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A first-principles study of cementite (Fe_3C) and its alloyed counterparts: Structural properties, stability, and electronic structure

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Abstract

As a part of our systematic study, the total energies and equilibrium cohesive properties of carbides with the structure of cementite (Fe_3C), and its alloyed counterparts (Fe_2MC , FeM_2C and M_3C with $\text{M}=\text{Al}$, Co , Cr , Cu , Fe , Hf , Mn , Mo , Nb , Ni , Si , Ta , Ti , V , W and Zr) are calculated employing electronic density-functional theory (DFT), all-electron PAW pseudopotentials and the generalized gradient approximation for the exchange-correlation energy. In this study, following properties are calculated: (i) Unit cell-internal and external parameters of binary and ternary cementites, (ii) Equation of state (EOS) parameters defining a few material constants, (iii) Zero-temperature heat of formation of binary and ternary cementites, (iv) Ground-state structure of Mn_3C , and (v) Electronic structure and selected magnetic properties. The bonding between M and C in M_3C is discussed based on analyses of calculated density of states and charge densities.

Key words: Ab initio phase stability; Cementite; Equation of state; Density of states; Electronic structure; Magnetic property

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1 Introduction

It is well known that cementite (Fe_3C) is a metastable phase in the binary Fe-C system. Notwithstanding its metastability, cementite is ubiquitous in low-, medium- and high-carbon steels. It is well established that the morphology and kinetics of cementite precipitates have a tremendous influence on the mechanical properties of steels. Historically, these factors have been manipulated by adding one or more alloying elements in steels to obtain desired microstructures, and hence properties.

In multicomponent steels, the precipitation of cementite (M_3C , where M represents substitutional elements and C is carbon) may take place in two extreme thermodynamic conditions: (i) orthoequilibrium, and (ii) paraequilibrium [1–3], representing corresponding kinetic behaviors. For example, in Fe-Cr-C alloys under orthoequilibrium regime cementite may dissolve up to its solubility limit of about 20 at.% Cr [4], while in ternary or higher orders alloys under paraequilibrium regime cementite may dissolve all substitutional alloying elements in amounts well beyond the equilibrium solubility limits. To predict and understand these behaviors, in conjunction with thermodynamic and kinetic softwares such as Thermo-Calc [5] and DICTRA [6], relevant properties of phases are needed [2,3]. The paucity of thermodynamic data, even in commercial databases, has been underscored by Miyamoto et al [7] while attempting to model the kinetics of cementite precipitation in multi-component alloys.

Lately, the Materials Genome Initiative (MGI) [8] and genomic approaches to materials design and discovery [9–14] have been advocated. Intrinsic to MGI and relevant approaches is the extensive usage of first-principles (quantum mechanics) calculations leading to the development of multi-component, multi-phase databases within CALPHAD formalism [15] to facilitate Integrated Computational Materials Engineering (ICME). Many important issues relevant to both MGI and ICME, especially first-principles calculations and their integration within CALPHAD formalism, were also underscored in our previous publication [16], but in the context of modeling phase stability of multi-component, multi-phase systems.

Usually, diffusion-controlled transformations lead to partitioning of alloying elements between phases but the martensitic transformation is a composition invariant transformation and it is driven by chemical forces. Hence, it is crucial to quantify the magnitude of driving force to model and predict martensitic transformation kinetics. In this context, a highly successful example is the development of **kMART**¹ (*k*inetics of **MAR**tensitic Transformation) database [17,18] that integrates solution thermodynamics within CALPHAD formalism and empirical modeling (temperature and composition dependence) of elastic properties [19] to assist the design of secondary hardening ultrahigh strength steels, an effort initiated by the Steel Research Group [9,20] at Northwestern University.¹

Notwithstanding the technological importance of steels containing cementite as one of the phases, until recently relatively little effort has been made to measure thermodynamic and elastic properties. Perhaps due to experimental difficulties, conventional reaction calorimetry has not been carried out to measure thermodynamic properties of Fe_3C . In 1972, Chipman [21] presented his assessment of free energy of formation of Fe_3C based on all data, as well as other assessments, available at the time. Subsequently, thermodynamic properties of Fe_3C were assessed and/or calculated by others [22–25]. In particular, Dick et al [25] calculated the free energy of formation of Fe_3C from first-principles that includes electronic, magnetic and vibrational excitations.

Besides thermodynamic properties, there have been several reports on hardness and isotropic (polycrystalline) elastic moduli of cementite [26–38]. Umemoto and co-workers [32,36] reported the effect of V, Cr, Mo and Mn on hardness and polycrystalline elastic moduli of Fe_3C .

The crystal structure of cementite, Fe_3C , is well established. It is orthorhombic with the space group $Pnma$ (no. 62). The Wyckoff positions of atoms are: C at $4c$ ($x_1, 0.25, z_1$); Fe^I at $4c$ ($x_2, 0.25, z_2$); Fe^{II} at $8d$ (x_3, y_3, z_3).

¹ The **kMART** database and its predecessors named MART, MART1, MART2, MART3, MART4, MART5 and mart.GG are unpublished and intellectual properties of one of us (GG) [18].

Also, it is well known that Fe_3C is metallic and ferromagnetic with a Curie temperature around 488 K.

Due to experimental difficulties in synthesizing single-phase cementite, attempts have been made to calculate structural properties using first-principles methods [25,39–42,44–48,50,24]. To the best of our knowledge, virtually all first-principles calculations have been carried out only for Fe_3C , and only a few attempts have been to investigate the stability of ternary cementite using first-principles methods. For example, Jang et al [48] studied the effect of Si on the stability of Fe_3C . To bridge the current knowledge gap associated with the multicomponent nature of real alloys, we have undertaken a systematic study of M_3Cs ($\text{M}=\text{Al}, \text{Co}, \text{Cr}, \text{Cu}, \text{Fe}, \text{Hf}, \text{Mn}, \text{Mo}, \text{Nb}, \text{Ni}, \text{Si}, \text{Ta}, \text{Ti}, \text{V}, \text{W}$ and Zr).

The substitutional alloying elements, M , are chosen to represent a wide variety of commercial alloys. Among these, only Fe_3C [21] and Mn_3C [51] with the structure of cementite (sp. gr. $Pnma$ (no. 62)) are present in respective binary phase diagrams, others from carbides having stoichiometry and crystal structure different from Fe_3C . However, elements, M , may dissolve, to a greater or lesser extent in Fe_3C , depending on the heat treatment of steels. An extreme case being the paraequilibrium transformation [1–3]. In this study, we report the effect of substitutional alloying element, M , on the zero-temperature stability of the virtual phase M_3C . The knowledge of energy landscape (enabled by computations) of M_3Cs is essential for mathematical modeling within CALPHAD formalism [15] for predictive modeling to facilitate design and processing of engineering alloys.

Like previous works on first-principles calculations of Fe_3C , here, we assume that M_3Cs are stoichiometric. However, a recent experimental study [52] of Fe_3C using pulsed-laser atom probe tomography reveals (APT) that Fe_3C has C-content several at.% (up to 8) higher than the stoichiometric value. At the same time, authors concluded that the origin of a large deviation from the stoichiometric value is unknown, and it is an open issue. Only three years later, Kitaguchi et al [53] reported that the apparent C-content in cementite, also using pulsed-laser APT, is 25.0 ± 1 at.%. They also concluded that there is no clear dependency on the cryogenic temperature or the laser pulse frequency on the measured carbon content. The latter C-content is close to the composition of M_3Cs used in this study.

This issue of non-stoichiometric Fe_3C has been investigated by the first-principles technique by Jiang et al [54]. Specifically, they calculated total energy of both C-rich and C-depleted Fe_3C using 128-atom supercell, and found that stoichiometric Fe_3C corresponds to the minimum energy configuration.

This paper is organized as follows. Section 2 describes the computational methodology employed in the current study. Section 3 presents the comparison of calculated equilibrium structural and cohesive properties of pure elements and M_3Cs in this study. These properties include equation of state parameters, lattice parameters, cell-internal degrees of freedom for atomic positions, and the zero temperature formation energies. This information is important, since they may be useful for comparison with future measurements using diffraction and other experimental techniques, and also may be used as input into future first-principles calculations which will reduce the computation time significantly. Section 4 presents zero-temperature heat of formation, selected magnetic properties, the electronic structure and nature of bonding in M_3C . Finally, Section 5 provides a summary of the findings of the present study.

2 Computational methodology

2.1 *Ab initio* total energy calculations

Over the past twenty years significant efforts have been devoted to developing computationally efficient approaches for calculating the properties of solids within the predictive framework of electronic density-functional theory (DFT, see, e.g., [57,58] and references therein).

All calculations presented here are based on the *ab initio* total-energy code, VASP (Vienna *ab initio* simulation package) [59–61], using pseudopotentials constructed by projector-augmented wave (PAW) method [62]

which retains the all-electron character. In the PAW method, a plane wave basis set is used to express auxiliary description of the electron density that is transformed into full density by projectors that add the effect of local atomic density. In practice, this loosely corresponds to a frozen-core approximation with a plane wave expansion of the valence electrons. The frozen-core approximation is not strictly necessary, and in fact, very recently a relaxed core PAW method has been proposed [63] that is shown to yield results with an accuracy comparable to the FP-LAPW (full potential-linearized augmented plane wave) method [64]. The PAW method includes non-linear core correction, accounts for core-core overlap, and is free of any shape approximation for both charge density and electronic potential. Therefore, PAW pseudopotentials are an improvement over Vanderbilt-type ultra-soft pseudopotential (USPP) [65].

We have used an expansion of the electronic wavefunctions in plane waves with a kinetic-energy cutoff of 500 eV, which is at least 30% more than the recommended default values. The PAWs employed in this work explicitly treat three ($_{13}\text{Al}$: $[\text{Ne}] 3s^2 3p^1$), four ($_{6}\text{C}$: $[\text{He}] 2s^2 2p^2$, $_{14}\text{Si}$: $[\text{Ne}] 3s^2 3p^2$, $_{22}\text{Ti}$: $[\text{Ar}] 3d^3 4s^1$, $_{40}\text{Zr}$: $[\text{Kr}] 4d^3 5s^1$, $_{72}\text{Hf}$: $[\text{Xe}] 5d^2 6s^2$), five ($_{23}\text{V}$: $[\text{Ar}] 3d^4 4s^1$, $_{73}\text{Ta}$: $[\text{Xe}] 5d^3 6s^2$), six ($_{24}\text{Cr}$: $[\text{Ar}] 3d^3 4s^1$, $_{42}\text{Mo}$: $[\text{Kr}] 4d^5 5s^1$, $_{74}\text{W}$: $[\text{Xe}] 5d^5 6s^1$), seven ($_{25}\text{Mn}$: $[\text{Ar}] 3d^5 4s^2$), eight ($_{26}\text{Fe}$: $[\text{Ar}] 3d^7 4s^1$), nine ($_{27}\text{Co}$: $[\text{Ar}] 3d^8 4s^1$), ten ($_{28}\text{Ni}$: $[\text{Ar}] 3d^{10}$) and eleven ($_{29}\text{Cu}$: $[\text{Ar}] 3d^{10} 4s^1$, $_{41}\text{Nb}$: $[\text{Kr}] 4p^6 4d^4 5s^1$) valence electrons to describe electron-ion interactions. In the case of Nb, a pseudopotential that includes semi-core $4p$ states as valence was used. Due to the importance of magnetism, relevant calculations for cementite containing Co, Cr, Fe, Mn or Ni were done employing spin polarized Hamiltonian; otherwise, non-spin-polarized Hamiltonian was employed. Nevertheless, in all calculations we have used generalized gradient approximation (GGA) for the exchange-correlation functional due to Perdew and Wang [66] with the Vosko-Wilk-Nussair [67] interpolation of the correlation energy. Brillouin-zone integrations were performed using Monkhorst-Pack [68] $\mathbf{k}$ -point meshes, and the Methfessel-Paxton [69] technique with the smearing parameter of 0.1 eV.

At first, extensive tests were carried out using different $\mathbf{k}$ -point meshes to ensure absolute convergence of the total energies of M and M_3C to within a precision of better than 1.0 meV/atom (≈ 0.1 kJ/mole). This is important because the axial ratio changes appreciably from one M_3C to another (see, Table 3). Based on preliminary tests, the $\mathbf{k}$ -point meshes chosen in our final calculations are listed in Table 1. Corresponding $\mathbf{k}$ -points in the irreducible Brillouin zone are also listed in Table 1. All calculations are performed using the precision setting "high" within VASP. With the chosen kinetic energy cut-off and $\mathbf{k}$ -point sampling, the total energy was converged numerically to less than 5×10^{-6} eV/atom with respect to electronic, ionic and unit cell degrees of freedom, the latter two relaxed using Hellman-Feynman forces with a preconditioned conjugate gradient algorithm. After structural optimization, Hellman-Feynman forces (when applicable) were less than 4 meV/Å and stresses in the unit cell were less than 0.35 kilo Bar in magnitude. With the chosen plane-wave cutoff and $\mathbf{k}$ -point sampling the reported formation energies are estimated to be converged to a precision of better than 2 meV/atom (≈ 0.2 kJ/mole).

Phase equilibria in the Mn-C system was established by Benz and co-workers [51], and it has been accepted in a recent CALPHAD modeling [55]. Among other Mn-C carbides, Mn_3C (having the structure of Fe_3C) is stable at high temperature (between 971 and 1052°C [51]), and its magnetic structure is not known. As a part of this systematic study, we have investigated the magnetic structure of Mn_3C using VASP and BGFM (Bulk Green's Function Method [70,71] codes. Specifically, we have calculated total energy of Mn_3C as a function of magnetic structure of Mn, as the latter is known to exhibit a rather complicated magnetic structures [56]. Magnetic moment calculations of magnetically disordered Mn_3C have been performed by means of Bulk Green's Function Method which is an implementation of the KKR-ASA Greens function technique [70,71] using an spd basis set and including the core electrons in the LDA self-consistency loop. The coherent potential approximation (CPA) [72] has been employed for modeling the disordered magnetic state within the disordered local moment (DLM) model [73,74].

2.2 Equation of state and formation energy

The zero-temperature equation of state (EOS) defines pressure-volume relationship. We have used the EOS due to Vinet et al [75] who assumed the interatomic interaction-versus-distance relation in solids can be expressed in terms of a relatively few material constants. In the EOS of Vinet et al [75] the pressure P is expressed in terms of bulk modulus (B_o), its pressure derivative (B'_o) and a scaled quantity (x):

$$P = 3B_o x^{-2}(1-x) \exp[\chi(1-x)] \quad (1)$$

with $x = (V/V_o)^{1/3}$ and $\chi = 3/2(B'_o - 1)$, where V_o is the equilibrium volume. Based on Eq. (1) and the relations between pressure and energy, the total energy (E) and volume-dependence of the bulk modulus can be expressed as

$$E(V) - E(V_o) = \frac{9B_o V_o}{\chi^2} \{1 - [\chi(1-x)]\} \exp[\chi(1-x)] \quad (2)$$

$$\frac{B(V)}{B_o} = x^{-2} [1 + (\chi x + 1)(1-x)] \exp[\chi(1-x)] \quad (3)$$

A common practice is to calculate total energy of the phase of interest as a function of volume. Then, the energy-volume relationship defines equilibrium energy ($E(V_o)$), the equilibrium volume (V_o), and the bulk modulus (B_o) as defined in the EOS (e.g., Eq. (2)). As an example, Fig. 1 shows the calculated energy-volume relationship of Fe_3C . The lattice parameters, a , b and c of cementite at the equilibrium volume are calculated by VASP by optimizing inter-atomic forces and stresses in the unit cell. It is to be noted that (Eq. (2) is valid for anisotropic solids like Fe_3C .

The zero temperature formation energy (per atom) of a binary M_3C is evaluated relative to the composition-averaged energies of the pure elements in their ground state structure:

$$\Delta E_f^\phi(\text{M}_3\text{C}) = E_{\text{M}_3\text{C}}^\phi - [0.75E_M^\theta + 0.25E_C^\psi] \quad (4)$$

where $E_{\text{M}_3\text{C}}^\phi$ is the total energy (per atom) of M_3C with the structure of cementite (ϕ), E_M^θ and E_C^ψ are the total energy (per atom) of M having bcc or cI2 (Cr, Fe, Mo, Nb, Ta, V, W), fcc or cF4 (Al, Cu, Ni), hcp of hP2 (Co, Ti, Hf, Zr), diamond cubic or cF8 (Si), complex cubic or cI58 (α -Mn) structure (θ), and graphite or hP4 (C) structure (ψ), respectively. Similarly, the zero temperature formation energy of a ternary cementite, $(\text{Fe,M})_3\text{C}$, may also be defined.

3 Results

3.1 Cohesive properties of pure elements M ($=\text{Al, Co, Cr, Cu, Fe, Hf, Mn, Mo, Nb, Ni, Si, Ta, Ti, V, W}$ and Zr) and C

The total energies of substitutional elements M and C, in their respective ground state structures are calculated as a function of volume. The resulting EOS and lattice parameters are presented in Table 2. In previous publications we compared the calculated cohesive properties of Al, Cu, Hf, Ti and Zr [76,77], and the calculated cohesive properties of Ni were presented in a separate publication [78]. While our previous studies made use of USPP pseudopotentials, a detailed comparison of calculated cohesive properties using PAW pseudopotentials and experimental data shows that lattice parameters agree to within 1-2%, B_o agree to within $\pm 5\%$, and B'_o agree to within 0.5-1.0 [79]. It has been pointed out that depending on the measurement technique, ultrasonic resonance, versus the initial slope of the locus of Hugoniot states in shock-velocity particle-

velocity coordinates, the value of B'_o may differ even though ideally they should be the same [79]. In fact, it is not uncommon that the B'_o predicted by ab initio techniques differs from the experimental value by as much as 30%.

Graphite has a layered structure with strong carbon bonds in the basal plane and weak van der Waals-type forces in the perpendicular direction. Table 2 shows that the calculated basal-plane parameter (a) of graphite agrees fairly well with experiments and previous reports [80,81,83], but its lattice parameter perpendicular to the basal plane (c) is overestimated by about 20%. The shortcomings of standard exchange-correlation functionals such as LDA and GGA in treating van der Waals-type forces within electronic DFT have been discussed elsewhere [82–84].

Recently, various GGA functionals have been tested for the predicted lattice parameters of pure elements [85]. The authors report that calculated and experimental lattice parameters may differ by 3 to 5%. Considering this global trend, our observation that calculated lattice parameters of Fe_3C agree within $\pm 1\%$ is certainly reasonable, and our calculations are reliable.

3.2 Phase stability and cohesive properties of M_3C

The EOS parameters of binary M_3Cs are summarized in Table 3. Experimentally, the EOS parameters have been determined only for Fe_3C using diamond-and-anvil apparatus [34,86–89]. Furthermore, previous computational studies employing FP-LAPW [42,48] and CASTEP [46] codes also reported EOS parameters of Fe_3C . In general, our B_o is higher than experimental values which could be due to the fact that experiments were conducted at room temperature or higher while calculated results correspond to 0 K. Nevertheless, our calculated B_o of Fe_3C shows a good agreement with other calculated results using both FP-LAPW and CASTEP codes. Also, our B'_o value is in reasonably good agreement with experimental data.

As seen in Table 3, the calculated B_o (at zero K) of Fe_3C is higher than most experimental data obtained at or near room temperature. An increase in bulk modulus with decreasing temperature is consistent with first-principles calculations [90] at finite temperatures.

The EOS parameters along with zero-temperature phase stability of binary M_3Cs , defined by the energy of formation (without zero-point energy), ΔE_f in Eq. 1 is also listed in Table 3. It is to be noted that ΔE_f values are negative for Cr, Hf, Nb, Ta, Ti, V and Zr. While these M-C systems are well known carbide formers, none of the equilibrium phase diagrams exhibits M_3C phase with the structure of cementite. At the same time, Fe_3C is a well known metastable phase in the Fe-C system. Ab initio calculation of Fe_3C yields a positive energy of formation. Specifically, our calculated ΔE_f value of Fe_3C is about 4.7 kJ/mol-atom while the assessed value reported by Gustafson [22] and Hallstedt et al [23] is about 27 kJ/mol-atom. FP-LAPW calculations by Jang et al [48] reports ΔE_f of Fe_3C to be about 21.5 kJ/mol-atom, while VASP calculations by Miyamoto et al [7] reports the same to be about 18.8 kJ/mol-atom.

Hallstedt et al [23] noted that due to various uncertainties the assessed ΔH_f of Fe_3C may differ by as much as 20 kJ/mol-atom. Furthermore, their assessment of thermodynamic properties [23] of Fe_3C show that the ΔE_f of Fe_3C is positive even at temperatures below 1250°C, while the first-principles calculations by Dick et al [25] show that its free energy of formation becomes negative only above 700°C. Based on first-principles calculations, Fang et al [24] also concluded that Fe_3C (with ΔE_f of about 24.2 kJ/mol-atom) is metastable relative to α -Fe and graphite, and contributions due to lattice vibrations and anomalous Curie-Weiss magnetic ordering are responsible for its predominance at high temperatures.

Like our calculations, Miyamoto et al [7] reported that energies of formation of Al_3C , Co_3C , Ni_3C , and Si_3C are positive. Djurovic et al [55] also calculated the heat of formation of Mn_3C from first-principles, and reported a value of -9.9 kJ/mol-atom, but with respect to diamond instead of graphite. Nevertheless, our calculated value of -6.65 kJ/mol-atom (ΔE_f of Mn_3C) agrees fairly well.

Comparing lattice parameters, we find that the calculated values for Cr_3C , Fe_3C and Mn_3C agree to within

$\pm 1.5\%$ of experimental values [32,91–95]. Furthermore, our calculated lattice parameters of Fe_3C agree to within $\pm 1\%$ of FP-LAPW values [42,48].

Analogous to binary cementites, the EOS of ternary cementites is also computed. However, as mentioned earlier, there are two metal sites I (at $4c$) II (at $8d$) in the unit cell, and we have calculated total energy of ternary cementites by substituting Fe with M in the unit cell of Fe_3C . These are designated as FeM_2C and Fe_2MC , respectively, in Table 4. In addition, the ΔE_f values of binary and ternary cementites presented in Table 3 and 4 may be used to define ternary interaction parameter(s) (or L-paramaters) to develop a database describing phase stability of multicomponent cementite in Thermo-Calc software [5]. Table 4 also shows that the substitution of Fe with M (either at site I or site II) decreases the magnetic moment (per cell) of alloyed M_3C .

Optimized unit-cell-internal parameters in binary cementites are listed in Table 5. We note a good agreement between calculated and measured (where available) Wyckoff positions listed in Table 5: agreement to within two significant figures is obtained for all non-symmetry-constrained Wyckoff positions between our calculations and reported experimental data. Optimized unit-cell-internal parameters in ternary cementites are listed in Table 6.

As mentioned in Section 2, experimentally the magnetic structure of Mn_3C is not known. Therefore, we have carried out a systematic study of total energy of Mn_3C as a function of its assumed magnetic states. This is important because, Hobbs et al [56] has shown that the magnetic structure of $\alpha\text{-Mn}$ can be very complex. In this study, total energy of Mn_3C is calculated with the assumption of its non-magnetic, ferromagnetic and non-collinear anti-ferromagnetic structures (nc-AFM). Furthermore, in the nc-AFM case additional assumption is made about the magnetization direction: [001], [011] and [111]. We find that the total energy corresponding to non-magnetic ferro magnetic states differ by only 0.12 mJ/mol-atom. Among the nc-AFM states considered, we find that the magnetization direction [001] yields lowest energy, thus we consider it to be the ground state. Furthermore, comparing total energies for [001], [011] and [111] magnetization directions, we find that the latter two are more positive by 18 and 17.9 mJ/mol-atom compred to that of [001] magnetization. To the best of our knowledge, this is the first attempt to search ground state structure of Mn_3C . Fully optimized geometry of Mn_3C is listed in Table 7.

4 Discussions

4.1 Density of states and electronic structure

In the following, we present both total and partial density of states (DOS) of several M_3Cs . For calculating partial DOSs and on-site magnetic moments we have used following values of Wigner-Seitz radii: $R_{WS}^C = 0.918$, $R_{WS}^{Co} = 1.386$ Å for Co_3C , $R_{WS}^C = 0.923$, $R_{WS}^{Cr} = 1.414$ Å for Cr_3C , $R_{WS}^C = 0.928$, $R_{WS}^{Fe} = 1.401$ Å for Fe_3C , $R_{WS}^C = 0.918$, $R_{WS}^{Mn} = 1.401$ Å for Mn_3C , and $R_{WS}^C = 0.937$, $R_{WS}^{Ni} = 1.397$ Å for Ni_3C . Furthermore, we have used the same Wigner-Seitz radius for all similar atoms in any M_3C . Our values of R_{WS} for Fe_3C are similar to those reported by others [42,48].

Electronic DOS of Fe_3C has been reported by Häglund et al [39], Chiou and Carter [40], Faraoun et al [42], and Jang et al [48]. Calculated total and partial DOSs are shown in Fig. 2, where the latter are computed using projections into site-centered C and Fe muffin-tin spheres mentioned above. The absence of band gap and the asymmetric nature of DOSs are consistent with metallic and ferromagnetic character of Fe_3C , respectively. Specifically, the ferromagnetic behavior is thought to originate from the asymmetry of up and down DOSs in upper valence band near the Fermi level [42].

Partial DOSs in Fig. 2, it may be noticed that Fe s and p states give only small contribution, and as expected the DOS is dominated by $3d$ states. We also find that in the region of valence band, about 4 to 7.6 eV below Fermi level, C p states are hybridized with Fe d states. In the unoccupied conduction band, delocalized Fe d

states are seen and its p and s contributions, once again, are negligibly small. By analyzing DOS of pure Fe and Fe_3C , Chiou and Carter [40] suggested the possibility of charge transfer from Fe to C, and also the polar covalent nature of Fe-C interaction.

We have calculated the total and bonding charge densities of Fe_3C . The latter, also called the deformation charge density, is defined as the difference (point-by-point, in space α , using identical FFT grid) between the self-consistent charge density ($\rho_{\text{solid}}(r)$) of the intermetallic (M_3C) and a reference charge density (ρ_α) constructed from the superposition of non-interacting atomic charge density (M and C) at the crystal sites. The bonding charge density ($\Delta\rho(r)$) is defined as [43]

$$\Delta\rho(r) = \rho_{\text{solid}}(r) - \sum_{\alpha} \rho_{\alpha}(r - r_{\alpha}) \quad (5)$$

It has been pointed out that the total charge density ($\rho_{\text{solid}}(r)$) reveals the distribution of interstitial and core charge; however, $\Delta\rho(r)$ provides a better picture of charge transfer and formation of directional bonding due to hybridization [43].

Figure 3 shows both (a) total and (b) bonding charge density of Fe_3C in the (001) plane. In Fig. 3(a) several Fe-Fe and C-Fe are the nearest neighbor distances are given. In Fig. 3(b), a significant charge redistribution leading to its accumulation in the interstitial region as well as in the proximity of C site between two Fe^I atoms may be seen. Combining angular momentum resolved DOS and the bonding charge density plot along with the results of Chiou and Carter [40], it may be concluded that the mechanisms of cohesion is governed by the combination of metallic bonding, the short-range band mixing between C- p and Fe- d states along with the long-range charge transfer (electrostatic) effect.

While DOS of Fe_3C has been reported in literature as mentioned above, we have also calculated total and partial DOS of Co_3C , and they are shown in Fig. 4. It is interesting to note that all important features in DOS of Co_3C are quite similar to that of Fe_3C shown in Fig. 2. It is reasonable to expect that the mechanisms of cohesion in Co_3C are also very similar to those in Fe_3C .

The total magnetic moment of Fe_3C and Co_3C are calculated to be 22.028 and 12 μ_B /unit-cell, respectively (or, 1.8356 μ_B /Fe-atom and 1.0 μ_B /Co-atom). DOS calculations suggest magnetic moments are contributed primarily, as expected, by Fe and Co 3d states. Using muffin-tin radii mentioned above, calculated spd contributions to on-site magnetic moments are summarized in Table 7. In the case of Fe_3C , the calculated on-site magnetic moments of Fe at 4c and 8d sites are 1.973 and 1.891 μ_B per Fe-atom, respectively, while in the case of Co_3C , the corresponding values of Co are 0.979 and 1.083 μ_B . Experimental data of site-resolved magnetic moments of Fe in Fe_3C is not available. Carbon on the other hand, in both Fe_3C and Co_3C , carries a negative magnetic moment -0.462 and -0.22 μ_B , respectively, primarily contributed by its p state as may be seen in corresponding partial DOS plots (up-spin contribution is smaller than down-spin contribution). In both Fe_3C and Co_3C , there is a small magnetic moment associated with the interstitial region as 3d states overflow from muffin-tin spheres. In Table 7, it is to be noted that on-site magnetic moments of Fe in Fe_3C , calculated by VASP-PAW (this study and Dick et al [25]) and those using FP-LAPW methods (Faraoun et al [42] and Jiang et al [48]) agree very well. Some minor disagreements between different studies are associated with uncertainties in defining the muffin-tin radii.

Figure 5 shows both (a) total and (b) bonding charge density of Co_3C in the (010) plane. In Fig. 5(a), several Co-Co and C-Co are the nearest neighbor distances are given. In Fig. 5(b), a significant redistribution of bonding charges lead to its accumulation in the interstitial region as well as in the proximity of C site between two Co^I atoms. Comparing Fig. 3 and Fig. 5, we conclude that essential features of bonding charge distribution in Fe_3C and Co_3C are every similar.

Figure 6 shows the unit-cell of Mn_3C , plotted using VESTA3 software [49] and based on the optimized geometry listed in Table 7. Total and partial DOS of Mn_3C , and they are shown in Fig. 7. To the best of our

knowledge, this is the first attempt to calculate and show DOS in the ground state structure of Mn_3C .

As we have already mentioned earlier, Mn_3C is one of two studied carbides with cementite structure present in existing binary phase diagrams (Fe-C and Mn-C). However, unlike Fe_3C , Mn_3C is stable only in the high temperature region between 1223 and 1323 K [51] and our results at 0 K show that Mn_3C has a negligibly small magnetic moment. However, this virtually non-magnetic state appears to be rather unstable as we have found that the system undergoes a so-called high-to-low spin state transition (see Fig. 8). Our results show that as the volume increases from its 0K equilibrium value the system undergoes a transition from a low-spin state with zero magnetic moments to a high-spin state with non-zero magnetic moments of both Mn sub-lattices.

In the case of Mn_3C , we have investigated a number of antiferromagnetic states aligned along [100], [110] and [111] magnetization directions. In all cases, the high-to-low spin state transition occurs at about $149 \text{ \AA}^3$. In addition, we have checked the disordered (high-temperature) magnetic state modeled by means of the disordered local moment model (DLM). The results have shown that the high-to-low spin state transition is observed in the DLM state as well (but at larger volumes of about $155 \text{ \AA}^3$). This finding indicates the likelihood of the so-called Invar- or Anti-Invar-like effects in the system [96–99] and should be investigated further in more detail. Though such an investigation goes beyond the scope of the present paper, based on the currently available data on high-to-low spin transitions in the system, we could suggest that our 0K data for Mn_3C should be taken with extra caution if used to describe the thermodynamic equilibrium at finite temperatures.

Similar calculations for Cr_3C , Mn_3C and Ni_3C show that, in contrast to Fe_3C and Co_3C , their total magnetic moment is negligibly small. Specifically, they are calculated to be 0.0002, 0.0085, and 0.0002 μ_B /unit-cell, respectively. Also, in all three cases calculated partial DOSs are symmetric in the entire valence region. Therefore, Cr_3C and Ni_3C are not predicted to be ferromagnetic. The salient features of DOS at Fermi-level (E_F) of above five M_3Cs are summarized in Table 9.

We have also calculated the effect of site occupancy of Cr in Fe_3C on the magnetic moment. The total magnetic moment decreases rapidly from 22.028 μ_B /unit-cell in Fe_3C to 7.703 and 3.148 μ_B /unit-cell in CrFe_2C and Cr_2FeC , mentioned in Section 4.1.2, respectively. Similarly, addition of Ni and Mn also decreases the total magnetic moment of Fe_3C . Therefore, we believe that with the addition of these elements in Fe_3C , its Curie temperature will decrease continuously.

5 Conclusions

We have carried out a comprehensive and systematic computational study of structural, elastic, thermodynamic properties, and electronic structure of Fe_3C and its alloyed counterparts (Fe_2MC , FeM_2C and M_3C ($\text{M}=\text{Al, Co, Cr, Cu, Fe, Hf, Mn, Mo, Nb, Ni, Si, Ta, Ti, V, W}$ and Zr)) having the orthorhombic crystal structure. Our systematic study makes use of electronic density functional theory in conjunction with pseudopotentials constructed by all-electron projector-augmented wave (PAW) method and GGA for the exchange-correlation functional. The following conclusions are drawn:

- (i) The zero-temperature equation of state (EOS) of M_3C defining a few material constants, along with their equilibrium lattice parameters and unit cell-internal degrees of freedom are calculated.
- (ii) Available experimental data of lattice parameter show a good agreement with calculated results.
- (iii) Among the cementites considered here, Fe_3C is the most widely studied experimentally. While the EOS parameters (see, Table 3) show a large scatter, several experimental values show a good agreement with our calculated value. The effect of third elements, such as V, Cr, Mo and Mn on the bulk modulus of Fe_3C is rationalized in terms of expected trend of our calculated EOS parameters.
- (iv) Based on computational results, we predict that the virtual phase Co_3C is ferromagnetic as demonstrated by relevant DOS plots, but such a prediction is yet to be experimentally verified.
- (v) We have carried out a systematic study of Mn_3C (with the structure of Fe_3C) as a function of its assumed magnetism structure. Total energy calculations help us establish the ground state structure of Mn_3C . Specifically,

we find that non-collinear antiferromagnetic structure with [001] magnetization direction is the ground state structure. To the best of our knowledge, this is the first such to establish the ground state structure of Mn_3C enabled by computations. It is hoped that experimentalists will investigate magnetic structure of Mn_3C using multiple techniques, such as neutron diffraction, Mössbauer spectroscopy etc to validate our computational results.

(vi) Site and angular-momentum DOS along with bonding charge densities are calculated to elucidate bonding mechanisms between C and M in M_3C . For the first time we show site and angular-momentum decomposed DOS of Mn_3C in its ground state structure.

(vii) Magnetic moment (per unit-cell) of Fe_3C and Co_3C is significant and their partial DOSs are asymmetric in the entire valence region, hence, they are ferromagnetic. On the other hand, magnetic moments (per unit-cell) of Cr_3C , Ni_3C and Mn_3C are negligibly small and their partial DOSs (up and down) are symmetric in the entire valence region, hence, they are not predicted to be ferromagnetic.

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7 List of Table Headings

Table 1. k -mesh used in our first-principles calculations of equation of state for pure elements and cementite (M_3C), and the corresponding number of k -points in the irreducible Brillouin zone (IBZ).

Table 2. The equation of state (EOS) parameters for pure elements at 0 K: the equilibrium energy (E_o , eV/atom), corresponding volume (V_o , $\times 10^{-3}$ nm³/atom), bulk modulus (B_o , in GPa) and its pressure derivative B_o' as defined in Eq. (3). The lattice constants are in nm, and the magnetic moments are in μ_B per atom. The structure of pure elements are bcc or cI2 (Cr, α -Fe, Mo, Nb, Ta, V, W), fcc or cF4 (Al, Cu, Ni), hcp or hP2 (Co, Hf, Ti, Zr), complex cubic or cI58 (α -Mn), diamond cubic or cF8 (Si), and graphite or hP4 (C).

Table 3. The equation of state (EOS) parameters for binary cementite, M_3C , at 0 K: the equilibrium energy (E_o , eV/atom), corresponding volume (V_o , $\times 10^{-3}$ nm³/atom), bulk modulus (B_o , in GPa) and its pressure derivative B_o' as defined in Eq. (3). The zero-temperature formation energy (ΔE_f) is in kJ/mol-atom, and the unit cell-external parameters (lattice constants) are in nm. The reference states are bcc or cI2 (Cr, α -Fe, Mo, Nb, Ta, V, W), fcc or cF4 (Al, Cu, Ni), hcp or hP2 (Co, Hf, Ti, Zr), complex cubic or cI58 (α -Mn), diamond cubic or cF8 (Si), and graphite or hP4 (C). Our calculated values are compared, where available, with previously reported results.

Table 4. The equation of state (EOS) parameters for ternary cementite, $(Fe,M)_3C$, at 0 K: the equilibrium energy (E_o , eV/atom), corresponding volume (V_o , $\times 10^{-3}$ nm³/atom), bulk modulus (B_o , in GPa) and its pressure derivative B_o' as defined in Eq. (3). In these ternary cementites two metal sites (I and II, as mentioned in Section I) are substituted by Fe and M, and represented as FeM_2C and Fe_2MC , respectively. The total magnetic moments (in μ_B per unit cell) of ternary cementites are also listed.

Table 5. Unit cell-internal parameters in binary cementite, M_3C . Our calculated values are compared, where available, with experimental data and previously calculated results.

Table 6. Calculated unit cell-internal parameters in ternary cementite, $(M_1,M_2)_3C$.

Table 7. Optimized unit-cell parameters of (Mn_3C)

Table 8. spd contributions of spin magnetic moments (in μ_B per unit cell) in M_3C . Our calculated values are compared, where available, with previously reported results.

Table 9. Total DOS (in states/eV/unit cell) at the Fermi level (E_F) in binary M_3C .

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Fig. 1 Calculated total energy, at zero temperature and without zero-point motion, as a function of volume of Fe_3C . The filled circles represent calculated points, and the line is a fit to EOS in Eq. (2) defining equilibrium energy ($E(V_0)$), the equilibrium volume (V_0), and the bulk modulus (B_0).

Fig. 2. Angular momentum and site decomposed electronic density of states, $n(E)$, of Fe_3C .

Fig. 3. Distribution of (a) total charge densities, and (b) bonding charge densities in the (001) plane of Fe_3C with the position of C atoms marked X. In (a), several Fe-Fe nearest neighbor distances are marked as $A = 2.446 \text{ \AA}$ ($\text{Fe}^{II}\text{-Fe}^{II}$), $B = 2.531 \text{ \AA}$ ($\text{Fe}^{II}\text{-Fe}^{II}$), $C = 2.620 \text{ \AA}$ ($\text{Fe}^{II}\text{-Fe}^{II}$) and $D = 2.632 \text{ \AA}$ ($\text{Fe}^I\text{-Fe}^{II}$), and C-Fe nearest neighbor distances are marked as $a = 1.989 \text{ \AA}$ (C-Fe^I), $b = 1.992 \text{ \AA}$ (C-Fe^{II}) and $c = 2.001 \text{ \AA}$ (C-Fe^{II}). The total charge density ranges from 14.225 ($\rho_{\min}(x)$) to 98.035 ($\rho_{\max}(x)$) $\text{e}/\text{\AA}^3$, while the bonding charge density ranges from -4.347 (depleted region: $\delta\rho(x)-$) to 3.355 (enhanced region: $\delta\rho(x)+$) $\text{e}/\text{\AA}^3$ due to redistribution of charges. The contour lines are drawn at an interval of (a) $8.4 \text{ e}/\text{\AA}^3$ and (b) $0.79 \text{ e}/\text{\AA}^3$.

Fig. 4. Angular momentum and site decomposed electronic density of states, $n(E)$, of Co_3C .

Fig. 5. Distribution of (a) total charge densities, and (b) bonding charge densities in the (010) plane of Co_3C with the position of C atoms marked X. In (a), several Co-Co nearest neighbor distances are marked as $A = 2.518 \text{ \AA}$ ($\text{Co}^I\text{-Co}^{II}$), $B = 2.553 \text{ \AA}$ ($\text{Co}^I\text{-Co}^{II}$), $C = 2.567 \text{ \AA}$ ($\text{Co}^I\text{-Co}^{II}$) and $D = 2.632 \text{ \AA}$ ($\text{Co}^I\text{-Co}^{II}$), and C-Co nearest neighbor distances are marked as $a = 1.932 \text{ \AA}$ (C-Co^I), $b = 1.978 \text{ \AA}$ (C-Co^I) and $c = 1.981 \text{ \AA}$ (C-Co^I). The total charge density ranges from 24.0 ($\rho_{\min}(x)$) to 223.0 ($\rho_{\max}(x)$) $\text{e}/\text{\AA}^3$, while the bonding charge density ranges from -9.03 (depleted region: $\delta\rho(x)-$) to 4.32 (enhanced region: $\delta\rho(x)+$) $\text{e}/\text{\AA}^3$ due to redistribution of charges. The contour lines are drawn at an interval of (a) $20.0 \text{ e}/\text{\AA}^3$ and (b) $1.36 \text{ e}/\text{\AA}^3$.

Fig. 6. Predicted ground-state structure of cell of Mn_3C showing its non-collinear magnetic structure with the direction of magnetization ($[001]$) is shown with arrows.

Fig. 7. Angular momentum and site decomposed electronic density of states, $n(E)$, of Mn_3C with $[001]$ as the direction of magnetization i.e., the predicted ground state structure shown in Fig. 6.

Fig. 8. On-site magnetic moments in Mn and C in the ground state structure of Mn_3C (shown in Fig. 5) as a function of unit cell volume, calculated using the CPA method, demonstrating high-spin and low-spin magnetic states of Mn with Mn^I and Mn^{II} refer to $4c$ and $8d$ sites, respectively, in the structure of Fe_3C .

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Fig. 1. Calculated total energy, at zero temperature and without zero-point motion, as a function of volume of Fe_3C . The filled circles represent calculated points, and the line is a fit to EOS in Eq. (2) defining equilibrium energy ($E(V_0)$), the equilibrium volume (V_0), and the bulk modulus (B_0).

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Table 1

k -mesh used in our first-principles calculations.....

Pure element			Cementite		
M	k -mesh	IBZ-kpoints	M_3C	k -mesh	IBZ-kpoints
Al	$24 \times 24 \times 24$	364	Al_3C	$16 \times 13 \times 17$	952
Co	$21 \times 21 \times 13$	336	Co_3C	$11 \times 8 \times 12$	144
Cr	$21 \times 21 \times 24$	286	Cr_3C	$11 \times 8 \times 12$	144
Cu	$20 \times 20 \times 20$	220	Cu_3C	$10 \times 8 \times 11$	120
α -Fe	$21 \times 21 \times 21$	286	Fe_3C	$11 \times 8 \times 12$	144
Hf	$30 \times 30 \times 19$	910	Hf_3C	$15 \times 10 \times 22$	440
α -Mn	$16 \times 16 \times 16$	120	Mn_3C	$11 \times 8 \times 13$	1144
Nb	$24 \times 24 \times 24$	364	Nb_3C	$11 \times 8 \times 15$	192
Ni	$20 \times 20 \times 20$	220	Ni_3C	$14 \times 10 \times 15$	144
Si	$15 \times 15 \times 15$	120	Si_3C	$16 \times 13 \times 19$	560
Ta	$24 \times 24 \times 24$	364	Ta_3C	$13 \times 9 \times 17$	315
Ti	$27 \times 27 \times 15$	675	Ti_3C	$15 \times 10 \times 22$	440
V	$24 \times 24 \times 24$	364	V_3C	$14 \times 10 \times 19$	350
W	$24 \times 24 \times 24$	364	W_3C	$19 \times 13 \times 22$	770
Zr	$32 \times 32 \times 20$	1122	Zr_3C	$14 \times 9 \times 20$	350
C	$35 \times 35 \times 10$	720	Al_2FeC	$11 \times 8 \times 12$	144 ^a
			Fe_2NiC	$8 \times 11 \times 12$	144
			$FeNi_2C$	$14 \times 10 \times 16$	280
			Fe_2SiC	$11 \times 11 \times 11$	216
			$FeSi_2C$	$11 \times 13 \times 13$	294
			Fe_2NbC	$8 \times 6 \times 9$	60 ^b

^a Also $FeAl_2Fe$, Co_2FeC , $CoFe_2C$, Cu_2FeC , $CuFe_2C$, Fe_2MoC

^b Also $FeNb_2Fe$, Fe_2VC , FeV_2C , Fe_2WC , FeW_2C .

Table 2

The equation of state (EOS) parameters for pure elements M and C at 0 K.....

M	EOS parameters				Lattice constants, in nm			Magnetic moment (in μ_B per atom)
	E_o	V_o	B_o	B_o'	a	b	c	
Al	-3.6972	16.575	74.36	4.66	0.40474			
Co	-7.0138	10.848	213.81	5.03	0.24034		0.40282	1.577
Cr	-9.4635	11.402	262.24	4.32	0.36359			0.0
Cu	-3.7272	12.016	137.67	5.21	0.36359			
α -Fe	-8.2079	11.346	179.18	6.42	0.28311			2.2
Hf	-9.8783	22.356	111.63	3.43	0.31979		0.50487	
α -Mn	-8.9639	10.748	279.42	4.53	0.85425			0.001
Mo	-10.912	15.688	267.14	4.3	0.31540			
Nb	-10.064	18.348	173.6	3.94	0.33231			
Ni	-5.4639	10.916	196.05	5.09	0.35213			0.6134
Si	-5.4315	20.434	88.88	4.35	0.54678			
Ta	-11.782	18.124	200.45	3.78	0.33095			
Ti	-7.7418	17.051	117.32	3.79	0.29203		0.46187	
V	-8.9208	13.187	187.07	3.80	0.29766			
W	-12.921	16.012	309.98	4.29	0.31756			
Zr	-8.4576	23.360	96.66	3.19	0.32309		0.51677	
C	-9.2397	11.813	1.326	15.15	0.24667		0.87287	

Table 3

The equation of state (EOS) parameters for binary cementite, M_3C , at 0 K.....

M_3C	EOS parameters				Lattice constants, in nm			ΔE_f (kJ/mol-at) (Ab initio, this stu
	E_o (eV/at)	V_o ($\text{\AA}^3/\text{at}$)	B_o (GPa)	B_o'	a	b	c	
Al_3C	-4.9101	14.782	74.27	4.28	0.58969	0.73565	0.54506	16.642
Co_3C	-7.4357	9.1674	236.53	5.61	0.49374	0.66996	0.44343	12.967
Cr_3C	-9.4837	9.7117	290.16	4.51	0.51947	0.66279	0.45113	-7.337
					0.51200 ^a	0.68000	0.45800	
Cu_3C	-4.5088	10.767	111.08	0.59	0.54075	0.67189	0.47448	57.477
Fe_3C	-8.4174	9.4728	213.84	4.06	0.50289	0.67262	0.44823	4.668
					0.50920 ^a	0.67410	0.45270	
			174 ^b	5.1 ^b	0.50787 ^c	0.67297	0.45144	
			175.4 $\pm$ 3.5 ^d	5.3 $\pm$ 0.3 ^d	0.50900 ^e	0.67480	0.45230	
			174.0 $\pm$ 6 ^f	4.8 $\pm$ 0.8 ^f	0.50910 ^f	0.67434	0.45260	
			105, 125 ^g		0.50620 ^g	0.67600	0.45300	
			175 ^h	4 ^h	0.50830 ^h	0.67360	0.45124	
					0.50890 ⁱ	0.67430	0.45230	
			235.13 ^j		0.50670 ^j	0.67140	0.45130	
					0.51280 ^k	0.6650	0.44620	
			142 ^l	4.6 ^l	0.50600 ^l	0.67400	0.45100	
			204 ^m	5 ^m	0.50400 ^m	0.67200	0.44800	
			204 ⁿ	5 ⁿ	0.50360 ⁿ	0.67240	0.44800	
			196 ^o	5.37 ^o	0.50530 ^o	0.67450	0.45030	
					0.4819 ^p	0.64774	0.42805	
					0.50080 ^q	0.67254	0.44650	
Hf_3C	-10.153	18.349	137.97	3.92	0.66095	0.98269	0.45201	-41.850
Mn_3C	-8.9898	9.4424	293.04	4.55	0.52175	0.67896	0.42643	-6.6512
					0.51100 ^r	0.67600	0.45300	
					0.51030 ^s	0.67870	0.45450	
					0.50800 ^a	0.67720	0.45300	
Mo_3C	-10.328	13.401	263.81	4.56	0.55621	0.80508	0.47869	15.987
Nb_3C	-10.128	15.552	196.24	3.97	0.61078	0.87925	0.46316	-26.022
Ni_3C	-6.3063	9.4243	203.47	5.89	0.49499	0.68049	0.44766	9.785
Si_3C	-5.812	12.482	104.45	4.72	0.57446	0.71450	0.48928	16.071
Ta_3C	-11.497	15.223	230.16	4.02	0.60762	0.86843	0.46151	-33.779
Ti_3C	-8.4984	14.606	135.20	4.36	0.61527	0.90569	0.41941	-36.819
V_3C	-9.2734	11.567	207.55	4.29	0.56274	0.78766	0.41941	-26.292
W_3C	-11.741	13.597	305.96	4.90	0.55759	0.80374	0.48538	25.020
Zr_3C	-9.0336	19.359	117.63	4.07	0.66906	1.00722	0.45962	-36.659

Expt. at 298 K: ^a [91], ^b [86], ^c [92], ^d [87], ^e [93], ^f [88], ^g [34], ^h [89]; LMTO, LDA at 0 K: ⁱ [39];
 FP-LAPW, GGA at 0 K: ^j [42], ^k [48]; VASP, USPP, GGA at 0 K: ^l [40]; VASP, PAW, GGA at 0 K:
^m [44], ⁿ [45], ^o [25]; CASTEP, USPP, LDA at 0 K: ^p [46]; CASTEP, USPP, GGA at 0 K: ^q [46]; Expt. at
 298 K: ^r [94], ^s [95].

Table 4

The equation of state (EOS) parameters for ternary cementite.....

M ₃ C	EOS parameters				Lattice constants, in nm			ΔE_f (mag-moment)
	E_o (eV/at)	V_o (Å ³ /at)	B_o (GPa)	B_o'	a	b	c	kJ/mol-atom (μ_B per cell)
Al ₂ FeC	-6.1659	10.783	156.23	5.07	0.50047	0.66919	0.52388	4.297 (1.56)
AlFe ₂ C	-7.3474	9.6304	191.22	5.17	0.51681	0.63381	0.47030	-0.888 (7.89)
Co ₂ FeC	-7.771	9.3236	219.79	5.54	0.49292	0.68093	0.44429	9.423 (15.73)
CoFe ₂ C	-8.1024	9.3675	210.00	5.42	0.49915	0.66819	0.44925	6.256 (18.60)
Cr ₂ FeC	-9.1432	9.4726	293.47	5.08	0.51165	0.65549	0.45186	-4.774 (3.15)
CrFe ₂ C	-8.761	9.3828	228.00	5.99	0.50152	0.68208	0.43822	1.807 (7.70)
Cu ₂ FeC	-5.7535	10.178	159.06	4.95	0.50825	0.69770	0.45901	45.478 (5.38)
CuFe ₂ C	-7.0834	9.7789	179.73	6.94	0.51894	0.67560	0.44623	25.271 (14.29)
FeMn ₂ C	-8.8695	9.0817	278.45	6.51	0.49727	0.64632	0.44195	-4.822 (2.89)
Fe ₂ MoC	-8.4174	9.473	213.86	4.07	0.50288	0.67254	0.44822	69.805 (22.02)
FeMo ₂ C	-8.3472	9.0983	225.17	4.86	0.49220	0.67265	0.43946	141.706 (5.12)
Fe ₂ NbC	-8.8858	11.085	184.59	8.85	0.53022	0.70868	0.47120	4.247 (9.18)
FeNb ₂ C	-9.4875	13.175	193.58	—	0.59524	0.71885	0.49132	-9.018 (4.79)
Fe ₂ NiC	-7.7025	9.4301	206.48	5.89	0.50640	0.67425	0.44181	7.453 (15.30)
FeNi ₂ C	-6.9646	9.5245	196.27	5.81	0.50213	0.68165	0.44533	12.453 (9.68)
Fe ₂ SiC	-7.7486	9.3258	258.82	5.68	0.52588	0.52116	0.54431	2.231 (0.0)
FeSi ₂ C	-6.7656	11.588	77.09	8.62	0.63732	0.52059	0.52750	30.067 (0.0)
Fe ₂ TaC	-9.4714	10.812	225.02	2.35	0.54140	0.70197	0.45423	-10.794 (10.13)
FeTa ₂ C	-10.139	12.631	253.58	4.96	0.51714	0.71527	0.54628	-100.28 (0.0)
Fe ₂ TiC	-8.6087	9.9887	238.32	5.92	0.54328	0.64767	0.45419	-24.991(7.34)
FeTi ₂ C	-8.6223	11.588	192.72	4.49	0.53336	0.69473	0.50030	-37.529 (0.0)
Fe ₂ VC	-8.7656	9.3636	228.80	6.53	0.50999	0.66753	0.45271	-11.709 (7.47)
FeV ₂ C	-9.0732	10.2040	259.12	4.61	0.50909	0.68027	0.47134	-24.174 (0.0)
Fe ₂ WC	-9.5236	10.484	230.90	10.33	0.51711	0.70259	0.46162	11.613 (4.56)
FeW ₂ C	-10.636	11.830	288.67	5.97	0.54470	0.71181	0.48793	17.961 (0.0)

Table 5

Unit cell-internal parameters in binary, M_3C ,.....

M_3C	Wyckoff position								
	C at $4c$			M^I at $4c$			M^{II} at $8d$		
	x	y	z	x	y	z	x	y	z
Al_3C	0.5	0.25	0.15639	0.49999	0.25	0.78399	0.25001	0.07423	0.25001
Co_3C	0.38097	0.25	0.05375	0.03861	0.25	0.84285	0.18048	0.06989	0.32887
Cr_3C	0.37303	0.25	0.06823	0.02768	0.25	0.84316	0.17615	0.05847	0.34200
Cu_3C	0.36348	0.25	0.04811	0.088669	0.25	0.78778	0.15389	0.06706	0.30746
Fe_3C	0.37654	0.25	0.61999	0.03577	0.25	0.83684	0.17686	0.06814	0.33200
	0.877(3) ^a	0.25	0.444(2)	0.0367(4)	0.25	0.8402(2)	0.1816(3)	0.0666(1)	0.3374(2)
	0.8942(9) ^b	0.25	0.4503(8)	0.0336(5)	0.25	0.8409(8)	0.1841(4)	0.0571(3)	0.3329(5)
	0.890 ^c	0.25	0.450	0.036	0.25	0.852	0.186	0.063	0.328
	0.877 ^d	0.25	0.440	0.038	0.25	0.837	0.176	0.068	0.332
	0.876 ^e	0.25	0.438	0.036	0.25	0.837	0.176	0.068	0.332
	0.3754 ^f	0.25	0.0621	0.0358	0.25	0.8398	0.1752	0.0662	0.3330
Hf_3C	0.12533	0.25	0.24996	0.12539	0.25	0.74996	0.37531	0.09293	0.24999
Mn_3C	0.37761	0.24999	0.064607	0.03082	0.24992	0.84014	0.18642	0.06544	0.34392
Mo_3C	0.12357	0.25	0.42221	0.30004	0.25	0.81837	0.39871	0.07240	0.29360
Nb_3C	0.19178	0.25	0.24999	0.22236	0.25	0.75001	0.44444	0.07795	0.24999
Ni_3C	0.38143	0.25	0.05437	0.04355	0.25	0.83454	0.17262	0.07313	0.32032
Si_3C	0.00002	0.25	0.29801	0.00001	0.25	0.69462	0.25002	0.05321	0.25001
Ta_3C	0.18958	0.25	0.24999	0.21756	0.25	0.75000	0.44104	0.07732	0.24999
Ti_3C	0.12554	0.25	0.25002	0.12576	0.25	0.75001	0.37554	0.09152	0.24999
V_3C	0.19158	0.25	0.24999	0.22219	0.25	0.74999	0.44427	0.07272	0.24999
W_3C	0.12458	0.25	0.41698	0.31384	0.25	0.80642	0.39713	0.07108	0.28855
Zr_3C	0.12498	0.25	0.24994	0.12497	0.25	0.74995	0.37498	0.09413	0.24998

Expt. at 298 K: ^aFruchart et al [91], ^bWood [89]FP-LAPW, GGA at 0 K: ^cFaraoun et al [42], ^dJang et al [48]VASP, USPP, GGA at 0 K: ^eChiou and Carter [40]VASP, PAW, GGA at 0 K: ^fJiang et al [44].

Table 6

Calculated unit cell-internal parameters in ternary cementite, $(M_1, M_2)_3C$

M_3C	Wyckoff position								
	C at $4c$			M_1 at $4c$			M_2 at $8d$		
	x	y	z	x	y	z	x	y	z
Al_2FeC	0.30323	0.25	0.05957	0.24631	0.05850	0.39604	0.02299	0.25	0.76179
$AlFe_2C$	0.37735	0.25	0.07354	0.01631	0.25	0.87511	0.17652	0.05553	0.35659
Co_2FeC	0.38192	0.25	0.06829	0.18067	0.07025	0.32781	0.03830	0.25	0.83449
$CoFe_2C$	0.37479	0.25	0.04996	0.03584	0.25	0.84260	0.17910	0.06943	0.33215
Cr_2FeC	0.36654	0.25	0.04544	0.18254	0.06483	0.34784	0.02884	0.25	0.84688
$CrFe_2C$	0.38308	0.25	0.08284	0.03498	0.25	0.83981	0.18207	0.06932	0.33978
Cu_2FeC	0.37576	0.25	0.01947	0.18479	0.07159	0.32987	0.04531	0.25	0.83809
$CuFe_2C$	0.38561	0.25	0.08386	0.04287	0.25	0.83525	0.17259	0.06949	0.32641
$FeMn_2C$	0.37686	0.25	0.05654	0.03058	0.25	0.847065	0.18541	0.06594	0.34506
Fe_2MoC	0.37661	0.25	0.06206	0.17694	0.06813	0.33206	0.03588	0.25	0.83679
$FeMo_2C$	0.38486	0.25	0.06959	0.04096	0.25	0.83874	0.18511	0.6803	0.33383
Fe_2NiC	0.37991	0.25	0.06121	0.03843	0.25	0.84	0.17702	0.06929	0.32898
$FeNi_2C$	0.37687	0.25	0.0539	0.03934	0.25	0.83631	0.17718	0.07332	0.32994
Fe_2SiC	0.37689	0.25	0.10485	0.15922	0.00692	0.32735	0.16146	0.25	0.51538
$FeSi_2C$	0.44157	0.25	0.11234	0.42746	0.25	0.48782	0.16146	0.51154	0.83462
Fe_2TaC	0.39091	0.25	0.11265	0.02856	0.25	0.86744	0.174	0.06711	0.34907
$FeTa_2C$	0.36423	0.25	0.05665	0.02839	0.25	0.77479	0.2366	0.05097	0.38199
Fe_2TiC	0.38657	0.25	0.09976	0.17332	0.25	0.87791	0.17354	0.05552	0.3533
$FeTi_2C$	0.35906	0.25	0.02441	0.05503	0.25	0.32735	0.16991	0.05751	0.32099
Fe_2VC	0.37431	0.25	0.05853	0.31584	0.55894	0.84978	0.02933	0.25	0.84376
FeV_2C	0.36491	0.25	0.04579	0.04076	0.25	0.82475	0.18924	0.06274	0.34484
Fe_2WC	0.39255	0.25	0.1111	0.03703	0.25	0.85042	0.17914	0.07197	0.33999
FeW_2C	0.36563	0.25	0.02748	0.03132	0.25	0.842	0.18572	0.06449	0.33193

Table 7
Optimized unit-cell parameters of (Mn₃C)

4.9319			
1.0000000000000000	0.0000000000000000	0.0000000000000000	
0.0000000000000000	1.3530589130000000	0.0000000000000000	
0.0000000000000000	0.0000000000000000	0.9016110700000000	
4	12		
Direct			
0.8776066300288038	0.2499924905883400	0.4353947802286977	C ₁ (4c)
0.6223900421644084	0.7500095369596544	0.9353935950052985	C ₂ (4c)
0.1223953370196245	0.7500078693232147	0.5646090315355626	C ₃ (4c)
0.3776064165574992	0.2499943290567520	0.0646076482659474	C ₄ (4c)
0.0308214147720112	0.2499924637063131	0.8401456392807957	Mn ₁ (4c)
0.4691782311675529	0.7500062391560809	0.3401463158011698	Mn ₂ (4c)
0.9691843002404233	0.7500054213872019	0.1598587897715630	Mn ₃ (4c)
0.5308198136658900	0.2499918906433852	0.6598486002457949	Mn ₄ (4c)
0.1864230323806817	0.0654481554587547	0.3439209946071911	Mn ₅ (8d)
0.3135844300132186	0.9345689044811587	0.8439165817284942	Mn ₆ (8d)
0.8135774314858071	0.5654440523645999	0.6560788317132286	Mn ₇ (8d)
0.6864174755231307	0.4345421310036489	0.1560879004936769	Mn ₈ (8d)
0.8135730427489699	0.9345691172617467	0.6560789084595641	Mn ₉ (8d)
0.6864178380347447	0.0654447242132189	0.1560825796827802	Mn ₁₀ (8d)
0.1864253524074417	0.4345406147906464	0.3439161975866369	Mn ₁₁ (8d)
0.3135792117897996	0.5654420596052765	0.8439136055936058	Mn ₁₂ (8d)

Table 8

spd contributions of spin magnetic moments.....

M ₃ C	C at 4c (in μ_B)			M ^I at 4c (in μ_B)			M ^{II} at 8d (in μ_B)		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
Co ₃ C	-0.01	-0.22	-0.006	-0.012	-0.066	3.918	-0.016	-0.134	8.662
Cr ₃ C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe ₃ C	-0.037	-0.462	0.012	-0.02	-0.112	7.892	-0.04	-0.108	15.124
			-0.06 ^a			7.92			13.92
						6.96 ^b			13.52
						6.96 ^c			13.52
						7.68 ^d			14.72
			-0.52 ^e			7.88			15.68
Mn ₃ C	0.0	0.0	-0.089 ^f	0.0	0.0	8.236	0.0	0.0	15.656
						0.016			-0.008
						0.0			0.0
Ni ₃ C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^a Total on-site moment: LMTO, LDA: Häglund et al [39]^b Korringa-Kohn-Rostoker-atomic sphere approximation (KKR-ASA), local Airy Gas: Khmelevskiy et al [41]^c VASP, USPP, GGA: Chiou and Carter [40]^d VASP, PAW, GGA: Dick et al [25]^e FP-LAPW, GGA: Faraoun et al [42], Jang et al [48].

Table 9

Total DOS.....

M ₃ C	Total DOS at E _F	
	(States/eV/cell)	
	<i>n</i> (E _F)↑	<i>n</i> (E _F)↓
Co ₃ C	4.13	15.46
Cr ₃ C	7.056	7.056
Fe ₃ C	5.12	5.74
Mn ₃ C	9.238	9.238
Ni ₃ C	5.252	5.252

Predicted ground-state structure of Mn₃C (a high-temperature phase and isotopic with Fe₃C), but having non-collinear magnetic structure with the direction of magnetization as [001].

Fig. 1

Computed density of states, DOS (Fig. 2), corresponding to the ground-state of Mn₃C (Fig. 1)

Fig. 2