



## Magnetic transition of iron carbide at high pressures

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### ABSTRACT

High-pressure experiments and first-principles calculations were performed to investigate the compressibility and the magnetic properties of the iron carbide system, Fe<sub>3</sub>C. The experimental data indicate that a significant reduction in volume occurs without any major structural changes at 55 GPa. Our calculations show that this reduction in volume corresponds to a magnetic collapse from the ferromagnetic to the non-magnetic state. The magnetic phase diagram of Fe<sub>3</sub>C indicates that the non-magnetic state is stable under the conditions of the Earth's inner core. The equation of state for non-magnetic Fe<sub>3</sub>C up to 400 GPa was also studied to assess this materials as a candidate as a major component of the Earth's inner core. The isothermal bulk modulus of non-magnetic Fe<sub>3</sub>C at 0 K was found to be about twice as high as the experimental value of ferromagnetic Fe<sub>3</sub>C. The density of non-magnetic Fe<sub>3</sub>C is much lower than that in the inner core, as determined from the PREM model. This indicates that it is not possible that Fe<sub>3</sub>C is a major component of the Earth's inner core.

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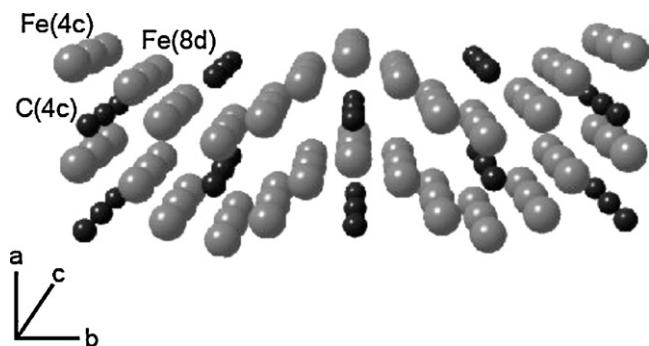
### 1. Introduction

It is generally accepted that the Earth's inner core is less dense than pure iron (e.g., Birch, 1952, 1968; Jeanloz, 1979; Mao et al., 1990), indicating that the chemical composition of the inner core is not pure iron. A significant portion of the inner core consists of lighter elements, such as C, S, O, Si and H (Jeanloz, 1990; Poirier, 1994). Wood (1993) proposed that the inner core might consist of Fe<sub>3</sub>C from a couple of aspects. The density of Fe<sub>3</sub>C determined from its equation of state at the pressure in the inner core agrees with that determined from seismic observations. Thermodynamic calculations on carbon-bearing iron systems show that Fe<sub>3</sub>C is the first crystalline phase to occur at high pressures corresponding to those at the inner core–outer core boundary. Moreover, carbon-rich Fe melts are formed during impact heating of the Earth's accretion and differentiation process because of the strong pressure dependence of the volatility of carbon. Therefore, an experimental investigation into Fe<sub>3</sub>C at extreme pressures and temperatures is an important contribution to the effort in testing the Fe<sub>3</sub>C inner core model. Recent high-pressure experiments have shown that the extrapolated equation of state for Fe<sub>3</sub>C could explain the density of the inner core (Scott et al., 2001; Li et al., 2002). In contrast, *ab initio* cal-

culations do not support the model of an Fe<sub>3</sub>C inner core (Vočadlo et al., 2002; Huang et al., 2005). This discrepancy between previous experimental results and calculations may be caused by the experimental uncertainties. Previous high-pressure experiments on the magnetic transition pressure from the ferromagnetic state to the non-magnetic state gave contradictory results. In some studies, no magnetic transition up to 73 GPa was observed (Scott et al., 2001; Li et al., 2002). In other experimental studies, evidence for a magnetic transition at ~5 GPa (Gao et al., 2008), ~10 GPa (Duman et al., 2005), ~25 GPa (Lin et al., 2004), and ~68 GPa (Fiquet et al., 2009) at ambient temperature was observed. Therefore, the extrapolation of the physical properties of ferromagnetic Fe<sub>3</sub>C to conditions at the inner core may be misleading. Moreover, it has not been clearly explained why the inconsistency in the magnetic transition pressure in previous experiments occurred. One possibility is that a significant hysteresis of the magnetic transition may disturb the magnetic ordering in Fe<sub>3</sub>C, because most of the previous experiments were performed at low temperatures, where the accumulated differential stress in the sample could not be released. In the case of FeO, the release of differential stress in the sample led to the detection of a reliable pressure for the magnetic transition related to the spin transition of the iron atoms (Ono et al., 2007). In contrast, *ab initio* calculations predict that non-magnetic Fe<sub>3</sub>C is stable at pressures above 60 GPa (Vočadlo et al., 2002) at 0 K, which is in disagreement with most experimental studies. It is known that the influence of the magnetic transition is non-negligible for various physical properties. This inconsistency among not only the previous experiments but also between the previous experiments

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**Fig. 1.** The regular pleated structure of cementite,  $\text{Fe}_3\text{C}$ . The grey and black squares denote the iron and carbon atoms, respectively. The space group of cementite is  $Pnma$ . In the case of the ferromagnetic phase, all the iron atoms are in the high spin state.

and calculations need to be resolved to understand the composition of the Earth's inner core.

$\text{Fe}_3\text{C}$  (cementite) has an orthorhombic structure with space group  $Pnma$ , and has 16 atoms in a conventional cell (Fig. 1). The structure can be viewed in terms of a pleated layer of iron atoms, derived from a close-packed hexagonal structure with carbon atoms occupying the interstitial sites (Fasisk and Jeffrey, 1965). At ambient pressure and temperature,  $\text{Fe}_3\text{C}$  is metallic and is ferromagnetically ordered. From the viewpoint of its crystallography,  $\text{Fe}_3\text{C}$  has two iron sites (4c and 8d) and one carbon site (4c). According to previous *ab initio* calculations, the two iron sites are magnetically non-equivalent (Häglund et al., 1991). The difference of magnetic moment between two iron sites from calculations was approximately corresponding to the uncertainty of experimental values (Hofer and Cohn, 1959). The experimentally determined structure was also confirmed by recent *ab initio* calculations (Vočadlo et al., 2002; Faraoun et al., 2006; Jiang et al., 2008). High-temperature experiments show that the magnetic transition from the ferromagnetic to the paramagnetic state occurs at  $\sim 485$  K (Vočadlo et al., 2002; Duman et al., 2004). Duman et al. (2004) also investigated the equation of state for  $\text{Fe}_3\text{C}$  up to 20 GPa, at temperature above the magnetic transition temperature (550 K). Their experiments showed a significant difference in the bulk modulus between room temperature and 550 K. This implies that the influence of the pressure-induced magnetic transition from the ferromagnetic to the non-magnetic state, which is accompanied by a spin transition of the iron atoms, on the physical properties, is non-negligible.

We used a high-pressure diamond anvil cell apparatus combined with laser annealing to investigate the influence on the hysteresis of the magnetic transition in  $\text{Fe}_3\text{C}$ . *Ab initio* calculations using density functional theory (DFT) were also carried out to reconcile the inconsistency in the transition pressure between experiments and simulations. We calculated the density of  $\text{Fe}_3\text{C}$  using data from our calculations to assess the  $\text{Fe}_3\text{C}$  inner core model.

## 2. Methods

The starting material used was polycrystalline  $\text{Fe}_3\text{C}$ , synthesized from pure iron and graphite powder in a platinum capsule at 1.5 GPa and 1373 K for a period of 2.0 h, using a piston-cylinder device (Yoshino et al., 2002). X-ray diffraction measurements, Raman spectroscopy data, and electron microprobe analysis confirmed the crystal structure and the composition of the product to be  $\text{Fe}_3\text{C}$  cementite.

High-pressure X-ray diffraction experiments were carried out in a motor-driven diamond anvil cell (Ono et al., 2007). A small sample

of polycrystalline  $\text{Fe}_3\text{C}$  sandwiched between pellets of NaCl powder was loaded into a 100  $\mu\text{m}$  diameter hole that had been predrilled into a rhenium gasket. A few grains of ruby powder were also loaded into the sample chamber to carry out a preliminary pressure calibration (Dorogokupets and Oganov, 2007). The NaCl acted as both a pressure-transmitting medium and a thermally insulating medium, and was also used as the primary pressure calibrant (Brown, 1999; Ono et al., 2006). The sample was heated after compression using a YAG laser to minimize any pressure inhomogeneity in the sample and to overcome the effect of any kinetics on any potential magnetic transition. The heating temperature was 1500–2000 K, and was recorded using a spectroradiometric method. The typical duration of heating of the sample (annealing) was 5–10 min, which produced data of sufficient quality to determine the cell parameters accurately. The sample was probed using angle-dispersive X-ray diffraction, located at the synchrotron beam lines, at the BL13A of Photon Factory (Japan) and the BL10XU of SPring-8 (Japan). Details of the synchrotron X-ray experiments have been described elsewhere (Ono et al., 2005a,b). The angle-dispersive X-ray diffraction patterns were obtained on an imaging plate of the X-ray data collection system (Rigaku, RAXIS). The pressure was calculated from the NaCl unit cell volume using the equation of state for NaCl developed by Brown (1999) and Ono et al. (2006).

The *ab initio* calculations based on DFT were performed using the VASP code (Kresse and Furthmüller, 1996). The interactions between the electrons and the ionic cores were described using the projector augmented wave (PAW) method with the generalized gradient approximations, known as PBE (Perdew et al., 1996). The Fe and C PAW potentials had the outermost cutoff radii of the valence orbitals of 1.164 and 0.794 Å, respectively. Single particle orbitals were expanded in plane waves with a plane-wave cutoff of 600 eV. The calculations were performed requiring a self-consistency convergence on the total energy of  $10^{-7}$  eV per simulation cell. Brillouin zone integration was performed using  $k$ -point sampling with an  $8 \times 8 \times 8$  Monkhorst-Pack grid on the  $\text{Fe}_3\text{C}$  primitive cell. With these  $k$ -point densities, the total energies converged to better than 0.5 meV/atom. The method used in our study has been described elsewhere (Ono et al., 2008).

## 3. Results

In the high-pressure experiments, the sample was compressed to  $\sim 15$  GPa at room temperature. Before laser heating was carried out, the diffraction pattern of the sample showed broad peaks, reflecting the presence of a compression-related differential stress. The sample was then heated for  $\sim 5$  min to  $\sim 1500$  K to relax the differential stress. No new diffraction peaks were observed during the laser annealing. After the required annealing period, the temperature was decreased gradually by controlling the laser power. This was carried out to avoid any differential stress during temperature quenching. The strain broadening of each peak in the diffraction pattern disappeared after heating. This implies that the differential stress in the sample decreased markedly after heating. Therefore, the sample was heated to relax the differential stress after each change in pressure. Only the diffraction data obtained after annealing were used in this study. A typical diffraction pattern of an  $\text{Fe}_3\text{C}$  sample and the pressure-transmitting medium are shown in Fig. 2. No structural phase transition of the  $\text{Fe}_3\text{C}$  sample was observed up to a maximum pressure of 66.5 GPa.

The diffraction peaks of  $\text{Fe}_3\text{C}$  were reasonably indexed based on orthorhombic symmetry, and there were four formula units of this phase per unit cell ( $Z=4$ ). The measured unit cell parameters and volumes are shown in Table 1. The observed variation in the cell parameters of  $\text{Fe}_3\text{C}$  with pressure is shown in Fig. 3. Although the anisotropy of cell compression was small, a remarkable phe-

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