

Structural characterization of temperature- and pressure-induced inverse↔normal spinel transformation in magnetite

G. Kh. Rozenberg,¹ Y. Amiel,¹ W. M. Xu,¹ M. P. Pasternak,¹ R. Jeanloz,² M. Hanfland,³ and R. D. Taylor⁴

¹*School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel*

²*Department of Earth and Planetary Science, University of California, Berkeley, California 94720, USA*

³*European Synchrotron Research Facility, Boîte Postale 220, 38043 Grenoble, France*

⁴*MPA-10, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

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High-precision powder x-ray diffraction and ⁵⁷Fe Mössbauer studies up to 20 GPa show that magnetite (Fe₃O₄) undergoes a reversible normal↔inverse transition with increasing pressure or decreasing temperature. There is no resolvable change in the spinel-type crystal structure or unit-cell volume at the phase transition. However, the volume of the tetrahedral (*A*) site increases (17%) and that of the octahedral (*B*) site decreases (~7%) as electron charge density is transferred from the *B* to the *A* site. The corresponding valence changes cause the inverse → normal transition with increasing pressure: Fe_A³⁺ → Fe_A²⁺ and Fe_B^{2.5+} → Fe_B³⁺. There is an intermediate mixed configuration region at pressure-temperature (*P-T*) conditions lying between those at which magnetite is normal, $T < T_{\text{norm}}(P)$, or inverse, $T > T_{\text{inv}}(P)$.

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Magnetite (Fe₃O₄) is a most fascinating natural mineral for technological and historical as well as scientific reasons. At ambient conditions it is a metallic ferrimagnet, occurring abundantly in the Earth as well as on Mars and other planets.¹ Magnetite, nicknamed lodestone, was used by early navigators to locate the magnetic North Pole, and it is synthesized naturally in living species such as fish and birds to be used as magnetoreceptors in their navigation.² With the recent development of nanotechnology, magnetite has become an important ingredient in the production of metallic and magnetic nanocomposites.³ In view of the interest in magnetite in so many fields of science, the structural, electronic, and magnetic properties of this mineral have been at the cutting edge of materials and minerals sciences for many decades. Magnetite is a mixed-valence Fe oxide, and it crystallizes in a cubic spinel structure at ambient pressure-temperature conditions.⁴

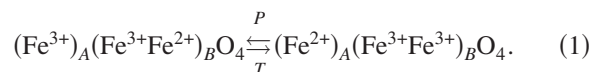
With the possible exception of magnetite, spinels generally exist as intermediate spinels, namely, as a mix of inverse and normal configurations with the general formula of $(M_{1-x}^{2+}M_x^{3+})_A(M_x^{2+}M_{1-x/2}^{3+}M_{1-x/2}^{3+})_B O_4$ where *x* denotes the degree of inversion. For the extreme cases of pure normal and pure inverse spinel, *x*=0 and 1, respectively. In both its artificial and natural forms, magnetite is exclusively an inverse spinel at ambient conditions.

Recent x-ray and neutron diffraction studies of cubic spinels, particularly aimed at investigating the effect of pressure upon *x*, concluded that in all cases the lattice parameter and therefore the unit-cell volume varies with *x*. Such was the case for the normal spinel NiAl₂O₄, for which Halevy *et al.*⁵ show (despite the lack of Rietveld analysis) that the reflections arising from the cation positions scale linearly with pressure and *x*. Temperature and pressure studies of the normal spinel MgAl₂O₄ by Mèducin *et al.*⁶ demonstrate the strong dependency of *x* upon the cation positions, and the work of Antao *et al.*⁷ with the intermediate spinel MgFe₂O₄ clearly shows the intimate relation between *x* and the lattice parameter *a* in the 0–6 GPa and 600–1200 K ranges of *P* and *T*. In this particular study, it was shown that even at

ambient *P-T* conditions a 25% change in *x* results in a 0.06 Å change in *a*.

Due to its purely inverse character at conditions near ambient, no detailed *P-T* diffraction studies have been carried out on Fe₃O₄ to search for structural changes depending on *x*. Indeed, recent measurements of the equation of state, *V(P)*, show no indication of an unusual change in volume of magnetite that could be associated with a change in inverse character over the 0–22 GPa range (Refs. 8 and 9, and references therein). In particular, Haavik *et al.*⁸ used Rietveld analysis and found that within their resolution no anomalies are observed in either octahedral or tetrahedral volumes that could point toward any change in inverse character over the pressure range 0–25 GPa.

In contrast, earlier ⁵⁷Fe Mössbauer spectroscopy (MS) studies¹⁰ in the vicinity of 120 K resulted in hyperfine interaction spectra consistent with an inverse $\overset{T < 120 \text{ K}}{\rightleftharpoons}$ normal spinel reversible transition which was designated as a *coordination crossover* (CC) transition (see Fig. 1 in Ref. 11). Specifically, changes in the hyperfine spectra are consistent with the following changes¹² in octahedral and tetrahedral site valences as a function of pressure and temperature:



In the present work, we undertook very precise powder x-ray diffraction experiments over the 0–20 GPa range at ambient *T* in order to search for crystal-structure evidence and to support the spectroscopy findings about this phase transition. Detailed MS measurements in the 0–27 GPa pressure and 300 K are presented. The sample we used for x-ray diffraction was composed of powdery magnetite obtained from a natural crystalline aggregate, embedded in a 200-μm-diameter by 40-μm-height cavity drilled in a stainless steel gasket (the synthesized sample used for high-pressure MS was enriched to 25% ⁵⁷Fe). Pressures were generated with a membrane-type diamond-anvil cell, with He

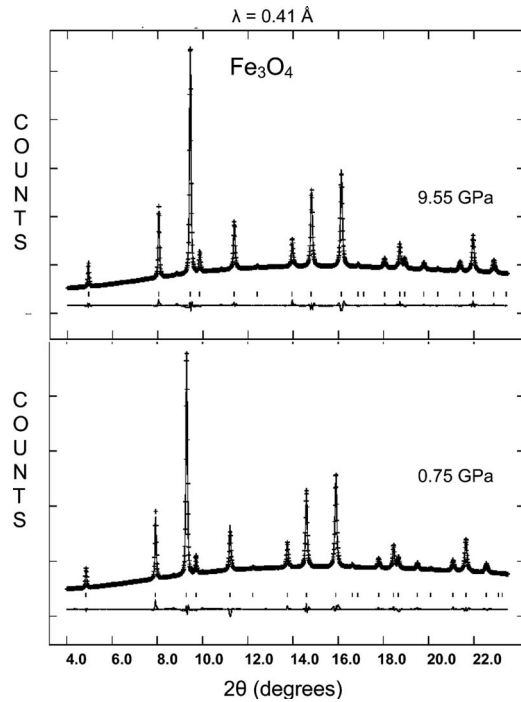


FIG. 1. Typical examples of analyzed integrated patterns of XRD spectra collected at 0.75 and 9.55 GPa at room temperature (RT) and the differences between the observed and calculated profiles. Marks show the calculated peak positions.

used as a pressure medium. X-ray diffraction (XRD) at ambient conditions showed reflections of Fe_3O_4 only. High-pressure XRD was performed in angle-dispersive mode at the ID09A beamline of the European Synchrotron Radiation Facility, Grenoble. Two sets of measurements to 20 GPa were obtained at room temperature using wavelength $\lambda = 0.416\,992$ and $0.409\,991$ Å, as well as two sets of isobaric measurements at $P = 1.3$ and 3.9 GPa, at temperatures of 130–300 K, with $\lambda = 0.417\,528$ and $0.417\,613$ Å, respectively. Pressure was measured using the Sm fluorescence technique.¹³ Diffraction images were collected with a MAR345 detector, and the images were integrated using the FIT2D program.¹⁴ Rietveld refinement of the crystal structure of magnetite at different pressures was done by means of the GSAS package.^{15,16} A 10-mCi Rh(⁵⁷Co) point source was used for MS.

The ideal spinel structure is cubic with space group $Fd\bar{3}m$ and $Z = 8$. The setting commonly used,¹⁷ with an inversion center at the origin, the tetrahedral cation at $(1/8, 1/8, 1/8)$ and the octahedral cation at $(1/2, 1/2, 1/2)$, was employed. The oxygen parameter in this setting is at u, u, u ($u \cong 0.25$). Representative diffraction patterns collected at 0.75 and 9.55 GPa are shown in Fig. 1. The molar volume is plotted as a function of pressure in Fig. 2(a), together with other results reported.^{8,9,18} One notices that the main deviation in $V(P)$ of previous data occurs at $P > 5$ GPa, differences probably caused by the presence of nonhydrostatic stresses. The He pressure medium used in the present experiments presumably provides more hydrostatic conditions, which seems to be confirmed by the narrow diffraction linewidths and excellent reproducibility of our measurements. The pressure-

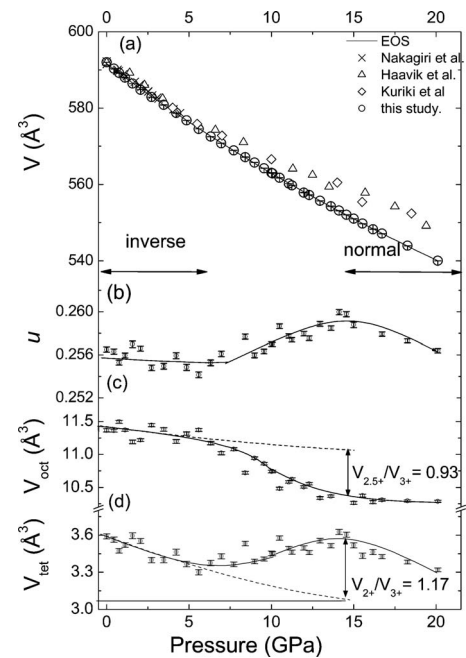


FIG. 2. (a) Pressure evolution of the volume of the unit cell of magnetite at RT (\circ). The solid line through the experimental points is described in the text. Symbols \times , \triangle , and \diamond correspond to data of the authors listed (Refs. 17, 8, and 9). (b) Pressure dependence of the oxygen atomic coordinate u . (c), (d) Pressure evolution of the octahedral and tetrahedral volumes, respectively. The solid curves in (b)–(d) serve only as guides to the eyes. Error bars were obtained from the GSAS fitting output. Pressure uncertainties ~ 0.1 GPa.

volume data fitted to the third-order Birch-Murnaghan (BM) equation of state¹⁹ yield a bulk modulus of 180.6(1.1) GPa, a pressure derivative $K'_0 = 4.33(13)$, and a unit-cell volume at 1 bar of $V_0 = 591.62(0.07)$ Å³. Unlike the results of many of the previous high-pressure x-ray diffraction studies, our bulk modulus is in excellent agreement with recent ultrasonic measurements of the elastic constants as a function of pressure, thus providing an independent validation of our experimental methods.²⁰

The pressure dependency of u is small over the 0–7 GPa range, rising slowly to 0.26 at ~ 15 GPa, and then decreasing slowly as the pressure reaches 20 GPa [Fig. 2(b)]. From these results, we can determine the pressure dependence of the octahedral (B -site) and tetrahedral (A -site) volumes, shown in Figs. 2(c) and 2(d), respectively. As can be seen, at $P > 7$ GPa there is a clear and concurrent growth of the A_{tet} -site and shrinkage of the B_{oct} -site volumes. Extrapolating the smoothly decreasing curves of V_{oct} (0–7 GPa) and V_{tet} (0–7 GPa) to 15 GPa [see dotted curves in Figs. 2(c) and 3(d)], we were able to estimate the fractional change of V_{tet} and V_{oct} at 15 GPa as $+0.17(2)$ and $-0.07(2)$, respectively. Based on the experimental values of Fe-O bonding distance measured in various Fe-containing spinels²¹ at ambient P , we calculate the fractional changes of V_{tet} and V_{oct} at the normal spinel state as $+0.22(3)$ and $-0.09(2)$, respectively, in good agreement with our experimental results. Thus, we conclude that the pressure-induced polyhedral volumes changes are caused by the inverse \leftrightarrow normal transition,²² in good accord with our previous Mössbauer data interpretation.¹⁰

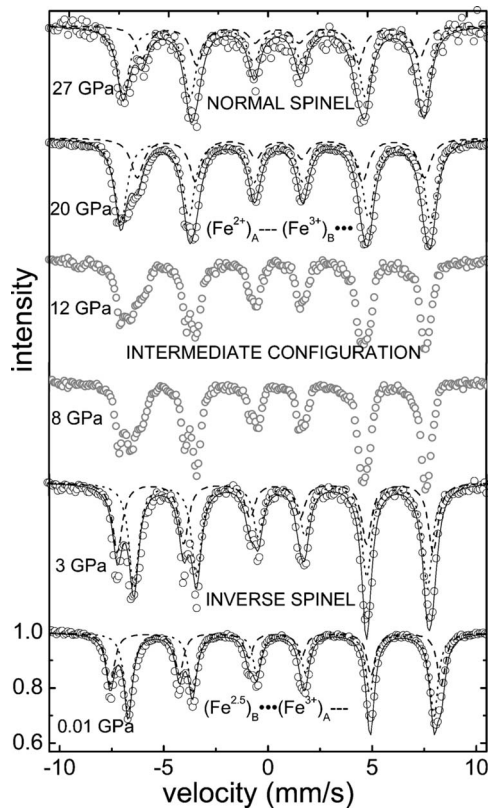


FIG. 3. Mössbauer spectra recorded at 300 K for various pressures. Most spectra were fitted with two magnetic components with all parameters free to vary, except that the linewidths were constrained to be equal for the two sites. The spectra at 0.01 and 3 GPa correspond to the inverse spinel phase in which the more abundant B site (\cdots) is occupied by two $\text{Fe}_B^{2.5+}$ cations, and the A site ($---$) by Fe_A^{3+} . Spectra corresponding to 8 and 12 GPa belong to the intermediate region and no satisfactory fits were achieved. The spectra at 20 and 30 GPa correspond to a normal spinel phase and were fitted with two components with a 2:1 abundance ratio. The more abundant curve (\cdots) corresponds to two Fe_B^{3+} ferric ions; the other component curve ($---$) to an Fe_A^{2+} ferrous ion occupying the tetrahedral site.

MS spectra up to 27 GPa at ambient temperature are shown in Fig. 3. The 0.01 MPa and 3 GPa spectra were fitted with two magnetic hyperfine-interaction components: one assigned to $\text{Fe}_B^{2.5+}$ and one to Fe_A^{3+} , with an abundance ratio of 2:1 and hyperfine fields of 44.8 and 41.0 T, respectively. This is the inverse spinel region. Beyond 5 GPa we were unable to fit the spectra using the inverse or the normal spinel model. This pressure range 7–15 GPa is designated as an intermediate region, perhaps corresponding to a mixture of inverse and normal spinel phases. At $P > 15$ GPa, a satisfactory fit using two sites with relative abundance of 2:1 gave hyperfine fields of 48.6 and 45.2 T. These spectral parameters are consistent with a normal spinel state, namely, Fe_B^{3+} and Fe_A^{2+} polyhedra with an abundance ratio $[\text{Fe}_B^{3+}]/[\text{Fe}_A^{2+}] = 2/1$.

The Mössbauer and x-ray diffraction results are highly consistent in documenting the inverse \leftrightarrow normal spinel transition in magnetite as a function of pressure and temperature. As can be seen by comparing Fig. 1 in Ref. 10 with Fig. 3 in

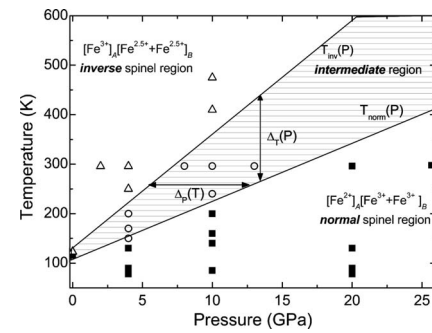


FIG. 4. The (P, T) phase diagram of the spinel configuration of magnetite in the stability pressure range of this structure. At $T < T_{\text{norm}}(P)$ spinel is in its normal configuration with $M_s = 3\mu_B$. At $T > T_{\text{inv}}(P)$ magnetite is an inverse spinel with $M_s = 2\mu_B$. The intermediate configuration defined by the two straight lines is discussed in the text. Thus, the Δ , \blacksquare , and \circ symbols correspond to inverse, normal spinel, and intermediate states, respectively.

this paper, the signature of the temperature-driven transition at ambient pressure is very similar to that of the pressure-driven transition at room temperature. With decreasing temperature, we witness the reversible transition from inverse to normal states within a temperature range of merely a few degrees. No temperature hysteresis is observed. As with the pressure-induced transition, the low-temperature inverse \leftrightarrow normal conversion shows no change in crystal symmetry or unit-cell volume, implying a second-order phase transition.

The corresponding phase diagram does exhibit an intermediate region, between normal and inverse states, that depends on both pressure and temperature (Fig. 4). $T_{\text{inv}}(P)$ and $T_{\text{norm}}(P)$ determine the limits of the inverse and normal regimes and can be expressed as

$$T_{\text{norm}}(P) = 118 + 11.3 [P(\text{GPa})] \text{ (K)},$$

$$T_{\text{inv}}(P) = 120 + 24.1 [P(\text{GPa})] \text{ (K)}. \quad (2)$$

At a given pressure or temperature, the intermediate state precedes the full conversion to a normal or inverse state during isothermal or isobaric conditions. The exact composition of the intermediate state is not clear, but we presume that it arises from configuration fluctuations resulting in a spatial distribution of x .

The mechanism behind the normal \rightarrow inverse conversion occurring at ~ 120 K at ambient pressure, and at higher temperatures at higher pressures, is not clear and raises fundamental questions about the nature of this peculiar second-order phase transition. Is it an electronic transition within the Fe-O mixed bands involving energies of the order of meV? Is it caused by a spatial rearrangement of the oxygen surrounding the Fe cations, again requiring a minuscule amount of energy? What drives this transition and what is its “order parameter”? Unlike other spinels that typically exhibit a (T, P) -induced inverse (or normal) \leftrightarrow fully disordered state ($x=2/3$) conversion with x varying gradually (see Refs. 5–7, and references therein), magnetite is completely different; the transition is inverse \leftrightarrow normal with x changing rather abruptly from 0 to 1 within a short range of pressure or temperature (Fig. 4).

Finally, Verwey²³ and later Mott²⁴ proposed that the low-temperature metal-insulator transition, the “Verwey transition,” at T_V is due to d -electron localization and related charge ordering (CO) occurring within the B site. However the revealed inverse \leftrightarrow normal transition precludes a CO within the B site since below T_V the Fe valences within the B sites are identical. Thus the d -electron localization concept proposed by Verwey and Mott for $T < T_V$ seems to be unrelated to the actual mechanism of the Verwey transition, and recent measurements by Rozenberg *et al.*¹¹ clearly show that the metal-insulator transition is related to a crystal-structural distortion as a function of pressure and temperature. We proposed that a p - p gap within this cubic-distorted region is probably responsible for the Verwey transition.²⁵

The consequence of the inverse \rightarrow normal conversion upon the magnetization of ferrimagnetic magnetite is significant. The net magnetization of the inverse spinel is given by the difference between the octahedral and tetrahedral sublattice magnetizations. On the octahedral sites there is one Fe^{3+} cat-

ion $[(5/2)\mu_B]$ and one Fe^{2+} cation $[(4/2)\mu_B]$ per formula unit, and on tetrahedral sites one Fe^{3+} cation. The expected magnetization of magnetite in the ordered case is therefore $M_s(\text{inverse}) = (5/2 + 4/2) - 5/2 = 2\mu_B$. But in normal spinel there are two Fe^{3+} cations in the B site and one Fe^{2+} cation in the A site, resulting in $M_s(\text{normal}) = (5/2 + 5/2) - 4/2 = 3\mu_B$; a 50% increase in the bulk magnetization.²⁶ Thus, if $T_{\text{norm}}(0 \text{ GPa})$ could be artificially increased to ambient temperatures, layer thicknesses or nanocrystal sizes required of Fe_3O_4 could be trimmed down by half.²⁷ Finally, we note that, given the conditions existing within the Earth, e.g., $\sim 2000 \text{ K}$ and 24 GPa at the top of the lower mantle, 670 km beneath the surface, magnetite within our planet is likely an inverse spinel in a disordered paramagnetic state.

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¹P. R. Buseck *et al.*, Proc. Natl. Acad. Sci. U.S.A. **98**, 13490 (2001).

²M. E. Deutschlander *et al.*, Nature (London) **400**, 324 (1999); W. Wiltschko *et al.*, J. Exp. Biol. **205**, 3031 (2002).

³P. Poddar *et al.*, Phys. Rev. B **65**, 172405 (2002); L. Tacacs, Nanostruct. Mater. **2**, 241 (1993).

⁴In the normal spinel structure, the divalent cation occupies the tetrahedral site A and the two trivalent cations occupy the octahedral site B , with a formula $M_A^{2+}(M^3+M^{3+})_B\text{O}_4$ whereas the inverse spinel corresponds to $M_A^{3+}(M^{2+}M^{3+})_B\text{O}_4$; the formulas for normal and inverse spinel of magnetite would be $\text{Fe}_A^{2+}(\text{Fe}_B^{3+}\text{Fe}_B^{3+})\text{O}_4$ and $\text{Fe}_A^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})_B\text{O}_4$, respectively. We have discussed elsewhere the evidence that magnetite is actually best represented by $\text{Fe}_A^{3+}(\text{Fe}^{2.5+}\text{Fe}^{2.5+})_B\text{O}_4$ at ambient conditions (Ref. 10), but we retain the above classical formulas for the present discussion as the latter has no effect on our analysis: the degree of inverse character can be unambiguously defined as the fractional population of trivalent cations (e.g., Fe^{3+}) in the tetrahedral site.

⁵I. Halevy *et al.*, J. Phys.: Condens. Matter **14**, 10511 (2002).

⁶F. Mèducin *et al.*, Am. Mineral. **89**, 981 (2004).

⁷S. M. Antao *et al.*, Am. Mineral. **90**, 1500 (2005).

⁸C. Haavik *et al.*, Am. Mineral. **85**, 514 (2000).

⁹A. Kuriki *et al.*, J. Phys. Soc. Jpn. **71**, 3092 (2002).

¹⁰M. P. Pasternak *et al.*, J. Magn. Magn. Mater. **265**, L107 (2003).

¹¹G. Kh. Rozenberg *et al.*, Phys. Rev. Lett. **96**, 045705 (2006).

¹²Recent high-pressure MS studies at RT [H. Kobayashi *et al.*, Phys. Rev. B **73**, 104110 (2006)] using nonenriched ⁵⁷Fe isotope claimed to be able to fit the data assuming the inverse spinel structure up to 18 GPa. The use of natural abundant Fe together with limitations in sample diameter imposed by the anvil culet dimensions resulted in spectra of relatively poor statistics (compare the spectra shown in Fig. 3 with that of Fig. 1 of the above reference). This together with the absence of low-temperature measurements impeded achievement of reliable hyperfine interaction parameters. It is noteworthy that the authors observed some changes in the MS parameters at $\sim 7 \text{ GPa}$, the pressure in which the inverse \rightarrow normal spinel just starts (see Fig.

4). Undoubtedly, had they reached higher pressures ($\geq 20 \text{ GPa}$) at RT, or with their operating pressures had reached lower temperatures, they would have observed the (P, T) inverse \leftrightarrow normal transitions.

¹³P. Comodi and P. F. Zanazzi, J. Appl. Crystallogr. **26**, 843 (1993).

¹⁴A. P. Hammersley, computer code FIT2D, ESRF, Grenoble, 1998.

¹⁵A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86 (unpublished), 1994.

¹⁶One unit-cell dimension, one atomic coordinate parameter, and the isotropic temperature factors were refined; altogether 24 variables. The 2Θ range used was $\approx 4^\circ - 23.5^\circ$ and contains 21 contributing Bragg reflections. Details of the refinements are χ^2 less than 0.3, w_{Rp} less than 0.02, and Rp less than 0.01.

¹⁷M. E. Fleet, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **B37**, 917 (1981).

¹⁸N. Nakagiri *et al.*, Phys. Chem. Miner. **13**, 238 (1986).

¹⁹O. L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, 1995).

²⁰H. J. Reichmann and S. D. Jacobsen, Am. Mineral. **89**, 1061 (2004).

²¹ $(\text{Fe}^{2+}\text{-O})_{\text{tet}} = 2.03 \text{ \AA}$, $(\text{Fe}^{3+}\text{-O})_{\text{tet}} = 1.89 \text{ \AA}$, $[(\text{Fe}^{2+}, \text{Fe}^{3+})\text{-O}]_{\text{oct}} = 2.113 \text{ \AA}$, and $(\text{Fe}^{3+}\text{-O})_{\text{oct}} = 2.06 \text{ \AA}$ (see Ref. 17).

²²Similar change of u and correspondingly of the polyhedral volume takes place also with temperature decrease. Thus at isobaric measurements at $P = 1.3$ and 3.9 GPa u reaches a value of 0.26 at 133 and 153 K, respectively.

²³E. J. Verwey, Nature (London) **144**, 327 (1939).

²⁴N. F. Mott, Festkoerperprobleme **19**, 331 (1979).

²⁵And, indeed, recent O K -edge resonant x-ray scattering by D. J. Huang *et al.* [Phys. Rev. Lett. **96**, 096401 (2006)] reveals that the O $2p$ states in the vicinity of the Fermi level exhibit a charge-orbital ordering with a double spatial periodicity with respect to the undistorted cubic phase.

²⁶Preliminary magnetic circular dichroism studies (F. Baudelet *et al.*, private communication) show a 50% jump in the x-ray signal intensity in the vicinity of 12 GPa.

²⁷<http://www.azonano.com/news.asp?newsID=100>, <http://www.nsti.org/procs/Nanotech2006v2/1/T61.317>