurities in carbon sites, but they sharply reduce the magnetic moments of the nearest iron atoms (especially the Fe<sub>s</sub> moments) and the magnetization.

**2.4 Effect of impurities on stability** We obtained the positive formation energy  $\Delta H = 0.06$  eV/atom for the unalloyed cementite. The experimental finding (0.05–0.07 eV/atom [27]) and the previous theoretical estimation ( $\Delta H = 0.2$  eV/atom [11]) also gave a positive value, testifying that Fe<sub>3</sub>C is a metastable bulk compound. To estimate the effect of 2p and 3p impurities on the stability of cementite we calculated the formation energies  $\Delta H$  for Fe<sub>3</sub>C–X taking into account the preferred site of impurity X. We found that  $\Delta H$  is negative only for cementite with boron (Table 1), i.e., boron stabilizes the orthorhombic cementite. Our calculations showed [7, 26] that the stability of cementite increases with boron concentration due to the

formation of much stronger Fe–B bonds in comparison with weak Fe–C bonds. This result points to high boron solubility in cementite. Indeed, it is known that boron can replace up to 80% of carbon and form borocementites [5]. Furthermore, we found that the stable boride Fe<sub>3</sub>B has a negative formation energy ( $\Delta H = -0.87$  eV/atom) and also crystallizes in the orthorhombic cementite-like structure with crystal parameters similar to those of cementite Fe<sub>3</sub>C. For other impurities substituting for carbon (X = N, O, P, S),  $\Delta H$  is positive for Fe<sub>3</sub>C<sub>0.75</sub>X<sub>0.25</sub> (Table 1). These impurities render a different effect on the cementite stability. We predict that phosphorus does not affect the stability of bulk Fe<sub>3</sub>C. A small stabilizing effect was obtained for nitrogen, while oxygen and sulfur destabilize the cementite. Aluminum and especially silicon, which we found to be preferable substitutes for iron, sharply increase the positive energy  $\Delta H$ , i.e., they lead to a very strong destabilization of cementite. Indeed, cementite may contain only low concentrations of Al impurities, while Si is known to suppress the formation of cementite.

**3 Conclusions** *Ab initio* calculations were performed to establish the effect of the 2p and 3p impurities on the structural, electronic, and magnetic properties of cementite. We predict that all 2p impurities and also phosphorus and sulfur replace the carbon atoms. The occupation of interstitial octa-sites by nitrogen and oxygen is energetically less favorable. Aluminum substitutes for the iron atoms in special positions, whereas silicon can occupy both special and general sites. We find that for cementite with 2p and 3p elements the Fermi level falls in the pseudogap between the bonding and antibonding impurity states and the impurity contribution to  $N(E_F)$  is small. The main changes in the total density of states occur at the bottom of the valence band, that puts the effect of 2p and 3p impurities apart from d impurities, which may have a high peak in DOS near  $E_F$  and strongly affect the electronic properties [15]. As a result, for Fe<sub>3</sub>C–X the Fermi level is located in the region of almost filled Fe3d<sup>↑</sup> states and in a local minimum of partly filled Fe3d<sup>↓</sup> states as is the case with undoped cementite and fcc Fe. The magnetization and the magnetic moments on the iron atoms in the special and general positions only slightly change with the appearance of impurities in the carbon sites, while they essentially decrease for impurities that substitute for iron (Al, Si). Cementite is a metastable bulk compound with positive formation energy and its stability strongly depends on the solubility of impurities. We predict that boron

and nitrogen promote stabilization of cementite and may be dissolved with the formation of stable (boron) or metastable (nitrogen) ternary cementite-like solid solutions. Aluminum and especially silicon sharply destabilize cementite and suppress its formation.

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