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Revisiting the Phase Transition of Magnetite under Pressure

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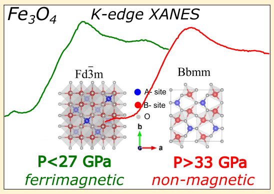
Supporting Information

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 structural transition at around 27 GPa from magnetite to a high-pressure phase h-Fe_3O_4 with the loss of the net ordered magnetic moments for both temperatures. The orthorhombic $CaTi_2O_4$-type (Bbmm) structure of the high-pressure phase h-Fe_3O_4 has been determined by combining experimental studies and theoretical simulations of the Fe K-edge X-ray absorption near-edge structure spectra. The long-time discussed pressure induced spin crossover, and inverse to normal spinel structure transitions in Fe_3O_4 can be deterministically excluded from the present study up to ∼65 GPa.



■ INTRODUCTION

Being the first discovered natural magnet, magnetite (Fe_3O_4) has a cubic inverse spinel structure ($Fd\bar{3}m$) with the chemical formula of AB_2O_4. The A-site ions are tetrahedrally (Td) coordinated, with the nominal Fe^{3+} ($S = -5/2$) configuration, while B-site ions are octahedrally (Oh) coordinated with equal distribution of Fe^{2+} ($S = 2$) and Fe^{3+} ($S = 5/2$). The opposite spin alignment of Fe ions on A- and B-sites leads to ferrimagnetism, resulting in a net moment of $M_{net} = +4\ \mu_B$ per formula unit, as compared to the experimental value of 4.07 μ_B.[1] The so-called Verwey transition[2−4] in magnetite, described as an abrupt 100-fold increase of electrical resistivity (metal−insulator transition) with decreasing temperature across $T_V \approx 124$ K, has been associated with 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-Fe_3O_4),[8−13] a number of electronic, magnetic, and structural transitions in magnetite have been reported around 8 GPa, including high spin (HS) to intermediate spin (IS) transition,[14] the pressure-tuned ideal inverse spinel structure,[15] the inverse to normal spinal,[7,16−19] as well as the occurrence of abnormal elastic and vibrational behaviors.[20] However, the scenario of inverse to normal spinal was not supported by neutron powder diffraction,[21] single-crystal X-ray diffraction (XRD),[22] and Fe K-edge X-ray magnetic circular dichroism (XMCD) spectroscopy.[14,23,24] The spin transition from HS to IS state of B-site Fe^{2+} ions at around 12 GPa[14] was later ruled out using the same Fe K-edge XMCD technique.[24] From the first-principles density functional theory,[25] the net magnetic moment of Fe_3O_4 should show an abrupt drop when entering into the high-pressure phase at P = 30 GPa with HS → IS and the net magnetization will be recovered at around $P \approx 70$ 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 = ∼30 and 70 GPa, respectively.[28]

The existing results differ from each other significantly, which may be due to the oxygen stoichiometry or the inhomogeneity of the magnetite used in those studies or the nonhydrostatic conditions with a 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 structure (XANES) spectra and XMCD spectra of a highly stoichiometric magnetite at Fe K-edge up to 65 GPa, together with the simulated XANES spectra of magnetite ($Fd\bar{3}m$) and $CaTi_2O_4$-type structure (Bbmm) h-Fe_3O_4. For pressures $P > 33$ GPa, Fe_3O_4 loses its ferrimagnetism and enters the h-Fe_3O_4 phase. The pressure induced charge transfer from octahedral B-site Fe^{2+} to bi-capped trigonal A-site Fe^{3+}, and the HS to IS or low spin (LS) transition is not observed up to 65 GPa in h-Fe_3O_4 in the present study.

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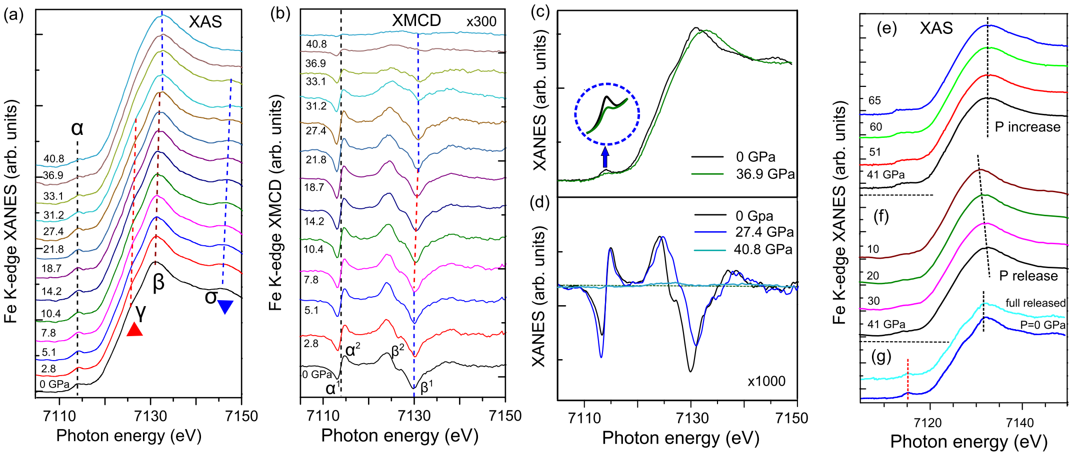

Figure 1. (a) Normalized XANES spectra collected at RT from 0 to 40.8 GPa and (b) corresponding normalized XMCD spectra. The prepeak positions of XANES and XMCD spectra, marked as α and α^1−α^2, remain constant with increasing pressure, while the energy of the main peak, marked as β and β^1−β^2, gradually shifts to higher energy and gets 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 spectra of h-Fe_3O_4 (e) from 40 to 65 GPa and (f) released from 40 to 10 GPa. (g) Fully recovered XANES spectrum profile when Fe_3O_4 is released to ambient pressure from 40 GPa.

■ METHODS

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 PTM of silicon oil and O_2 or Ne gas, was 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 Figure S1 in the Supporting Information). Pressures were calibrated based on the pressure-induced Ruby fluorescence spectra shift. XANES spectra were collected at the Fe K-edge (7112 eV) with a fixed helicity with magnetic field $H = 0$. XMCD spectra were recorded 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 simulations for magnetite ($Fd\bar{3}m$) and high-pressure (Bbmm) phases of h-Fe_3O_4 have been performed by first-principles calculations based on full multiple scattering theory using the MXAN code.[30]

■ RESULTS AND DISCUSSION

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 (RT) 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 because of 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 $P \approx 27.4$ GPa and reaches the minimal value at $P \approx 35$ 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 Figure 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 Figure 1a as γ and σ, respectively, gradually disappear.

Figure 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 intrasite exchange interactions with polarized 3d states, the so-called p−d hybridization.[31] Therefore, the size of the XMCD signal is expected to be proportional to the net magnetic moment of 3d states. Peak α (β) in the XMCD spectra of the Fe K-edge is split into two components having opposite signs 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 decrease to zero at 41 GPa as shown in Figure 1b. Here, $H_{\alpha^1-\alpha^2}$ is the sum of absolute value of the height of the XMCD signals α^1 and α^2. Similar pressure-induced change of the XMCD signal of β^1 and β^2 will be discussed later. From 0 to 27.4 GPa, $H_{\beta^1-\beta^2}$ decreases only slightly. Above 27.4 GPa, 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 Figure 1d. The XANES spectra, including the line shape, remain unchanged with pressure increasing from 41 to 65 GPa (Figure 1e) or reducing from 41 to 10 GPa (Figure 1f). The XANES spectrum of Fe_3O_4 is recovered when the pressure is totally released (Figure 1g).

Fe K-edge XANES has been proved to be a 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 65 GPa, the unchanged energy position of the prepeak indicates no valence change of A-site Fe^{3+} (Figure 1c inset), which rules out a transition from the inverse to normal spinel Fe_3O_4 under pressure as proposed in refs.[7,16−19]

The pressure-induced changes of energy position of the main peak β (E_β) (white line) and the normalized intensity (according to the intensity at 300 K, ambient pressure) of the prepeak α (I_α, defined as the height of peak α in Figure 2a

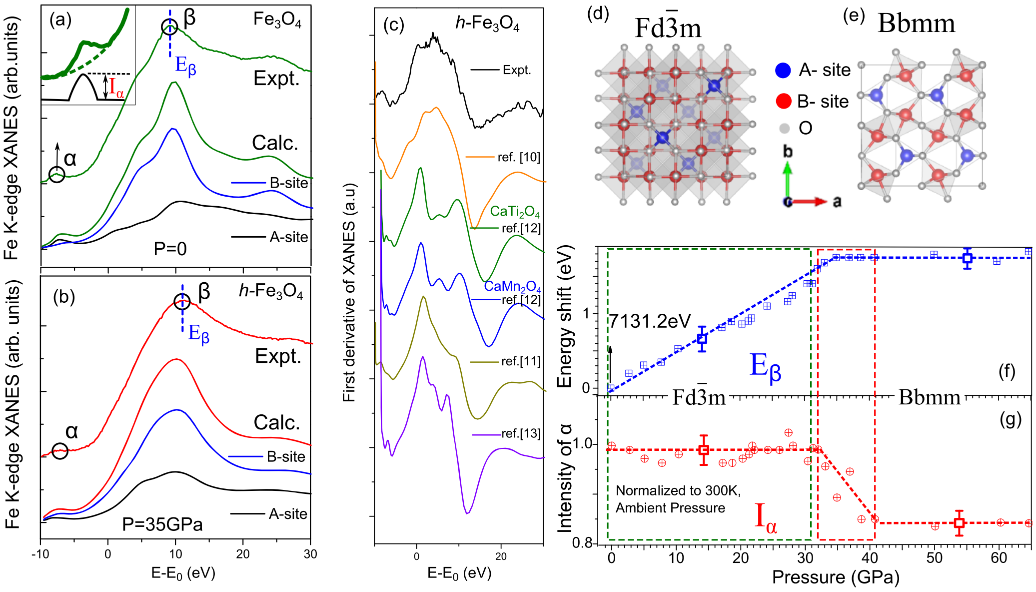

Figure 2. Pressure-dependent XANES of Fe_3O_4. Experimental and calculated XANES spectra with separated A- (black line) and B-site contributions (blue line) of Fe_3O_4 at (a) $P = 0$ and (b) $P = 35$ GPa. (d) Magnetite structure ($Fd\bar{3}m$) and (e) h-Fe_3O_4 with $CaTi_2O_4$-type (Bbmm)[10] are used for the calculation of $P = 0$ and $P = 35$ GPa, respectively. The first derivative of the experimental and theoretical simulated XANES, using the structure from refs,[10,13] is 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 prepeak α (I_α, defined in the inset of Figure 1a) are shown in (f,g), indicating that h-Fe_3O_4 starts to appear at $P \approx 30$ GPa. The error bars represent the standard deviation of the value from data evaluation.

inset) are shown in Figure 2f,g. Unlike the 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 structures. According to calculations (see Figure S2 in the Supporting Information), without structural change the pressure-induced lattice compression will only give energy shifts for XAS profile because of the reduction of the Fe−O bonds, while the pre-edge peak position, intensity, and the XANES shape remain unchanged, as observed for $P < 27.4$ GPa. The reduced I_α and the change of spectral profile of the main peak β at $P > 27.4$ GPa indicate the formation of a new lattice structure, that is, the high-pressure phase h-Fe_3O_4. According to XRD results, h-Fe_3O_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 Figure 1e; because h-Fe_3O_4 has a compact crystal structure[9−12] compared to magnetite ($Fd\bar{3}m$), 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, whereas 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 show that the XANES spectra of such structures for h-Fe_3O_4 with a charge transfer between B-sites and A-sites have a very different spectrum profile compared to the experimental spectrum (Figure S3 in the Supporting Information). We also checked the most recent proposed crystal structure from single-crystal XRD;[13] the simulated XANES is almost close to the experimental results, except for a weak shoulder peak (marked in Figure S3f in the Supporting Information) because of 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. In Figure 2a,b, the experimental XANES spectra of Fe_3O_4 at $P = 0$ and 35 GPa are shown together with the calculated XANES using the magnetite structure ($Fd\bar{3}m$, Figure 2d) and h-Fe_3O_4 with $CaTi_2O_4$-type (Bbmm, Figure 2e).[10] The separated A- (black line) and B-site (blue line) contributions are also reported. In Figure 2c, the first derivative of the experimental and theoretical simulated XANES, using the structure from refs,[10,13] is 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-Fe_3O_4. Besides, the valence of Fe ions was confirmed to be 3+ at A-sites (4c site) and a mixture of 2+ and 3+ at B-sites (8f site) in the h-Fe_3O_4 phase, respectively. Thus, we rule out the charge transfer between B-site and A-site Fe ions through the structure transition.

Having established the coordination of the Fe^{2+} and Fe^{3+} ions, as the second step we evaluated the local structure by exploiting the high sensitivity of XANES to the Fe−O bond-length 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 refs,[11,12] where the A-site (B-site) Fe−O bond lengths are relatively long (short), provides a theoretical XANES that is also slightly different from the experimental one (see Tables S3−S5 and Figure S3 in the Supporting Information). A fairly nice simulation (Figure 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 the Supporting Information). No evidence of charge transfer or spin transition was observed in h-Fe_3O_4 because the XANES spectra remain unchanged up to 65 GPa at 300 K (see Figure 1e).

Pressure response of the XMCD signal $\alpha^1{-}\alpha^2$ and $\beta^1{-}\beta^2$, normalized to the intensity at 300 K and ambient pressure, is

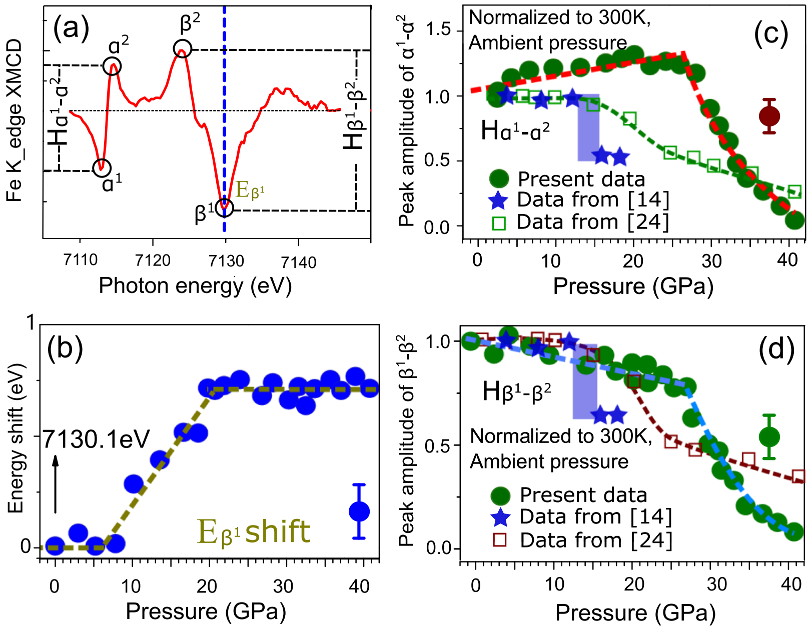

Figure 3. Pressure-induced changes of the XMCD spectra of Fe_3O_4. Defined from XMCD (a), the pressure-induced changes of peak β^1 energy (E_{β^1}) and the intensities of the XMCD peaks ($H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$), representing the absolute height from α^1 to α^2 and from β^1 to β^2, are shown in (b−d) with the error bars, and the XMCD intensity extracted from refs[14,24] are also shown for comparison. The intensity of XMCD starts to decrease at ∼27.4 GPa when entering h-Fe_3O_4 for the present data. The error bars represent the standard deviation of the value from data evaluation.

shown in Figure 3. Slight changes of the peak height of $\alpha^1-\alpha^2$ and $\beta^1-\beta^2$, defined in Figure 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 of XMCD signal ($H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$) was observed up to $P = 27.4$ GPa from our results as shown in Figure 3c,d ruling out the sharp spin-state transition of B-site Fe^{2+} proposed in ref 14 between 12 and 16 Gpa, as marked in Figure 3c,d. 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 → IS or HS → LS transition. The energy shift of the XMCD peak β^1 (E_{β^1}, Figure 3b) is related to the pressure-induced energy shift of the XANES main peak β (E_β) resulting from the short Fe−O bonding length. Here, we see a rapid decrease of $H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$ from 27 to 40 GPa. The disappearance of the XMCD signal indicates the loss of net ordered magnetic moment in the h-Fe_3O_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 300 K. Besides, the phase transition is more sensitive to the sample quality under investigation. In Figure 3c,d, the XMCD intensity extracted from ref 24 is listed for comparison. For the micrometer-sized magnetite commercial powder with broad Verwey transition, the phase transition from magnetite Fe_3O_4 to h-Fe_3O_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 to 15 GPa and non-zero XMCD intensity up to 41 GPa. A much sharp phase transition from 27 to 35 GPa has been observed according to the XMCD intensity of the present data. The data of ref 14 with a sharp fall of the magnetization was obtained from the powders ground from a high-purity single crystal. The fall of the magnetization was proposed as the HS−LS spin transition supported by the X-ray emission spectra experiment in ref 14. However, this spin transition has been excluded recently from more accurate Fe K_β X-ray emission spectra of single-crystal magnetite at high pressures.[20] The pressure standard Cu powders were mixed with the magnetite sample in the DAC in ref 14, and this may be responsible for the drops of XMCD intensity, as well as the Fe $K_{\beta'}$ satellite peak in the X-ray emission spectra observed in the pressure range from 12 to 16 GPa.

There are four possible scenarios to explain the loss of XMCD signal: (1) h-Fe_3O_4 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 $T = 20$ K were measured and shown in Figure 4a,b, respectively. Similar to RT, h-Fe_3O_4 is formed at around 30−40 GPa. Disappearance of the XMCD signal at low temperature ($T = 20$ K) under high pressure ($P = 40, 71$ GPa) demonstrates that a decrease of T_c below RT under high pressure can be ruled out. Although the previous resistivity measurements had shown controversial results,[27,28] neither of them shows any sharp drop of resistivity in the h-Fe_3O_4 phase; therefore, we can exclude the scenario of magnetic collapse.

The scenario of structure change-induced magnetic frustration or antiferromagnetic ordering cannot be excluded here. The first-principle calculations[33] pointed out that the strong antiferromagnetic coupling (J_{A-B}) between the A- and B-site Fe ions dominates in magnetite Fe_3O_4. Entering the h-Fe_3O_4, the antiferromagnetic exchange coupling between A- and B-site Fe ions may get depressed. Besides, in h-Fe_3O_4, the A-site Fe

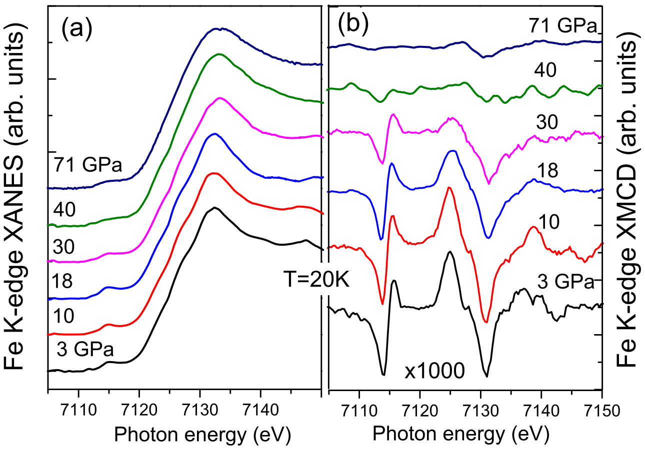

Figure 4. Pressure-dependent Fe K-edge XANES and XMCD spectra at T = 20 K. Fe_3O_4 enters into the h-Fe_3O_4 phase with P > 30 GPa with the reduced prepeak α in XANES (a) and disappeared XMCD (b) signal, $H_{\alpha^1-\alpha^2}$ and $H_{\beta^1-\beta^2}$, at 20 K.

ions form chains along the c-axis and the antiferromagnetic (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-site Fe ions losing net magnetic moment in h-Fe_3O_4. Even a pure AFM order[13] with all spins coupled antiparallel along the c-axis may form if AFM J_{A-A} is strong enough in h-Fe_3O_4. In both cases, the XMCD signal would be very small for a small applied field as μ_0H = 1.3 T used in our measurements. Further, first-principle calculations[33] are desirable to confirm whether these scenarios are the cause of the loss of the net ordered moment in h-Fe_3O_4. According to the Mössbauer spectroscopy,[13] the HS−LS transition scenario of B-site Fe^{3+} in h-Fe_3O_4 was suggested to start at 50 GPa; however, no evidence of the transition was observed from the present XANES and XMCD results.

■ CONCLUSIONS

To conclude, phase transitions of Fe_3O_4 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-Fe_3O_4 has a $CaTi_2O_4$ (Bbmm) structure. The drop in XMCD intensity of h-Fe_3O_4 is interpreted in terms of a complete suppression of the magnetic order because of the strong magnetic frustration or antiferromagnetic ordering. Both the scenarios of spin crossover and charge transfer have been deterministically ruled out. Mössbauer spectroscopy investigation[13] proposed second-order HS to LS transition in B-site Fe^{3+} of h-Fe_3O_4 from 50 to 80 GPa, but this statement requires further confirmation form XANES or Fe K_β-resonant X-ray emission spectra, which is more sensitive to pressure-induced spin transition.[20,34,35]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b04140.

Verwey transition of Fe_3O_4, theoretical XANES calculation of Fe_3O_4 and h-Fe_3O_4, and discussion of the crystal structure (PDF)

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Notes

The authors declare no competing financial interest.

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