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Computational searches for iron carbide in the Earth's inner core

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We have used density-functional-theory methods together with a structure searching algorithm to determine stable structures and stoichiometries of mixtures of iron and carbon at high pressures and zero temperature. The most favorable stoichiometries at Earth's inner-core pressures (∼350 GPa) are those with between about 20% and 35% carbon atoms. The most stable stoichiometries were found to be (Fe and C), Fe_3C, Fe_7C_3, and Fe_2C. The latter has not to our knowledge been discussed previously in relation to the Earth's core. The stoichiometries Fe_4C and Fe_5C_2 were found to be close to stability at Earth's inner-core pressures. We find that Fe_7C_3 is unstable to decomposition into $Fe_3C + 2Fe_2C$ at pressures greater than ∼330 GPa. At 150 GPa only Fe, C, Fe_3C, and Fe_7C_3 are stable. Formation of Fe/C compounds is energetically more favorable at 350 GPa than at 150 GPa. We also report a new phase for Fe_3C with *Cmcm* symmetry to be more stable than the well-known cementite phase at 350 GPa. A number of pressure-induced phase transitions are identified in Fe_3C, Fe_3C_2, FeC, Fe_8C, and FeC_2. The lowest enthalpy Fe/C phases were found to be metallic at the pressures studied.

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I. INTRODUCTION

The Earth's inner core is believed to be composed primarily of Fe with about 8% Ni and 8% –12% of other light elements.[1] The identities of these light elements have yet to be fully determined, although various arguments favor O, Si, C, S, and H as the most likely candidates.[2] Wood[1] suggested that there might be a significant amount of C in the Earth's core, and the likely stoichiometries of the most stable Fe/C compounds at high pressures have been discussed. In particular, Fe_3C and Fe_7C_3 have been proposed as significant phases.[1–5] There is evidence for the formation of other phases at low pressures such as Fe_5C_2[6] and Fe_2C.[7,8]

The great difficulties involved in making measurements on the Earth's core and in performing laboratory experiments under similar conditions have stimulated a number of theoretical studies. Atomistic simulations have been performed on pure Fe under inner-core conditions using density functional theory (DFT) methods[9] and some studies have included impurities.[10–12] In this work we have searched for stable structures of Fe and C with stoichiometries: Fe_8C, Fe_6C, Fe_4C, Fe_3C, Fe_5C_2, Fe_7C_3, Fe_2C, Fe_3C_2, Fe_2C_3, FeC, FeC_2, and FeC_3. The small percentage of Ni present within the core can safely be ignored for our purposes. We have used a convex hull diagram to determine which of the Fe/C stoichiometries would be likely to form at inner-core pressures. We have also investigated pressure-induced phase transitions for each stoichiometry.

II. FERROMAGNETISM IN FE/C AT HIGH PRESSURES

Many Fe/C structures show magnetism at low pressures arising from the large magnetic moment of the Fe atom. Magnetism is generally reduced and eventually destroyed under strong compression because the electronic states tend to become delocalized. Ferromagnetism leads to a gain in exchange energy at the cost of kinetic energy, but the small volumes that arise at high pressures mean that it is increasingly important to smooth out the electronic charge density so as to reduce the kinetic energy. Experimental studies have shown that ferromagnetism in Fe_3C cementite collapses at about 55 GPa.[13] This result is supported by first-principles DFT calculations which show that the ferromagnetic order in Fe_3C ceases at around 60 GPa.[14] Recent DFT calculations[4] have predicted that the magnetic moment of Fe_7C_3 collapses at about 67 GPa, although experiment suggests lower values.[5] Pure iron is nonmagnetic at pressures above about 15 GPa, where it transforms from the ferromagnetic body-centered-cubic phase to the hexagonal-close-packed phase (hcp) in which ferromagnetism is frustrated.[15] The nonmagnetic hcp structure remains the most stable phase of iron to pressures far above the highest we have investigated of about 350 GPa.[16] We performed spin-polarized DFT calculations for structures of Fe_3C, Fe_3C_2, Fe_5C_2, and Fe_2C, but found no evidence for ferromagnetism in these systems at 70 or 350 GPa. In conclusion, it is very unlikely that magnetism plays a significant role in the Fe/C system at the large pressures used in this investigation, and magnetic effects are not included in the results presented below.

III. RANDOM STRUCTURE SEARCHING

The structures most likely to be found in nature lie at or close to the global minimum of Gibbs free energy. Finding the global minimum in the potential energy surface is difficult because the number of local minima increases exponentially with system size.[17] The complexity of this problem falls into the category of NP hard (nondeterministic polynomial time hard). For such problems it is believed (but not proved) that no algorithm can be designed which is guaranteed to find the global minimum in a time which scales as a polynomial in the number of degrees of freedom. Exponential scaling algorithms, which could guarantee to find the global minimum, are conceptually simple. Such an algorithm would have to locate all minima and calculate their energies in order to determine the global minimum. However, the exponential scaling of this algorithm makes it unfeasible for large systems. It is for this reason that we use a nondeterministic method for finding the global minimum.

The approach we use is called *ab initio* random structure searching (AIRSS),[18] which has already proven to be successful in predicting structures at high pressures which have subsequently been verified by experiments.[19,20] The principle behind AIRSS is to randomly sample the local minima. In this process starting structures are generated with randomly chosen atomic positions and cell lattice vectors which give a reasonable volume. Each starting structure corresponds to a random coordinate lying in a basin of attraction of the potential energy surface. We then use the CASTEP plane-wave DFT code[21] to relax the structure to the local enthalpy minimum. This process is repeated many times with different random starting structures and the search is terminated when the lowest enthalpy structure has been found several times, or when the available computing resources have been exhausted. Some structures can only be created with unit cells containing several formula units (fu). We have performed searches using multiple formula units where feasible with cells containing up to 20 atoms. As the number of atoms in the cell is increased, the process of searching becomes more expensive and thus a balance needs to be struck between feasibility and obtaining a reliable result.

The pressures within the inner core are thought to be in the range 330–360 GPa.[22] All of our searches were performed at zero temperature using a fixed pressure of 350 GPa. The final structures were determined using a two-step procedure. We first used the AIRSS technique in a medium-quality calculation which was optimized for computational speed. The medium quality settings consisted of a k-point sampling grid of spacing of $2\pi \times 0.07$ Å^{-1} and a plane-wave cut-off energy of 350 eV. Structures were relaxed until the lowest enthalpy phase was found several times, which typically required about 100 relaxations. The low enthalpy structures for each stoichiometry were then further relaxed in a higher-quality calculation consisting of a finer k-point sampling grid of spacing of $2\pi \times 0.03$ Å^{-1} and a plane-wave cut-off energy of 1000 eV. Such higher quality calculations are not particularly expensive because each structure is already close to its local enthalpy minimum. In all of our calculations we used the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange correlation functional.[23]

We used ultrasoft pseudopotentials[24] to represent the cores of the Fe and C atoms. For structure searching we used a fairly soft Fe pseudopotential in which only the $4s$ and $3d$ electrons were treated explicitly, while for C we treated the $2s$ and $2p$ electrons explicitly. We found the overlap of the pseudopotential cores on neighboring atoms to be very small at 350 GPa, and we judged that these pseudopotentials were adequate for searching purposes. For the higher quality calculations we used a Fe pseudopotential in which the $3s$, $3p$, $4s$, and $3d$ electrons were treated explicitly. This pseudopotential has been successfully tested up to terapascal pressures.[16] Both the searching and high quality relaxations were performed by constraining the up- and down-spin densities to be equal, which prevents magnetic moments from developing.

A completely unbiased search can often be inefficient, especially when dealing with large numbers of atoms. We can improve the efficiency of a search by imposing a bias. For example, one can generate initial structures by randomly packing structural units rather than individual atoms. The structural units should be chosen to be consistent with the chemistry of the system. The simplest example in the Fe/C system would be to choose chemical units containing Fe–C bonds in preference to Fe–Fe or C–C bonds. Once a structural unit containing m fu has been chosen, we can apply a space group with n symmetry operations to generate an initial structure with $m \times n$ fu. For example, we used this type of approach when searching for structures of Fe_3C with 4 fu, as unconstrained searches with 16-atom cells are costly. Random structure searching was first performed on 1 fu of Fe_3C at 350 GPa. The lowest enthalpy structure was then used as a structural unit and a space group with four symmetry operations was chosen at random and applied to create a larger 4 fu initial structure. Another useful bias is to reject all initial structures in which the smallest bond length is less than some predefined value. Structures in which atoms are very close are extremely high in enthalpy and we found that the geometry optimization sometimes fails when the starting configuration is unrealistic. We therefore rejected initial structures in which the atoms were too close together, using various minimum separations between 0.5 and 1 Å, so that the shortest bond length encountered in a relaxed structure of ∼1.3 Å was substantially larger than the minimum separation. This bias helps to preserve the chemical bonds of the chosen structural units. In this study we have relaxed a total of about 4000 structures.

IV. RESULTS FROM STRUCTURE SEARCHING

To assess the stability of the phases with respect to decomposition into different compounds we use a convex hull diagram. To construct this diagram we also need the enthalpy of pure iron in the hcp structure, which calculations show to be the lowest in enthalpy at 350 GPa, and the enthalpy of carbon diamond. Both of these calculations were performed with high quality settings. The formation enthalpy per atom of a compound with respect to its elements is

$$\Delta H = \frac{H_{\mathrm{s}} - (N_{\mathrm{Fe}} H_{\mathrm{Fe}} + N_{\mathrm{C}} H_{\mathrm{C}})}{N_{\mathrm{C}} + N_{\mathrm{Fe}}}, \tag{1}$$

where N_x and H_x are the number of atoms and enthalpy per atom of element x, respectively, and H_{s} is the enthalpy of the structure. A negative ΔH indicates that a structure is stable with respect to decomposition into its elements, although it may be unstable with respect to decomposition into two compounds of different stoichiometries. Only structures on the convex hull are thermodynamically stable and those lying above the convex hull are less likely to form. Fe_7C_3 is known to adopt a structure with $P6_3mc$ symmetry and 20 atoms in the primitive cell at low pressures.[25,26] We did not attempt to find this structure by an unconstrained search because of its large unit cell. We performed random structure searching

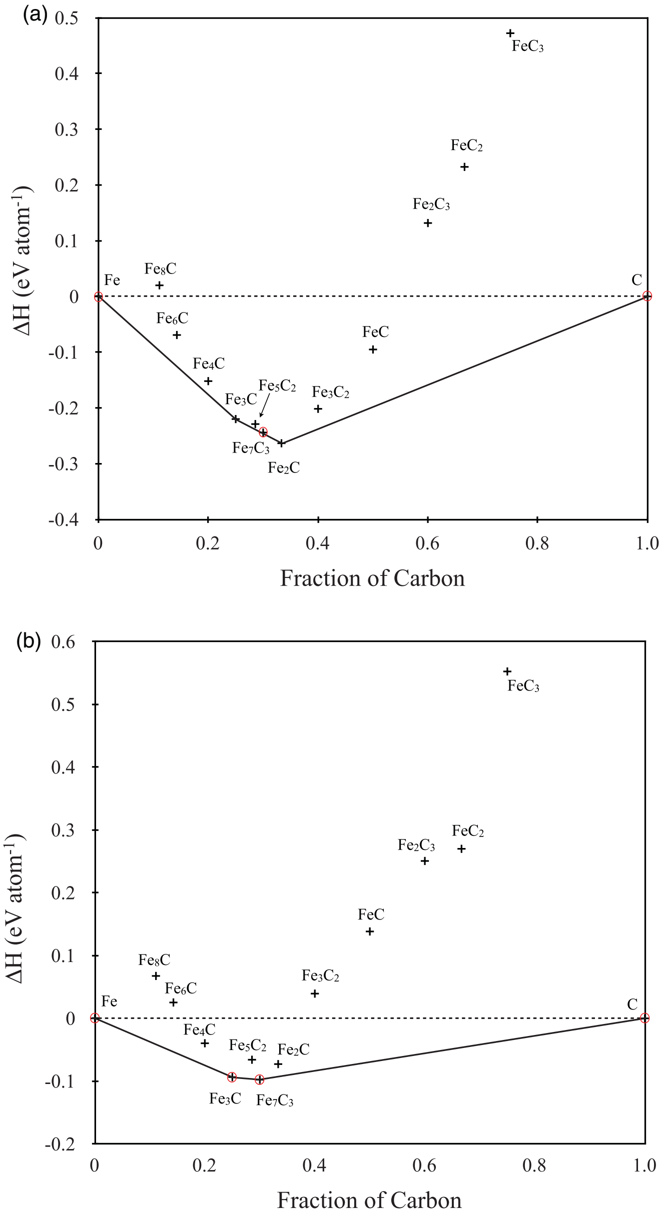

FIG. 1. (Color online) Convex hull plot for various stoichiometries of Fe and C at (a) 350 GPa and (b) 150 GPa. The red-circled points are structures known prior to this work.

at 350 GPa on 1 fu of Fe_7C_3 and 1 fu with two symmetry operations but did not find a structure with a lower enthalpy than the known $P6_3mc$ phase. Our most stable structure was 1.04 eV per fu higher in enthalpy than the $P6_3mc$ phase. The search with 4 fu of Fe_3C using starting structures consisting of randomly placed four-atom Fe_3C units gave a number of different relaxed structures, including the cementite structure of $Pnma$ symmetry, which is known to be stable at low pressures and a new lower enthalpy structure with $Cmcm$ symmetry, which was also found in the 2 fu searches. Note that the FeC_3 structure shown in Fig. 3 consists of layers of hcp iron and diamond, which clearly shows that segregation into the elements is favorable. The details of the new Fe/C structures found in our searches are given in the supplemental material.[27]

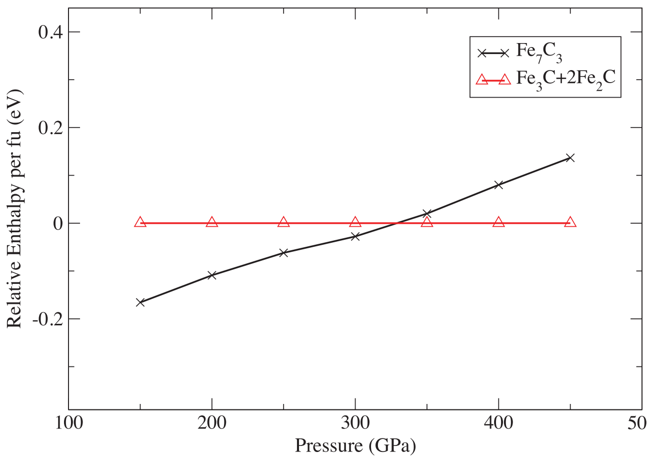

FIG. 2. (Color online) Variation of the enthalpies of Fe_7C_3 and of $Fe_3C + 2Fe_2C$ with pressure, showing that $Fe_3C + 2Fe_2C$ is more stable above ∼330 GPa.

The convex hull diagram of Fig. 1(a) shows that the compounds which are most likely to form in equilibrium at 350 GPa are Fe_3C, Fe_5C_2, Fe_7C_3, Fe_2C, Fe, and C. Fe_3C and Fe_2C lie directly on the hull while Fe_5C_2 and Fe_7C_3 lies very close to it. Figure 2 shows that Fe_7C_3 is energetically unstable to decomposition into $Fe_3C + 2Fe_2C$ at pressures greater than ∼330 GPa. It is worth noting that some stoichiometries, such as Fe_4C, lie fairly close to the hull and therefore might also form at 350 GPa. Figure 1(a) shows that the most favorable structures at 350 GPa have C fractions in the range 20% to 35%. The convex hull diagram of Fig. 1(b) shows that the compounds most likely to form in equilibrium at 150 GPa are Fe_7C_3, Fe_3C, Fe, and C.

As can be seen in Fig. 3, the most stable structures at each stoichiometry containing C fractions of less than one half do not contain any C–C close contacts. The C atoms tend to avoid one another in the Fe/C structures, but when the C fraction is greater than one half this is no longer possible and so C–C close contacts are formed. Fe–Fe close contacts are found even in structures with high C content. The convex hull diagrams of Fig. 1 show that structures with C fractions of greater than one half tend to be unstable. The Fe/C system is stable against decomposition into Fe and C so that, at zero temperature and pressures of 150 or 350 GPa, the formation of Fe/C compounds is energetically favorable.

V. PHASE TRANSITIONS

Random structure searching yields a considerable amount of data which can, for example, be used to predict pressure-induced phase transitions. Expanding the enthalpy around a pressure p_0 at which a search is performed gives

$$H(p) = H(p_0) + (p - p_0)\left.\frac{dH}{dp}\right|_{p_0} + \frac{1}{2}(p - p_0)^2\left.\frac{d^2H}{dp^2}\right|_{p_0} \cdots . \tag{2}$$

The second-order derivative in Eq. (2) can be written in terms of the bulk modulus, whose evaluation would require substantial computational effort. We find, however, that a

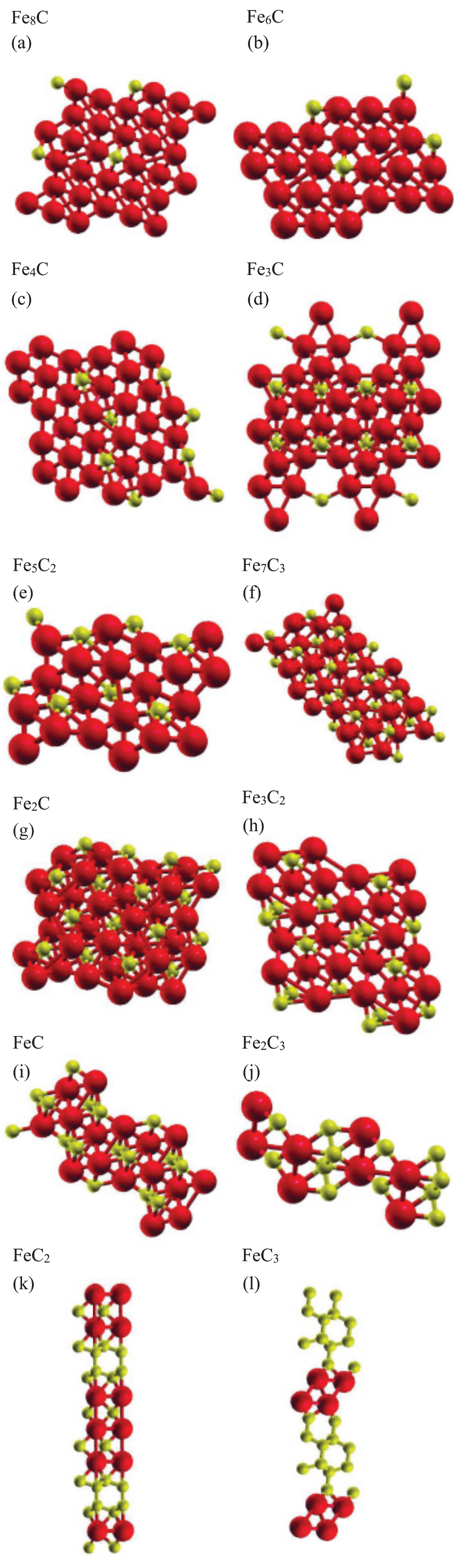

FIG. 3. (Color online) Structures for various stoichiometries of Fe and C found from searching at 350 GPa. The structures are those listed in Table I.

TABLE I. The lowest enthalpy structures found in the searches at 350 GPa which are pictured in Fig. 3. Z_1 and Z_2 are the number of formula units used in the searches and the number of formula units in the primitive unit cell, respectively. $A \times B$ denotes a search with A formula units and B symmetry operations.

Stoichiometry	Z_1	Z_2	Space Group
Fe_8C	1	1	$C2/m$
Fe_6C	1, 1 × 2	1	$C2/m$
Fe_4C	1, 2, 1 × 3	2	$P2_1/m$
Fe_3C	1, 2, 3, 1 × 4	2	$Cmcm$
Fe_5C_2	1, 1 × 2	1	$C2/m$
Fe_7C_3	1, 1 × 2	2	$Cmc2_1$
Fe_2C	1, 2, 3, 2 × 2, 2 × 3, 3 × 2	4	$Pnma$
Fe_3C_2	1, 2, 1 × 3, 1 × 4	2	$P2_1/m$
FeC	2, 3, 4, 2 × 3, 2 × 4	2	$Cmcm$
Fe_2C_3	1, 1 × 2, 1 × 3	1	$R3m$
FeC_2	2, 3, 4	3	$P\bar{3}m1$
FeC_3	1, 1 × 2, 1 × 3, 1 × 4	2	$Fmm2$

useful approximation can be obtained by neglecting the second-order term and using the fact that the first derivative of H with respect to pressure p is the volume, so that

$$H(p) \approx H(p_0) + v_0(p - p_0), \tag{3}$$

where v_0 is the volume of the phase at p_0. The quantities $H(p_0)$ and v_0 are calculated during the structure search, and therefore Eq. (3) can be used to estimate the enthalpies of the phases at any pressure p. This allows the estimation of phase transition pressures, which we refined by performing further DFT calculations in the pressure region of interest. It should be noted that we use Eq. (3) only in the preliminary analysis of our search data and none of the results reported in this paper depend on this approximate relation. The data in Fig. 4 shows that the linear approximation of Eq. (3) works well for these systems over quite large pressure ranges.

Figure 4(a) shows that a phase transition in Fe_8C between a structure with Cm symmetry and one with $C2/m$ symmetry occurs at 170 GPa. Figure 4(b) shows the enthalpy-pressure plot for Fe_3C, relative to the cementite phase. From this data we predict that Fe_3C will undergo a phase transition at 326 GPa from cementite to a new structure of $Cmcm$ symmetry, which could be the most stable at inner core pressures. Our results are consistent with high pressure experiments, which have shown that the cementite phase is stable up to at least 187 GPa.[28] The $Cmcm$ phase was found to lie close in enthalpy to cementite with an enthalpy difference of 0.015 eV per fu at 350 GPa. The relative stability of the $Cmcm$ phase with respect to cementite was found to increase linearly with pressure beyond 350 GPa. Figure 5 shows that the volumes per fu for each structure are also similar, with the $Cmcm$ phase possessing a volume which is 0.107 Å^3 per fu smaller than cementite at 350 GPa. Note that the agreement between the experimental and theoretical data in Fig. 5 improves at higher pressures.

Figure 4(c) shows the enthalpy-pressure plot for Fe_3C_2, relative to the $P2_1/m$ phase. At lower pressures, Fe_3C_2 is predicted to adopt a structure with Cm symmetry but a transition is predicted to occur at 113 GPa to a new phase with $P2_1/m$ symmetry. Figure 4(d) shows the enthalpy-pressure

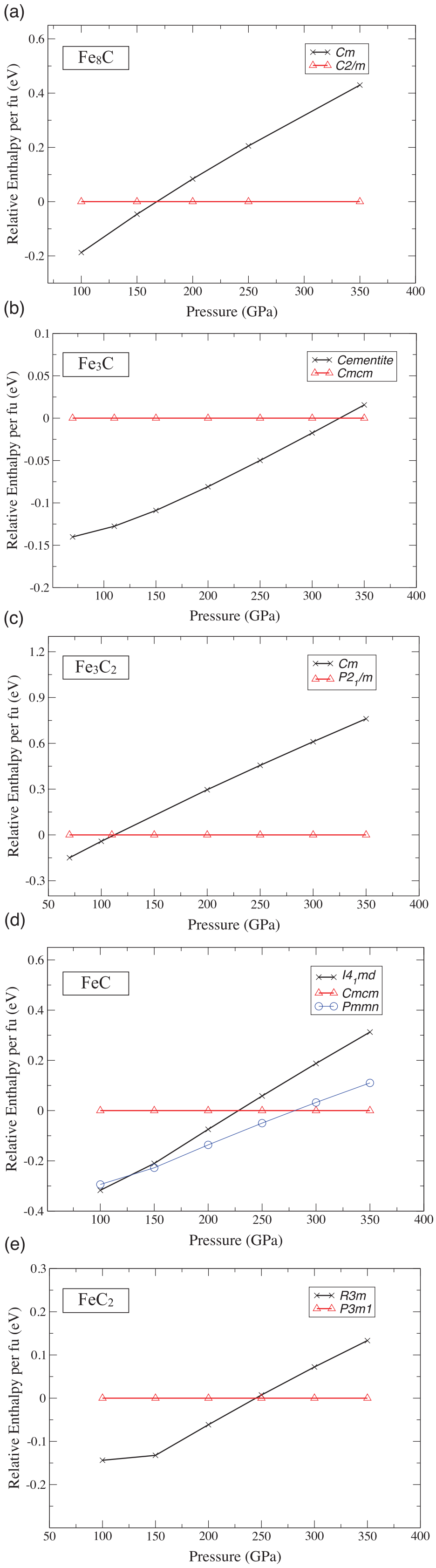

FIG. 4. (Color online) Plots of relative enthalpy against pressure for (a) Fe_8C, (b) Fe_3C, (c) Fe_3C_2, (d) FeC, and (e) FeC_2. The reference structures appear as horizontal lines at 0 eV.

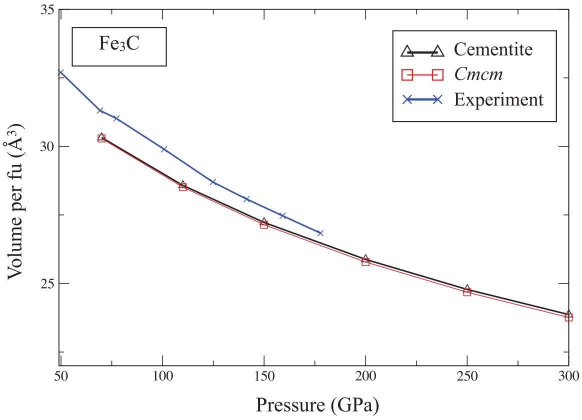

FIG. 5. (Color online) Volume-pressure plot for the Fe_3C cementite and *Cmcm* structures. Experimental data for the cementite structure are also shown.[28]

plot for FeC, relative to the *Cmcm* phase. At lower pressures, FeC adopts a structure with $I4_1md$ symmetry and a phase transition occurs at 129 GPa to a new structure with *Pmmn* symmetry. At 279 GPa this structure transforms to the high pressure *Cmcm* phase. Across the pressure range a different structure with $P2_1/m$ symmetry was found to be very close in enthalpy to the *Cmcm* structure. At 350 GPa the enthalpy difference between the two structures was found to be 0.11 eV per fu. Finally, Fig. 4(e) shows a phase transition in FeC_2. At lower pressures FeC_2 is predicted to adopt a structure of $R3m$ symmetry but at 252 GPa it transforms to a structure of $P\bar{3}m1$ symmetry.

It should be remembered that our study is for zero temperature, while the temperatures within the Earth's inner core lie in the range 5000–7000 K.[29] Finite temperatures give rise to contributions to the free energy from vibrations and electronic excitations. Calculating the relative stabilities of different phases at finite temperatures requires the calculation of their chemical potentials, which is possible using DFT methods, although it is an arduous task.[9,29] It is possible to calculate finite temperature effects within DFT simulations using, for example, the quasiharmonic approximation to calculate the phonon frequencies or by performing classical molecular dynamics simulations. Thermal effects could also be calculated within the quasiharmonic Debye model,[30] although this is unlikely to give an accurate description of the differences in free energies between phases. We have not attempted such work here, although providing candidate structures for high-pressure Fe/C phases is an essential building block for such studies.

VI. DENSITY OF ELECTRONIC STATES

Analysis of the electronic densities of states of the phases was performed using the LINDOS CODE[31] which uses a linear extrapolation method.[32,33] Figure 6 shows the densities of states for the two phases of Fe_3C and for the remaining stoichiometries found to lie on the convex hull. A Gaussian smearing of width 0.3 eV was applied to the density of states in all cases. Figure 6 show a significant density of states at the Fermi energy and these phases are metallic. Using the

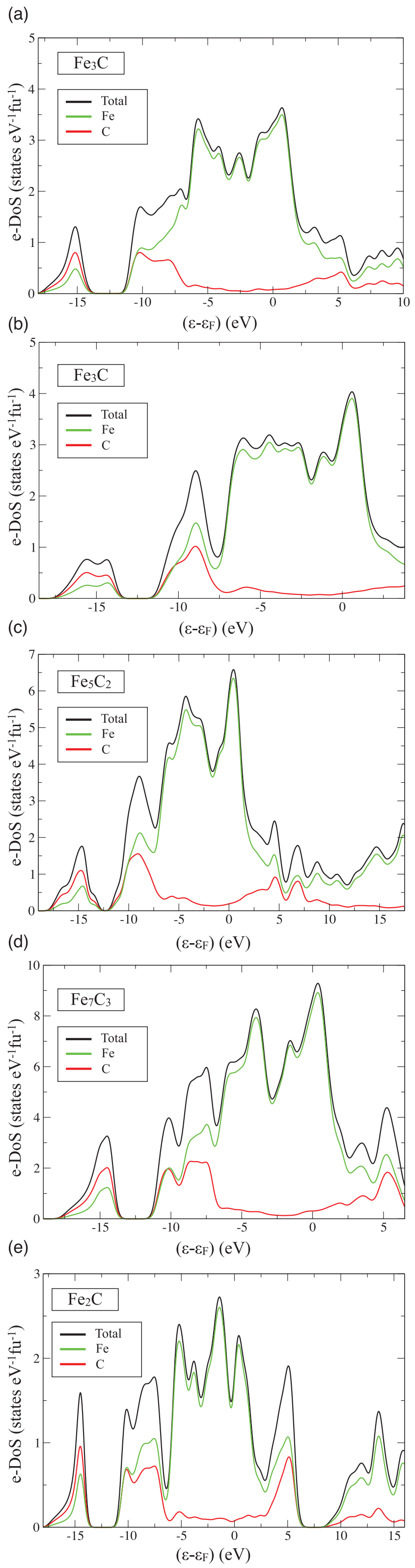

FIG. 6. (Color online) Electronic densities of states for (a) the cementite and (b) *Cmcm* phases of Fe_3C, and for the lowest enthalpy structures lying close to or on the convex hull at 350 GPa for (c) Fe_5C_2 and (d) Fe_7C_3 and Fe_2C. Each plot shows the total density of states and its decomposition into contributions from Fe and C. The Fermi energies are at 0 eV.

integrated density of states, we found that the Fe 3*s* and Fe 3*p* states lie at, respectively, ∼87 and ∼54 eV below the Fermi energy in both Fe_3C phases. The full widths at half maxima of the Fe 3*s* and Fe 3*p* states were found to be ∼0.8 and ∼1.7 eV, respectively. In addition, the C 2*s* states lie ∼15 eV below the Fermi level, as can be seen in Fig. 6. The C-derived 2*p* levels lie at 7–12 eV below the Fermi energy, and almost all of the occupied electronic density of states above the C-2*p* levels arises from the Fe *d* bands. We used LINDOS to investigate the remaining stoichiometries of interest to us, namely, Fe_5C_2, Fe_3C_2, Fe_8C, FeC, FeC_2, Fe_2C, and Fe_7C_3. The lowest enthalpy phases for each stoichiometry were found to be metallic across the pressure range investigated.

VII. CONCLUSIONS

Very little information about the high-pressure behavior of Fe/C compounds is currently available. We have predicted stable phases of 12 different Fe/C compounds at pressures in the range 70–350 GPa. We predict that the well-known cementite phase of Fe_3C transforms to a structure of *Cmcm* symmetry at 326 GPa. Our study suggests that Fe_3C and Fe_7C_3 are the most favorable phases at 150 GPa, with Fe_5C_2 and Fe_2C also being quite favorable. We find that Fe_3C, Fe_7C_3, Fe_5C_2, and Fe_2C are energetically competitive at 350 GPa. We have demonstrated that it is energetically favorable for Fe_7C_3 to decompose into $Fe_3C + 2Fe_2C$ at pressures greater than ∼330 GPa. We are not aware of any previous suggestions that Fe_5C_2 or Fe_2C might be close to stability at core pressures, and our study suggests that these stoichiometries should be considered on an equal footing to the Fe_3C and Fe_7C_3 stoichiometries considered previously. The maximum enthalpy gain on forming Fe/C compounds is calculated to be 0.10 eV per atom at 150 GPa and about 0.26 eV per atom at 350 GPa. It is of course always possible that even more stable Fe/C structures exist than the ones that we have found, which would make formation of Fe/C compounds even more favorable at high pressures. At both 150 and 350 GPa we find that phases containing large fractions of C are not stable.

Static diamond-anvil-cell experiments are very difficult at the pressures found within the Earth's inner core and consequently no such experimental studies of the Fe/C system have been reported at the relevant pressures. Theoretical studies are therefore of particular importance in this area. It is very important to determine the zero-temperature structures and stoichiometries of the system and their energetics, and our work represents a significant advance in this endeavor. Future theoretical work could involve studying the candidate structures that we have identified at finite temperatures using quasiharmonic methods and molecular dynamics simulations.

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[1] B. J. Wood, Earth Planet. Sci. Lett. **117**, 593 (1993).

[2] G. Fiquet, J. Badro, E. Gregoryanz, Y. Fei, and F. Occelli, Phys. Earth Planet. Int. **172**, 125 (2009).

[3] O. T. Lord, M. J. Walter, R. Dasgupta, D. Walker, and S. M. Clark, Earth Planet. Sci. Lett. **284**, 157 (2009).

[4] M. Mookherjee, Y. Nakajima, G. Steinle-Neumann, K. Glazyrin, X. Wu, L. Dubrovinsky, C. McCammon, and A. Chumakov, J. Geophys. Res. **116**, B04201 (2011).

[5] Y. Nakajima, E. Takahashi, N. Sata, Y. Nishihara, K. Hirose, K. Funakoshi, and Y. Ohishi, Am. Mineral. **96**, 1158 (2011).

[6] E. Bauer-Grosse, C. Frantz, G. Le Caer, and N. Heiman, J. Non-Cryst. Solids **44**, 277 (1981).

[7] C. M. Fang, M. A. van Huis, and H. W. Zandbergen, Scr. Mater. **63**, 418 (2010).

[8] Z. Q. Lv, S. H. Sun, P. Jiang, B. Z. Wang, and W. T. Fu, Comput. Mater. Sci. **42**, 692 (2008).

[9] M. J. Gillan, D. Alfè, J. Brodholt, L. Vočadlo, and G. D. Price, Rep. Prog. Phys. **69**, 2365 (2006).

[10] L. Vočadlo, D. Alfè, M. J. Gillan, I. G. Wood, J. P. Brodholt, and G. D. Price, Nature (London) **424**, 536 (2003).

[11] L. Huang, N. V. Skorodumova, A. B. Belonoshko, B. Johansson, and R. Ahuja, Geophys. Res. Lett. **32**, L21314 (2005).

[12] A. S. Côté, L. Vočadlo, and J. P. Brodholt, J. Phys. Chem. Solids **69**, 2177 (2008).

[13] S. Ono and K. Mibe, Phys. Earth Planet. Int. **180**, 1 (2010).

[14] L. Vočadlo, J. Brodholt, D. P. Dobson, K. S. Knight, W. G. Marshall, G. D. Price, and I. G. Wood, Earth Planet. Sci. Lett. **203**, 567 (2002).

[15] K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, and K. Amaya, Nature (London) **412**, 316 (2001).

[16] C. J. Pickard and R. J. Needs, J. Phys. Condens. Matter **21**, 452205 (2009).

[17] F. H. Stillinger, Phys. Rev. E **59**, 48 (1999).

[18] C. J. Pickard and R. J. Needs, J. Phys. Condens. Matter **23**, 053201 (2011).

[19] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).

[20] C. J. Pickard and R. J. Needs, Phys. Rev. B **76**, 144114 (2007).

[21] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, Z. Kristallogr. **220**, 567 (2005).

[22] L. Stixrude and R. E. Cohen, Geophys. Res. Lett. **22**, 125 (1995).

[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[24] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[25] F. H. Herbstein and J. A. Snyman, Inorg. Chem. **3**, 894 (1964).

[26] C. M. Fang, M. A. van Huis, and H. W. Zandbergen, Phys. Rev. B **80**, 224108 (2009).

[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.84.174110 for details of the structures obtained in this study.

[28] N. Sata, K. Hirose, G. Y. Shen, Y. Nakajima, Y. Ohishi, and N. Hirao, J. Geophys. Res. **115**, B0920 (2010).

[29] D. Alfè, M. Gillan, and G. D. Price, Earth Planet. Sci. Lett. **195**, 91 (2002).

[30] M. A. Blanco, E. Francisco, and V. Luaña, Comput. Phys. Commun. **158**, 57 (2004).

[31] A. J. Morris and C. J. Pickard, LINDOS version 1.3 User Manual (University College, London, 2010).

[32] C. J. Pickard and M. C. Payne, Phys. Rev. B **59**, 4685 (1999).

[33] C. J. Pickard and M. C. Payne, Phys. Rev. B **62**, 4383 (2000).