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RESEARCH LETTER

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Key Points:

- Between 1 and 2.5 wt % C can explain the core density deficit
- Carbon increases V_p , decreases V_s , increases shear wave splitting, and the anisotropy of the seismic waves
- Carbon can be a major light element in the core

Supporting Information:

- Supporting Information S1

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The influence of carbon on the seismic properties of solid iron

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Abstract The mechanical properties of C-doped hexagonal close-packed (hcp) iron are studied at high pressure from first-principles calculations. The energy required for doping with C as an interstitial impurity is 246 meV/1 wt % C at 120 GPa for one unit cell of hcp Fe and increases almost linearly with pressure. The density deficit of the inner core can be matched for 1 to 2.5 wt % in hcp Fe, depending on the thermal profile. Carbon doping in hcp iron increases the compressional seismic wave velocity, decreases the shear wave velocity, while increasing the shear wave splitting and seismic anisotropy. In general, the presence of C in the inner core helps in explaining the observed seismic properties, though it cannot be considered the only light element.

1. Introduction

Geochemical evidence, e.g., mass balance calculations, analysis of iron meteorites, element partitioning [McDonough and Sun, 1995], and geophysical information, e.g., density, seismic wave velocities, and seismic anisotropy [Anderson, 2003] suggest that the Earth's core is formed of an Fe-based alloy containing Ni and one or more lighter elements. All of the geochemically favored light elements possibly present in the core, H, C, O, Mg, Si, P, or S would be found in small amounts [Poirier, 1994; Antonangeli et al., 2010; Badro et al., 2007; Lin et al., 2002; Takafuji, 2005; Wood, 2008; Wood et al., 2008; Rubie et al., 2011], i.e., typically less than 5 wt %. As there are no such C-poor stoichiometric compounds known to date, most likely these impurities are dissolved in the solid hexagonal Fe-Ni alloy. Hence, a meaningful approach is to study these doped alloys.

Here the focus is on the Fe-C system. While the Fe-C phase diagram at ambient pressure conditions is extremely well documented [Chipman, 1972] due to its technological importance, there is no study of the solubility of C in the Fe alloys at the extreme conditions characteristic to the Earth's solid core. Several C-rich stoichiometric phases have been synthesized experimentally at lower pressures or proposed computationally.

In experiments, two phases have been synthesized and characterized: Fe_3C and Fe_7C_3 . Fe_3C has been extensively studied in experiments up to about 70 GPa [Lin et al., 2004; Wood et al., 2004; Duman et al., 2005; Gao et al., 2008; Rouquette et al., 2008; Fiquet et al., 2009; Sata et al., 2010; Ono and Mibe, 2010; Gao et al., 2011; Prescher et al., 2015; Litasov et al., 2013] and in first-principles calculations [Wang et al., 2005; Vocadlo et al., 2002; Mookherjee, 2011]. It is found naturally in meteorites as the mineral cohenite; it has a complex orthorhombic structure with $Pnma$ space group, formed of pairs of Fe triangular prisms with the C atoms filling the voids between these prisms. The magnetic spin transition, the equation of state, and the seismic wave velocities have been recorded and computed. Two experimental studies showed the formation of Fe_7C_3 around 5–7 GPa [Lord et al., 2009] suggesting that the Fe-C system at core conditions should involve Fe_7C_3 rather than Fe_3C . Several structures with hexagonal $P6_3mc$ or with orthorhombic $Pnma$ symmetries have been proposed so far for Fe_7C_3 with the hexagonal being more stable [Fang et al., 2009]. Recent measurements on single crystals of Fe_7C_3 suggest yet another orthorhombic modification with $Pbca$ symmetry. The latter yields Poisson ratio values that are remarkable close to the measured ones for the inner core [Prescher et al., 2015]. While geochemical mass balance considerations would rule out the presence of a phase rich in carbon of up to 8.4 wt % in the inner core, these new experimental findings advocate a major role for carbon in the quest for the best candidates for the light elements of the Earth's core.

In the Fe-rich half of the Fe-C binary, several theoretical stoichiometries have been investigated in first-principles calculations FeC [Bazhanova et al., 2012], Fe_5C_2 [Zhao et al., 2015], Fe_2C , and Fe_4C [Bazhanova et al., 2012; Zhao et al., 2015], with the Fe_2C stable at core pressures. Here a different approach is taken wherein

the hexagonal close-packed (hcp) phase of iron is doped with light element impurity at the 1–2 wt % level. Similarly to a previous study on H-doped iron [Caracas, 2015], here the effect of carbon doping on the elastic, seismic, and compressional properties of hcp iron is investigated from first-principles calculations.

2. Computational Details

First-principles calculations based on the planar augmented wave functions (PAW) formalism [Blochl, 1994] were performed using the generalized gradient approximation [Perdew *et al.*, 1996] for the exchange-correlation functional of the density functional theory, in the ABINIT implementation [Torrent *et al.*, 2008; Gonze *et al.*, 2002, 2009]. More details about the PAW method can be found in the original papers dealing with the theory [Blochl, 1994] or implementation [Torrent *et al.*, 2008].

The electron density was sampled in the reciprocal space (in the first Brillouin zone) using a grid of special high-symmetry \mathbf{k} points [Monkhorst and Pack, 1976]. Just as usual with plane wave calculations, and similarly to the standard norm-conserving pseudopotentials, the kinetic energy cutoffs and the density of the \mathbf{k} -point grid were consecutively and independently raised while monitoring the convergence of the total energy and the residual stresses. The final grid of \mathbf{k} points for the hcp unit cell of iron was $16 \times 16 \times 12$. The supercells that host the carbon atoms had grids reduced according to their size. The kinetic energy cutoff for the wave functions on the coarse mesh was 16 Ha (1Ha = 27.2116 eV), and the cutoff for the wave functions on the finer grid inside the PAW spheres was 48 Ha. This set of parameters ensured an accuracy of the calculation on the order of a few kilobars in pressure, of the milliHartree per hcp unit cell in energy, and better than 4 GPa for the elastic constants.

The elastic constants tensors were computed using the linear stress-strain relations. Positive and negative uniaxial strains of 1% were applied along each of the x and z axes of the unit cell and shear strains in the basal and vertical planes. In each case, the atomic positions were relaxed under fixed unit cell geometry. Linear fits between the residual stresses and the imposed strains yielded the elasticity. The seismic wave velocities were obtained after computing the bulk elastic moduli, K , and the shear elastic moduli, G , in the Voigt-Reuss-Hill formulation.

All simulations reported here were performed at static conditions (i.e., $T = 0$ K). This is a large approximation with respect to the actual temperatures of the core, which affects the absolute values of certain seismic properties [Vocadlo *et al.*, 2009]. Here the focus is on the relative effect of chemistry; the validity of this effect at the high temperatures of the core remains to be investigated in later studies.

3. Results and Discussion

Because of the small atomic radius compared to Fe, the C atoms were added interstitially in the hcp structure. There are two possible interstitial defect sites in the hcp structure: at the b (0,0,0) and at the c (1/3,2/3,3/4) positions. Tests of the two configurations in a $2 \times 2 \times 1$ hcp supercell with eight Fe atoms showed that the first position has about 5.5 eV/supercell lower enthalpy than the latter, with a weak variation under pressure.

The enthalpy of formation of various impurities was estimated according to the reactions: $\text{FeC}_x = (1 - 3^*x)\text{Fe} + x\text{Fe}_3\text{C}$ and $\text{FeC}_x = \text{Fe} + x\text{C}$. Here FeC_x is C-doped hcp Fe, Fe_3C has the cementite structure, and C has diamond structure. The energy required for doping scales linearly with the amount of C incorporated, with weak configurational dependence. The defect energy increases almost linearly with pressure from 246 meV/1 wt % C at 120 GPa to 398 meV/1 wt % per one Fe hcp unit cell when using the cementite structure as C reference, and from 211 meV/1 wt % C at 120 GPa to 310 meV/1 wt % per one Fe hcp unit cell when using the diamond structure as C reference. Another theoretical study [Huang *et al.*, 2005] analyzing the enthalpy of formation of 6 wt % C defects in both hcp and body-centered cubic iron found a nonlinear dependence with pressure. Nevertheless, all the theoretical results suggest that at equilibrium, or close to it, iron would stay rather carbon-poor when performing experiments in the diamond anvil cell without heating.

The incorporation of carbon has a direct effect on the volume of hcp Fe as shown in Figure 1. The increase is almost linear with the amount of carbon and is roughly independent of pressure over the entire stability range of the hcp phase. But the relative effect is different for the a and c parameters. As a result, the c/a ratio increases when increasing the amount of carbon. It is also more dependent on the actual configuration of the defects than on other measures. The combined increase of both a and c parameters results in an increase of

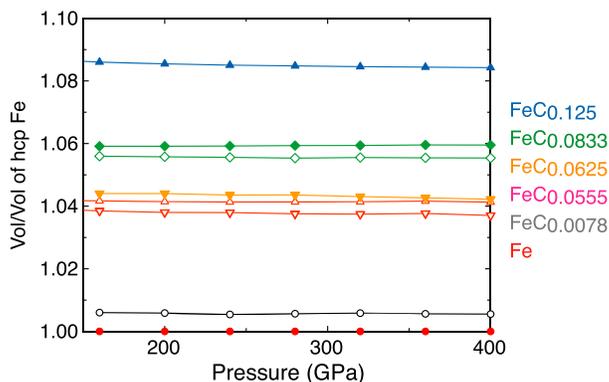


Figure 1. Density variation as a function of pressure for several C concentrations in hexagonal-close packed iron.

the specific volume and a decrease of the density. The latter is linear with the amount of carbon: the density decreases by about 2.8% per each 1 wt % added carbon, slightly more at lower pressures (2.83 at 160 GPa) than at higher pressure (2.80 at 400 GPa). Assuming a thermal dilatation that is independent of the amount of carbon, this corresponds to adding about 1 wt % C in order to fit the density deficit of the inner core in the cold regime and up to 2.5 wt % in the hot regime [Anderson and Isaak, 2002].

To study the effect of carbon on the elastic properties of hcp Fe, two concentrations were studied: $\text{FeC}_{0.0625}$ and $\text{FeC}_{0.125}$, corresponding, respectively, to $2 \times 2 \times 2$ and $2 \times 2 \times 1$ supercells. In both cases the symmetry is partially broken and reduced to trigonal; there are seven nonzero elastic constants: $C_{11} = C_{22}$, C_{33} , C_{12} , $C_{13} = C_{23}$, $C_{44} = C_{55}$, C_{66} , and $C_{56} = C_{14} = -C_{24}$. The elastic constants increase almost linearly with pressure. The effect on the bulk moduli of hcp iron is surprisingly weak (Figure 2). At 320 GPa pressure the bulk modulus of pure iron computed at 1407 GPa, increases to 1413 GPa for $\text{FeC}_{0.0625}$, and at 1419 GPa for $\text{FeC}_{0.125}$. This corresponds to less than 10.8 GPa increase for each 0.1 mol % C, or 4.6 GPa for each 1 wt % additional C into hcp Fe. The increase is constant with pressure. The effect of carbon is more visible on the shear modulus, which decreases with addition of carbon: about 15.3 GPa decrease for each 0.1 mol % C, or 65.2 GPa for each 1 wt % additional C into hcp Fe. These trends are different from Fe_3C and show the importance of the crystal structure on elastic properties.

The weak dependence of the bulk moduli with the carbon content is reflected also in the change in compressional wave velocities, V_p . Figure 3 shows the variation of seismic wave velocities in a Birch plot—as a

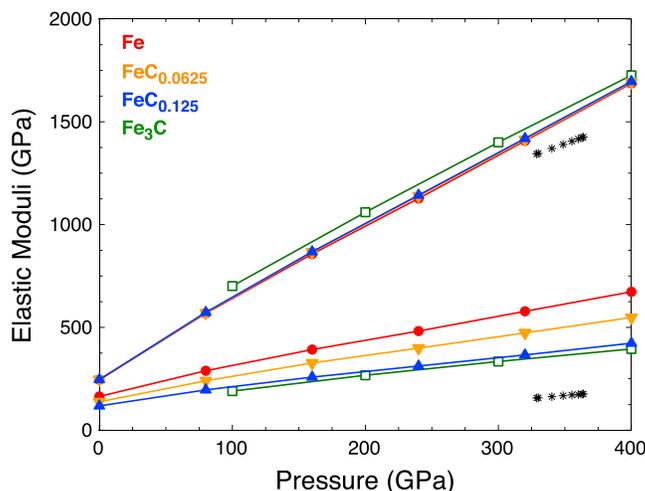


Figure 2. Bulk and shear elastic moduli in the Voigt-Reuss-Hill average for C-bearing hexagonal-close packed iron. Comparison with stoichiometric orthorhombic Fe_3C . Preliminary reference Earth model (PREM) values (with black stars) are only indicative, due to the temperature difference, which tends to reduce the elastic moduli. Carbon has a surprisingly weak effect on the bulk modulus of iron when dissolved in its structure.

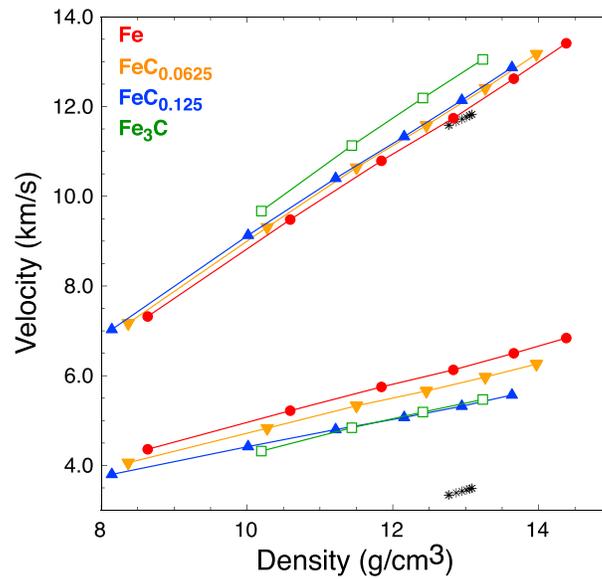


Figure 3. Seismic wave velocities of C-bearing hcp iron, compared with stoichiometric orthorhombic Fe₃C. PREM values (with black stars) are only indicative, due to the temperature difference, which tends to reduce the velocities.

function of density. In the amounts considered here, carbon increases V_p of hcp iron with about 0.1–0.15 km/s. There is only a small difference between FeC_{0.0625} and FeC_{0.125}. The shear wave velocities, V_s, show instead a clear decrease with the amount of carbon (Figure 3) relative to V_s of hcp Fe. The decrease is not linear and is enhanced by the presence of C. It is also interesting to note that V_s of hcp FeC_{0.125} is comparable to V_s of cohenite Fe₃C. While our simulations confirm the trends already observed in the literature, our findings also suggest that it is not necessarily needed to have various C-rich stoichiometric phases with different structures in the inner core, like Fe₃C or Fe₇C₃ [Gao *et al.*, 2011, 2008; Chen *et al.*, 2014; Prescher *et al.*, 2015], to obtain a significant lowering of the shear velocities; a small amount of carbon dissolved into iron would be enough, as proposed earlier [Fiquet *et al.*, 2009].

It is known that pure hcp Fe has a relatively low Poisson ratio, of about 0.32 at inner core pressures, compared to about 0.45 of PREM (Figure 4). It has been already suggested that the addition of C to Fe, as in Fe₃C, raises the Poisson ratio and thus has the desired effect when trying to fit PREM [Gao *et al.*, 2011]. Fe₇C₃ has values which are similar to PREM [Prescher *et al.*, 2015]. But such stoichiometric phases would doubtfully be major components of the Earth’s core, as they are too rich in carbon. But the present calculations show that even

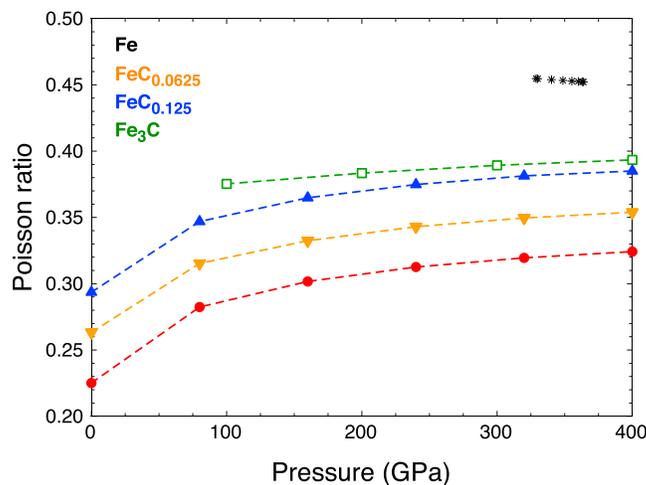


Figure 4. Poisson ratio of C-bearing hcp iron in comparison with stoichiometric orthorhombic Fe₃C and with PREM (with black stars). C doping considerably increases the Poisson ratio of Fe.

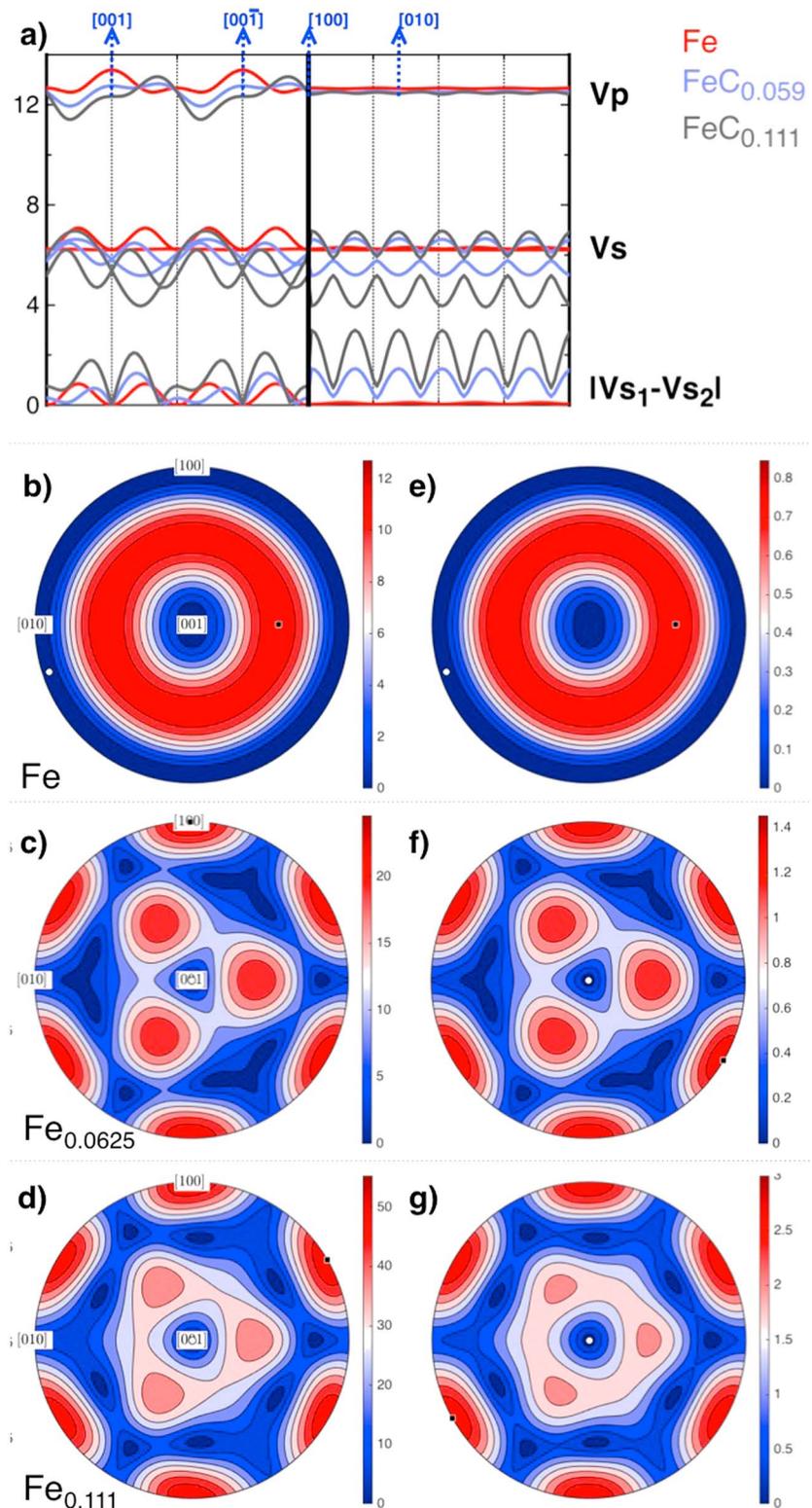


Figure 5. Seismic anisotropy of C-bearing hcp iron. (a) Compressional, V_p , shear, V_s , wave velocities, and shear wave splitting, $|V_{s1} - V_{s2}|$, for waves traveling in planes perpendicular to the [100] and [001] directions, respectively, in the left and right halves of the diagram for several C contents. (b–g) Stereographic representations of the seismic anisotropy as a function of C content. Anisotropy of the seismic shear waves V_s for, respectively, (b) hcp Fe, (d) ordered trigonal FeC_{0.0625}C, and (f) ordered trigonal FeC_{0.125}C. (c, e, and g) Shear wave splitting for the same compositions.

in the small amounts considered here the effect is already positive. $\text{FeC}_{0.125}$ has a Poisson ratio of about 0.38, very close to the one of cementite Fe_3C , at about 0.39.

The anisotropy of both Vp and Vs waves as well as the Vs splitting are strongly affected by the presence of carbon. This was already observed in other Fe-C stoichiometric compounds at low pressure. Figure 5a shows the seismic wave velocities as a function of propagation direction through single crystals for the compositions considered above. The addition of carbon departs the position of the maximum of Vp from the vertical polar axis, increases the anisotropy of Vp in the basal plane, approaches the maximum of Vs to the vertical polar axis, and increases the amount of shear wave splitting. These effects are more visible in a stereographic representation (Figures 5b–5g of the anisotropy and the splitting of the S waves). The presence of ordered C defects breaks the hexagonal symmetry, and as a result the travel pattern of the seismic waves changes. The anisotropy of Vp waves increases with the addition of C: from about 12% for pure iron it doubles for $\text{FeC}_{0.0625}$ and the trend continues to $\text{FeC}_{0.125}$. The maximum of the shear wave splitting increases from about 0.8 km/s for pure iron to 1.4 km/s for $\text{FeC}_{0.0625}$ and 3 km/s for $\text{FeC}_{0.125}$, the latter value representing almost 40% from the Vs maximum. However, in a realistic situation this change would be somehow smoothed out by the configuration disorder of carbon, even if it would still be present. Nevertheless, the presence of carbon in the inner core would relax the constraints one needs to put on the texture of pure hcp Fe aggregates in order to fit the observed seismic anisotropy [Romanowicz *et al.*, 2016].

In conclusion, the addition of C as a light element is done as an interstitial doping impurity in the hcp structure. Its effect on the seismic wave velocities of pure iron is to increase Vp and to decrease Vs, in agreement with the constraints put on the light elements in the core. The seismic anisotropy is greatly enhanced, with the fastest axis of Vp propagation tilted away from the hexagonal axis of Fe. In particular, this aspect helps in relaxing the strong textural constraints put today on pure iron aggregates [Romanowicz *et al.*, 2016]. But the increase of anisotropy of Vs is opposite to the current observations. Thus, carbon is certainly not the only light element as it cannot explain the totality of the seismic observations of the inner core. Future studies will require taking into account both the temperature effects as well as the multicomponent alloying of iron in order to elucidate the nature of the light elements present in the Earth's core.

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