

High-pressure structural studies of hematite Fe_2O_3

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Structural studies and a full-profile refinement of the high-pressure phases of hematite (Fe_2O_3) were carried out to 76 GPa using x-ray synchrotron powder diffraction. It was found that pressure induces a progressive distortion of the corundum-like hematite structure (HP1), culminating in a structural phase transition (HP2) at ~ 50 GPa. At first sight the powder diffraction data obtained for HP2 could be equally explained in terms of either an orthorhombic perovskite or a $\text{Rh}_2\text{O}_3(\text{II})$ -type structure, but by a comparative analysis of the O-O bond length for both structures, recent Mössbauer spectroscopy results, and *ab initio* calculations allowed for the unambiguous assignment of the HP2 phase to the $\text{Rh}_2\text{O}_3(\text{II})$ -type structure. As a result of the phase transition the following changes are observed: (i) a substantial decrease in the Fe-O distances with a slight increase in Fe-Fe distances which led to a reduced cell volume, (ii) a diminution of the Fe-O-Fe bond distortion, and, (iii) a reduction in the distortion of the FeO_6 octahedron. The structural transition coincides with a previously reported insulator-metal transition due to the electronic Mott transition. It is suggested that the unusual volume reduction of 10% is accounted by the combined crystallographic and electronic phase transition, the latter resulting into a substantial reduction of the ionic radii and consequently of the Fe-O bond lengths due to electron delocalization attributed to a *charge-transfer* gap closure. The mechanism of the combined structural, electronic, and magnetic transformations is discussed.

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I. INTRODUCTION

The majority of trivalent *transition-metal* (TM) oxides crystallize in a corundum-type structure. In general the importance of these oxides in technology and earth sciences have stimulated extensive high-pressure (HP) studies to elucidate their mechanical, electronic, and structural properties.¹ Among corundum-type TM oxides, the HP characteristics of hematite ($\alpha\text{-Fe}_2\text{O}_3$) drew particular attention because of its geophysical impact regarding the role of ferric and ferrous oxides in the dynamics and composition of the earth lower mantle.²⁻⁸

At ambient pressure the trigonal $\alpha\text{-Fe}_2\text{O}_3$ (space group $R\bar{3}c$) is a wide-gap antiferromagnetic insulator, and can be considered as an archetypal *Mott* insulator.⁸ Its equation of state has been studied to 50 GPa, above which it undergoes a sluggish structural phase transition.⁷ However, comprehensive HP studies of its cell geometry were done by three groups^{3,4,9} only to ~ 10 GPa, and their results and conclusions are still ambiguous. While Lewis and Drickamer⁹ concluded that the c/a values are pressure *independent*, Sato and Akimoto³ observed a pressure variation of the cell geometry, namely, a reduction in c/a values with pressure increase while Finger and Hazen⁴ deduced that to 5 GPa the two free internal coordinates z_{Fe} and x_{O} are practically unchanged with pressure. It is quite possible that for a low compressible compound such as hematite, the 0–10 GPa range might be too small to infer properties to pressures of 50 GPa, the phase we designate as HP1.

For a long time the structure and other properties of the HP Fe_2O_3 phase ($P > 50$ GPa), designated by us as HP2,

was ambiguous. The first HP studies using shock waves were carried out in the late 1960s.² They gave sufficient evidence for the existence of a *denser* HP2 phase. In the early 1980s *static* compression experiments with diamond-anvil cells^{6,7,10} DAC's confirmed the existence of a HP2 phase above ~ 50 GPa, with a considerably smaller volume. On the basis of the relatively poor x-ray data recorded using conventional sources, two possible structures of HP2 have been proposed: an *orthorhombic perovskite*, which by its virtue has to be composed of two kinds of Fe cations, or a *distorted corundum* of $\text{Rh}_2\text{O}_3(\text{II})$ type, composed of a single cation.⁶ At about the same time Mössbauer spectroscopy (MS) studies^{5,6,11} done at 300 K, up to 70 GPa, reported the onset of a nonmagnetic component at ~ 50 GPa, coexisting with a magnetic component characterized by a relatively smaller hyperfine field. It was concluded that the HP2 phase of Fe_2O_3 is a perovskite with the an ABO_3 formula, containing two iron sites characterized by the disproportionated charges, $\text{Fe}^{2+}(\text{A})$ and $\text{Fe}^{4+}(\text{B})$ having different coordination numbers.^{6,12} Thus the decrease in volume could be qualitatively explained to be due to the increase in the coordination number of one of the cations.

Recent combined synchrotron x-ray-diffraction (XRD), MS, and electrical resistance studies to ~ 80 GPa, by Pasternak *et al.*,⁸ unambiguously resolved the nature of the HP2 phase concluding that it contains a *single* nonmagnetic Fe^{3+} cation site. Also, the concurrent collapse of magnetism and the onset of an insulator-metal transition were explained on the basis of a pressure-induced *breakdown of the electronic d-d correlation* (the *Mott* transition). Thus, according to these data, the distorted A_2O_3 corundum structure

TABLE I. The refined structural parameters of HP1 at various pressures.

Pressure (GPa)	a (Å)	c (Å)	z_{Fe}	y_{O}
2.9	5.0162(3)	13.6739(15)	0.3553(1)	0.3108(10)
6.5	5.0082(3)	13.6467(11)	0.3557(1)	0.3080(10)
12.9	4.9865(4)	13.5016(19)	0.3511(1)	0.3225(12)
18.9	4.9666(4)	13.4251(16)	0.3547(1)	0.3228(10)
30.3	4.9180(7)	13.1983(22)	0.3541(1)	0.3355(12)
38.3	4.8823(6)	13.0100(22)	0.3539(1)	0.3392(13)
46.0	4.8454(14)	12.8180(40)	0.3527(2)	0.3560(16)
55.4	4.8369(18)	12.7520()	0.3528(3)	0.3498(19)

[Rh₂O₃(II) type] is the only one appropriate for HP2 Fe₂O₃ polymorph.

This paper documents a full-profile refinement of both HP1 and HP2 crystallographic phases based on extensive powder synchrotron XRD data, combined with *ab initio* calculations to particularly elucidate the structure of the HP2 phase. As will be shown, this work adds insights into the HP1 structure at high pressure and its structural behavior *preceding* and *accompanying* the first-order phase transition concurring with the *Mott* transition. Such a type of analysis, combining the structural and electronic phase transitions, is reported for the first time, to our knowledge.

II. EXPERIMENT

X-ray-diffraction studies were performed up to 76 GPa in the angle-dispersive mode at the ID30 beamline of ESRF, employing a TAU miniature *opposing-plates* DAC.¹³ A sample of spectroscopically pure Fe₂O₃, mixed with ruby chips, used for pressure calibration, was loaded into a cavity of 100 μm in diameter and 30–40- μm thickness, drilled in 301 SS gaskets. Argon was used as a pressurizing medium. Diffraction images were collected at a $\lambda = 0.4246$ Å wavelength, using an image plate with exposure times of ~ 5 min. The image data were integrated using the FIT2D program,¹⁴ and the resulting diffraction patterns were analyzed with the GSAS (Ref. 15) and PEAKFIT 4.0, programs. The uncertainties in the lattice parameters reported in Tables I and II are from the GSAS fitting output.

III. RESULTS AND DISCUSSION

Total-energy and electronic structure calculations were performed using the full-potential linear muffin-tin-orbital

(FPLMTO).¹⁶ The calculations were based on the local-density approximation (LDA) and the generalized gradient approximation (GGA). The Hedin-Lundqvist¹⁷ and Perdew-, Burke-Ernzerhof¹⁸ parametrizations for the exchange and correlation potential were employed. Basis functions, electron densities, and potentials were calculated without any geometrical approximation.¹⁶ These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l = 8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres), and in a Fourier series in the interstitial region. The muffin-tin sphere occupied approximately 55% of the unit cell. The radial basis functions within the muffin-tin spheres were linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site, principal as well as orbital atomic quantum numbers. Outside the muffin-tin spheres the basis functions were combinations of Neuman or Hankel functions.^{19,20} In the present calculations we made use of pseudocore $3p$ and valence-band $4s$, $4p$, and $3d$ basis functions for Fe, and valence-band $2s$, $2p$, and $3d$ basis functions for O, with two corresponding sets of energy-band $2s$, $2p$, and $3d$ basis functions for O, with two corresponding sets of energy parameters—one appropriate for the semicore $3p$ states and the other for valence states. The resulting basis formed a single, fully hybridizing basis set. This approach was previously confirmed to give a well-converged basis.¹⁶ The special k -point method²¹ was used for sampling the irreducible wedge of the Brillouin zone. In order to speed up the convergence, we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRy.

The HP1 phase. The corundumlike trigonal α -Fe₂O₃ structure could be completely characterized in a hexagonal

TABLE II. The refined structural parameters of HP2 at 76 GPa.

Space group	Orthorhombic perovskite model <i>Pbnm</i>	Rh ₂ O ₃ (II) model <i>Pbcn</i>
a (Å)	4.6208(17)	6.6428(19)
b (Å)	4.9808(22)	4.6003(18)
c (Å)	6.6685(18)	4.9263(15)
Fe1	0.5 0.0 0.5	0.126(3) 0.755(2) 0.030(1)
Fe2	0.492(4) 0.559(1) 0.25	
O1	0.076(5) 0.516(3) 0.25	0.869(8) 0.626(3) 0.089(2)
O2	0.126(5) 0.141(2) 0.569(2)	0.0 0.048(4) 0.25

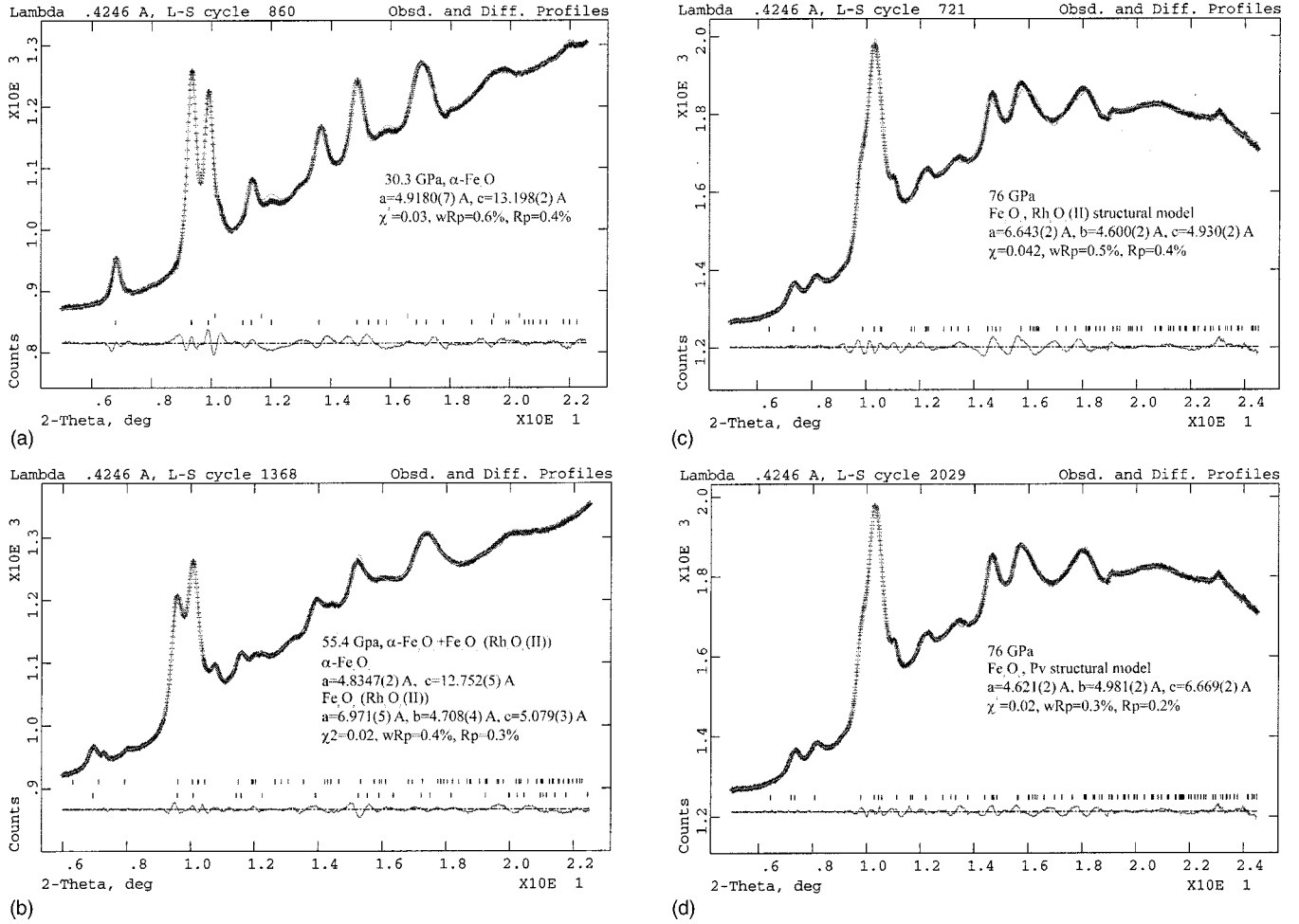


FIG. 1. Typical examples of analyzed integrated patterns of spectra collected at (a) 30.3 GPa (HP1 lower ticks; Ar, upper ticks); (b) 55.4 GPa (HP1, lower ticks; HP2, upper ticks); (c) assuming a $\text{Rh}_2\text{O}_3(\text{II})$ structural model; (d) 76 GPa, assuming an orthorhombic perovskite model for HP2. The GSAS program package was used

setting by the two lattice parameters a and c , the position of the iron atom on the three-fold axis (z_{Fe}), and the oxygen position along a twofold axis (x_{O}). Those parameters have been refined from powder x-ray-diffraction data at pressures up to 55 GPa. At pressures to 38 GPa, diffraction patterns could be fully explained by the sole presence of the HP1 phase and Ar [see Fig. 1(a)], while for $P > 40$ GPa reflections of the HP2 phase started to appear [see Fig. 1(b)]. Despite the large and complex background, it was possible to obtain a good fitting quality for all refined patterns, χ^2 being less than 0.04, w_{Rp} less than 0.6%, and Rp less than 0.4%. Results of the structural refinement to 55 GPa are presented in Table I. The standard deviations of the oxygen positions are higher than that of the (heavier) iron, and increase slightly with a pressure increase. Structural results from our powder diffraction data refinement at 2.9 GPa can be compared with the single-crystal XRD data of Finger and Hazen.⁴ At 3.14 GPa they reported $z_{\text{Fe}}=0.35517(12)$ and $x_{\text{O}}=0.3051(14)$, which are close to our data at 2.9 GPa, namely, 0.3553(1) and 0.3108(10), respectively.

The data for molar volumes as functions of the pressure were fitted using the Birch-Murnaghan equation of state²²

$$P = 1.5K_0[(V_0/V)^{5/3}][1 - 0.75(4 - K'_0)\{(V_0/V)^{2/3} - 1\}], \quad (1)$$

where K_0 , K'_0 , and V_0 are the bulk modulus, its pressure derivative, and the unit-cell volume at 1 bar and 300 K, respectively. The theoretical fit using $K_0=258(6)$ GPa, $K'_0=4$ (fixed), and $V_0=301.76(5)$ Å³ is shown in Fig. 2. Sato and Akimoto³ proposed two values of K_0 , e.g., 231(10) GPa for $P < 3$ GPa and 178(4) GPa for $3 < P < 10$ GPa. Finger and Hazen⁴ proposed a value of 225(4) GPa from data obtained to 5 GPa, and Olsen *et al.* proposed a value of 230(5) GPa from data collected in the energy dispersive mode to 50 GPa. Our value of K_0 derived from angle dispersive data to 50 GPa is consistently higher than that of Refs. 3, 4, and 7, but our experimental molar volume V_0 fits very well with that derived by Olsen *et al.*⁷ at 50 GPa (Fig. 2).

The c/a value, which for an ideal HCP corundum-type structure is 2.833, decreases with pressure (see Fig. 3), in agreement with previous studies performed at considerably lower pressures.^{3,4} This is a common feature in corundum-type transition-metal oxides.¹ A decrease in c/a with pressure may point either to a bonding distortion or to an uneven

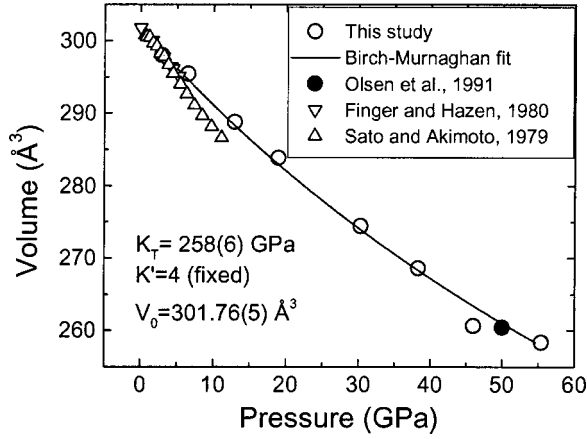


FIG. 2. The variation with pressure of the volume unit cell of HP1. The solid line is a theoretical fit using a third-order Birch-Murnaghan equation of state with variables $K_0=258(6)$ GPa, $K'_0=4$ (fixed), and $V_0=301.76(5)$ cm³/mol.

modification of the M - O - M bond lengths, which consequently may affect the electronic properties of the metal ion (M).²³ This has been the case in V_2O_3 and Ti_2O_3 , which are known to undergo a pressure-induced insulator-metal transition.¹ For α - Al_2O_3 and probably Cr_2O_3 , which do not demonstrate insulator-metal transitions, the c/a ratio is practically independent of pressure.^{24,25}

In the hematite composition, the FeO_6 octahedra share one face and three edges with their neighbors (Fig. 4). The shared octahedral faces are comprised of three Fe-O bonds with the shortest Fe-O distances $d_{Fe-O(F)}$ and of one Fe-Fe bond with $d_{Fe-Fe(F)}$ distance. The shared edges are comprised of the remaining three Fe-O bonding with $d_{Fe-O(E)}$ distances and three Fe-Fe second-neighboring bonding with $d_{Fe-Fe(E)}$ distances. The expression \mathcal{D}_{Fe-O} , which characterizes the degree of Fe-O distortion in the FeO_6 -octahedron, can be written as

$$\mathcal{D}_{Fe-O} = (d_{Fe-O(E)} / d_{Fe-O(F)} - 1),$$

and, similarly for the Fe-Fe neighbors,

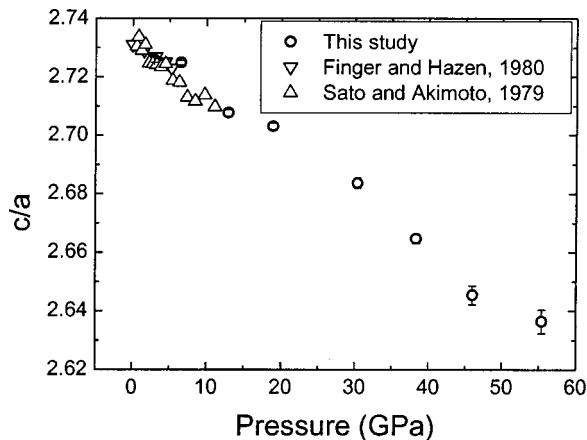


FIG. 3. Variation of c/a with pressure in the HP1 phase.

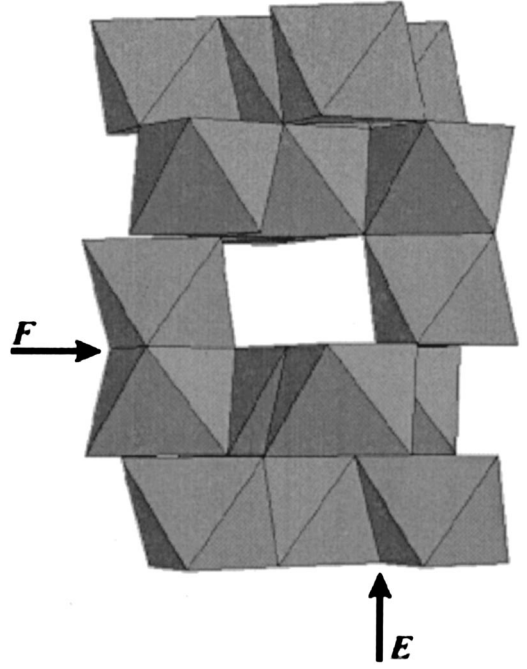


FIG. 4. Polyhedral model of the hematite structure (F , marked faced sharing octahedra, E , edge-sharing octahedra).

$$\mathcal{D}_{Fe-Fe} = (d_{Fe-Fe(E)} / d_{Fe-Fe(F)} - 1).$$

The pressure dependencies of the Fe-O and Fe-Fe mean distances and of the degree of distortion of the FeO_6 octahedron are shown in Figs. 5(a) and 5(b). While in general the mean distances decrease linearly and moderately with pressure, the degree of distortion increases significantly. This leads to the conclusion that shorter Fe-O bonds belonging to the shared faces decrease with pressure, considerably more than those belonging to the shared edges (see Table III). A feature characterizing the octahedral symmetry, namely, the octahedral angle variance $\Delta\theta$ (Ref. 26) that expresses the mean deviation of the O-Fe-O angles from the ideal octahedron value of $\theta=90^\circ$ can be written as

$$\Delta\theta = \sum_{j=1}^{12} (\theta_j - 90)^2 / 11. \quad (2)$$

It is noteworthy that, with increasing pressure, the octahedron becomes more regular with respect to angle distortion $\Delta\theta$ [Fig. 5(c)], but less with respect to the Fe-O and Fe-Fe distances.

HP2 phase. Diffraction patterns collected at $P > 46$ GPa contained reflections of the high-pressure phase (HP2), in addition to those of Ar and α - Fe_2O_3 (HP1). Although all previous studies^{6-8,10} agreed with an orthorhombic phase assignment to HP2, its structure was never refined, leading to different interpretations concerning its structural assignment. Two possible structural models were considered: the *orthorhombic perovskite* (OPv) type^{6,7,10,12} and the Rh_2O_3 (II) type^{6,8} (Fig. 6). Structural refinement analyses for both models were carried out [see Figs. 1(c) and 1(d), and Table II] using data collected at 76 GPa, the pressure at which HP1 is

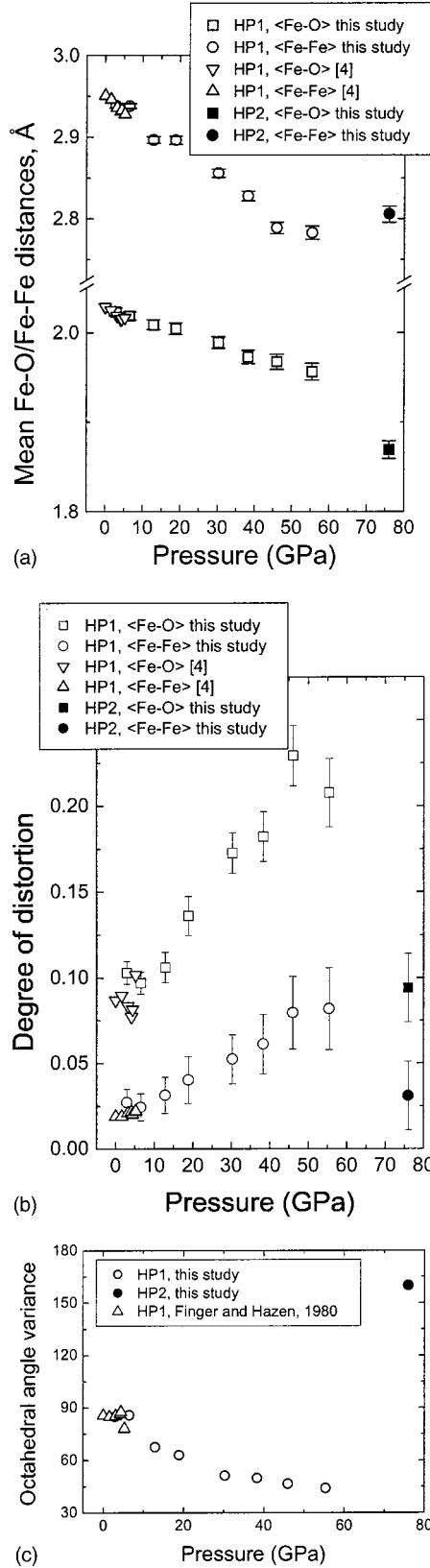


FIG. 5. Pressure dependencies of various structural features of HP1: (a) the mean Fe-O distance and the mean *second-neighbor* Fe-Fe distances, (b) the degree of distortion of the FeO_6 octahedra, and (c) the octahedral angle variance.

TABLE III. Selected interatomic distances and angles for HP1 and HP2 phases^{a,b,c} (in Å and degrees).

Parameter	2.9 GPa	46 GPa	76 GPa
Fe-O	1.924(2) [3] ^a (F) ^b	1.771(7) [3] (F)	1.772(4)
	2.122(3) [3] (E) ^b	2.158(7) [3] (E)	1.835(4)
			1.847(6)
			1.887(4)
Fe-Fe	2.880(2) (F)	2.632(8) (F)	1.905(4)
	2.958(2) [3] (E)	2.841(9) [3] (E)	1.956(6)
			2.669(6)
			2.774(7)
Fe-O1-Fe ^c	85.4(1)	75.1(4)	2.848(7)
	93.8(1) [2]	92.1(4) [2]	2.882(7) [2]
	120.9(1)	126.6(4) [2]	126.8(1)
	131.2(1) [2]	132.6(4)	107.9(1)
Fe-O2-Fe			126.8(1)
			131.6(2)
			89.0(2)
			95.8(2) [2]
		121.6(2)	
		126.6(2) [2]	

^aNumbers in square brackets show the multiplicity of the parameters.

^b(F): distances corresponding to the shared faces; (E): distances corresponding to the shared edges.

^c $\alpha\text{-Fe}_2\text{O}_3$ contains only one type of oxygen atoms

completely transformed to HP2.²⁷ As can be seen, despite the high quality of the refinement following the superior x-ray data of the present work, unequivocal assignment to either structural model is still impossible. Though visually, the fit with OPv “looks” slightly better; statistically the mere 0.1% difference in wRp or Rp is not enough for a definitive assignment.²⁸ By close inspection of the derived interatomic distances for the proposed structures one finds that the shortest O-O distances in the OPv refinement is merely 2.05 Å, too small for a realistic value.²⁹ However, following the $\text{Rh}_2\text{O}_3(\text{II})$ -type structure refinement, the shortest O-O distance (corresponding to the shared octahedra edges) is ~ 2.26 Å, which is in good agreement with the O-O distances measured in the high-pressure silica modification.^{30–32} Furthermore, for an OPv structure one must assume *two different kinds of iron cations*, arising, say, from two iron *charge states* (Fe^{2+} and Fe^{4+}) positioned at the two crystallographic sites FeO6 and FeO8 polyhedra.³³ However the recent Mössbauer data⁸ unequivocally demonstrated that for $P > 72$ GPa there is only one *single* nonmagnetic Fe^{3+} spectral component. No doubt, this is the strongest argument against assigning an orthorhombic perovskite structure.³⁴

Structural and electronic aspects of the HP1→HP2 transition. We carried out total-energy calculations for Fe_2O_3 for two different type of structures, HP1 being of the corundum type and HP2 of the $\text{Rh}_2\text{O}_3(\text{II})$ type (Fig. 7). The calculations employing the LDA and GGA methods suggest a

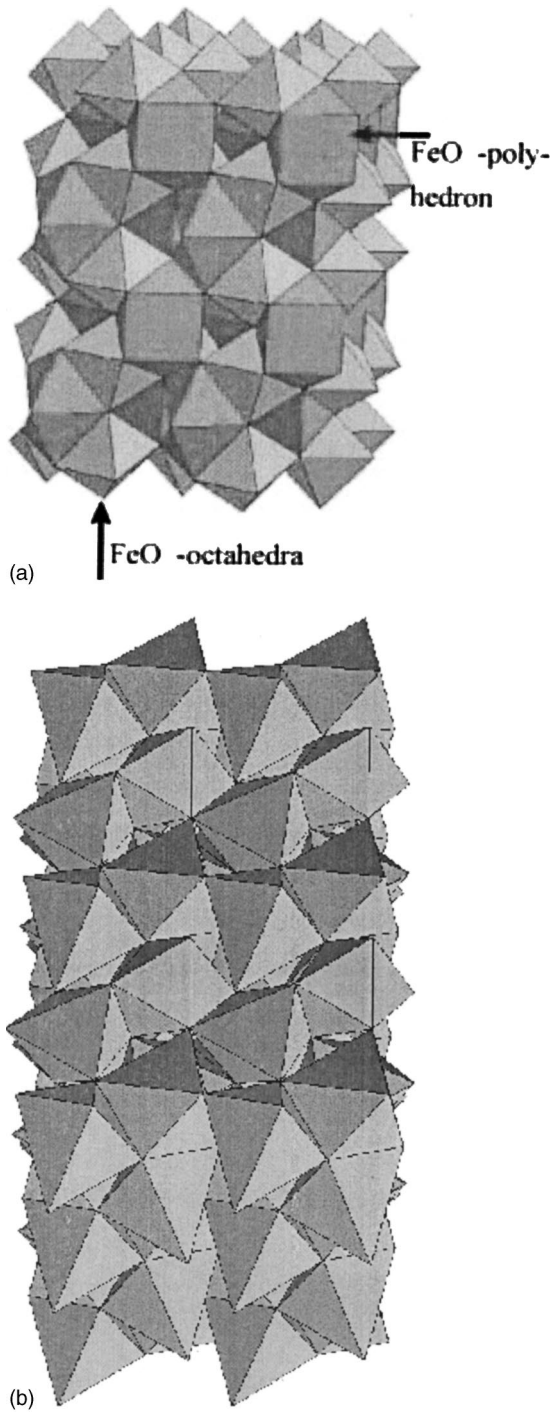


FIG. 6. Polyhedral models of possible HP2 Fe_2O_3 structures: (a) orthorhombic perovskite, (b) $\text{Rh}_2\text{O}_3(\text{II})$.

HP1 \rightarrow HP2 transition taking place at $P > 20$ and 25 GPa, respectively. This is in reasonable agreement with the present experimental observations. We have also tested the possibility of HP2 being OPv , by comparing its relative stability to that of $\text{Rh}_2\text{O}_3(\text{II})$ at 76 GPa.³⁵ The calculated total-energy value of $\text{Rh}_2\text{O}_3(\text{II})$ phase is 25 mRy/f.u. lower than that of the perovskite, thereby favoring this HP2 assignment. Thus our *ab initio* calculations confirm the experimental finding of a Rh_2O_3 -type phase. The calculated transition pressures are

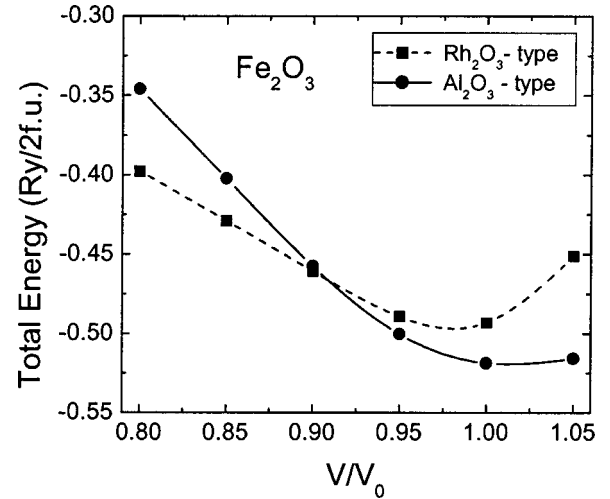


FIG. 7. The total energy of corundum-type and $\text{Rh}_2\text{O}_3(\text{II})$ -type structures of Fe_2O_3 as a function of volume obtained by FPLMTO (GGA) calculations.

somewhat lower than the experimental one. Kinetic barriers of the phase transformation process might be the reason; also, one may go beyond LDA and GGA calculations such as LDA+ U to simulate the real physical conditions.

The structural transition from the corundum to the Rh_2O_3 -II type involves minor crystallographic changes. It involves a 180° rotation of every other octahedra sheet, along with a translation; namely, five of the six coordinating oxygen atoms remain intact whereas only the sixth oxygen position is altered.³⁶ The Rh_2O_3 -II structure is related to the corundum, in that it contains pairs of FeO_6 octahedra with shared faces, the difference being that each octahedron shares only two edges with other octahedra rather than three for the case of corundum. The Fe-O distances, which in the hematite structure (HP1) correspond to the three longest bonds through the common edges (Fe-O_E), are substantially reduced at the transition, while the other three distances, corresponding in hematite to the shortest bonds through the common face (Fe-O_F , Table III), increase slightly. At the transition the $\langle \text{Fe-O-Fe} \rangle$ bond angle of the latter bonds increase by $\sim 12\%$, an indication of a reduced bonding distortion. Linear extrapolation to 76 GPa of the $\langle \text{Fe-O} \rangle$ distance in HP1 shows that, following the phase transition to HP2, it is reduced by 3.2%, concurrent with a decrease in the distortion of the FeO_6 octahedra and a slight increase of the mean Fe-Fe distance [see Figs. 5(a) and 5(b)]. The changes at the transition can be summarized as follows: (i) a substantial decrease in Fe-O with a slight increase in Fe-Fe distances, (ii) a reduction of the Fe-O-Fe bond distortion, and (iii) a reduction of the FeO_6 octahedral distortion.

The pressure-induced transformation from the corundum to a Rh_2O_3 -II structure seems to be quite general. This is the case with Rh_2O_3 , that transforms at 6.5 GPa, after annealing, with a volume reduction of 3.2%.³⁶ *Ab initio* quantum-mechanical calculations predicted that such a transition would also occur with the analogous Al_2O_3 , at 80 GPa, followed by a 2.2% reduction in the molar volume.³⁴ In agreement with this prediction, XRD measurements³⁷ revealed

that the transformation occurs at ~ 100 GPa and ~ 1000 K, accompanied by a volume decrease of 4%. However it should be emphasized that in contrary to Fe_2O_3 , in both cases the volume decrease at the transition is considerably smaller, and no significant changes in the electronic structure are observed.³⁶ Thus we conclude that the crystallographic transition of the corundum phase of hematite into a Rh_2O_3 -II structure is, by itself (as in Rh_2O_3), not sufficient to explain the large volume decrease; fundamental electronic processes must take place to explain the significant volume shrinkage. In what follows, we tackle this problem.

The majority of binary and ternary TM oxides are magnetic insulators, the insulating properties emanating from the strong electronic correlation phenomena inherent to the d bands. These so-called *Mott* insulators³⁸ are characterized by optical large $d-d$ gaps U , separating the upper empty d band from the lower filled one [the *Mott-Hubbard* (MH) gap], or by a $p-d$ gap Δ , separating the upper d -band from the lower filled ligand p -band [the *charge-transfer* (CT) gap]. Apart from their insulating nature, these materials are characterized by large magnetic moments, and become antiferromagnetic below T_N . The effect of pressure on a Mott insulator will be to close the $d-d$ or $p-d$ gap, leading to the breakdown of the d -electrons correlation. This concurs with the collapse of the magnetic moment. This is exactly what happened in the HP1 \rightarrow HP2 pressure-induced transition.⁸ Thus it is obvious that a considerable fraction of the unusually large volume reduction ($\sim 10\%$) in the HP1 \rightarrow HP2 transformation must be attributed to the Mott transition. An interpretation of this reduction in terms of the individual Fe-O and Fe-Fe lengths shrinkage is not simple, a major reason being that the crystallographic phase transition is not isostructural.

A clue to the specific contribution of the correlation breakdown to the bonding alterations can be obtained by comparing the present results with those obtained for the pressure-induced phase transition in an analogous Rh_2O_3 system.^{36,39} The transition from an α - Rh_2O_3 phase to a Rh_2O_3 -II phase follows a volume contraction of 3.2%, which primarily affects the $\langle\text{Rh-Rh}\rangle$ distance, which decreased by about 3% with a corresponding minor adjustment of the RhO_6 octahedra, and no change was observed in the $\langle\text{Rh-O}\rangle$ nearest-neighbor distance. But in Fe_2O_3 , as mentioned, one observes a *large decrease* in the $\langle\text{Fe-O}\rangle$ nearest-neighbor distances, while the $\langle\text{Fe-Fe}\rangle$ distances barely changes. What is the significance of the Fe-O nearest-neighbor bond contraction opposed to that of the Fe-Fe and bond contraction? From the few crystallographic studies following correlation breakdown in TM compounds it was found that in the case of a *temperature-induced* isostructural transition in the CT insulators RNiO_3 ($R = \text{Pr, Nd, Eu, and Sm}$) (Ref. 40) the Ni-O distances decreased, whereas for the similar transition in the MH insulators V_2O_3 and Cr_2O_3 - V_2O_3 (Ref. 41) only V-V distances changed. This finding may suggest that a closure of the $p-d$ CT gap is the mechanism responsible for the correlation breakdown transition in Fe_2O_3 . This hypothesis corresponds well with an analysis carried out by Bocquet *et al.*⁴² within the framework of the *cluster model*, according to which α - Fe_2O_3 at ambient pressure is a CT insulator with a gap $\Delta \sim 3.4$ eV versus a MH gap $U \sim 7$ eV.

The mechanism that triggers this transition is complex, due to the fact that electronic and structural changes occur simultaneously, and it is difficult to pinpoint their respective roles. At this point it is noteworthy to mention that up to 40 GPa, the pressure at which the HP1 to HP2 transition is established, the temperature dependence of the resistance is typical of an insulator.⁴³ Furthermore, the characteristics of the $R(T)$ curves to 40 GPa barely change with pressure, with no hint whatsoever of a gap closure. Also, within the HP1 phase, the Fe- O_E bonds through the common edges are not decreased; they even exhibit a slight increase with pressure, and the Fe-O-Fe bond angle barely changes (see Table III), all these hindering the formation of a conducting network at HP1, and thus suggesting that such a network could be formed only at the HP2 phase.

IV. CONCLUSIONS

Detailed high-pressure x-ray powder diffraction of the orthorhombic phase was carried out by a refinement of the data at pressures between 3 and 76 GPa. A pressure-induced progressive distortion of the corundumlike hematite structure was observed, signifying the increasing asymmetry of the FeO_6 octahedra, which culminated in a structural phase transition from a corundum-type structure to a Rh_2O_3 (II)-type structure (HP1 \rightarrow HP2). Interestingly, powder diffraction data for the HP2 phase could be equally well explained in terms of both orthorhombic perovskite and Rh_2O_3 (II)-type structures. However, a comparative analysis of the O-O bond lengths for both structures and recent Mössbauer studies allowed a definite classification of the HP2 polymorph phase to a Rh_2O_3 (II) structure. This conclusion is in full agreement with the total-energy, FPLMTO calculations, which predicted that at 76 GPa the perovskite is less stable than the Rh_2O_3 (II)-type structure.

Analysis of XRD data showed that the main changes at the transition are (i) a substantial decrease in the Fe-O distance and a slight increase in the Fe-Fe distance, (ii) a reduction in the Fe-O-Fe bond distortion, and (iii) a reduction in the distortion of the FeO_6 octahedron. The cell volume undergoes a large reduction of $\sim 10\%$, attributed to the substantial decrease of the Fe-O distances. The structural transition coincides with an insulator-metal transition and the collapse of magnetic state (correlation breakdown). A comparative analysis of the bond alteration occurring at the transition, between Rh_2O_3 and Fe_2O_3 systems, suggests that electronic modifications significantly affects the Fe-O bonds, resulting in their large shrinkage, leading to a volume decrease in Fe_2O_3 . The fact the Fe-O bonding is largely affected by the correlation breakdown implies that *charge-transfer* gap closure is the mechanism responsible for metallization, concurring with the collapse of the magnetic moments. The respective roles of structural and electronic changes at the combined phase transition in Fe_2O_3 were discussed.

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