Structural, electronic, and magnetic properties of iron carbide Fe$_7$C$_3$ phases from first-principles theory

C. M. Fang, M. A. van Huis, and H. W. Zandbergen

Materials Innovation Institute (M2I), 2628 CJ Delft, The Netherlands

Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

(Received 29 June 2009; revised manuscript received 17 November 2009; published 22 December 2009)

I. INTRODUCTION

In the early 1980s, Bauer-Grosse and co-workers investigated the crystallization processes of amorphous Fe$_7$C$_{25}$ alloys that had been prepared by the sputter-deposition technique. Using transmission electron microscopy (TEM), they found that Fe$_7$C$_3$ crystallizes first. Fe$_7$C$_3$ or more generally Fe$_M$C$_3$ (M=Cr, Mn, W, etc.) phases are formed in various preparation and thermal treatment processes of alloys and steels. Examples are white cast alloys, Cr-containing ferrite steels, and high-speed steels. Fe$_7$C$_3$ forms also as a byproduct of carburization of ferrite. Audier and co-workers obtained Fe$_7$C$_3$ microcrystals by disproportioning CO on Fe at 500 °C. By means of milling of Fe$_7$C$_{25}$ powder mixture, Campbell and co-workers were able to make Fe$_2$C$_2$.

Fe$_7$C$_3$ phases exhibit attractive electronic and magnetic properties. Tsuzuki and co-workers found that Fe$_7$C$_3$ crystals form in carburization of ferrite as well for the sake of comparison. The relative stability of the two Fe$_7$C$_3$ phases is addressed by means of total-energy calculations with high accuracy and the electronic and magnetic properties are characterized. The information obtained here is helpful to understand the formation and stability of the Fe$_7$C$_3$ phases and contributes to a complete understanding of the structural, electronic, and magnetic properties that are of interest to industrial applications.

II. DETAILS OF CALCULATION METHOD

All calculations were carried out using the first-principles’ Vienna ab initio simulation program (VASP) code employing the density-functional theory (DFT) within the projector-augmented wave (PAW) method. The generalized gradient approximation (GGA) was employed for the exchange and correlation energy terms, since it proved that the (spin-polarized) GGA approximation describes spin-polarized Fe better than the (spin-polarized) local-density approximation (LDA). The cutoff energy of the wave functions was 500.0 eV. The cutoff energy of the augmentation functions was 644.5 eV. The electronic wave functions were sampled on an 8×8×12 grid with 70 k points, 4×8×12 with 105 k points, and 10×8×12 with 210 k points, in the irreducible Brillouin zone (BZ) of the bcc cell and the primitive cell of diamond, respectively. Magnetism of the iron carbides has been calculated for different orderings, The Wigner-Seitz radius is set to be 1.4 Å for Fe and 1.0 Å for C, respectively, for calculations of partial density of states.
and local magnetic moments of atoms. Tests of \( k \) mesh and cutoff energies showed a good convergence (well within 1 meV/atom).

### III. Calculation Results and Discussion

#### A. Definition of formation enthalpy

The formation enthalpy (\( \Delta H \)) of an iron carbide (\( \text{Fe}_x\text{C}_m \)) with respect to the pure elemental solids (\( \alpha \) phase of Fe and graphite) can be described as

\[
\Delta H = H(\text{Fe}_x\text{C}_m) - [nH(\text{Fe}) + mH(\text{C})].
\]

To compare the relative stability of different iron carbides, we use the formation enthalpy per atom (\( \Delta H_f \)),

\[
\Delta H_f = \Delta H/(n + m).
\]

At \( T=0 \) K and \( p=0 \) Pa, the formation enthalpy is equal to the difference of the calculated energies, i.e., \( \Delta H(\text{Fe}_x\text{C}_m) = \Delta E(\text{Fe}_x\text{C}_m) \) when the zero-vibration contribution is ignored.

We first performed total-energy calculations using the settings described in Sec. II for the elemental solids, \( \alpha \)-Fe, and diamond. \( \alpha \)-Fe has a bcc structure. The calculated lattice parameter \( a=2.831 \) Å and the local moment \( M = 2.21 \mu_B/\text{Fe} \) which agree well with the experimental values (\( a=2.866 \) Å and \( M = 2.12 \mu_B/\text{Fe} \)) (Ref. 39) and with former theoretical calculations, e.g., as obtained using ultrasoft pseudopotentials (Ref. 39) and the all-electron method (Ref. 40). The calculated energy for \( \alpha \)-Fe is 8.310 eV/atom.

Elemental carbon exhibits mainly two phases: graphite and diamond. The ground state of carbon is graphite. Experiments have determined that at \( T=0 \) K and \( p=0 \) Pa, graphite is about 17 meV per atom more stable than diamond. Graphite exhibits a layered structure. The interlayer bonding is largely determined by van der Waals interactions, which cannot be correctly described by conventional DFT methods. In recent years, many efforts have been made to calculate the interlayer interaction of layered compounds, including graphite, using other theoretical methods. The diamond phase, though, can be well addressed with the DFT method used in this work. We therefore adopt the following approach. First, the valence electron energy of diamond is calculated, after which the well-established value of 17 meV per atom is subtracted from the diamond’s energy in order to find the valence electron energy for graphite. The calculated lattice parameter for diamond is 3.5713 Å, in good agreement with the experimental value (3.5668 Å at 300 K) and former theoretical calculations.

#### B. Stability of the \( \text{Fe}_7\text{C}_3 \) phases

As mentioned before, \( \text{Fe}_7\text{C}_3 \) has two forms (see Fig. 1). Herbstein and Snyder determined it to be hexagonal and isostructural to \( \text{Ru}_7\text{B}_3 \) with space group \( \text{P6}_3\text{mc} \). The other form has an orthorhombic lattice. Table I shows the calculated lattice parameters of the \( \text{Fe}_7\text{C}_3 \) forms, as well as for \( \theta \)-Fe\(_2\)C. Table II shows the calculated coordinates of atoms and local magnetic moments which were obtained from the difference of the integrated densities of states for the spin-up (majority) and spin-down (minority) electrons in the spheres of the atoms.

First we discuss the calculated results of \( \theta \)-Fe\(_2\)C. The calculated lattice parameters are slightly smaller than the reported experimental values (less than 1%, see Table I). Our calculated lattice parameters (\( a=5.037, b=6.720, \) and \( c=4.842 \) Å) agree well with former theoretical results as well (\( a=5.058, b=6.703, \) and \( c=4.506 \) Å) by Shein and co-workers using the similar method we use here and (\( a=5.079, b=6.7137, \) and \( c=4.5133 \) Å) by Farad and co-workers using the full-potential linearized augmented plane-wave (FP-LAPW) method. The calculated results for \( \theta \)-Fe\(_2\)C (cementite) and \( \alpha \)-Fe can be used as tests of our method and settings.

The calculated lattice parameters for \( \text{Fe}_7\text{C}_3 \) phases are listed in Table I. Our calculations reproduce well the experimental values for the lattice parameters of both hexagonal and orthorhombic cells (within 1%, see Table I). Using the semiempirical atomistic method, Xie and co-workers performed calculations for the \( \text{Fe}_7\text{C}_3 \) phases. Their calculated lattice parameters differ significantly from the experimental data, as shown in Table I. They also reported that the \( h \)-Fe\(_7\)C\(_3 \) is favored over the \( o \) form. That disagrees with our calculations. Note that in Table I, for the sake of comparison to the lattice parameters \( h \)-Fe\(_7\)C\(_3 \), we employ the nonstandard space group \( \text{Pnmc} \) instead of \( \text{Pnma} \). It is also noted that the lengths of the \( a \) and \( c \) axes of the orthorhombic cell are very close to those the hexagonal cell within about 0.5%. The length (11.7324 Å) of the \( b \) axis of

![FIG. 1. (Color online) Atomic structure of \( h \)-Fe\(_7\)C\(_3 \) (left-hand side) and \( o \)-Fe\(_7\)C\(_3 \) (right-hand side). (a) Projection of \( h \)-Fe\(_7\)C\(_3 \) along the hexagonal \( (110) \) axis and (b) projection of \( o \)-Fe\(_7\)C\(_3 \) along the corresponding orthorhombic \( (100) \) axis. (c)–(f) Projections of \( h \)-Fe\(_7\)C\(_3 \) and \( o \)-Fe\(_7\)C\(_3 \) along the \( c \) axis. (c) and (d) show only one half of the unit cell (along the \( c \) axis) so that a single Fe layer in the \( (001) \) plane is displayed. (e) and (f) show the projection of the full unit cell so that the octahedrons A (and also B, in the case of the \( o \) phase) can be easily identified. The big black and small white (blue) balls represent Fe and C (C2 in the \( o \) phase), respectively. Solid lines represent the boundaries of the unit cell.)](Image 323x623 to 434x690)
TABLE I. Summary of calculated results (lattice parameters, formation enthalpies, etc.). (a) For $\theta$-Fe$_2$C: orthorhombic with space group $Pmna$ (nr. 62). (b) For $h$-Fe$_7$C$_3$ with space group $P63mc$ (nr. 186). (c) For $o$-Fe$_7$C$_3$ with space group $Pmcn$ (nr. 62).

<table>
<thead>
<tr>
<th>(a) Lattice</th>
<th>PAW-GGA (present)</th>
<th>PAW-GGA</th>
<th>FP-LAPW-GGA</th>
<th>Exp. (4.2 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.0368</td>
<td>5.058</td>
<td>5.0679</td>
<td>5.082</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>6.7203</td>
<td>6.703</td>
<td>6.7137</td>
<td>6.733</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.4818</td>
<td>4.506</td>
<td>4.5133</td>
<td>4.514</td>
</tr>
<tr>
<td>$V$ ($Å^3$)</td>
<td>151.71</td>
<td>152.77</td>
<td>153.56</td>
<td>154.40</td>
</tr>
<tr>
<td>$\Delta H_f$ (meV/at.)</td>
<td>20.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) Lattice</th>
<th>PAW-GGA (present)</th>
<th>Atomistic</th>
<th>Exp. $^{21,27}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>6.8243</td>
<td>7.187</td>
<td>6.88</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.4939</td>
<td>4.235</td>
<td>4.54</td>
</tr>
<tr>
<td>$V$ ($Å^3$/f.u.)</td>
<td>90.62</td>
<td>94.72</td>
<td>93.05</td>
</tr>
<tr>
<td>$\Delta H_f$ (meV/at.)</td>
<td>38.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(c) Lattice</th>
<th>PAW-GGA (present)</th>
<th>Atomistic</th>
<th>Exp. $^{21,27}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>6.8570</td>
<td>6.953</td>
<td>6.879</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>11.7324</td>
<td>13.740</td>
<td>11.940</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.5183</td>
<td>4.991</td>
<td>4.540</td>
</tr>
<tr>
<td>$V$ ($Å^3$/f.u.)</td>
<td>90.87</td>
<td>119.20</td>
<td>93.22</td>
</tr>
<tr>
<td>$\Delta H_f$ (meV/at.)</td>
<td>22.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The orthorhombic cell is very close to that of the hexagonal cell ($\sqrt{3}a=11.8200$ Å; here $a$ is the length of $a$ axis of the hexagonal cell).

Next we compare the local structures of the two Fe$_7$C$_3$ phases. Figure 1 shows projections of the Fe$_2$C$_3$ structures along different directions. As shown in Fig. 1(a), viewed along the (110) axis of $h$-Fe$_7$C$_3$, the C atoms are arranged in two parallel lines ($z=0.1886$ and 0.6886, respectively), while the Fe atoms form two layers along the $c$ axis (centered at $z=0$ and $\frac{1}{2}$, respectively). Each layer is composed of two Fe sublayers. Figure 1(b) shows the projection of $o$ phase along the (100) axis. The C atoms form two uneven planes, while the Fe atoms form two bulged layers displacing a regular sine curve. Figures 1(c) and 1(d) show the lattices of only one Fe layer for the structures of both the $o$ and $h$ forms, respectively. As shown in Figs. 1(c) and 1(d), the similarity between the two Fe$_7$C$_3$ structures is very apparent. In both cases, the Fe atoms form squares and triangles and two-dimensional (2D) hexagonal rings. That agrees with the former discussions about the lattice similarity between the $h$ and $o$ phases. $^{22-27}$ Two Fe triangles at closing layers form a prism. There are some differences. One important difference between the two structures is that there is only one type of Fe prisms in the $h$ phase [Fig. 1(e)] while there are two different Fe octahedra in the cell of the $o$ phase [Fig. 1(f)]. $^{22-27}$ One Fe octahedron is the same as that in the $h$ phase ($A$ type), while the other one is $B$ type formed by turning $A$ octahedron $180^\circ$ along the $c$ axis. $^{23,24}$

Different possibilities for magnetic ordering of the Fe atoms in the Fe$_7$C$_3$ phases were considered. All calculations with different input configurations for magnetic ordering resulted in ferromagnetic ordering for both phases, which is in good agreement with experimental findings. $^8$

The calculated lengths of chemical bonds of atoms and the local electronic and magnetic properties are listed in Table II. First we discuss the coordination of carbon atoms in the carbide phases. All the carbon atoms in the Fe$_7$C$_3$ phases are coordinated by six Fe atoms, with Fe-C bonds ranging from 1.96 to 2.04 Å, which is similar to the bond lengths in Fe$_3$C cementite. It is notable that the C2 atoms in the $o$-Fe$_7$C$_3$ have an extra Fe-C bond with a slightly longer length of about 2.22 Å, as shown in Table II. Therefore, it is better to describe the C2 atoms being 6+1 coordinated. Meanwhile the C1 atoms have two extra Fe-C bonds with a length of about 2.45 Å. The latter is similar to the carbon atoms in the $h$ form and in the cementite phase (Table II). The Fe atoms in the structures have high Fe coordination numbers (between 11 and 12). In the next section, the atomic arrangements are discussed together with the electronic structure of the compounds.

Table I also includes the calculated formation enthalpies for the two types of Fe$_7$C$_3$, as well as for $\theta$-Fe$_3$C cementite. The calculations show that the $o$-Fe$_7$C$_3$ is almost as stable as $\theta$-Fe$_3$C cementite (formation enthalpies 22.0 and 20.6 meV/atom, respectively). The calculations also show that the orthorhombic lattice has higher stability than the hexagonal one (formation enthalpies 22.0 and 38.9 meV/atom, respectively). In other words, the $o$ phase is about 0.17 eV per Fe$_7$C$_3$ more stable than the $h$ phase. This result disagrees with recent atomistic calculations, where the hexagonal phase was predicted to be more stable than the orthorhombic one. $^{28}$ Our results are in good agreement, though, with recent first-principles calculations. $^{29}$
TABLE II. Calculated coordinates of atoms, chemical bonds, and local electronic and local magnetic moments: (a) for $\theta$-Fe$_3$C; (b) for $h$-Fe$_3$C; (c) for $\alpha$-Fe$_3$C.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a, y/b, z/c$</th>
<th>Bonds ($\text{Å}$)</th>
<th>Electronic configuration at $\text{Fe 3d}$</th>
<th>$M$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Fe1  | 8d   | 0.1763, 0.0678, 0.3318 | -Fe1: 2.45, 2.50, 2.53(×2), 2.62(×2)  
-Fe2: 2.50, 2.58, 2.63, 2.64, 2.67 | -C: 1.99, 2.00, (2.39)  
-Fe1: 2.50(×2), 2.58(×2), 2.64(×2), 2.67(×2)  
-Fe2: 2.64(×2) | 4.22$^\dagger$  
2.30$^\ddagger$  
1.88 |
| Fe2  | 4c   | 0.0357, $\frac{1}{2}$, 0.8373 | -C: 1.96, 1.99  
-Fe1: 1.99(×2), 2.00(×2), (2.39(×2)) | -Fe2: 1.96, 1.99 | 4.26$^\dagger$  
2.25$^\ddagger$  
1.97 |
| C    | 4c   | 0.8766, $\frac{1}{2}$, 0.4379 | -Fe2: 1.96, 1.99 | - | -0.14 |
| (b)  |      |                |                   |                                          |             |
| Fe1  | 2b   | 1/3, 2/3, 0.4022 | -Fe2: 2.51(×3), 2.64(×3), 2.69(×3)  
-Fe3: 2.62(×3) | -C: 1.98(×3) | 4.16$^\dagger$  
2.44$^\ddagger$  
1.70 |
| Fe2  | 6c   | 0.5456, 0.4544, 0.4089 | -Fe1: 2.51, 2.64, 2.69  
-Fe2: 2.48(×2), 2.49(×2)  
-Fe3: 2.61(×2), 2.62(×2) | -C: 2.04(×2), (2.44(×2))  
-Fe1: 2.62  
-Fe2: 2.61(×2), 2.62(×2) | 4.46$^\dagger$  
2.05$^\ddagger$  
2.03 |
| Fe3  | 6c   | 0.1225, 0.8775, 0.5833 | -Fe1: 2.62  
-Fe2: 2.61(×2), 2.62(×2)  
-Fe3: 2.51(×2), 2.67(×4) | -C: 1.93, 2.00(×2)  
-Fe1: 1.98 | 4.01$^\dagger$  
2.51$^\ddagger$  
1.46 |
| C    | 6c   | 0.1866, 0.8134, 0.1886 | -Fe2: 2.04(×2), (2.44(×2))  
-Fe3: 1.93, 2.00(×2) | -Fe3: 1.93, 2.00(×2) | -0.12 |
| (c)  |      |                |                   |                                          |             |
| Fe1  | 4c   | 1/4, 0.6276, 0.0809 | -C1: 1.92  
-C2: 1.98(×2)  
-Fe2: 2.56(×2)  
-Fe3: 2.51, 2.53, 2.69  
-Fe4: 2.59(×2), 2.69(×2) | 4.06$^\dagger$  
2.55$^\ddagger$  
1.49 |
| Fe2  | 4c   | 1/4, 0.1988, 0.2927 | -C2: 1.99(×2)  
-Fe5: 2.50(×2) | -Fe5: 2.50(×2) | 4.18$^\dagger$  
2.36$^\ddagger$  
1.79 |

C. Electronic structure and magnetic properties of Fe$_3$C$_3$ phases

The partial and total density of states (DOS) for the two Fe$_3$C$_3$ phases and $\theta$-Fe$_3$C cementite are shown in Fig. 2. As shown in Fig. 2(a), the Fe 4s states have their density of states at around −7.5 to −6.5 eV and are mixed with the C 2p state. The Fe 4p states show no specific peaks. As a whole, the valence band is dominated by the Fe 3d states and
there are no significant contributions from Fe 4s, 4p states. Therefore, in Figs. 2(b) and 2(c), only the partial densities of states of the Fe 3d states are presented. Table III summarizes the characteristics of the electronic structures of the Fe₅C₃ phases and θ-Fe₅C. As shown in Fig. 2, the shapes of partial DOS of the Fe atoms in the Fe₅C₃ phases and θ-Fe₅C cementite are very similar. The calculations also show that the number of electrons in the 3d states in the Fe spheres are almost the same (about 6.5 electrons) for the Fe₅C₃ phases and θ-Fe₅C phase. This indicates that the Fe-Fe interactions are similar for the three phases. Figure 2 also shows the dispersion character of the semicore C 2s states. This indicates that although C 2s electrons belong to semicore states, they also contribute to valence interactions. A gap is present between the low-energy range (C 2s states) and the upper-energy range (C 2p and Fe 3d states). The C 2p states dominate the lower part of the valence band from the bottom (about −7.5 to about −4.3 eV). However, there are also some unoccupied C 2p states above the Fermi level as shown in Fig. 2. This indicates that the iron carbides are not completely ionic, considering the difference of their electronegativities (the Pauling scale, 1.83 for Fe vs. 2.55 for C). For the itinerant spin-polarized Fe 3d electrons, we integrate the occupied density of states in the Wigner-Seitz sphere of an atom, so that we can obtain the local magnetic moment in the sphere from the difference of the occupied spin-up (or majority) and spin-down (minority) densities of states. The local magnetic moment in a C sphere is about −0.12μB, originating from the hybridization between C 2p and Fe 3d states. There are apparent differences in the shapes of Fe 3d density of states as shown in Fig. 2. The corresponding local chemical environments are shown in Table II. For all the iron atoms, the Fermi level is at the top of the Fe 3d states for the spin-up electrons as shown in Fig. 2. Therefore, the Fe atoms are
almost fully spin polarized, in line with electronic structure of α-Fe.39,50,51

The local magnetic moments in the Fe spheres show small differences, 1.88 $\mu_B$ for Fe1 and 1.97 $\mu_B$ for Fe2 in α-Fe$_7$C$_3$, as shown in Table II. This corresponds with a similar local chemical bonding, as well as a similar local electronic structure Fig. 2. As shown in Table II, there are Fe atoms having small magnetic moments: 1.46 $\mu_B$ for Fe3 in the h-Fe$_7$C$_3$ and 1.49 $\mu_B$ for Fe1 in o-Fe$_7$C$_3$, originating from the Fe-C bonding. Table II shows that Fe atoms with short Fe-C bonds (about 1.93 Å) have a lower occupation of the spin-up 3d states (Fig. 2). Moreover, the Fe2 atom in h-Fe$_7$C$_3$ and the Fe5 atom in o-Fe$_7$C$_3$ have a local moment of about 2.0 $\mu_B$. Those types of Fe have long Fe-C bonds (>2.0 Å). These results agree with the general convention that strong Fe-C bonding can reduce the local magnetic moment of Fe atoms.

D. Formation of the Fe$_7$C$_3$ phases

The coordination numbers (CNs) for Fe atoms by other Fe atoms for the three structures in Table II are in the range between 11 and 12. These numbers are much larger than that in α-Fe (CN=8), but close to that in γ-Fe (CN=12). This can be understood from the fact that the Fe sublattices of the
**TABLE III. Characteristics of the electronic structures of the Fe$_7$C$_3$ phases and $\theta$-Fe$_7$C.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>$h$-Fe$_7$C$_3$</th>
<th>$o$-Fe$_7$C$_3$</th>
<th>$\theta$-Fe$_7$C</th>
<th>$\theta$-Fe$_7$C$^a$</th>
<th>$\theta$-Fe$_7$C$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandwidth of C 2s (eV) (range)</td>
<td>2.2 $\downarrow$</td>
<td>2.6 $\downarrow$</td>
<td>2.2 $\downarrow$</td>
<td>$\sim 2.3$ $\downarrow$</td>
<td></td>
</tr>
<tr>
<td>(−14.1 to −11.9) $\uparrow$</td>
<td>(−14.0 to −11.4) $\uparrow$</td>
<td>(−13.7 to −11.5) $\uparrow$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bandwidth of C 2p (eV) (range)</td>
<td>2.8 $\downarrow$</td>
<td>3.1 $\downarrow$</td>
<td>3.0 $\downarrow$</td>
<td>2.9 $\downarrow$</td>
<td>2.8 $\downarrow$</td>
</tr>
<tr>
<td>(−7.3 to −4.5) $\uparrow$</td>
<td>(−7.6 to −4.5) $\uparrow$</td>
<td>(−7.7 to −4.7) $\uparrow$</td>
<td>(−7.7 to −4.8) $\uparrow$</td>
<td>(−7.5 to −4.7) $\uparrow$</td>
<td></td>
</tr>
<tr>
<td>3.5 $\downarrow$</td>
<td>3.4 $\downarrow$</td>
<td>3.2 $\downarrow$</td>
<td>3.3 $\downarrow$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(−7.5 to −4.0) $\downarrow$</td>
<td>(−7.3 to −3.9) $\downarrow$</td>
<td>(−7.5 to −4.1) $\downarrow$</td>
<td>(−7.4 to −4.2) $\downarrow$</td>
<td>(−7.4 to −4.1) $\downarrow$</td>
<td></td>
</tr>
<tr>
<td>Bandwidth of Fe 3d (eV) (range)</td>
<td>4.6 $\downarrow$</td>
<td>4.4 $\downarrow$</td>
<td>4.5 $\downarrow$</td>
<td>4.5 $\downarrow$</td>
<td>$\sim 4.5 \uparrow$</td>
</tr>
<tr>
<td>(−4.6 to 0.0) $\uparrow$</td>
<td>(−4.4 to 0.0) $\uparrow$</td>
<td>(−4.5 to 0.0) $\uparrow$</td>
<td>(−4.5 to 0.0) $\uparrow$</td>
<td>(−4.5 to 0.0) $\uparrow$</td>
<td></td>
</tr>
<tr>
<td>6.0 $\downarrow$</td>
<td>5.6 $\downarrow$</td>
<td>6.3 $\downarrow$</td>
<td>6.0 $\downarrow$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(−3.7 to +2.3) $\downarrow$</td>
<td>(−3.3 to +2.3) $\downarrow$</td>
<td>(−3.6 to +2.7) $\downarrow$</td>
<td>(−3.4 to +2.6) $\downarrow$</td>
<td>(−3.5 to +2.6) $\downarrow$</td>
<td></td>
</tr>
<tr>
<td>DOS at $E_F$ states/eVFe</td>
<td>0.3 $\downarrow$</td>
<td>0.3 $\downarrow$</td>
<td>0.4 $\downarrow$</td>
<td>$\sim 0.4 \downarrow$</td>
<td></td>
</tr>
<tr>
<td>0.8 $\downarrow$</td>
<td>0.8 $\downarrow$</td>
<td>0.5 $\downarrow$</td>
<td>$\sim 0.5 \downarrow$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 47.  
$^b$Reference 48.

Fe$_7$C$_3$ structures, being similar to that of $\theta$-Fe$_7$C, are basically distorted closed packed structures (Fig. 1). Therefore, the Fe sublattices play a determining role in the structures of Fe$_7$C$_3$. In order to analyze this further, the Fe sublattices of the phases have been calculated for several configurations of Wyckoff site occupancies. The influence of magnetic ordering was taken into account as well.

As shown in Table II, there are four kinds of atoms in the $h$-Fe$_7$C$_3$. Fe1 atoms are positioned at $2b$, Fe2 and Fe3 at two sets of the 6c sites while C atoms are at 6c. In the lattice, the Wyckoff 2a sites are unoccupied. Therefore, we assumed several possible structural configurations including changes in chemical composition. For $o$-Fe$_7$C$_3$, there are seven kinds of atoms: five types of Fe atoms with three of them at three sets of 4c sites and two of them at two sets of 8d sites. Furthermore, two kinds of carbon atoms are positioned at 4c and 8d sites. Considering the Fe-Fe atomic environment, all the Fe atoms in the $o$ phase are strongly bonded to each other (Table II) and therefore we only consider possible carbon deficiency. Table IV lists the possible changes and arrangements of atoms for the orthorhombic Fe$_7$C$_3$ phase.

**TABLE IV. Calculated results (lattice parameters, formation enthalpies).** FM represents for the ferromagnetic ordering and FR for a ferrimagnetic ordering.

<table>
<thead>
<tr>
<th>Model</th>
<th>Atoms at Wyckoff sites</th>
<th>Formula/magnetism</th>
<th>Lattice (Å)</th>
<th>$\Delta E$ (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic, space group: $Pnma$ (nr. 62)</td>
<td>Fe: 4c, 4c, 8d</td>
<td>Fe$_7$C$_3$/FM</td>
<td>$a=6.8570$ b = 11.7324 c = 4.5183</td>
<td>22.0</td>
</tr>
<tr>
<td>Model a</td>
<td>C: 4c, 8d</td>
<td>Fe$_7$C$_3$/FM</td>
<td>$a=6.9491$ b = 11.7883 c = 4.3340</td>
<td>74.8</td>
</tr>
<tr>
<td>Model b</td>
<td>Fe: 4c, 4c, 8d</td>
<td>Fe$_7$C$_2$</td>
<td>$a=6.9491$ b = 11.7883 c = 4.3340</td>
<td>74.8</td>
</tr>
<tr>
<td>Model c</td>
<td>C: 8d</td>
<td>Fe$_7$C$_1$</td>
<td>$a=6.8453$ b = 11.9606 c = 4.2168</td>
<td>161.6</td>
</tr>
<tr>
<td>Model d</td>
<td>Fe: 4c, 4c, 8d</td>
<td>Fe$_7$C$_0$</td>
<td>$a=7.0824$ b = 11.8679 c = 4.0630</td>
<td>226.0</td>
</tr>
</tbody>
</table>

| Hexagonal, space group $P6_3mc$ (186) | Fe: 2b, 6c, 6c | Fe$_7$C$_3$/FM | $a=6.8243$ c = 4.4939 | 38.9 |
| Model 1 | C: 6c | Fe$_7$C$_3$/FM | $a=7.1129$ c = 4.3340 | 318.2 |
| Model 2 | Fe: 6c, 6c | Fe$_7$C$_3$/FM | $a=6.5548$ c = 4.5332 | 196.2 |
| Model 3 | C: 6c | Fe$_7$C$_3$/FM | $a=7.0483$ c = 4.7518 | 400.5 |
| Model 4 | Fe: 2b, 6c, 6c | Fe$_7$C$_3$/FM | $a=6.4897$ c = 4.0691 | 329.5 |
Table IV shows that the pure Fe sublattices in \( \text{o-Fe}_7\text{C}_3 \) are more stable than those in the \( \text{h-Fe}_7\text{C}_3 \). Moreover, the \( \text{o-Fe}_7\text{C}_3 \) has a formation enthalpy of just 74.8 meV/atom relative to that of the elemental solids. In other words, the formation of a carbon vacancy has a low energetic cost of 0.45 eV. These results indicate that the \( \text{o-Fe}_7\text{C}_3 \) may exhibit C deficiency. In contrast, the Fe sublattices in the \( \text{h-Fe}_7\text{C}_3 \) structure are less stable than those of \( \text{o} \) phase and the carbon atoms play a crucial role in the stabilization of the hexagonal structure, particular in nonstoichiometric environments.

Experimental observations revealed that in steels, the \( \text{o} \)-form phase occurs more frequently than the \( \text{h} \) phase\( ^{30} \) and that there are a number of polytypes of \( \text{Fe}_7\text{C}_3 \).\( ^{27} \) The formation of polytypes originates from twinning or antiphase ordering of \( \text{Fe}_7\text{C}_3 \).\( ^{27} \) The formation of amorphous alloys\( ^{1–3} \) and carburization of iron.\( ^{9–13} \) It is well known that complex processes such as nucleation and growth of a carbide in amorphous alloys, carburization, and precipitation in steels depend on many factors, such as chemical composition, thermal history, temperature, and interface interactions with the other phases. Our calculations show that the \( \text{o-Fe}_7\text{C}_3 \) has a more stable Fe sublattice and may contain carbon (vacancy) defects. Therefore the stability of \( \text{o-Fe}_7\text{C}_3 \) is not strongly dependent on the carbon content in steels and the nucleation of \( \text{o-Fe}_7\text{C}_3 \) in steels is easier than that of the \( \text{h} \) form. In general, \( \text{o-Fe}_7\text{C}_3 \) is formed in residual austenite with stacking faults. The cavities of the Fe sublattices in the \( \text{o} \) phase will then trap carbon atoms from the environment. Moreover, as pointed out by several authors, order and disorder defects cause the polytypism of \( \text{Fe}_7\text{C}_3 \).\( ^{27} \) On the other hand, it has been reported that carburization of ferrite will produce mainly nanosized particles of \( \text{h-Fe}_7\text{C}_3 \) from chemically produced C clusters.\( ^{9–13} \) For the nanocrystals obtained by methods such as carburization of iron, the defects causing the formation of different \( \text{Fe}_7\text{C}_3 \) lattices may not be observed by methods such as x-ray diffraction. Audier and co-workers obtained microcrystals of \( \text{o-Fe}_7\text{C}_3 \) by disproportioning CO on Fe at 500 °C,\( ^{14} \) suggesting that the \( \text{h} \) phase transformed into the \( \text{o} \) phase (through stacking fault generation) as the nanoparticles increase in size.

IV. CONCLUSIONS

Total energy and electronic structure calculations were performed for the two basic lattices of \( \text{Fe}_7\text{C}_3 \) and for \( \text{h-Fe}_7\text{C}_3 \) cementite, the most common carbide in steels. Total energy calculations show that the \( \text{Fe}_7\text{C}_3 \) phases are slightly less stable that \( \text{h-Fe}_7\text{C}_3 \), in agreement with experimental observations. Moreover, \( \text{o-Fe}_7\text{C}_3 \) is preferred to the \( \text{h} \) form at \( T = 0 \) K and \( p = 0 \) Pa, in contrast to recent semiempirical atomic calculations.\( ^{28} \) Both forms of \( \text{Fe}_7\text{C}_3 \) exhibit ferromagnetic ordering. All the Fe atoms are at a high-spin state. The Fe atoms with a short Fe-C bond (\( < 1.95 \) Å) have smaller local magnetic moments. The calculations also show that the Fe sublattices in the \( \text{o-Fe}_7\text{C}_3 \) structure exhibit higher stability than the Fe sublattice in the \( \text{h} \) form. Furthermore, a surprisingly low-energy cost was found for carbon-vacancy formation in \( \text{o-Fe}_7\text{C}_3 \) lattices. The more diverse structure and low carbon-vacancy energy likely enhance the formation of \( \text{o-Fe}_7\text{C}_3 \) in steels.

ACKNOWLEDGMENTS

We appreciate kind help and discussions with M. H. F. Sluiter (Delft University of Technology). D. Hanlon and S. Celotto (Corus RDT) are acknowledged for useful discussion. The authors acknowledge financial support from the Materials Innovation Institute (M2i), Project No. MC5.06280, and from the Stichting Techniek en Wetenschap (STW), Project No. 07532, The Netherlands.
265 (1968).