

## Magnetic transition in compressed Fe<sub>3</sub>C from x-ray emission spectroscopy

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The magnetic properties of iron in cementite (Fe<sub>3</sub>C) have been measured by x-ray emission spectroscopy in a diamond cell up to 45 GPa. The Fe-K<sub>β</sub> fluorescence peaks reveal that Fe<sub>3</sub>C undergoes a magnetic collapse at approximately 25 GPa, consistent with theoretical predictions. This transition is likely to be a second-order phase transition without a major structural change. The magnetic collapse transition is expected to affect the elastic and thermodynamic properties of Fe<sub>3</sub>C; the nonmagnetic phase predicted theoretically has a higher incompressibility and density than the magnetic state. Our results support recent theoretical and thermodynamic calculations indicating that Fe<sub>3</sub>C is unlikely to be the major component in the Earth's inner core.

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Cementite (Fe<sub>3</sub>C, cohenite in its natural form) in the orthorhombic structure (*Pnma*) is a metallic ferromagnet and transforms to the paramagnetic state at a Curie temperature of 483 K. The structure consists of hexagonal close packed layers of iron atoms with carbon atoms occupying interstitial sites. The iron atoms occupy two different sites with slightly different magnetic moments.<sup>1</sup>

Based on the extreme abundance of carbon in C1 carbonaceous chondrites (3.2 wt %) and the geophysical properties of iron carbide (Fe<sub>3</sub>C), carbon has been proposed as a potential light element constitute of the Earth's core.<sup>2-5</sup> The extrapolated equation of state (EOS) of Fe<sub>3</sub>C, based on the estimation at ambient conditions, is consistent with carbon being a major light element in the core.<sup>2</sup> However, recent theoretical calculations predict that cementite (Fe<sub>3</sub>C) in the orthorhombic structure (space group *Pnma*) undergoes a magnetic phase transition from a low-pressure magnetically ordered state to a high-pressure nonmagnetic state at 60 GPa and 0 K.<sup>6</sup> At ambient pressure, a ferromagnetic to paramagnetic transition in Fe<sub>3</sub>C occurs at 480 K as revealed by time-of-flight neutron powder diffraction experiments.<sup>1</sup> The magnetic phase has very low volumetric coefficients of the thermal expansion ( $<1.8 \times 10^{-5} \text{ K}^{-1}$ ) close to the behavior of invar alloys, whereas the average thermal expansion coefficient of the nonmagnetic state is  $4.1 \times 10^{-5} \text{ K}^{-1}$  at room pressure.<sup>1,6</sup> First-principles calculations also show that the nonmagnetic phase has a high bulk modulus ( $K_0$ ) of 316 GPa [with the pressure derivative of the bulk modulus ( $K'_0$ ) of 4.3]. The possible transition has consequences for the possible presence of carbon in the Earth's core.<sup>1,2,6</sup> These theoretical and thermodynamic calculations of the EOS of the nonmagnetic phase show that both the density and incompressibility of Fe<sub>3</sub>C differ from values derived from the seismological data for the core, precluding Fe<sub>3</sub>C as the major inner-core forming phase.<sup>6</sup> On the other hand, *in situ* x-ray diffraction experiments showed that Fe<sub>3</sub>C is stable in the

orthorhombic structure up to 73 GPa and that its  $K_0$  and  $K'_0$  values are very similar to those used to support the presence of carbon in the core;<sup>7,8</sup> however, slight volume and axial ratio discontinuities were observed at  $\sim 30$  GPa.<sup>7</sup> Therefore, further study of the magnetic and elastic properties across the predicted magnetic transition of Fe<sub>3</sub>C under high pressures is desirable for an improved understanding of the possible presence and abundance of carbon in the Earth's inner core.<sup>2,6</sup>

X-ray emission spectroscopy (XES) using a highly intense synchrotron x-ray source is a technique well-suited to address the magnetic transition of iron in Fe<sub>3</sub>C. The XES provides direct information on the local magnetic properties of iron atoms.<sup>9-12</sup> Recently, this technique has been widely used to study magnetic transitions in iron-containing systems such as FeS, Fe<sub>2</sub>O<sub>3</sub>, (Mg<sub>0.83</sub>,Fe<sub>0.17</sub>)O, and iron alloys, providing a deeper understanding of magnetic and electronic properties of important planetary materials at high pressures.<sup>13-18</sup> The magnetic state of Fe is characterized by the appearance of the satellite emission peak ( $K'_\beta$ ) located at the lower energy region of the main emission peak ( $K_{\beta 1,3}$ ) of  $\sim 7058$  eV, which is a result of the  $3p-3d$  core-hole exchange interaction in the final state of the emission process. On the other hand, the collapse of the magnetization of Fe is characterized by the disappearance of the low-energy satellite due to the loss of  $3d$  magnetic moment.<sup>9-12</sup> Although the satellite peak of the magnetic state in metals is not as intense as that in Mott insulators,<sup>13-18</sup> the appearance and disappearance of the satellite peak as an indicator of the magnetic transition is firmly established in studies of local magnetic moments in metals such as Fe, Fe-Ni invar alloy, and Fe<sub>3</sub>Pt.<sup>14-16</sup>

Motivated by the prediction of the magnetic collapse of Fe<sub>3</sub>C under high pressures,<sup>6</sup> we report the study of the magnetic transition of Fe<sub>3</sub>C using XES in a diamond anvil cell. The Fe-K<sub>β</sub> fluorescence spectra up to 45 GPa reveal that a magnetic collapse, which can be attributed to either high-

spin to low-spin transition or correlation breakdown (hereafter we use magnetic and nonmagnetic states), occurs in  $\text{Fe}_3\text{C}$  at 25 GPa, consistent with first-principles theoretical calculations.<sup>6</sup> In the light of this new observation, we reexamine previous EOS data for the magnetic state at pressures lower than 30 GPa and the nonmagnetic state at pressures higher than 30 GPa.<sup>7</sup> The nonmagnetic state has a  $K_0$  of  $288 (\pm 42)$  GPa with a fixed  $K'_0$  of 4, which is similar to theoretical predictions using spin-restricted calculations.<sup>6</sup> This study also demonstrates the usefulness of the XES method in revealing physical properties of important planetary materials in the deep Earth.

XES experiments of the  $\text{Fe-K}_\beta$  were carried out at the undulator beamline 16-ID-D of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A monochromatic x-ray beam of 14.41 keV with a FWHM of less than 1 eV was focused down to 20  $\mu\text{m}$  vertically and 60  $\mu\text{m}$  horizontally at the sample position. The  $\text{Fe-K}_\beta$  emission spectra were collected through the Be gasket by a one-meter Rowland circle spectrometer in the vertical scattering geometry.<sup>13</sup> The use of the vertical geometry minimizes the x-ray emission background from Fe impurities in the gasket material and minimizes the effects of pressure gradients for large samples. A Si (333) single-crystal wafer glued onto a spherical substrate of one-meter radius was used as the analyzer and a Peltier-cooled silicon detector (AMPTTEK XR\_100CR) was used to detect the emitted x-ray fluorescence. Helium gas was filled in the flight tubes of the x-ray path in the Rowland circle spectrometer to reduce the absorption by air. The counting time for each XES spectrum was about one hour and typically five spectra were collected at the same pressure and coadded. The total count for the summed spectrum was about 6000 counts at the maximum.

The starting material, polycrystalline  $\text{Fe}_3\text{C}$ , was synthesized from pure iron and graphite powder in an MgO capsule at 2 GPa and 1273 K, using a piston-cylinder device at the Geophysical Laboratory.<sup>8</sup> X-ray diffraction and electron microprobe analysis showed that the sample had the pure cementite structure ( $\text{Fe}_3\text{C}$ , space group  $Pnma$ ). The sample was loaded into the sample chamber of a diamond cell with flat diamonds with a culet size of 400  $\mu\text{m}$ . A beryllium gasket was pre-indented to a thickness of 30  $\mu\text{m}$  and a hole of 300  $\mu\text{m}$  was drilled in it. Subsequently, an amorphous boron-epoxy mixture (4:1 by weight) was inserted into the drilled hole and a smaller hole of 80  $\mu\text{m}$  in diameter was drilled and used as the sample chamber.<sup>19</sup> The use of the amorphous boron gasket insert increases the thickness of the sample and reduces the nonhydrostatic stress.<sup>19</sup> The sample was approximately 60  $\mu\text{m}$  in diameter, nearly matching the x-ray beam size. A few ruby chips were placed on top of the sample for pressure measurements using the  $R_1$  ruby luminescence peak and a nonhydrostatic pressure scale.<sup>20</sup> The pressure uncertainty ( $1\sigma$ ) was estimated from multiple pressure measurements in different ruby chips.

Figure 1 shows the XES spectra of the  $\text{Fe-K}_\beta$  fluorescence lines up to 45 GPa. All spectra show a main  $\text{Fe-K}_{\beta_{1,3}}$  peak located at 7058 eV. Moreover, a  $\text{Fe-K}'_\beta$  satellite peak located at 7045.5 eV appears in the spectra below 25 GPa. The satellite peak disappears at pressures above 25 GPa, indicating a magnetic transition at 25 GPa. The appearance and disap-

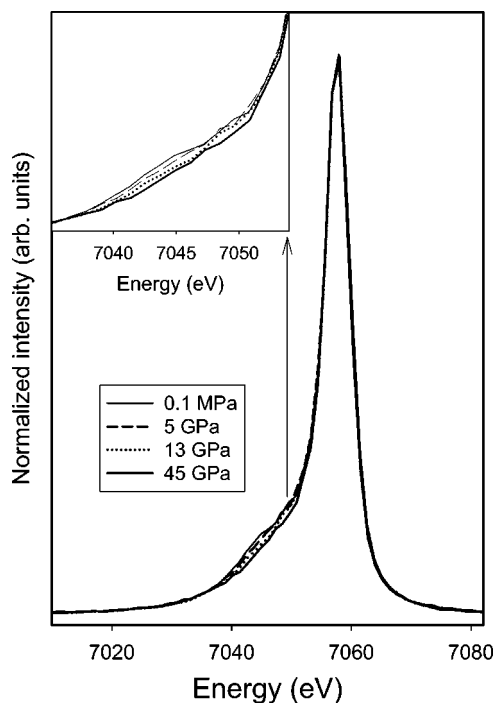


FIG. 1. Representative  $\text{Fe-K}_\beta$  fluorescence spectra at high pressures. The XES spectra were normalized to unity and shifted in energy to compensate for the pressure-induced shift of the line maximum based on the main fluorescence peak ( $\text{K}_\beta$ ) at 7058 eV. The shift is approximately linear at a rate of 16 meV/GPa. The presence of the satellite peak ( $\text{K}'_\beta$ ) is characteristic of the magnetic state at 0, 5, and 13 GPa whereas the absence of the satellite peak at 45 GPa indicates the collapse of the magnetization.

pearance of the satellite peak are characteristic of the magnetic state and the nonmagnetic state, respectively, as has been well established in experimental and theoretical studies of transition metal compounds.<sup>9–18</sup> Based on theoretical calculations of 3d transition metal compounds within the multiplet approach, the  $3p^1 3d^1$  final state contributes mainly to the main emission peak ( $\text{Fe-K}_{\beta_{1,3}}$ ) at 7058 eV. The satellite peak ( $\text{Fe-K}'_\beta$ ) is predominantly due to the final state configurations where the total spin of the 3p core orbital is aligned opposite to the spin of the 3d valence electrons (the core-hole electron interaction in the final state of  $3p^1 3d^1$ ).<sup>10–12</sup> The 3p-3d exchange stabilization yields a lower energy state, and therefore the splitting between these two regions is a result of the 3p-3d exchange interaction. Thus, the presence of the satellite peak indicates the existence of the local magnetic moment arising from the 3d valence orbital. We note that the intensity of the satellite peak in the magnetic state is relatively low, similar to that of pure iron and iron Invar alloys (Fe-Ni and  $\text{Fe}_3\text{Pt}$  alloys) but much lower than that of iron oxides such as  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $(\text{Fe}_{0.17}, \text{Mg}_{0.83})\text{O}$ .<sup>13–18</sup>

Figure 2 shows the integrated intensity of the satellite peak as a function of pressure to illustrate the pressure-induced magnetic transition more clearly. The intensity at  $\sim 7045.5$  eV was determined by subtracting the XES spectrum with a nonmagnetic state (no satellite) at 45 GPa, after shifting and normalizing all the spectra to the peak intensity at 7058 eV. The intensity of the satellite peak decreases with

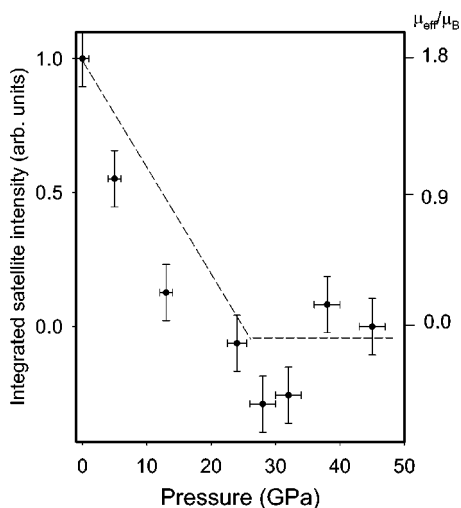


FIG. 2. Integrated intensity of the satellite peak as a function of pressure. The intensity of the satellite peak was obtained by subtracting each spectrum from the one at 45 GPa (highest pressure). The errors in integrated intensity were propagated from statistical errors in original spectra. The decrease in intensity below 25 GPa indicates that the magnetic moment in  $\text{Fe}_3\text{C}$  decreases with increasing pressure in the magnetic  $\text{Fe}_3\text{C}$ . A magnetic transition occurs at 25 GPa. The right vertical axis shows the effective iron magnetic moment ( $\mu_{\text{eff}}$ ) based on the intensity of the satellite peak and the magnetic moment measured at ambient conditions (Ref. 9). The solid line is a guide to the eyes.

increasing pressure up to 25 GPa, indicating that the magnetic moment of Fe in  $\text{Fe}_3\text{C}$  is decreasing. Above 25 GPa the satellite peak intensity does not change, indicating a nonmagnetic state theoretically predicted.<sup>6</sup> The magnetic to nonmagnetic transition has also been observed recently in a similar iron compound,  $\text{Fe}_3\text{S}$ , at approximately 18 GPa by XES and synchrotron Mössbauer spectroscopy experiments.<sup>21</sup> It is also conceivable that other  $\text{Fe}_3\text{X}$  compounds such as  $\text{Fe}_3\text{P}$  undergo similar phase transitions at high pressures.

In light of the magnetic transition in cementite at 25 GPa, we re-examined previous EOS data up to 73 GPa.<sup>7</sup> Although these studies do not suggest any observation of a first order structural transition in  $\text{Fe}_3\text{C}$ , the compression data clearly showed a discontinuity at  $\sim 30$  GPa in the axial ratios ( $c/a$  and  $b/a$ ) and in the pressure-volume plot. A volume reduction of approximately 2–3% can be seen at  $\sim 30$  GPa.<sup>7</sup> This discontinuity is consistent with the presence of the observed magnetic transition. Theoretical calculations predict the magnetic collapse due to correlation breakdown above 60 GPa at 0 K (Fig. 3).<sup>6</sup> If we assume that our room temperature measurements are consistent with theoretical calculations (the predicted transition is at higher pressures and 0 K), this transition is likely to be a magnetic collapse transition without a major structural change. The collapse of magnetism could be attributed either to the high-spin to low-spin transition or to the correlation breakdown. Further magnetic measurements at high pressures such as Mössbauer studies and direct magnetic measurements would help to resolve this ambiguity. The magnetic collapse of Fe in iron-containing compounds can also cause a volume reduction across the transition; in

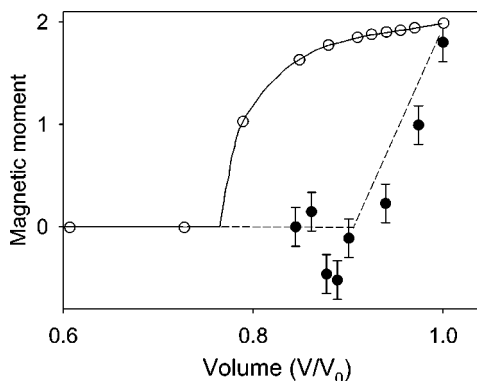


FIG. 3. Magnetic moment of  $\text{Fe}_3\text{C}$  as a function of volume. First-principles calculations predicted magnetic collapse due to correlation breakdown at 60 GPa and 0 K (Ref. 6) (open circles and a solid line). A magnetic transition, which can be attributed to either high-spin to low-spin transition or correlation breakdown, is observed to occur at 25 GPa and 300 K in this study. The average spin is inferred from the satellite intensity and shown as solid circles (the dashed line is a guide to the eye). Thus, we observe a transition to a nonmagnetic state, which is also supported by the available structural data above 25–30 GPa at room temperature. While the magnetic state can be stabilized at low temperatures and higher pressures, no low-temperature experimental data are available at present.

$\text{Fe}_2\text{O}_3$ , the volume change due to the magnetic collapse could be as big as 7%.<sup>17</sup> Therefore, the volume change of 2–3% is likely due to the magnetic collapse. First-principles calculations also show that the nonmagnetic phase has a high  $K_0$  of 316 GPa with a  $K'_0$  of 4.3, affecting the interpretation of the possibility of carbon in the Earth's core.<sup>2,6</sup> Since the magnetic transition is known to significantly affect elastic and thermodynamic properties,<sup>6,21</sup> we refit previous EOS data separately to the magnetic state and nonmagnetic state.<sup>22</sup> The magnetic state has a  $K_0$  of 179.4 ( $\pm 7.8$ ) and  $K'_0$  of 4.8 ( $\pm 1.6$ ), whereas the nonmagnetic state has a  $K_0$  of 288 ( $\pm 42$ ) GPa with a fixed  $K'_0$  of 4. We note that the EOS of the whole data set assuming no phase transition yields a  $K_0 = 175$  ( $\pm 4$ ) and  $K'_0 = 5.2$  ( $\pm 0.3$ ).<sup>7</sup> These analyses show that the magnetic transition significantly affects the compressibility of the  $\text{Fe}_3\text{C}$ , consistent with the conclusions from neutron diffraction studies at ambient pressure and theoretical calculations at high pressures.<sup>1,6</sup> Thus, the determination of the physical properties of the nonmagnetic  $\text{Fe}_3\text{C}$  phase is important for inferring the presence of carbon in the Earth's inner core and for estimating its amount given that the high pressure and temperature conditions that prevail there ensure the presence of the nonmagnetic state. The density and incompressibility of the nonmagnetic  $\text{Fe}_3\text{C}$  phase have been theoretically calculated and compared with that of the Earth's inner core.<sup>6</sup> Our results support the conclusion that  $\text{Fe}_3\text{C}$  is unlikely to be a major phase in the inner core.<sup>6</sup>

In summary, measured x-ray emission spectra in  $\text{Fe}_3\text{C}$  demonstrate that  $\text{Fe}_3\text{C}$  undergoes a magnetic transition from a magnetic state to a nonmagnetic state at approximately 25 GPa, consistent with theoretical predictions. Since x-ray dif-

fraction studies up to 73 GPa did not reveal any structural phase transition in this pressure range,<sup>7</sup> it is likely that this is a second-order magnetic transition. The magnetic state has a higher compressibility than that of the nonmagnetic state, consistent with theoretical predictions.<sup>6</sup> Our results indicate that Fe<sub>3</sub>C is unlikely to be a major component in the Earth's inner core. Further studies at low temperature would provide a direct comparison with available theoretical results.

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- <sup>1</sup>I. G. Wood, L. Vocadlo, K. S. Knight, D. P. Dobson, W. G. Marshall, G. D. Price, and J. Brodholt, *J. Appl. Crystallogr.* **37**, 82 (2004).
- <sup>2</sup>B. Wood, *Earth Planet. Sci. Lett.* **117**, 593 (1993).
- <sup>3</sup>F. Birch, *J. Geophys. Res.* **57**, 227 (1952).
- <sup>4</sup>J. P. Poirier, *Phys. Earth Planet. Inter.* **85**, 319 (1994).
- <sup>5</sup>J. Li and Y. Fei, in *The Mantle and Core*, edited by R.W. Carlson (Oxford, 2003), Vol.2 of *Treatise on Geochemistry*, edited by H. D. Holland and K. K. Turekian (Elsevier-Pergamon), p. 521.
- <sup>6</sup>L. Vocadlo, 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).
- <sup>7</sup>H. P. Scott, Q. Williams, and E. Knittle, *Geophys. Res. Lett.* **28**, 1875 (2001).
- <sup>8</sup>J. Li, H. K. Mao, Y. Fei, E. Gregoryanz, M. Eremets, and C. S. Zha, *Phys. Chem. Miner.* **29**, 166 (2002).
- <sup>9</sup>J. Häglund, G. Grimvall, and T. Jarlborg, *Phys. Rev. B* **44**, 2914 (1991).
- <sup>10</sup>G. Peng, X. Wang, C. R. Randall, J. A. Moore, and S. P. Cramer, *Appl. Phys. Lett.* **65**, 2527 (1994).
- <sup>11</sup>G. Hölzer, M. Fritsch, M. Deutsch, J. Härtwig, and E. Förster, *Phys. Rev. A* **56**, 4554 (1997).
- <sup>12</sup>X. Wang, F. M. F. de Groot, and S. P. Cramer, *Phys. Rev. B* **56**, 4553 (1997).
- <sup>13</sup>J. P. Rueff, C. C. Kao, V. V. Struzhkin, J. Badro, J. Shu, R. J. Hemley, and H. K. Mao, *Phys. Rev. Lett.* **82**, 3284 (1999).
- <sup>14</sup>J. P. Rueff, M. Krisch, Y. Q. Cai, A. Kaprolat, M. Hanfland, M. Lorenzen, C. Masciovecchio, R. Verbeni, and F. Sette, *Phys. Rev. B* **60**, 14510 (1999).
- <sup>15</sup>J. P. Rueff, A. Shukla, A. Kaprolat, M. Krisch, M. Lorenzen, F. Sette, and R. Verbeni, *Phys. Rev. B* **63**, 132409 (2001).
- <sup>16</sup>J. P. Rueff, M. Krisch, and M. Lorenzen, *High Press. Res.* **22**, 53 (2002).
- <sup>17</sup>J. Badro, G. Fiquet, V. V. Struzhkin, M. Somayazulu, H. K. Mao, G. Shen, and T. Le Bihan, *Phys. Rev. Lett.* **89**, 205504 (2002).
- <sup>18</sup>J. Bardo, G. Fiquet, F. Guyot, J. P. Rueff, V. V. Struzhkin, G. Vankó, and G. Monaco, *Science* **300**, 789 (2003).
- <sup>19</sup>J. F. Lin, J. Shu, H. K. Mao, R. J. Hemley, and G. Shen, *Rev. Sci. Instrum.* **74**, 4732 (2003).
- <sup>20</sup>H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).
- <sup>21</sup>J. F. Lin, Y. Fei, W. Sturhahn, J. Zhao, H. K. Mao, and R. J. Hemley, *Earth Planet. Sci. Lett.* **226**, 33 (2004).
- <sup>22</sup>R. Jeanloz, *Geophys. Res. Lett.* **8**, 1219 (1981).