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Revisiting the phase transition of magnetite under pressure

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Abstract

Using a highly stoichiometric magnetite, the pressure-induced phase transitions of Fe_3O_4 have been revisited here by performing Fe K-edge x-ray absorption and magnetic circular dichroism measurements up to $P=65$ GPa at room temperature and 71 GPa at 20 K. We have observed a structure transition at around 27 GPa from magnetite to a high pressure phase $h\text{-Fe}_3\text{O}_4$ with the loss of the net ordered magnetic moments for both temperature. The orthorhombic CaTi_2O_4 -type (Bbmm) structure of the high

pressure phase h -Fe₃O₄ has been determined by combining experimental studies and theoretical simulations of the Fe K-edge XANES. The long time discussed pressure induced spin crossover and inverse to normal spinel structure transitions in Fe₃O₄ can be deterministically excluded from present study up to ~ 65 GPa.

Being the first discovered natural magnet, magnetite (Fe₃O₄) has a cubic inverse spinel structure (Fd $\bar{3}$ m) with the chemical formula of AB₂O₄. The A-site ions are tetrahedrally (Td) coordinated, with the nominal Fe³⁺ (S=5/2) configuration, while B-site ions are octahedrally (Oh) coordinated with equal distribution of Fe²⁺ (S=2) and Fe³⁺ (S=5/2). The opposite spin alignment of Fe ions on A- and B-sites leads to ferrimagnetism, resulting in a net moment of $M_{\text{net}} = +4 \mu\text{B}$ per formula unit, as compared to the experimental value of $4.07 \mu\text{B}$.¹ The so called Verwey transition²⁻⁴ in magnetite, described as an abrupt hundred-fold increase of electrical resistivity (metal-insulator transition) with temperature decreasing across $T_V \sim 124\text{K}$, has been associated to charge ordering and three-site distortions of Fe ions^{5,6} with a gap opening in the electronic band structure.⁷

Before entering the high pressure phase around $P=30$ GPa (h -Fe₃O₄),⁸⁻¹³ a number of electronic, magnetic, and structural transitions in magnetite have been reported around 8 GPa, including HS to IS transition,¹⁴ the pressure-tuned ideal inverse-spinel structure,¹⁵ the inverse to normal spinel,^{7,16-19} as well as the occurrence of abnormal elastic and vibrational behaviors.²⁰ However, the scenario of inverse to normal spinel was not supported by neutron powder diffraction,²¹ single-crystal x-ray diffraction²² and Fe K-edge x-ray magnetic circular dichroism spectroscopy (XMCD).^{14,23,24} The spin transition from high spin (HS) to intermediate spin (IS) state of B-site Fe²⁺ ions at around 12 GPa,¹⁴ was later ruled out using the same Fe K-edge XMCD technique.²⁴ From first-principles density-functional theory,²⁵ the net magnetic moment of Fe₃O₄ should show an abrupt drop when entering into the high-pressure phase at $P=30$ GPa with HS \rightarrow IS and the net magnetization will be recovered at around $P \sim 70$ GPa with the post-spinel structural phase (Bbmm).¹² Another ab initio study concluded

that Fe_3O_4 had no spin transition in Fe^{2+} up to 45 GPa,²⁶ confirmed by the Fe K_β X-ray emission spectra of single-crystal magnetite at high pressures.²⁰ Besides, Xu et al., showed an incipient metallic behavior in Fe_3O_4 coupled to a magnetic moment collapse at a higher pressure of 50 GPa,²⁷ while Muramatsu et al., claimed the metal-insulator-semiconductor transition at $P \sim 30$ and 70 GPa respectively.²⁸

The existing results differ from each other significantly, which may due to the oxygen stoichiometry or the inhomogeneity of the magnetite used in those studies, or the nonhydrostatic conditions with different pressure transmitting medium (PTM). Thus the phase transition of magnetite under pressure requires further careful investigation. In this paper, we present experimental X-ray absorption near edge spectra (XANES) and XMCD spectra of a highly stoichiometric magnetite at Fe K-edge up to 65 GPa, together with the simulated XANES spectra of magnetite ($\text{Fd}\bar{3}\text{m}$) and CaTi_2O_4 -type structure (Bbmm) $h\text{-Fe}_3\text{O}_4$. For pressures $P > 33$ GPa, Fe_3O_4 loses its ferrimagnetism and enters the $h\text{-Fe}_3\text{O}_4$ phase. The pressure induced charge transfer from octahedral B-site Fe^{2+} to bicapped trigonal A-site Fe^{3+} , and the HS to IS or LS transition are not observed up to 65 GPa in $h\text{-Fe}_3\text{O}_4$ in present study.

High-pressure XANES and XMCD measurements at the Fe K-edge at $T = 20$ and 300 K, have been performed at ODE beamline at synchrotron SOLEIL, France.²⁹ Magnetite of micrometer-sized powders ground from a high-quality single crystal with 99.999% purity, together with the pressure transmitting medium of silicon oil, O_2 or Ne gas, were subject to high pressure up to 71 GPa in diamond-anvil cell (DAC). The sample qualities, including the stoichiometry and the homogeneity of the single crystal were checked by careful resistivity measurement, which has an extremely sharp Verwey transition at 124 K (see Fig. S1 in Supplementary). Pressures were calibrated based on the pressure induced Ruby fluorescence spectra shift. XANES were collected at the Fe K-edge (7112 eV) with a fixed helicity with magnetic field $H = 0$. XMCD was obtained through the deviation of XANES under a magnetic field of $H = 1.3$ T applied parallel or antiparallel to the beam helicity. Fe K-edge XANES

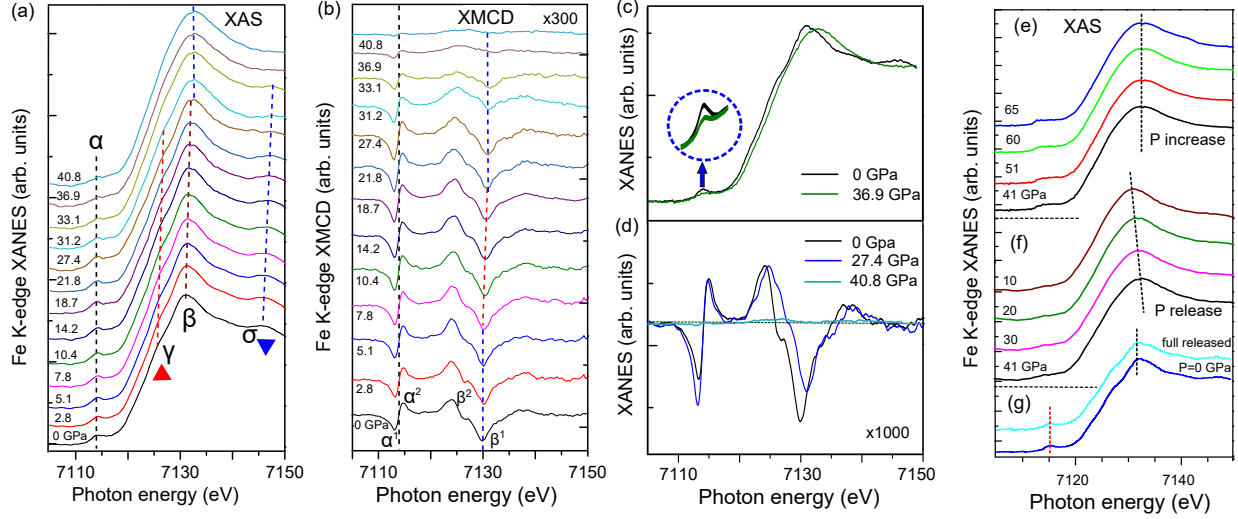


Figure 1: (a) The normalized XANES collected at RT from 0 to 40.8 GPa and (b) the corresponding normalized XMCD. The pre-peak positions of XANES and XMCD, marked as α and α^1 - α^2 , keep constants with pressure increasing while the energy of the main peak, marked as β and β^1 - β^2 gradually shift to higher energy and saturated at ~ 27.4 GPa. (c) XANES spectra of Fe_3O_4 at $P=0$ and 37 GPa and (d) XMCD spectra of Fe_3O_4 at $P=0$, 27.4 and 41 GPa. XANES of h - Fe_3O_4 (e) from 40 to 65 GPa and (f) released from 40 GPa to 10 GPa. (g) The fully recovered XANES spectrum profile when Fe_3O_4 is released to ambient pressure from 40 GPa.

simulations for magnetite ($\text{Fd}\bar{3}\text{m}$) and high pressure (Bbmm) phases of h - Fe_3O_4 have been performed by first principle calculations based on full multiple scattering theory using the MXAN code.³⁰

The normalized Fe K-edge XANES and XMCD spectra of Fe_3O_4 from $P = 0$ to 65 and back to 0 GPa at room temperature are shown in Figure 1. The XANES spectrum consists of a main peak at 7132 eV, labeled as β , and a pre-edge peak at 7114 eV, labeled as α , which are generally assigned to $1s$ - $4p$ dipole transition and $1s$ - $3d$ quadruple transition due to $3d/4p$ hybridization, respectively. Pre-edge peak α is mainly originated from Fe^{3+} at the tetrahedral sites.^{14,24} The energy position of peak α (E_α) does not change with pressure up to 65 GPa, however, its intensity starts to decrease at $P \sim 27.4$ GPa and reaches the minimal value at $P \sim 35$ GPa. The main peak β does not show any visible change of line-shape under pressure below 27.4 GPa except for a slight increase in the white line intensity and a gradual/continual shift to higher energy. Above 27.4 GPa the spectral profile of the main

peak β shows a sharp change: it moves to higher energy as shown in Fig. 1c, where we show a comparison of spectra taken at $P = 0$ and 36.9 GPa and at the same time the weak peaks at 7126 and 7145 eV, labeled in Fig.1 (a) as γ and σ respectively, gradually disappear.

Fig. 1b reports the corresponding XMCD spectra as a function of external pressure up to 40.5 GPa. It is generally accepted that the XMCD signal at the 3d transition metal K-edge arises from spin polarization of 4p states, which is originated from on-site and intra-site exchange interactions with polarized 3d states, the so called $p-d$ hybridization.³¹ Therefore the size of XMCD signal is expected to be proportional to the net magnetic moment of 3d states. Peak α (β) in the XMCD spectra of Fe K-edge is split into two components having opposite sign and labeled as α^1 and α^2 (β^2 and β^1). The XMCD signal of α^1 and α^2 does not exhibit clear change until 27.4 GPa followed by a rapid decreasing to zero at 41 GPa as shown in Fig.1b and Fig.3c. Here $H_{\alpha^1-\alpha^2}$ is sum of absolute value of the height of XMCD signal α^1 and α^2 . Similar pressure induced change of XMCD signal of β^1 and β^2 is shown in Fig.3d. From 0 to 27.4 GPa, the $H_{\beta^1-\beta^2}$ decreases only slightly. Above 27.4GPa it decreases quickly to zero at 40 GPa. The changes of the XMCD spectra are shown by the data recorded at $P=0$, 27.4 and 41 GPa and reported in Fig. 1d. The XANES, including the line shape remains unchanged with pressure increased from 41 to 65 GPa (Fig.1e), or reduced from 41 to 10 GPa (Fig.1f). The XANES of Fe_3O_4 gets recovered when the pressure is totally released (Fig. 1g).

Fe K-edge XANES has been proved to be powerful tool for the precise structural characterization of transition metal oxides, including the chemical and electronic properties. For an inverse to normal spinel structure transition, the pre-edge α is sensitive to the valence state and a roughly 2 eV shift to lower energy is expected from Fe^{3+} and Fe^{2+} ions.³² Up to the maximum pressure of 65GPa, the unchanged energy position of the pre-peak indicates no valence change of A-site Fe^{3+} (Fig.1c inset), which rules out a transition from the inverse to normal spinel Fe_3O_4 under pressure as proposed in ref.^{7,16-19}

The pressure induced changes of energy position of the main peak β (E_β) (whiteline)

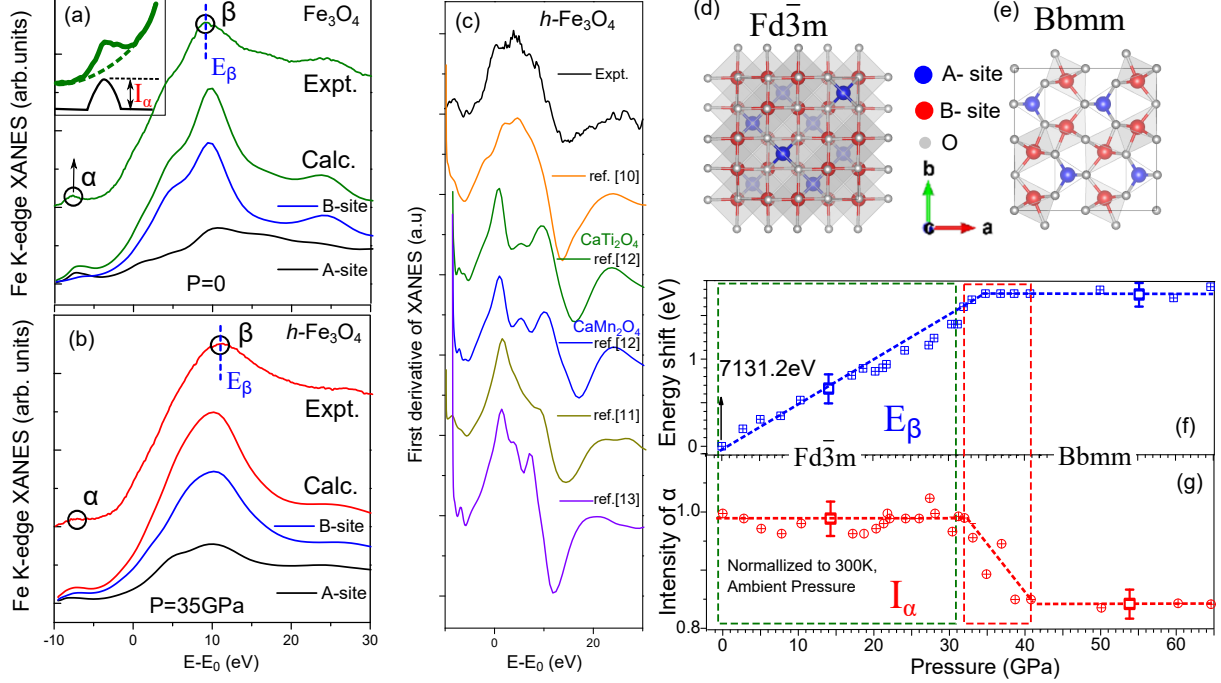


Figure 2: Pressure dependent XANES of Fe_3O_4 . Experimental and calculated XANES spectra with separated A (black line) and B site contributions (blue line) of Fe_3O_4 at (a) $P=0$ and (b) $P=35\text{ GPa}$. The (d) magnetite structure ($\text{Fd}\bar{3}\text{m}$) and (e) $h\text{-Fe}_3\text{O}_4$ with CaTi_2O_4 -type (Bbmm)¹⁰ are used for the calculation of $P=0$ and $P=35\text{ GPa}$, respectively. First derivative of the experimental and theoretical simulated XANES, using the structure from ref.,^{10–13} are listed in (c). Defined from the XANES, the pressure induced changes of the energy of the main peak β (E_β) and the intensity of the pre-peak α (I_α , defined in the inset of Fig.1a) are shown in (f) and (g), indicates that the $h\text{-Fe}_3\text{O}_4$ starts to appear at $P\sim 30\text{ GPa}$. The error bars represent the standard deviation of the value from data evaluation.

and the normalized intensity (according to the intensity at 300K, ambient pressure) of the pre-peak α (I_α , defined as the height of peak α in Fig.2a inset) are shown in Fig. 2e and 2f. Unlike pre-edge peak α that is sensitive to local symmetry, the profile of the main peak β is sensitive to both local and long range crystal structure. According to calculations (see Fig.S2 in supplementary materials), without structural change the pressure induced lattice compression will only give energy shifts for XAS profile due to the reduction of the Fe-O bonds, while the pre-edge peak position, intensity and the XANES shape remain unchanged, as we observed for $P < 27.4\text{ GPa}$. The reduced I_α and the change of spectral profile of the main peak β at $P > 27.4\text{ GPa}$ indicate the formation of a new lattice structure, that is, the high pressure phase $h\text{-Fe}_3\text{O}_4$. According to x-ray diffraction results, the $h\text{-Fe}_3\text{O}_4$ may

have the structure of CaTi_2O_4 -type (Bbmm)¹⁰⁻¹² or CaMn_2O_4 -type (Pbcm).⁹ Above 40 GPa I_α remains nearly unchanged and the energy position of the main peak β exhibits a weak energy shift as a function of pressure as shown in Fig.1e, since $h\text{-Fe}_3\text{O}_4$ has a compact crystal structure⁹⁻¹² compared to magnetite ($\text{Fd}\bar{3}\text{m}$), it exhibits a weak pressure response.

In these proposed structural models^{9,11,12} all Fe^{3+} ions are located on B-sites (8f site) with an octahedral coordination, while the Fe^{2+} ions are located on the A-sites (4c site) with an eightfold coordination (bi-capped trigonal prismatic) and much longer Fe-O bonds than in the B-sites. Our calculations shows that the XANES of such structures for $h\text{-Fe}_3\text{O}_4$ with a charge transfer between B-sites and A-sites, have very different spectrum profile compared to the experimental spectrum (Fig.S3 in supplementary). We also checked the most recent proposed crystal structure from single crystal XRD,¹³ the simulated XANES comes near to the experimental results, except for a weak shoulder peak (marked in Fig.S3f in the supplementary), due to the similar lower valence of A-site Fe ions in this structure. Our calculated XANES spectra are, on the other hand, in fairly good agreement with the experimental XANES spectrum, if a Bbmm structure with the Fe^{2+} ions located in the B-sites, is considered. Please see Fig. 2a and 2b, where the experimental XANES spectra of Fe_3O_4 at $P=0$ and 35GPa are shown together with the calculated XANES. The separated A- (black line) and B-sites (blue line) contributions are also reported. In Fig.2c, the first derivative of the experimental and theoretical simulated XANES, using the structure from ref.,¹⁰⁻¹³ are listed for comparison. Here, the experimental results can only be well simulated with the CaTi_2O_4 structure reported in ref.¹⁰ Our data analysis therefore supports the CaTi_2O_4 structure of $h\text{-Fe}_3\text{O}_4$. Besides, the valence of Fe ions were confirmed to be 3+ at A-sites (4c site) and mixed of 2+ and 3+ at B-sites (8f site) in the $h\text{-Fe}_3\text{O}_4$ phase, respectively. Thus we rule out the charge transfer between B-sites and A-sites Fe ions through the structure transition.

Having established the coordination of the Fe^{2+} and Fe^{3+} ions, as second step we evaluated the local structure by exploiting the high sensitivity of XANES to the Fe-O bond-length

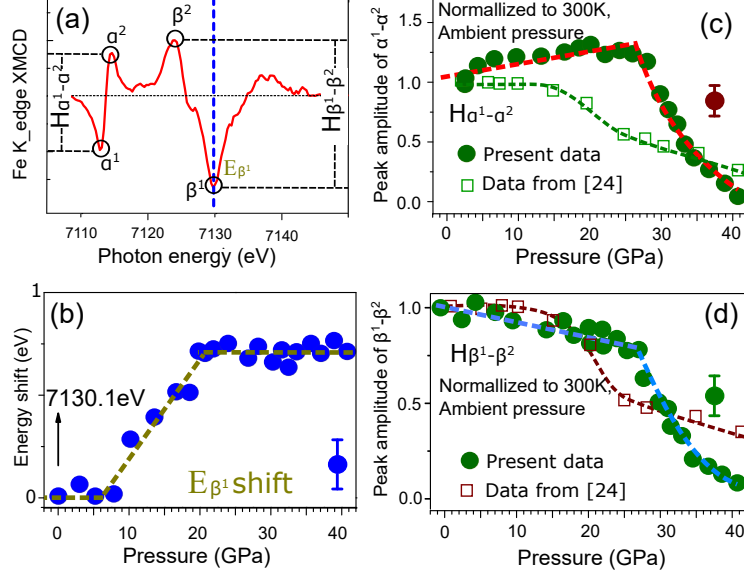


Figure 3: Pressure induced changes of the XMCD spectra of Fe_3O_4 . Defined from the XMCD (a), the pressure induced changes of peak β^1 energy (E_{β^1}), and the intensities of the XMCD peaks ($H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$), representing the absolute height from α^1 to α^2 and from β^1 to β^2 , are shown in (b), (c) and (d) with the error bars, and the XMCD intensity extracted from ref.²⁴ are also shown for comparison. The intensity of XMCD starts to decrease at ~ 27.4 GPa when entering the $h\text{-Fe}_3\text{O}_4$ for the present data. The error bars represent the standard deviation of the value from data evaluation.

distribution. No good fit of the XANES spectra could be obtained in the case of the heavily distorted cation environment of the CaMn_2O_4 -type structure (Pbcm). Using the oxygen position of the Bbmm structure proposed in,^{11,12} where the A-site (B-site) Fe-O bond-lengths are relatively long (short), provides a theoretical XANES that is also somewhat different from the experimental one (see Table. S3-5 and Fig.S3 in supplementary materials). A fairly nice simulation (Fig. 2b) of the experimental spectra was obtained for the Bbmm structure when using the oxygen positions given by Haavik et al.¹⁰ (see Table.S2 in supplementary materials). No evidence of charge transfer or spin transition was observed in $h\text{-Fe}_3\text{O}_4$ since the XANES spectra keep unchanged up to 65 GPa at 300K (see Fig. 1e).

Pressure response of XMCD signal $\alpha^1-\alpha^2$ and $\beta^1-\beta^2$, normalized to the intensity at 300K and ambient pressure, are listed in Fig. 3. Slight changes of the peak height of $\alpha^1-\alpha^2$ and $\beta^1-\beta^2$, defined in Fig. 3a as $H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$, respectively, have been observed from 0 to 27.4 GPa followed by a rapid decrease to 0 from 27.4 to 40 GPa. Here, no abrupt change

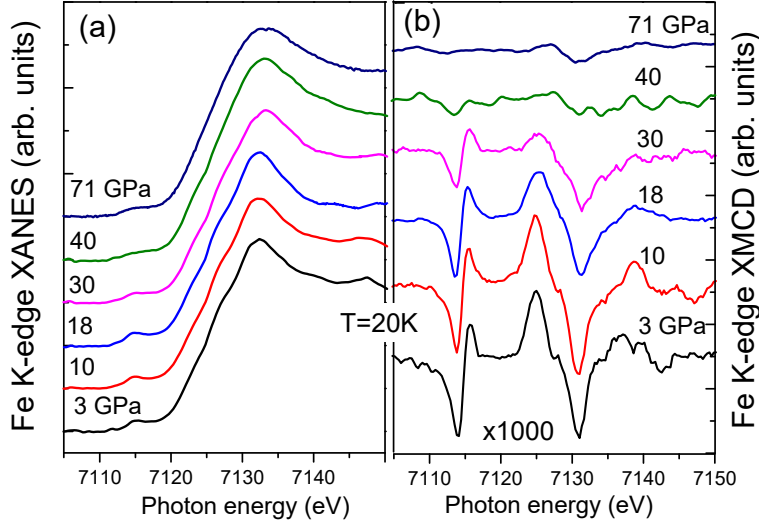


Figure 4: Pressure dependent Fe K-edge XANES and XMCD spectra at $T=20\text{K}$. Fe_3O_4 enters into the $h\text{-Fe}_3\text{O}_4$ phase with $P>30\text{GPa}$ with the reduced pre-peak α in XANES (a) and disappeared XMCD (b) signal, $H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$ at 20K .

of XMCD signal ($H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$) was observed up to $P=27.4\text{ GPa}$ from our results as shown in Fig. 3c and 3d ruling out the sharp spin state transition of B-site Fe^{2+} proposed in Ref.¹⁴ Our results are in agreement with very recent high pressure experimental Fe K_β X-ray emission spectra on Fe_3O_4 ,²⁰ which showed no loss of local spin moment under pressure below 20 GPa and excluded the HS \rightarrow IS or HS \rightarrow LS transition. The energy shift of the XMCD peak β^1 (E_{β^1} , Fig. 3b) is related to the pressure induced energy shift of the XANES main peak β (E_β) resulting from the shorten Fe-O bonding length. Here we see a rapid decrease of $H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$ from 27 GPa to 40 GPa . The disappearance of XMCD signal indicates the loss of net ordered magnetic moment in $h\text{-Fe}_3\text{O}_4$ phase.

The pressure induced phase transition of Fe_3O_4 was considered to be sensitive to the hydrostatic conditions when different PTMs are used. However, our XANES and XMCD results of Fe_3O_4 are the same when different PTMs of silicon oil, O_2 or Ne were used up to 65 GPa at 300K . Besides, the phase transition are more sensitive to the sample quality under investigation. In Fig.3c and 3d, the XMCD intensity extracted from ref.²⁴ are listed for comparison. For the micrometer-sized magnetite commercial powder with broad Verwey transition, the phase transition from magnetite Fe_3O_4 to $h\text{-Fe}_3\text{O}_4$ may also be observed in a

broad pressure range. In ref.²⁴ the phase transition starts at 10-15 GPa and not completed up to 41 GPa, resulting in the decrease of XMCD intensity from 10-15 GPa and non-zero XMCD intensity up to 41 GPa. A much sharp phase transition from 27-35 GPa has been observed according to the XMCD intensity of present data.

There are four possible scenarios to explain the loss of XMCD signal: (1) h -Fe₃O₄ phase is paramagnetic as the ordering temperature drops, (2) the so-called magnetic collapse into a nonmagnetic metallic state, (3) the complete suppression of the magnetic order due to magnetic frustration or (4) the formation of antiferromagnetic order in the new structure. Pressure dependent XANES and XMCD spectra at T=20K were measured and shown in Fig. 4(a) and (b), respectively. Similar to room temperature, h -Fe₃O₄ is formed at around 30-40 GPa. Disappearance of XMCD signal at low-temperature (T=20K) under high-pressure (P=40, 71 GPa) demonstrate that a decrease of T_c below room temperature under high pressure can be ruled out. Although the previous resistivity measurements had shown controversial results,^{27,28} neither of them show any sharp drop of resistivity in h -Fe₃O₄ phase, therefore we can excluded the scenario of magnetic collapse.

The scenario of structure change induced magnetic frustration or antiferromagnetic ordering can not be excluded here. The first principle calculations³³ pointed out that the strong antiferromagnetic coupling (J_{A-B}) between the A- and B-sites Fe ions dominates in magnetite Fe₃O₄. Entering the h -Fe₃O₄, the antiferromagnetic exchange coupling between A- and B-sites Fe ions, may get depressed. Besides, in the h -Fe₃O₄ the A-sites Fe ions form chains along the c-axis and the AFM coupling between the A-sites is not anymore weak but probably of the same order as the AFM coupling between the A and B sites. Such a change of the dominant magnetic coupling might lead to the magnetic frustration in A- and B-sites Fe ions losing net magnetic moment in h -Fe₃O₄. Even a pure AFM order¹³ with all spins coupled antiparallel along the c-axis may form if AFM J_{A-A} is strong enough in h -Fe₃O₄. In both cases the XMCD signal would be very small for a small applied field as $\mu_0 H=1.3$ T used in our measurements. Further first principle calculations³³ are desirable to confirm whether

these scenarios are the cause of the loss of the net ordered moment in h -Fe₃O₄. According to the Mössbauer spectroscopy,¹³ the HS-LS transition scenario of B-site Fe³⁺ in h -Fe₃O₄ was suggested to start at 50 GPa, however, no evidence of the transition was observed from the present XANES and XMCD results.

To conclude, phase transitions of Fe₃O₄ have been revisited by performing Fe K-edge XAS and XMCD measurements under pressure. The comparison of the XANES spectra measured at P>30 GPa, with theoretical simulations from MXAN indicates that the high pressure phase h -Fe₃O₄ has a CaTi₂O₄ (Bbmm) structure. The drop in XMCD intensity of h -Fe₃O₄ interpreted in terms of a complete suppression of the magnetic order due to the strong magnetic frustration or antiferromagnetic ordering. Both the scenarios of spin-crossover and charge transfer have been deterministically ruled out. Mössbauer spectroscopy investigation¹³ proposed second order high to low spin transition in B-site Fe³⁺ of h -Fe₃O₄ from 50 to 80 GPa but this statement requires further confirmation from XANES or Fe K _{β} -resonant x-ray emission spectra, which is more sensitive to pressure induced spin transition.^{20,34,35}

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References

- (1) Weiss, P.; and Forrer, R.; La saturation absolue des ferromagnétiques et les lois d'approche en fonction du champ et de la température. Ann. Phys. (Paris) **1929**, 12, 279.
- (2) Verwey, E. J. W.; Electronic Conduction of Magnetite (Fe₃O₄) and its Transition Point at Low Temperatures. Nature (London) **1939**, 144, 327.
- (3) Walz, F.; The Verwey transition - a topical review. J. Phys. Condens. Matter **2002**, 14, R285.
- (4) Garcia, J.; and Subias, G.; The Verwey transition-a new perspective. J. Phys. Condens. Matter **2004** 16, R145.

- (5) Wright, J.P.; Attfield, J.P. and Radaelli, P.G.; Long Range Charge Ordering in Magnetite Below the Verwey Transition. Phys. Rev. Lett. **2001** 87, 266401; Charge ordered structure of magnetite Fe_3O_4 below the Verwey transition. Phys. Rev. B **2002** 66, 214422.
- (6) Senn, M.S.; Wright, J.P. and Attfield, J.P.; Charge order and three-site distortions in the Verwey structure of magnetite, Nature **2012** 481, 173.
- (7) Rozenberg, G.Kh.; Pasternak, M.P.; Xu, W.M.; *et al.*; Origin of the Verwey Transition in Magnetite, Phys. Rev. Lett. **2006** 96, 045705.
- (8) Mao, H.-K.; Takahashi, T.; Bassett, W.; *et al.*; Isothermal compression of magnetite to 320 KB, J. Geophys. Res. **1974** 79, 1165.
- (9) Fei, Y.; Frost, D.J.; Mao, H.-K.; *et al.*; In situ structure determination of the high-pressure phase of Fe_3O_4 , Am. Mineral. **1999** 84, 203.
- (10) Haavik, C.; Stolen, S.; Fjellvag, H.; *et al.*; Equation of state of magnetite and its high-pressure modification: Thermodynamics of the Fe-O system at high pressure, Am. Mineral. **2000** 85, 514.
- (11) Dubrovinsky, L.S.; Dubrovinskaia, N.A.; McCammon, C.; *et al.*; The structure of the metallic high-pressure Fe_3O_4 polymorph: experimental and theoretical study, J. Phys.: Condens. Matter **2003** 15, 7697-7706.
- (12) Ricolleau, A.; Fei, Y.; Equation of state of the high-pressure Fe_3O_4 phase and a new structural transition at 70 GPa, Am. Mineral. **2016** 101, 719.
- (13) Greenberg, E.; Xu, W.M.; Nikolaevsky, M.; *et al.*; High-pressure magnetic, electronic, and structural properties of MFe_2O_4 (M=Mg, Zn, Fe) ferric spinels, Phys. Rev. B **2017** 95, 195150.
- (14) Ding, Y.; Haskel, D.; Ovchinnikov, S.G.; *et al.*; Novel Pressure-Induced Magnetic Transition in Magnetite (Fe_3O_4) Phys. Rev. Lett. **2008** 100, 045508.

- (15) Ovsyannikov, S.V.; Shchennikov,V.V.; Todo, S.; Uwatoko, Y.; A new crossover in Fe_3O_4 magnetite under pressure near 6 GPa: modification to 'ideal' inverse cubic spinel?, J. Phys. Condens. Matter. **2008** 20, 172201.
- (16) Rozenberg, G.Kh.; Hearne, G.R.; and Pasternak, M. P.; Nature of the Verwey transition in magnetite (Fe_3O_4) to pressures of 16 GPa, Phys. Rev. B **1996** 53, 6482.
- (17) Todo, S.; Takeshita, N.; Kanehara, K.; Mori, T.; and Môri, M.; Metallization of magnetite (Fe_3O_4) under high pressure J. Appl. Phys. **2001** 89, 7347.
- (18) Pasternak, M.P.; Xu, W.M.; Rozenberg, G.Kh.*et al.*; Pressure-induced coordination crossover in magnetite; the breakdown of the Verwey-Mott localization hypothesis J. Magn. Magn. Mater. **2003** 265, L107.
- (19) Rozenberg, G.Kh.; Amiel, Y.; Xu, W.M.; *et al.*; Structural characterization of temperature- and pressure-induced inverse-normal spinel transformation in magnetite, Phys. Rev. B **2007** 75, 020102.
- (20) Lin, J-F.; Wu, J.; Zhu, J.; *et al.*; Abnormal elastic and vibrational behaviors of magnetite at high pressures, Sci. Rep. **2014** 4, 6282.
- (21) Klotz, S.; Steinle-Neumann,G.; Strässle, Th.; *et al.*; Magnetism and the Verwey transition in Fe_3O_4 under pressure, Phys. Rev. B **2008** 77, 012411.
- (22) Gatta, G. D.; Kantor, I.; Ballaran, T.B.; *et al.*; Effect of non-hydrostatic conditions on the elastic behaviour of magnetite: An in situ single-crystal X-ray diffraction study, Phys. Chem. Miner. **2007** 34, 627.
- (23) Subias, G.; Cuartero, V.; Garcia, J.; *et al.*; Pressure-induced magnetic transition in Fe_3O_4 and CoFe_2O_4 spinels, J. Phys.: Conf. Ser. **2009** 190, 012089.
- (24) Baudalet, F.; Pascarelli, S.; Mathon, O.; *et al.*; Absence of abrupt pressure-induced magnetic transitions in magnetite, Phys. Rev. B **2010** 82, 140412(R).

- (25) Ju, S.; Cai, T.-Y.; Lu, H.-S.; and Gong, C.-D.; Pressure-Induced Crystal Structure and Spin-State Transitions in Magnetite (Fe_3O_4) J. Am. Chem. Soc. **2012** 134, 13780-13786.
- (26) Bengtson, A.; Morgan, D.; Becker, U.; Spin state of iron in Fe_3O_4 magnetite and h- Fe_3O_4 , Phys. Rev. B **2013** 87, 155141.
- (27) Xu, W.M.; Machavariani, G.Y.; Rozenberg, G.K.; Pasternak, M.P.; Mössbauer and resistivity studies of the magnetic and electronic properties of the high-pressure phase of Fe_3O_4 , Phys. Rev. B **2004** 70, 174106.
- (28) Muramatsu, T.; Gasparov, L.V.; Berger, H.; Hemley, R.I.J.; Struzhkin, V.V.; Electrical resistance of single-crystal magnetite (Fe_3O_4) under quasi-hydrostatic pressures up to 100 GPa, J. Appl. Phys. **2016** 119, 135903.
- (29) Baudelet, F.; Nataf, L.; Torchio, R.; New scientific opportunities for high pressure research by energy-dispersive XMCD, High Pres. Res., **2016** 36(3): 429~444.
- (30) Benfatto, M.; Congiu-Castellano, A.; Daneile, A.; Longa, S.D.; MXAN : a new software procedure to perform geometrical fitting of experimental XANES spectra, J. Synchrotron Radiat, **2001** 8, 267-269.
- (31) Schütz, G.; Wagner, W.; Wilhelm, W.; *et al.*; Absorption of circularly polarized x rays in iron, Phys. Rev. Lett. **1987** 58, 737.
- (32) Arrio, M.-A.; Rossano, S.; Brouder, Ch.; Galois, L.; Calas, G.; Calculation of multipole transitions at the Fe K pre-edge through p-d hybridization in the Ligand Field Multiplet model, Europhys. Lett. **2000** 51, 454.
- (33) Leonov, I.; Yaresko, A.N.; Antonov, V.N.; Anisimov, V.I.; Electronic structure of charge-ordered Fe_3O_4 from calculated optical, magneto-optical Kerr effect, and O K-edge x-ray absorption spectra, Phys. Rev. B **2006** 74, 165117.
- (34) Rueff, J.-P.; Shukla, A.; Inelastic x-ray scattering by electronic excitations under high pressure, Rev. Mod. Phys. **2010** 82, 847.

- (35) Shen, G.; Mao, H.-K.; High-pressure studies with x-rays using diamond anvil cells, Rep. Prog. Phys. **2017** 80, 016101.