Structurally hidden magnetic transitions in Fe$_3$C at high pressures

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We report a Mössbauer spectroscopic study of cementite (Fe$_3$C) in a diamond anvil cell up to 88 GPa. The hyperfine parameters reveal a two-stage loss of magnetism in Fe$_3$C: a ferro-to-paramagnetic transition around 8–10 GPa and a spin transition at about 22 GPa. Full structural refinement based on single-crystal x-ray diffraction data collected at pressures up to ∼50 GPa reveals that there are no structural changes associated with the electronic transitions in Fe$_3$C. Our Rapid Communication resolves the long-standing controversy regarding the nature of phase transitions in Fe$_3$C at high pressures.

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I. INTRODUCTION

Carbon is one of the candidate light elements for the Earth's core.[1] The importance of carbon for the Earth's interior has motivated many high-pressure experimental and computational investigations of iron carbide Fe$_3$C (mineral name cohenite), both for its potential as an accessory mineral of the Earth's lower mantle and as one of the probable components of the Earth's inner core. Moreover, Fe$_3$C is a common component of steels and has interesting physical properties—it is a metallic ferromagnet with a Curie temperature of 483 K and exhibits the Invar effect in the ferromagnetic (FM) state below T_C.[2–4]

At ambient conditions, the cementite structure has orthorhombic symmetry (space group *Pnma*) with two independent iron positions (one iron surrounded by 12 other iron atoms, while the other has 11 iron neighbors). Carbon is surrounded by six iron atoms forming a trigonal prism (Fig. S1).[5]

Despite the large number of investigations, the transition pressure from the ferromagnetic state to the paramagnetic (PM) or nonmagnetic (NM) state is still highly debated. Investigations directly probing the atomic or electronic structure of iron revealed transition pressures of ∼6 GPa by synchrotron Mössbauer spectroscopy (nuclear forward scattering),[6] 10 GPa by x-ray magnetic circular dicroism[7] (XMCD) and 25 GPa by x-ray emission spectroscopy (XES);[8] whereas, by means of indirect methods, several different effects at higher pressures were observed which the investigators attributed to a change in the electronic state of iron: a softening of phonon frequencies observed by inelastic x-ray scattering (IXS) around 68 GPa[9] and a change in behavior of lattice parameters above 55 GPa observed by x-ray diffraction.[10] Furthermore, *ab initio* calculations suggest that the nonmagnetic state becomes stable only above 60 GPa.[11]

The span of the transition pressure range is too large to be attributed to different pressure calibrations or experimental uncertainties. If we assume that different investigations employed the same well-characterized iron carbide starting material, the only plausible explanation for the discrepancies is that different investigations probed different transitions in Fe$_3$C that led to different observable effects which only can be detected by specific methods.

In order to clarify these phase transition(s), we performed a Mössbauer spectroscopic study of Fe$_3$C up to 88 GPa and a single-crystal x-ray diffraction study up to 47 GPa, both measured in a diamond anvil cell. Mössbauer spectroscopy is one of the traditional methods addressing magnetic properties of iron-bearing materials; it provides direct information on the magnetic and electronic properties of iron atoms. Furthermore, single-crystal x-ray diffraction provides precise and unambiguous information on the effect of magnetic or electronic transition(s) on crystal structure.

II. EXPERIMENTAL DETAILS

The Fe$_3$C sample powder for the Mössbauer spectroscopic study was synthesized from a mixture of 80 wt.% carbon and 20 wt.% iron (∼95% enriched in ^{57}Fe) treated at 5 GPa and 1200 °C for 3 h in a MgO capsule using a multianvil press at the Bayerisches Geoinstitut. We employed a LaCrO$_3$ heater assembly and controlled temperature based on a W$_{75}$Re$_{25}$/W$_{97}$Re$_3$ thermocouple. X-ray diffraction and Mössbauer spectroscopy confirmed that the synthesized material consisted mainly of Fe$_3$C but with an excess of carbon. Fe$_3$C was cleaned from the carbon by magnetic separation. The single crystals were synthesized from pure iron in a carbon capsule at 5 GPa and 1300 °C in a multianvil press.

Diamond anvil cells with diamond culet sizes of 250 μm and a rhenium gasket with a 120-μm diameter hole were employed. Neon gas was used as a pressure-transmitting medium to improve hydrostaticity,[12] and the fluorescence of ruby chips was used to measure pressure[13] before and after each measurement, whereby the error was calculated from the difference in both values.

^{57}Fe Mössbauer spectra were recorded at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ^{57}Co high specific activity source in a 12-μm-thick Rh matrix. The velocity scale was calibrated relative to a 25-μm-thick α-Fe foil using the positions certified for (former) National Bureau of Standards reference material No. 1541; linewidths of 0.36 mm/s for the outer lines of α-Fe were obtained at room temperature. Spectra took 1 to 6 days each to collect, and Mössbauer spectra were fitted to Lorentzian line shapes using the software package MossA.[14]

Single-crystal high-pressure diamond anvil cell experiments were conducted at ID09a at the European Synchrotron Radiation Facility. Diffraction data were collected at 293 K using the MAR555 flatpanel detector, radiation with a wavelength of 0.4148 Å, beam size of 10 × 10 μm^2, and a crystal-to-detector distance of about 310 mm. An ω-scanning range of $-30°$ to $+30°$ was collected with $0.5°$ scanning step and an exposure time of 1 s per frame. The data were processed using the CRYSALIS software [Oxford Diffraction (2006) CrysAlis RED, Version 1.171.31.8. Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK]. Crystal structure refinements of integrated intensities were carried out using the SHELX-97 WinGX version.[15]

III. RESULTS AND DISCUSSION

The refined unit-cell parameters and atomic positions are listed in Table S1.[5] We found no evidence of structural transitions up to 47 GPa (highest pressure achieved in our single-crystal x-ray diffraction experiments), and we could refine structures at all pressures based on about 100 observed unique independent reflections with R1 factors better than 8% (Table S1).[5] Distances between iron atoms and between iron and carbon decrease continuously with pressure (Fig. 1). For a first approximation, the compressional behavior of Fe_3C can be described by a single isothermal third-order Birch-Murnaghan equation of state, giving, for the entire studied pressure range, a bulk modulus $K = 161(2)$ GPa and its first pressure derivative $K' = 5.9(2)$ (Fig. 1). However, the Birch-normalized pressure (F_e) against the Eulerian strain (f) plot (a more sensitive representation of the same data) shows a change in slope around 24 GPa, indicating a change in compressional behavior, which may reflect specific changes in the electronic or magnetic state of Fe_3C. One of the best and most direct
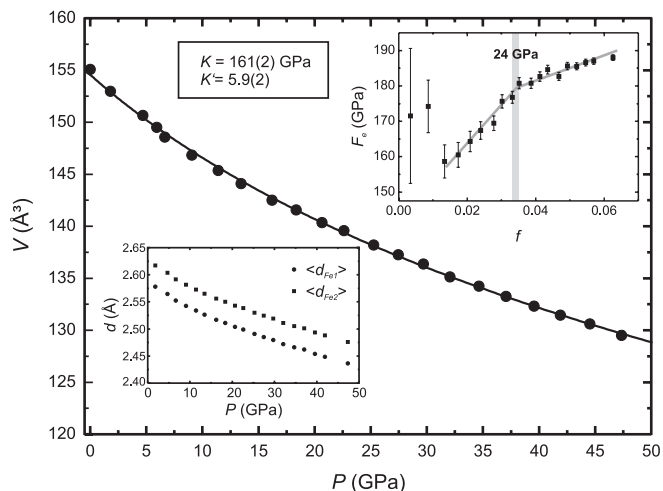

FIG. 1. Volume-pressure data for Fe_3C with fitted third-order Birch-Murnaghan equation of state. The upper insets shows a plot of the Eulerian strain (f) against Birch-normalized pressure (F_e). A change in compressional behavior is visible around 24 GPa. The lower inset shows the mean Fe-Fe of the separate iron-site distances to their coordinating iron atoms. Individual distances can be seen in Figs. S4 and S5.[5]
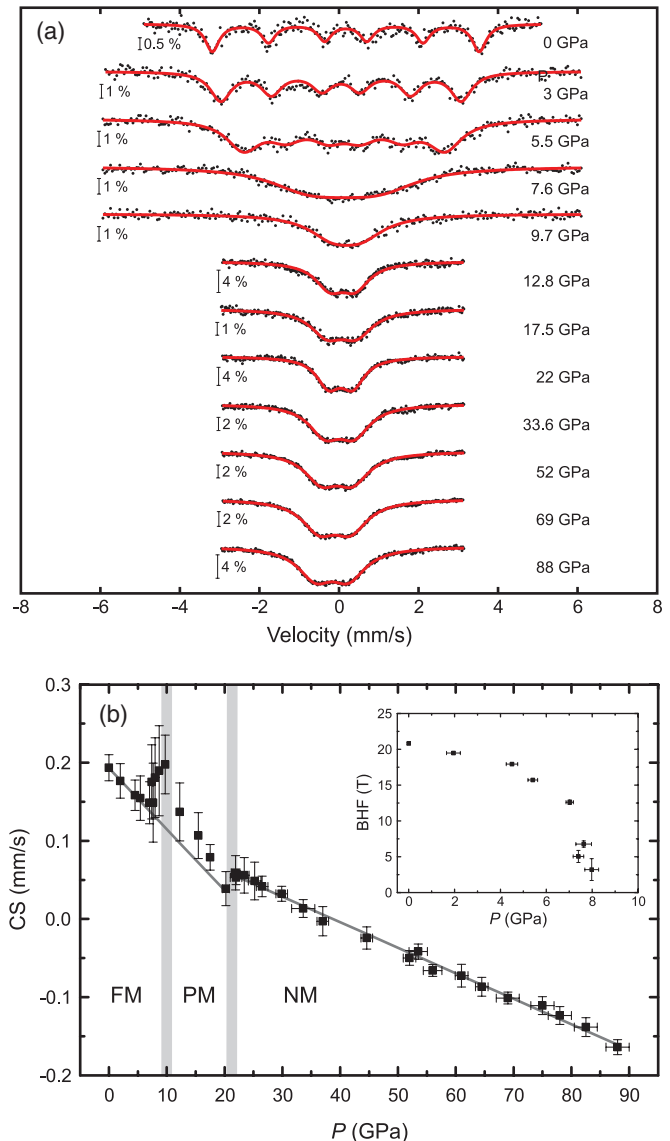

FIG. 2. (Color online) (a) Selected ambient temperature Mössbauer spectra of Fe_3C over the whole pressure range studied. (b) Variation in the CS (relative to α-Fe) of Fe_3C showing two transitions—ferromagnetic (FM) to paramagnetic (PM), and paramagnetic to nonmagnetic (NM). Error bars of the CS are shown as 2σ. The inset shows the variation in the BHF of Fe_3C as a function of pressure at ambient temperature. Error bars of the BHF are shown as 2σ.

methods to elucidate the nature of the changes is Mössbauer spectroscopy.

Fe_3C has two nonequivalent Fe sites which result in two sextets with nearly equal magnetic hyperfine field (BHF) and central shift (CS) at room temperature[16] in the Mössbauer spectrum. However, the statistics of our data measured in a diamond anvil cell with a high nonresonant background level were only sufficient to fit the data with a single sextet. This is an acceptable approximation since the parameters of the two different sites are nearly equal.[16] Selected spectra from the entire pressure range are shown in Fig. 2(a). The variation in the BHF and CS with increasing pressure is shown in Fig. 2(b). BHF is generally proportional to the average Fe

magnetic moment, and it approaches zero at around 8 GPa, indicating that the net magnetic moment of the material is lost. Consequently, the data were fitted to a doublet above this pressure. The FWHM of the doublet drops exponentially from pressures starting at 8 GPa to around 20 GPa, and then, the value stays constant up to 88 GPa (Fig. S2).[5]

The CS variation with pressure can be divided into three parts [Fig. 2(b)]. First, up to 8 GPa, the CS decreases linearly with increasing pressure. Second, from 8 to 22 GPa, the CS shows a sharp increase followed by a more gradual decrease, where the maximum is situated around 10 GPa. Third, from 22 to 88 GPa, the CS decreases linearly but with a slope different from previous values. The anomalous behavior in the CS variation is also observed if the data at pressures above 8 GPa are fit to a sextet instead of a doublet. Therefore, the jump is independent of the fitting model.

The data essentially show two regions of discontinuity in the variation of hyperfine parameters with pressure: the first from 8 to 11 GPa and the second from 20 to 23 GPa. In the region from 8 to 11 GPa, the loss of ferromagnetism in Fe_3C is observed as a decrease in the BHF. Furthermore, the loss of the BHF near 8 GPa is accompanied by an increase in the CS. This parameter is influenced by two effects—the chemical isomer shift (which is a measure of s-electron density at the nucleus) and the second-order Doppler shift [(SOD), which is a measure of mean-squared velocities of the Mössbauer active atoms]. An increase in chemical isomer shift is contrary to the expected increase in s-electron density at the nucleus with increasing pressure since the excited state of the ^{57}Fe nucleus is smaller than the ground state. Consequently, the increase in the CS can only be explained by a change in the SOD.

To estimate the contribution of the SOD to the CS, δ_{SOD}, we approximated the chemical isomer shift by fitting a straight line through the three lowermost pressure points (at 0, 1.95, and 4.5 GPa) and assumed that the remaining contribution to the CS could be used to calculate the change in mean-squared velocity $\langle v^2 \rangle$ due to the SOD. The variation in mean-squared velocity can be calculated by $\Delta \langle v^2 \rangle = 2c\delta_{SOD}$,[17] where c is the speed of light in vacuum. The result of this calculation suggests phonon softening in the region of the ferro-to-paramagnetic transition (Fig. S3).[5] The maximum of this curve is at 10 GPa, which is slightly higher than the pressure indicated by the rapidly decreasing BHF at around 8 GPa. The decrease in the BHF before phonon softening occurs can be understood as the loss of long-range order (which the BHF is sensitive to) before the transition is complete at the local scale.

The interpretation of the transition in Fe_3C at around 10 GPa observed by Mössbauer spectroscopy as a transformation from the ferro-to-paramagnetic state agrees with our structural results, i.e., the absence of any discontinuous changes in structure or compressional behavior. Indeed, such ferro-to-paramagnetic transitions in many metals (pure iron, for example) and compounds occur structurally unnoticed.

The second transition region around 22 GPa shows a small jump and a change in slope in the CS variation as a function of pressure. The change in slope suggests a reconfiguration of the shielding electrons on iron atoms which affects the variation in the CS with respect to pressure. According to our single-crystal x-ray diffraction data and previously reported x-ray diffraction results,[10,18–20] there are no structural phase transitions up to at least 55 GPa. The jump can only be attributed to a spin transition of the iron atoms with a loss of magnetic moment (paramagnetic to nonmagnetic transition). This conclusion is supported by XES results which also suggest high-spin to low-spin crossover at 25 GPa.[8]

In ionic or covalent materials, spin transitions are usually accompanied by a change in interatomic distance due to a decrease in the size of the atom. This results in a volume decrease, e.g., for $CaFe_2O_4$ and $FeCO_3$, there is a volume drop of 8.4%[21] and 10%,[22] respectively. In metals, the physical process is less clear; however, spin transitions in metals are usually accompanied by structural phase transitions; e.g., in Fe, a bcc-hcp transition[23–26] and in Co, a hcp-fcc transition.[27–30] In Fe_3C, we did not observe any structural changes at 22 GPa, but stiffening of the material on compression above this pressure is clearly visible on a f-F_e plot (Fig. 1). Thus, Fe_3C demonstrates that pressure-induced spin crossover is not always associated with first-order structural transformations.

Theoretical *ab initio* calculations predict[11] magnetic collapse at 60 GPa (at higher pressures than we observed) and a significant increase in bulk modulus in the nonmagnetic phase (to $K_0 = 316$ GPa and $K' = 4.3$). In fact, fitting our experimental data using a third-order Birch-Murnaghan equation of state for pressures below the spin transition (i.e., below 22 GPa) gives $K_0 = 145(3)$ GPa and $K' = 8.5(7)$, while the interval of 22–47 GPa gives $K_0 = 172(1)$ GPa and $K' = 5.1(1)$. Thus, our experimental observations reproduce, at least qualitatively, the lattice stiffening predicted theoretically across the magnetic-to-nonmagnetic transition of Fe_3C.

IV. CONCLUSION

Our combined single-crystal structural and Mössbauer spectroscopy studies of Fe_3C provide a reconciliation of previous conflicting reports. The ferro-to-paramagnetic transition observed between 8 and 10 GPa corresponds to the transition observed in nuclear forward scattering[6] and XMCD[7] experiments, while observed changes in XES spectra[8] are consistent with the high-to-low spin transformation that we found at around 22 GPa. The second order ferro- to paramagnetic transition is accompanied by a pressure-induced phonon softening which is large enough to be resolved by a variation in CS with pressure.

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