



# Experimental constraints on the sound velocities of cementite Fe<sub>3</sub>C to core pressures

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## ABSTRACT

Sound velocities of cementite Fe<sub>3</sub>C have been measured up to 1.5 Mbar and at 300 K in a diamond anvil cell using the nuclear resonant inelastic X-ray scattering (NRIXS) technique. From the partial phonon density of states (pDOS) and equation of state (EOS) of Fe<sub>3</sub>C, we derived its elastic parameters including shear modulus, compressional ( $V_P$ ) and shear-wave ( $V_S$ ) velocities to core pressures. A pressure-induced spin-pairing transition in the powdered Fe<sub>3</sub>C sample was found to occur gradually between 10 and 50 GPa by the X-ray Emission Spectroscopy (XES) measurements. Following the completion of the spin-pairing transition, the  $V_P$  and  $V_S$  of low-spin Fe<sub>3</sub>C increased with pressure at a markedly lower rate than its high-spin counterpart. Our results suggest that the incorporation of carbon in solid iron to form iron carbide phases, Fe<sub>3</sub>C and Fe<sub>7</sub>C<sub>3</sub>, could effectively lower the  $V_S$  but respectively raise the Poisson's ratio by 0.05 and 0.07 to approach the seismically observed values for the Earth's inner core. The comparison with the preliminary reference Earth model (PREM) implies that an inner core composition containing iron and its carbon-rich alloys can satisfactorily explain the observed seismic properties of the inner core.

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## 1. Introduction

Iron (Fe) is widely accepted as the predominant constituent of the Earth's liquid outer core and solid inner core (Birch, 1964; Li and Fei, 2014). The core density deficit indicated the presence of considerable amount of lighter elements in the core, i.e., hydrogen (H), carbon (C), oxygen (O), silicon (Si), and sulfur (S) (Hirose et al., 2013; Li and Fei, 2014). Despite numerous concerted efforts from mineral physics, geochemistry, cosmochemistry, and seismology, the identity and abundance of the light constituents remain controversial. Alloying of one or more light elements with Fe at elevated pressure and temperature is found to substantially change the elastic properties such as density and sound velocities, essential to account for the core density deficit and sound velocity discrepancy (Hirose et al., 2013; Li and Fei, 2014). As such, understanding the high pressure–temperature ( $P$ – $T$ ) behaviors of liquid and solid Fe alloyed with lighter elements is integral to gaining insights into the compositions of Earth's various layers,

the conditions under which the core and mantle segregated, the temperature regimes of the core and mantle, and the core–mantle interactions.

The plausibility of carbon as the principal light element in the Fe-dominant core originated partly from the observations of its high abundance as an element in the Solar System and carbonaceous chondrites and its high affinity to liquid Fe at the core–mantle segregation conditions (Wood, 1993; Wood et al., 2013; Chen and Li, 2016). As suggested by cosmochemical and geochemical studies, the evaporative loss of volatiles to space and the core formation may have caused the relative depletion of carbon in the bulk silicate Earth (BSE) in comparison with the Sun and carbonaceous chondrites (Wood et al., 2013; Chen and Li, 2016). The latter process involving the sequestration of Fe and lighter elements such as carbon from the mantle to the core was thought to have left behind isotopic signatures with elevated  $^{56}\text{Fe}/^{54}\text{Fe}$  and  $^{13}\text{C}/^{12}\text{C}$  ratio of the terrestrial basalts relative to chondrites and other terrestrial planetary bodies (Wood et al., 2013; Horita and Polyakov, 2015; Shahar et al., 2016).

The two common Fe carbide phases considered for the inner core are Fe<sub>3</sub>C and Fe<sub>7</sub>C<sub>3</sub> (Wood, 1993; Gao et al., 2008; Naka-

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jima et al., 2009; Lord et al., 2009; Chen et al., 2014; Chen and Li, 2016). Cementite ( $\text{Fe}_3\text{C}$ ) was initially proposed as the most likely carbide phase for the inner core, on the basis of thermodynamics calculations (Wood et al., 2013). At inner core boundary (ICB) condition,  $\text{Fe}_3\text{C}$  was considered to be the first phase to crystallize from an Fe–C–(S) liquid with merely 0.3% carbon (Wood et al., 2013). With a renewed interest more recently, the Fe–C–(S) system has been explored at higher pressures and temperatures (Nakajima et al., 2009; Dasgupta et al., 2009; Lord et al., 2009; Fei and Brosh, 2014). The revised phase diagrams of the Fe–C system from new high-pressure data suggested that  $\text{Fe}_7\text{C}_3$  would be the first phase crystallizing from Fe–C liquids at ICB conditions (Lord et al., 2009; Nakajima et al., 2009; Fei and Brosh, 2014; Liu et al., 2016b), although experimental verifications at higher pressures are required. *Ab initio* calculations, however, reported conflicting results. Based on recent first-principles calculations on  $\text{Fe}_7\text{C}_3$ , the hexagonal  $\text{Fe}_7\text{C}_3$  phase is suggested to become stable above 150 GPa, whereas the orthorhombic  $\text{Fe}_7\text{C}_3$  phase is more stable below approximately 100 GPa (Raza et al., 2015). Zero kelvin theoretical structure prediction calculations have revealed that  $\text{Fe}_3\text{C}$  may adopt a new structure other than the cementite at core pressures and  $\text{Fe}_7\text{C}_3$  may decompose to more stable stoichiometries such as  $\text{Fe}_2\text{C}$  and  $\text{Fe}_3\text{C}$  at inner core pressures (Bazhanova et al., 2012).

The magnetic transitions have been found to profoundly affect the physical properties of Fe alloys, such as density and sound velocities (Chen and Li, 2016). As a viable candidate that may exist in the inner core,  $\text{Fe}_3\text{C}$  has been reported to undergo magnetic transitions at high pressures. First-principles density functional theory (DFT) calculations have predicted that the ferromagnetic order in  $\text{Fe}_3\text{C}$  ceases at approximately 60 GPa (Vočadlo et al., 2002), but experiments suggest lower transition pressures (Lin et al., 2004b; Ono and Mibe, 2010). Recent DFT calculations suggested that a magnetic collapse of  $\text{Fe}_7\text{C}_3$  occurring at approximately 67 GPa, though much lower values were reported by experimental studies (Chen et al., 2014; Liu et al., 2016a).

Mineral physics investigations of the candidate Fe carbides have indicated that the alloying of carbon with Fe may be necessary to explain the seismic observations of the core (Gao et al., 2009; Chen et al., 2012, 2014; Prescher et al., 2015; Chen and Li, 2016; Liu et al., 2016a). Recent studies suggested that the inner core may contain significant fraction of  $\text{Fe}_7\text{C}_3$  in order to explain the anomalously low shear-wave (S-wave) velocity of the inner core (Chen et al., 2014) and its high Poisson's ratio ( $\nu$ ) (Prescher et al., 2015). There are still debates on which Fe carbide phase could be stable at the inner core conditions. Nevertheless, the sound velocity measurements of Fe carbides to core pressures are still limited. To date, the sound velocities measurements for  $\text{Fe}_3\text{C}$  have been limited to  $\sim 70$  GPa (Gao et al., 2008; Fiquet et al., 2009). In this study, we determined both the  $V_P$  and  $V_S$  of  $\text{Fe}_3\text{C}$  up to 153 GPa at 300 K in a panoramic diamond anvil cell (DAC), employing the nuclear resonant inelastic X-ray scattering (NRIXS) technique. Our X-ray Emission Spectroscopy (XES) measurements revealed the pressure-induced magnetic or spin-pairing transition in  $\text{Fe}_3\text{C}$ , significantly influencing the elastic properties. We evaluated and discussed the effect of carbon on the acoustic properties of Fe under core conditions.

## 2. Experimental methods

### 2.1. Starting materials and high pressure experiments

The powered  $\text{Fe}_3\text{C}$  sample was synthesized from a mixture of 94.45%  $^{57}\text{Fe}$ -enriched Fe powder (Cambridge Isotope Laboratories Inc., #FLM-1812-0) and graphite powder (Sigma-Aldrich, #282863) at an atomic ratio of Fe:C = 2.922:1 (Gao et al., 2009). The starting material was equilibrated at 2 GPa and 1373 K for 4 h in a

multi-anvil press. The synthesized sample was probed by X-ray diffraction and conventional Mössbauer spectroscopy and found to be fine powder and pure  $\text{Fe}_3\text{C}$  (Gao et al., 2009).

The sample was then mechanically compressed to a pellet with a thickness of 15  $\mu\text{m}$ . The sample assemblage was sandwiched by two NaCl layers and loaded into a sample chamber of  $\sim 75$   $\mu\text{m}$  in diameter drilled in cubic boron nitride (cBN) insert in an X-ray-transparent beryllium (Be) gasket. A panoramic DAC equipped with two 150  $\mu\text{m}$  culet size double-bevel diamond anvils ( $8^\circ$  angle) was used to generate high pressure, as described in Gao et al. (2009). The pressures of the sample at and below 107 GPa were determined by the ruby fluorescence of a few ruby spheres placed next to the sample (Mao et al., 1986) and the Raman spectra of the diamond anvil on top of the sample (Akahama and Kawamura, 2004). At pressures higher than 107 GPa, the pressures are solely determined by the Raman spectra of diamonds collected before and after each measurement. The discrepancies between ruby and diamond pressures are typically within  $\pm 5$  GPa, even at 107 GPa in this study.

### 2.2. XES measurements at high pressures

The XES measurements of  $\text{Fe}_3\text{C}$  were performed in Sector 16-ID-D of the Advanced Photon Source (APS), Argonne National Laboratory. The technical details were described in Chen et al. (2014). The powdered sample was loaded in neon pressure medium and compressed in a panoramic DAC. Ruby spheres were loaded near the sample for pressure determination (Mao et al., 1986). The XES spectra for  $\text{Fe}_3\text{C}$  were normalized to unity in integrated intensity and analyzed using the Integrated Absolute Difference method (Vanko et al., 2006). The integrated spectra area differences between the  $K'_\beta$  satellite peaks of  $\text{Fe}_3\text{C}$  at high pressures and the low spin state reference spectrum of  $\text{FeS}_2$  at 0 GPa. were calculated based on the integrated spectral area within 7035–7050 eV. The absolute values of the area differences were used as a proxy for the total spin momentum (Vanko et al., 2006; Chen et al., 2014).

### 2.3. NRIXS measurements at high pressures

The NRIXS experiments were performed at the Sector 3-ID-B of the APS, as described in Gao et al. (2009). The size of the X-ray beam was  $< 10$   $\mu\text{m}$  in diameter, and the energy resolution was  $\sim 1$  meV. At each pressure, NRIXS spectra were collected by tuning the X-ray energy within  $-70$  to 95 meV around the  $^{57}\text{Fe}$  nuclear transition energy of 14.4125 keV (corresponding to a wavelength of 0.86025 Å). Multiple NRIXS spectra were collected until sufficient counts were obtained at each pressure. NRIXS spectra were collected at 0, 26, 45, 65, 82, 107, 119, 130, and 153 GPa for one DAC loading. Typically, 6 to 26 NRIXS spectra were collected at each pressure from ambient to the highest pressure of 153 GPa in order to obtain sufficient counts for reliable velocity determination. The summed NRIXS spectrum at each pressure was then used to derive the phonon density of state (pDOS) (Sturhahn and Jackson, 2007).

The partial pDOS of Fe in  $\text{Fe}_3\text{C}$  was extracted from the NRIXS spectra at each pressure using the PHOENIX software program (Sturhahn, 2000). At a given pressure, Debye sound velocity ( $V_D$ ) was derived from a parabolic fitting to the low-energy region of the pDOS using the following relationship:

$$\rho V_D = \frac{3\tilde{M}}{2\pi^2\hbar^3} \frac{E^2}{g(E)} \quad (1)$$

where  $\rho$  is the density of the  $^{57}\text{Fe}$ -enriched sample,  $g(E)$  is the pDOS as a function of energy  $E$ ,  $\hbar$  ( $h/2\pi$ ) is the reduced Planck

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