

## Supplementary information

### Revisiting the phase transition of magnetite under pressure

K. Chen,<sup>1,2</sup> F. Baudelet,<sup>2</sup> Y. Mijiti,<sup>2,3</sup> L. Nataf,<sup>2</sup> A. Di Cicco,<sup>3</sup> Z. Hu,<sup>4</sup> S. Agrestini,<sup>4</sup> A. C. Komarek,<sup>4</sup> J. Haines,<sup>5</sup> J. Rouquette,<sup>5</sup> Q. Kong,<sup>2</sup> T-C. Weng<sup>1</sup>

<sup>1</sup> Center for High Pressure Science & Technology Advanced Research, 1690 Cailun Rd, 201203 Shanghai, China

<sup>2</sup> Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

<sup>3</sup> Physics Division, School of Science and Technology, University of Camerino, I-62032 Camerino (MC), Italy.

<sup>4</sup> Max Planck Institute for Chemical Physics of Solids, Noethnizer Strasse 40, 01187 Dresden, Germany

<sup>5</sup> ICGM, CNRS, Université de Montpellier, ENSCM, Montpellier, France

#### I : Verwey transition of Fe<sub>3</sub>O<sub>4</sub>

The Verwey transition refers to a low-temperature phase transition in magnetite at around 124K and the attendant changes in its magnetic, electrical, and thermal properties. The temperature and physical expression of the Verwey transition are highly sensitive to the stress state of magnetite and the stoichiometry. Non-stoichiometry in the form of metal cation-substitution or partial oxidation can lower the transition temperature or suppress it entirely [1]. The quality of the single crystal magnetite (Fe<sub>3</sub>O<sub>4</sub>) sample was checked by careful electrical resistance measurements, which exhibit the presence of a very sharp Verwey transition at 124 K.

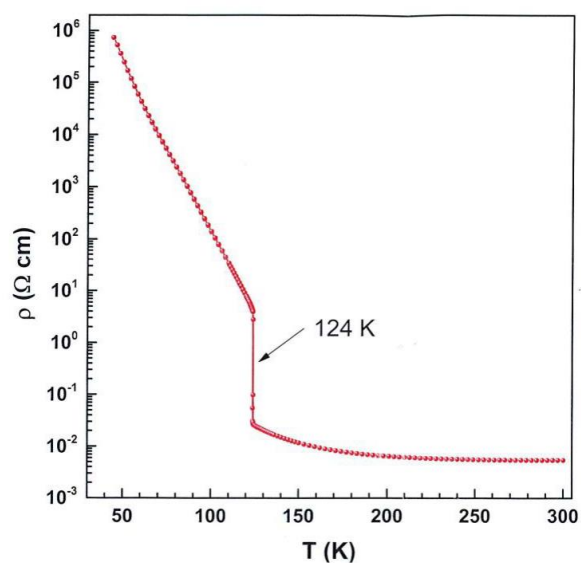


Fig.S1: Verwey transition of single crystal magnetite at 124K

#### II. Theoretical XANES calculation of Fe<sub>3</sub>O<sub>4</sub> and *h*-Fe<sub>3</sub>O<sub>4</sub>

Fe K-edge XANES simulations for magnetite (Fd-3m) and high pressure phases (Bbmm) of *h*-Fe<sub>3</sub>O<sub>4</sub> at different pressurization steps have been performed by first principle calculations based on full multiple scattering theory using the MXAN code [2]. We have considered the real part of the Hedin-Lundqvist exchange potential and broadened the calculated spectrum by a Lorentzian with half-width of 3.0 eV to

account the experimental broadening. In order to simulate the charge relaxation around the core hole, we have used the excited configuration of the photo-absorber.

Considering the different lattice site occupations of Fe atoms, we have run two separate calculations for Fe absorber atoms at A- and B- sites and linearly combined the calculations results with the ratio of 1:2 to represent the simulated XANES spectra. Spherical clusters of 173 and 179 atoms were used for A- (8a) and B- (16d) site calculations for ambient phase of the magnetite (Fd-3m) and 177 atoms clusters were used for both A- (4c) and B- (8f) site calculations in case of *h*-Fe<sub>3</sub>O<sub>4</sub> (Bbmm or Pbcm). Atomic clusters for each calculation correspond to different pressurization steps were generated according to the unit cell parameters of Fe<sub>3</sub>O<sub>4</sub> and *h*-Fe<sub>3</sub>O<sub>4</sub> (Bbmm) obtained by interpolating the crystal parameter values for various pressures reported in the work [3].

Our XANES calculation for *h*-Fe<sub>3</sub>O<sub>4</sub> according to the CaTi<sub>2</sub>O<sub>4</sub> (space group Bbmm) type structural parameters reported by C. Haavik et al.[3] nicely reproduced the experimental spectral features after P=35 GPa. Intensity difference of pre-peak contributions from A-site atoms at ambient and high pressure phases, as shown in Figure 2a and b in the main text, explains the decrease of pre-peak at high pressure, which evidences the coordination crossover from tetrahedral to more symmetric eightfold coordination of Fe in CaTi<sub>2</sub>O<sub>4</sub> type structure. It suggests no charge transfer between A and B site Fe ions. However, the experimental spectrum is quite different from the calculated spectrum using the structure determined from Ricolleau (CaTi<sub>2</sub>O<sub>4</sub> and CaMn<sub>2</sub>O<sub>4</sub>) [4], and Dubrovinsky [5], as shown in Fig.S3c, d, and e, respectively. The most recent structure from Greenberg [6] using single crystal XRD measurements comes near to the experimental XANES spectra, expect for the weak should below the main peak, as shown in Fig.3f. The crystal structures used for the simulations are listed in Table S1-S6.

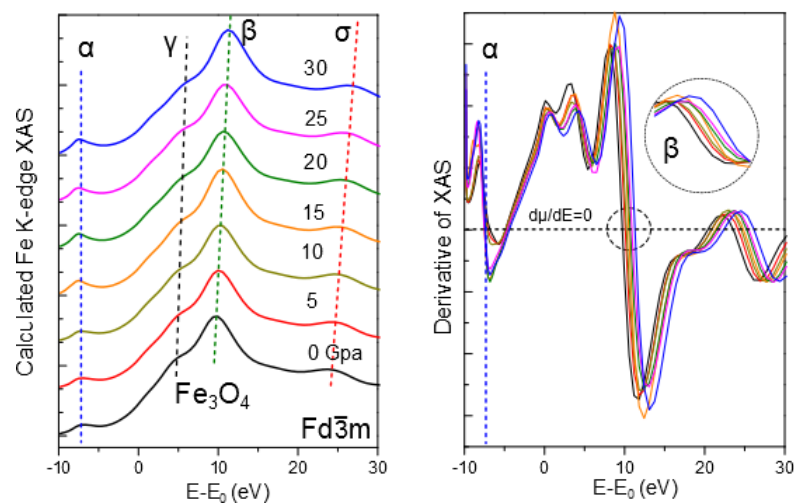


Fig.S2: Calculated XANES (left) and derivative of XAS (right) of Fe<sub>3</sub>O<sub>4</sub> (Fd-3m) with pressure increased up to 30 GPa.

**Table S1.** Atomic coordinates and unit cell parameters for Fe<sub>3</sub>O<sub>4</sub> at P=0 GPa [1].

Atom	Site	x	y	z
Fe1	8a (tet)	0.125	0.125	0.125
Fe2	16d (oct)	0.5	0.5	0.5
O	32e	0.2549	0.2549	0.2549
Space group Fd-3m , a = b = c = 8.3965 Å Fe1-O 1.88626 x4 Fe2-O 2.06042 x6				

**Table S2.** Atomic coordinates and unit cell parameters for h-Fe<sub>3</sub>O<sub>4</sub> of CaTi<sub>2</sub>O<sub>4</sub> type at 40 GPa by Haavik et al.[3]

Atom	Site	x	y	z
Fe1	4c	0.375	0.25	0
Fe2	8f	0.135	0.087	0
O1	4c	0.005	0.25	0
O2	8f	0.214	0.605	0
O3	4a	0.5	0	0
Space group Bbmm , a = 9.273 Å b = 9.239 Å c = 2.75 Å Fe1-O1 1.82711 x2 Fe2-O2 1.91920 Fe1-O2 2.08829 x4 Fe2-O1 1.92902 Fe1-O3 2.58428 x2 Fe2-O2 1.96810 x2 Fe2-O2 2.02444 x2				

**Table S3.** Atomic coordinates and unit cell parameters for h-Fe<sub>3</sub>O<sub>4</sub> of CaTi<sub>2</sub>O<sub>4</sub> type at 44.7 GPa by Ricolleau et al.[4]

Atom	Site	x	y	z
Fe1	4c	0.383	0.25	0
Fe2	8f	0.1365	0.0713	0
O1	4c	0.0486	0.25	0
O2	8f	0.243	0.6014	0
O3	4a	0.5	0	0
Space group Bbmm , a = 9.231 Å b = 9.248 Å c = 2.707 Å Fe1-O1 2.04386 x2 Fe2-O2 1.77511 x2 Fe1-O2 2.25198 x4 Fe2-O1 1.83900 Fe1-O3 2.54882 x2 Fe2-O2 1.87390 Fe2-O2 1.96435 x2				

**Table S4.** Atomic coordinates and unit cell parameters for h-Fe<sub>3</sub>O<sub>4</sub> of CaMn<sub>2</sub>O<sub>4</sub> type at 44.7 GPa by Ricolleau et al.[4]

Atom	Site	X	y	z
Fe1	4c	0.782	0.3675	0.25
Fe2	8f	0.277	0.1128	0.0726
O1	4c	0.718	0.25	0
O2	8f	0.209	0.2001	0.25
O3	4a	0.260	0.4903	0.1022
Space group Pbcm , a= 2.707 Å b= 9.248 Å c=9.231 Å Fe1-O2 1.93203 Fe2-O3 1.71141 Fe1-O2 2.19149 Fe2-O2 1.83504 Fe1-O3 2.19669 x2 Fe2-O3 1.86312 Fe1-O3 2.26889 x2 Fe2-O1 1.86659 Fe1-O1 2.55666 x2 Fe2-O3 1.87480 Fe2-O1 2.08539				

**Table S5.** Atomic coordinates and unit cell parameters for  $h\text{-Fe}_3\text{O}_4$  of  $\text{CaTi}_2\text{O}_4$  type at 41 GPa by Dubronivsky et al.[5]

Atom	Site	x	y	z
Fe1	4c	0.386	0.25	0
Fe2	8f	0.135	0.076	0
O1	4c	0.048	0.25	0
O2	8f	0.210	0.616	0
O3	4a	0.5	0	0
Space group Bbmm, a = 9.326 Å b = 9.288 Å c = 2.7555 Å				
	Fe1-O1	2.04469 x2	Fe2-O1	1.80835
	Fe1-O2	2.06125 x4	Fe2-O2	1.91556
	Fe1-O3	2.55382 x2	Fe2-O3	1.99539 x2
			Fe2-O3	2.03120 x2

**Table S6.** Atomic coordinates and unit cell parameters for  $h\text{-Fe}_3\text{O}_4$  of  $\text{CaTi}_2\text{O}_4$  type at 28.4 GPa by Greenberg et al. [6]

Atom	Site	x	y	z
Fe1	4c	0.3723	0.25	0
Fe2	8f	0.1295	0.0780	0
O1	4c	0.0240	0.25	0
O2	8f	0.217	-0.116	0
O3	4a	0.5000	0.000	0
Space group Bbmm, a = 9.290 Å b = 9.320 Å c = 2.820 Å				
	Fe1-O1	1.99354 x2	Fe2-O1	1.87891
	Fe1-O2	2.05816 x4	Fe2-O2	1.98240
	Fe1-O3	2.61463 x2	Fe2-O3	1.99096 x2
			Fe2-O3	2.03643 x2

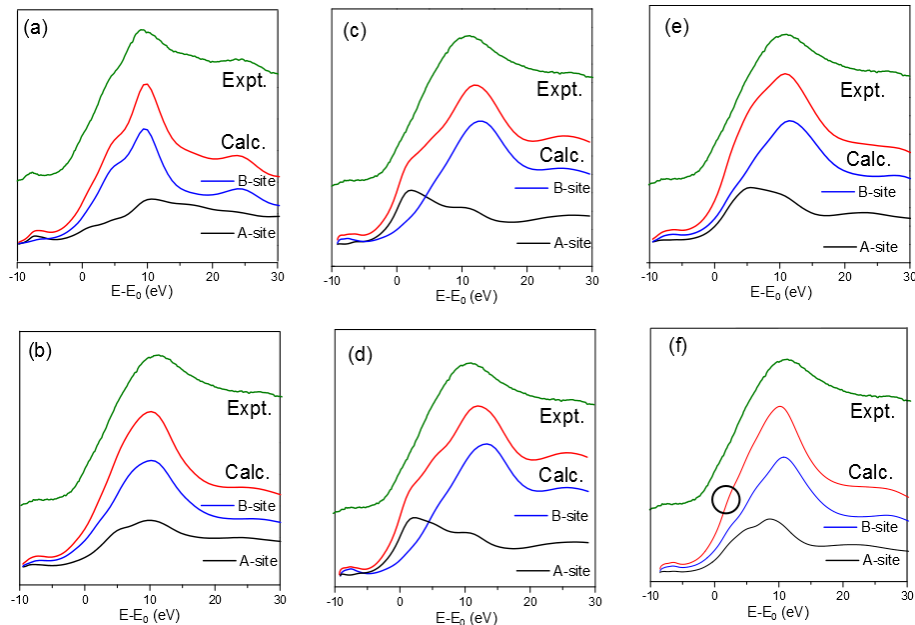


Fig.S3: Calculated XANES (red line) of  $\text{Fe}_3\text{O}_4$  using the  $Fd\text{-}3m$  (a) and  $h\text{-Fe}_3\text{O}_4$  structure from (b) Haavik [3], (c) Ricolleau ( $\text{CaTi}_2\text{O}_4$ ) [4], (d) Ricolleau ( $\text{CaMn}_2\text{O}_4$ ) [4], (e) Dubrovinsky [5] and (f) Greenberg [6], experimental XANES (green line) at  $P=0$  and 35GPa are listed for comparison.

### III Discussion of the crystal structure

XANES is sensitive to the symmetry around the photon-absorbing atom. Therefore, when a phase transformation occurs with a modification of the local symmetry, the XANES will change. Thus, if different possible structures are proposed from XRD, one can compare the experimental XANES and the simulated one for each structure. This allows discriminating between the proposed structures, as shown in Fig.S3. XANES simulated using MXAN code based on the proposed XRD structures [3-6] are listed, with the separated contributions from A (4c) and B (8f) sites Fe ions. Here, to discuss about the possible charge transfer with structure change, we kept using A and B sites for h-Fe<sub>3</sub>O<sub>4</sub>, which represents the 4c and 8f sites, respectively.

We did the same simulation based on the structure parameters determined from the single crystal XRD (Fig.S3f). We realized that the simulated XANES comes near to the experimental results (much better than those shown in Fig.S3c, d and e), except for the weak shoulder peak marked in Fig.S3f. In the structure, A-site Fe ions behave a slightly lower valence state compared to B-sites Fe ions. This is in contradiction to the Mossbauer spectroscopy results which suggests the charge states of Fe<sup>3+</sup> (A), Fe<sup>2+</sup> (B) and Fe<sup>3+</sup> (B). The lower valence of A-site Fe ions contributes to the weak shoulder peak in Fig.S3f. Using the structure determined by Haavik [Am. Mineral. 85, 514], the experimental XANES (Fig.S3b) is nicely reproduced; with Fe ions in A site behaving a higher valence compared to the Fe ions in B-sites. The charge states of Fe ions in h-Fe<sub>3</sub>O<sub>4</sub> from the structure by Haavik [Am. Mineral. 85, 514] are in good agreement with the Mossbauer spectroscopy results [6].

We compared the atomic positions listed in Tables in the supplementary. The x-coordinate of O1 is quite different in the CaTi<sub>2</sub>O<sub>4</sub> structures from different authors (Haavik: 0.005, Ricolleau: 0.0486, Dubronivisky: 0.048 and Greenberg: 0.024). Thus the Fe1-O1 bond lengths (Haavik: 1.83Å, Ricolleau: 2.04Å, Dubronivisky: 2.04Å and Greenberg: 1.99Å) and the averaged Fe1-O bond length (Haavik: 2.15Å, Ricolleau: 2.27Å, Dubronivisky: 2.18Å and Greenberg: 2.18Å) are different from each other. Considering the smaller ionic radius of Fe<sup>3+</sup>, it favors the structure proposed by Haavik et al with the shortest averaged Fe1-O bond length.

Thus, combining with the experimental and theoretical simulated XANES, the crystal structure and atomic positions of high pressure phase Fe<sub>3</sub>O<sub>4</sub> was determined with high precision. And in h-Fe<sub>3</sub>O<sub>4</sub> the eightfold coordinated Fe ion holds the 3+ while the FeO<sub>6</sub> octahedra holds 3+ and 2+.

#### References:

- [1] R. Aragón, D. J. Buttrey, J. P. Shepherd, and J. M. Honig, Phys. Rev. B, 31, 430 (1985).
- [2] M. Benfatto, A. Congiu-Castellano, A. Daneile and S. D. Longa, J. Synchrotron Rad, 8, 267-269 (2001).
- [3] C. Haavik, S. Stolen, H. Fjellvag, M. Hanfland, and D. Häusermann, Am. Mineral. 85, 514–523 (2000).
- [4] A. Ricolleau, Y. Fei, Am. Mineral. 101, 719 (2016).
- [5] L. S. Dubrovinsky, N.A. Dubrovinskaia, C. McCammon, G.Kh.Rozenberg, R. Ahuja, J.M. Osorio-Guillen, V. Dmitriev, H-P. Weber, T.Le. Bihan and B. Johansson, J. Phys.: Condens. Matter 15,7697-7706 (2003).
- [6] E. Greenberg, W. M. Xu, M. Nikolaevsky, E. Bykova, G. Garbarino, K. Glazyrin, D. G. Merkel, L. Dubrovinsky, M. P. Pasternak, and G. Kh. Rozenberg, Phys. Rev. B, 95, 195150 (2017).