Breakdown of the Mott-Hubbard State in Fe_2O_3: A First-Order Insulator-Metal Transition with Collapse of Magnetism at 50 GPa

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Electronic and structural properties of the high-pressure phase of Fe_2O_3 were determined by combining the methods of Mössbauer spectroscopy, x-ray diffraction, and electrical resistance, $R(P,T)$, to 80 GPa. Because of a first-order phase transition taking place in the 50–75 GPa range and accompanied by a volume decrease of $\sim 10\%$, a breakdown of the electronic d-d correlation occurred, leading to a Mott transition, a metallic and a nonmagnetic single Fe^{3+} electronic state. The high-pressure structure is of the distorted Rh_2O_3-II type. The accommodation of the denser phase within this six-coordinated structure is attributable to the metallic state. [S0031-9007(99)09286-8]

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More than half of the binary transition metal (TM) compounds and the majority of the undoped TM oxides are magnetic insulators that order antiferromagnetically below a certain Néel temperature (T_N). The localization of carriers in those so-called Mott insulators results from strong on-site Coulomb repulsion within the $3d$ band. Its insulating nature [1] is commensurate to an effective energy-gap U, far exceeding the d-band width W, splitting the d band into upper (empty) and lower (filled) subbands. In view of the "Coulomb" nature of the gap, it is expected that in ionic insulators, such as the binary TM oxides, very high pressures will be needed to reach the $W/U \gg 1$ regime. In this regime the d-electron correlation collapses, giving rise to an insulating-metal transition concurring with a magnetic moment breakdown, a phenomenon often called the *Mott* transition. Indeed, as shown by Cohen *et al.* [2] for the case of binary TM oxides, the Mott transition could be attained only at pressures close to 200 GPa. Pasternak *et al.* experimentally observed a pressure-induced Mott transition in the highly covalent NiI_2, [3] using the combined methods of ^{129}I Mössbauer spectroscopy (MS), x-ray diffraction (XRD), and electrical conductivity in diamond anvil cells (DAC's). The isostructural transition was second order and quasi-isochoric. The question then arises whether in the case of a first-order phase transition resulting in a reduction in volume, such a TM-oxide Mott insulator might undergo a Mott transition.

In this Letter we report the observation of such a transition attributable to a huge volume reduction, the first-order phase transition in α-Fe_2O_3 (hematite) at 50 GPa. As will be shown, this work is important not only to the elucidation of such a basic phenomenon as the Mott transition, but also to ultimately untangling the baffling nature of the high-pressure phase of hematite.

Fe_2O_3, a wide-gap antiferromagnetic insulator ($T_N = 956$ K [4]) can be regarded as archetypal of a Mott insulator. Motivated primarily by its importance in the earth sciences, high-pressure studies of this corundum-type mineral have been extensively performed since the early days of high-pressure physics. As early as in the mid-1960s shock-wave experiments were performed by McQueen and Marsh [5] who reached energy densities not available at that time in conventional static pressure cells. Based on those experiments Reid and Ringwood [6] proposed a new denser structure formed in the 60–120 GPa range. In the mid-1980s, static high-pressure conventional XRD studies carried out with DAC's by Yagi and Akimoto [7] and Suzuki *et al.* [8] confirmed the onset of a new denser phase at $\sim$50 GPa. This structure could be equivocally assigned either to the "distorted corundum," Rh_2O_3-II type [9] or to an orthorhombic perovskite [8] structure. Toward the late 1980s with the advent of synchrotron radiation facilities, XRD measurements using the energy-dispersive mode were carried out to 67 GPa by Staun Olsen *et al.* [10]. They reported the onset of a first-order phase transition at $\sim$50 GPa accompanied by a drastic volume reduction of about 10% and assigned an orthorhombic structure to this new phase. Yet, despite improved experimental data of the XRD patterns, the authors did not unambiguously differentiate between the Rh_2O_3-II corundum type and the *perovskite* structures.

Concurrent with the discovery of the new high-pressure dense phase by XRD investigation, Mössbauer experiments carried out at 300 K by Suzuki *et al.* [8], Syono *et al.* [11], and Nasu *et al.* [12] revealed a nonmagnetic component at $\sim$50 GPa, coexisting with a magnetic phase to highest pressure of 70 GPa, and assigned to the dense state. The authors also noticed that the hyperfine field, H_{hf}, in the 56–70 GPa range, was somewhat smaller than that of the low-pressure (LP) phase. It was concluded and since then accepted that the high-pressure (HP) phase of Fe_2O_3 is characterized by "two kinds of iron ions with different crystallographic sites in the same crystal structure" [8]. To accommodate the two kinds of iron, the authors had no choice but to opt for the perovskite option with the ABO$_3$ formula, where A and B stand for Fe^{2+} and Fe^{4+}, respectively. Furthermore, because of the nonmagnetic feature of one of the components, it was assigned to a low-spin (*paired*-spin) state. Thus, based on the MS data the HP phase of hematite has since then been tabbed "the high-pressure, low-spin phase of hematite." Electrical resistance studies by Knittle and Jeanloz to 65 GPa [13] showed a drastic reduction in the resistivity upon crossing this phase transition. Based on the estimated value of the resistivity, they concluded that the HP phase is a semiconductor.

In this study we have performed extensive measurements, up to 80 GPa, with XRD in the angle-dispersive mode [14], MS, and electrical resistivity R employing the TAU miniature piston/cylinder DAC [15] with anvils having 0.3-mm flats. Ruby fluorescence was used for pressure measurements. For XRD and MS [16] samples were encapsulated in 150-μm diameter by 25-μm-high cavities drilled in SS and Re gaskets, respectively. Argon was used as a pressurizing medium. For resistivity studies the ring surrounding the sample cavity drilled in a SS gasket was coated with fine Al$_2$O$_3$ powder mixed with epoxy for the purpose of electrical insulation of the 5-μm-thick Pt electrodes, and the four-probe method was used. The average distance between electrodes was 40 μm. At selected pressures, particularly in the vicinity and above the phase transition, the temperature dependencies of $R(P)$ and of MS were carried out in the range 4–300 K using a *dip-stick* sample holder immersed into a He-storage Dewar and a top-loaded cryostat [17], respectively. The pressure uncertainty was ~5%.

Mössbauer spectra of Fe$_2$O$_3$ characteristic of various pressure ranges taken at 300 K are shown in Fig. 1 (a–d). Up to ~45 GPa the only spectral component is that of the LP phase (a, b), arising from the $^6A_{1g}$ high-spin state and characterized by $H_{\mathrm{hf}} = 51$ T, a typical value of the hyperfine field for ionic ferric oxide bonding. In the 50–55 GPa range a nonmagnetic quadrupole-split component emerges (c), designated as the HP component, *coexisting* with the 51 T magnetic-split LP component. In the 60–70 GPa range (d) the relative abundance of the LP component keeps on decreasing, and we note that the H_{hf} at 300 K of the magnetic component is slightly reduced, by about 10%; this magnetic phase in the mixed region is designated as an intermediate phase (IP). For $P > 72$ GPa, the only spectral component observed in the 4–300 K range is that of the nonmagnetic HP phase (e) and is characterized by a quadruple-split spectrum. The lack of a magnetic ordering down to 4 K prompted us to conclude that this single HP component reflects not a $^6A_{1g}$ paramagnetic configuration, but rather a nonmagnetic state [18]. This signals the breakdown of the d-d electronic correlation, and that will be accompanied by metallization.

The pressure variation of the resistance $R(P)$ at 300 K is shown in Fig. 2. As can be seen a precipitous decrease occurs at the onset of the phase transition in which $R(P)$ is reduced by more than 6 orders of magnitude [19]. The resistivity value at 80 GPa and 300 K was estimated to be $1.5(7) \times 10^{-6}$ Ωm, typical of a metal. To further explore the HP electronic state we carried out $R(T)$ measurements at various pressures (see inset of Fig. 2). As shown, the $R(T$, 17 GPa) curve for the LP regime is typical of an insulator, and the $R(T$, 59 GPa) curve with its positive dR/dT is characteristic of a metallic state. In the range 42–59 GPa the sample behaves as a mixture of insulating and metallic states with the HP metallic abundance increasing with pressure.

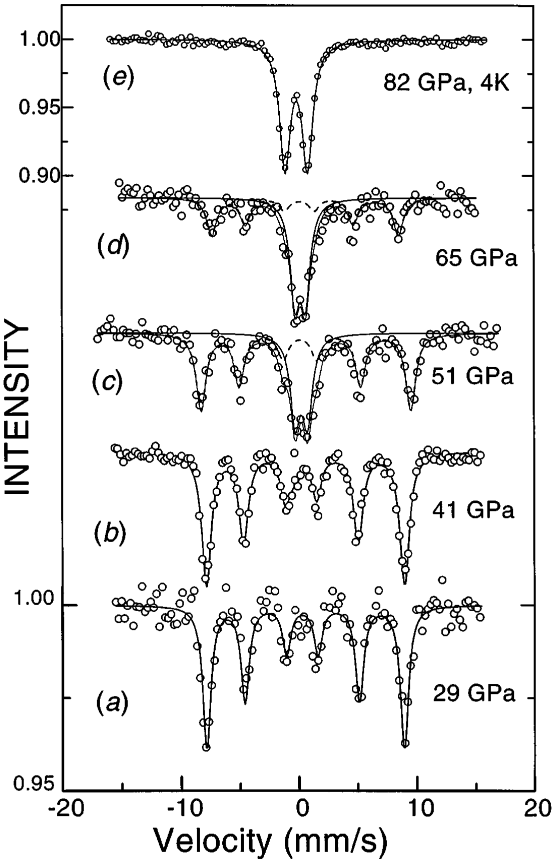

FIG. 1. Typical Mössbauer spectra recorded at 29, 41, 51, 65, and 82 GPa. The solid line is a curve derived from a least-squares-fit program assuming one magnetic component (a, b), magnetic and nonmagnetic components (c, d), and a pure quadrupole-split component with a splitting QS = 2 mm/s (e). At 82 GPa a spectrum similar to that at 4 K was recorded at 300 K with a smaller value of QS. The lack of a magnetic component at $P > 72$ GPa to the lowest temperature signals the onset of a pure metallic state (see text).

The diffraction patterns typical of the LP, IP, and HP regimes are shown in Fig. 3. The LP diffraction pattern (a) fits very well with the corundum phase (space group $R\bar{3}c$). The diffraction lines corresponding to the HP phase first appear at ~45 GPa, and the diffraction pattern recorded at 46 GPa (b) is characteristic of IP, the intermediate regime where both LP and HP phases coexist. Diffraction patterns (c) of the pure HP recorded at 70 GPa can be precisely indexed to the distorted

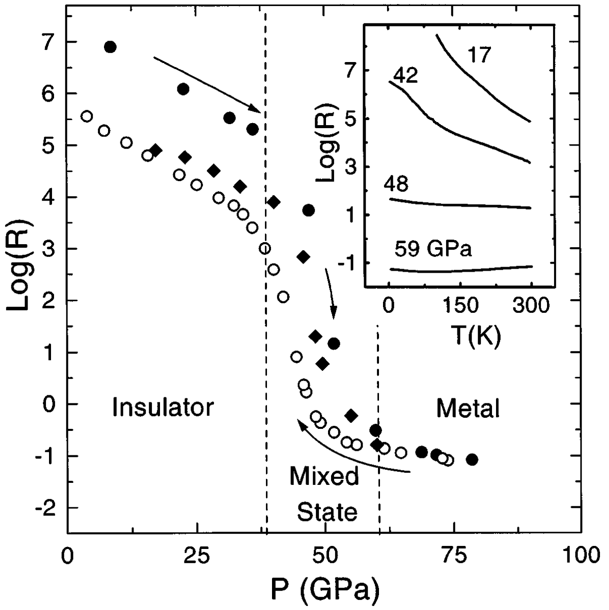

FIG. 2. The pressure dependence of the logarithm of the resistance recorded at 300 K. The solid circles (●) are data points recorded during the first cycle of compression, solid diamonds (◆) at the successive compression cycles, and open circles (○) at successive decompression cycles. The large change in the resistance between the first and the successive compression cycles is explained as due to compacting of the powder sample. Note the big decrease in R of the sample, by more than 6 orders of magnitude until its full metallization at $P > 60$ GPa (see text). The vertical dotted lines set the boundaries between the insulating LP, mixed intermediate, and metallic (HP) phases. The inset shows the temperature dependence of the Log(R) at the various phases: at 17 GPa it behaves as an insulator, at 42 and 48 as an insulator-metal mixed phase, and at 59 GPa as a metal with $dR/dT > 0$.

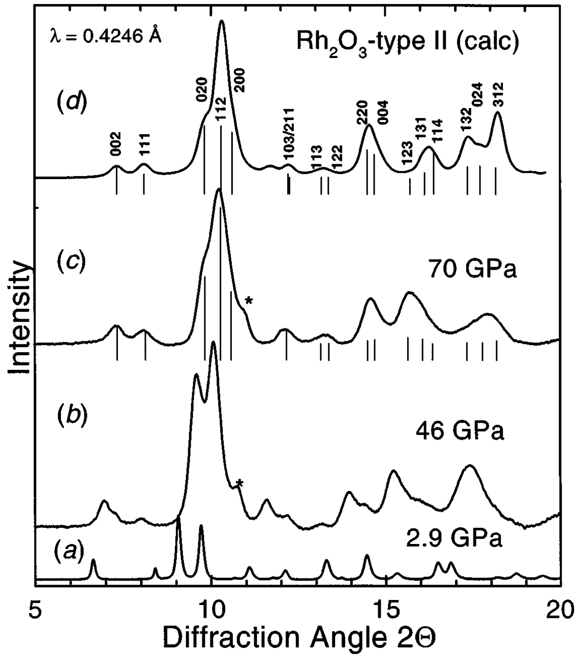

FIG. 3. Angle-dispersive x-ray diffraction patterns of hematite at different pressures. (a) α-Fe$_2$O$_3$ corundum structure (space group $R\overline{3}c$) at 2.9 GPa, typical of the LP phase; (b) mixed phase patterns recorded at 46 GPa; (c) Rh$_2$O$_3$-II structure (space group *Pbna*) recorded at 70 GPa, typical of the HP phase; (d) calculated pattern for the Rh$_2$O$_3$-II structure. The vertical lines in (c) and (d) denote the fitted and the calculated positions and intensities. The pattern of the calculated structure in (d) was obtained on the basis of the lattice parameters derived from the fitting at 70 GPa. Note the excellent agreement between derived and calculated patterns. The $*$ symbol in (b) and (c) may arise from the ruby probe used as a pressure marker.

corundum phase, Rh$_2$O$_3$-II type, with space group *Pbna* (3d) [20].

It is noteworthy that Reid and Ringwood's [6] and subsequent crystallographers' explanation of the huge decrease in volume was based on the conjecture of increase in the coordination number of the cation. Since the ferric-corundum structure could not accommodate the enhanced coordination number, the valence disproportionation model resulting in "two iron" sites, i.e., $\mathrm{Fe}_2^{3+}\mathrm{O}_3 \rightarrow (\mathrm{Fe}^{2+}\mathrm{Fe}^{4+})\mathrm{O}_3$, was invoked. Such a model leads automatically to a perovskite structure. The subsequent incomplete Mössbauer studies [10–12] carried to ~70 GPa somehow corroborated this conjecture suggesting that the HP phase is indeed characterized by two distinct Fe components. Those two spectral components were attributed to two different Fe cations (Fe^{2+} and Fe^{4+}), one of which could be in a low-spin, diamagnetic, state explaining the nonmagnetic component. Now it is clear that a large pressure distribution in the DAC for the Mössbauer experiments associated with their (alcohol mixture) pressure medium, particularly the one experiment carried out to 72 GPa [12], and a lack of experimental data at the higher pressures, led to the wrong and biased disproportionation model. Thus, for years the perovskite ABO$_3$ structure has been adopted, ruling out the A_2O$_3$ corundum structure which can be assigned only in the case of a single cation, e.g., Fe^{3+}.

The present studies unambiguously clarify the nature of the high-pressure *electronic* and *structural* states of hematite. Upon reaching $V/V_0 \sim 0.82$ (50 GPa), a first-order phase transition occurs resulting in a colossal collapse in volume. This collapse prompts the closure of the *p-d charge-transfer* gap (Δ) or the *d-d* Mott-Hubbard gap (U), leading to the breakdown of the *d-d* correlation and resulting in a metallic phase with zero moments. The filling of the conduction band due to electron delocalization is commensurate with an effective decrease of the cationic radius, namely, of the crystal volume. Therefore, the metallization of the HP phase of hematite allows for the accommodation of a dense state with no need for increasing the coordination number [21]. Following this quasi-isostructural transition from a corundum α-Fe$_2$O$_3$ structure to a distorted corundum Rh$_2$O$_3$-II, the Fe^{3+} cations remain sixfold coordinated.

Though we understand now the properties of the HP phase of hematite, the fundamental issue regarding the mechanism that triggers this phase transition still remains unsolved. The very detailed pressure-induced Mott-transition experiment performed in NiI_2 [2] showed that metallization did not involve any volume change as was manifested by the ^{129}I isomer shift, a very sensitive probe of the electron density on the atomic scale, and by the XRD data. A *temperature-induced* Mott transition documented for the rare-earth nickelates, (RNiO$_3$, $R =$ Pr, Nd, Eu, and Sm [22] also resulted in a quasi-isochoric transition with a minute volume reduction of about 0.2% and associated with the onset of metallization. Therefore the mechanism of the Mott transition by itself does not have to mitigate a first-order phase transition with such a volume collapse. Finally it should be noted that if one extrapolates the equation of state of the low-pressure phase, using the bulk modulus parameters as derived by Ref. [10], the 10% volume reduction, in the absence of a phase transition, would have ultimately occurred at $\sim$200 GPa. Calculations by Cohen *et al.* [2] for several TM oxides showed that for the particular case of MnO in which the high-spin state configuration of Mn^{2+} is the same as of Fe^{3+} (d^5), the Mott transition also occurs at $\sim$200 GPa.

In conclusion the present series of experimental data determines unequivocally the nonmagnetic metallic state of hematite induced by a precipitous volume decrease at 50 GPa. The insulator-metal transition results from the breakdown of the d-d correlation resulting in a nonmagnetic metal. The insulating and metallic phases coexist in the 42–58 GPa pressure range. Also, the ambivalence regarding the electronic state of Fe and the HP structure is now clarified. The structural transition is minor, from the corundum type to a distorted corundum Rh_2O_3-II type, with both composed of Fe^{3+} cations sixfold coordinated to oxygens. The geological implications of this finding are quite compelling. At depths corresponding to the inner mantle, hematite is metallic with a resistivity as high as that of metallic iron.

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[19] Note that following the first compression cycle (filled circle curve), $R(P)$ upon decompression reaches a value that is lower at $\sim$5 GPa. Successive compression and decompression cycles are reproducible. This phenomenon can be explained as due to compacting of the sample during the first compression cycle.

[20] The reliability factor $R = \sum |d_{\text{obs}} - d_{\text{calc}}| \sum d_{\text{obs}}$, was found to be 0.2%, a rather low value considering the high-pressure conditions of the sample. d_{obs} and d_{calc} are the observed and calculated d-spacing values, respectively.

[21] This interpretation is consistent with the observation that Al_2O_3 transforms from the corundum to the Rh_2O_3-II at $\sim$100 GPa, with no significant change in electronic structure with a volume decrease of $<4\%$. N. Funamori and R. Jeanloz, Science **278**, 1109 (1997).

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