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Mössbauer and resistivity studies of the magnetic and electronic properties of the high-pressure phase of Fe_3O_4

W. M. Xu, G. Yu. Machavariani,* G. Kh. Rozenberg, and M. P. Pasternak
School of Physics and Astronomy, Tel-Aviv University, 69978, Tel Aviv, Israel

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The high-pressure phase of magnetite, *h*-Fe_3O_4, has been studied by Mössbauer spectroscopy, and electrical conductivity to pressure of 140 GPa and in the 5–573 K temperature range. Mössbauer studies following annealing at 573 K and 34 GPa reveal three equal-abundant iron species within two magnetic sublattices, I and II: Fe^{3+}(I) sublattice with hyperfine field typical of six-coordinated ferric ions and magnetic ordering temperature $T_M(\mathrm{I}) > 600$ K at 34 GPa and a combined Fe^{3+}(II) and Fe^{2+} species forming a magnetic sublattice II with $T_M(\mathrm{II}) \sim 300$ K at 34 GPa. Starting at 50 GPa the Fe^{3+}(I) moment gradually collapses becoming nonmagnetic at $P > 80$ GPa. This moment collapse is explained in terms of a charge-transfer *d-p* gap closure mechanism. T_M(II) decreases with pressure, and to 120 GPa, the highest pressure reached with Mössbauer spectroscopy, Fe^{3+}(II) remains magnetically ordered. Resistance studies with a nonannealed and highly stoichiometric sample at 300 K reveal a sharp increase in R at the onset of the *h*-Fe_3O_4 phase ($P > 25$ GPa), reaching a 25-fold maximum at ~45 GPa, after which it shows a precipitous decrease in the 45–70 GPa range after which it decreases gradually with pressure reaching 10-fold reduction at 140 GPa. The sharp increase in R is attributed to a gap opening once *h*-Fe_3O_4 is formed. Starting at $P > 50$ GPa, coinciding with *partial* correlation breakdown of the Fe^{3+}(I) sublattice, a sluggish onset of metallization is observed manifested by a positive $d\mathrm{R}/d\mathrm{T}$.

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I. INTRODUCTION

As one of the oldest known magnetic materials and an important constituent of the earth's interior, magnetite (Fe_3O_4) has been the focus of high-pressure (HP) studies[1–3] for many years. At ambient temperature conditions magnetite has an *inversed* spinel structure in which (Fe^{2+}, Fe^{3+}) occupies the octahedral, Fe^{3+} the tetrahedral site, and undergoes a structural phase transition above ~25 GPa. Mao *et al.*[1] assigned a monoclinic symmetry for the high-pressure phase, henceforth designated as *h*-Fe_3O_4, with all Fe atoms positioned in sixfold coordinated sites. Recent and more accurate powder high-pressure x-ray diffraction (XRD) experiments by Fei *et al.*,[4] carried out in samples following temperature annealing, resulted in the assignment of an orthorhombic instead of monoclinic symmetry, proposing a $CaMn_2O_4$-type structure with space group *Pbcm*. On the basis of bond lengths analysis they concluded that the Fe^{3+} ions are sixfold coordinated in highly distorted FeO_6 octahedra and the Fe^{2+} are eightfold coordinated. In similar studies Haavik *et al.*[5] deduced a similar structure, a $CaTi_2O_4$-type (*Bbmm*), composed of less distorted octahedra. This assignment was later confirmed by Dubrovinsky *et al.*[6] and their *ab initio* calculations were on par with the structural refinement assignment. Whereas the structural features of *h*-Fe_3O_4 seem to be rather well established, this is not the case for its electronic and magnetic properties, in particular the individual ferric and ferrous spin states and magnetic ordering. Resistivity studies by Morris and Williams[7] advocated semiconductor-like features to at least 48 GPa. Similar conclusions were obtained by Dubrovinsky *et al.* at 51 GPa who observed semiconductor-like behavior in the 90–420 K range and only after annealing at ~1050 K $d\rho(T)/dT$ changed its sign, from negative to positive.

Ambient temperature ^{57}Fe Mössbauer spectroscopy (MS) studies of *h*-Fe_3O_4 ($T > T_N$) have been carried out by Pasternak *et al.*[8] Two broad quadrupole-split components were observed from which a structural model was suggested: tetrahedral and octahedral sites similar to the ambient pressure inverse spinel structure were assigned as the *building blocks* of the *h*-Fe_3O_4 phase. With lack of low-temperature MS studies in this work in which magnetic properties become available once $T < T_N$, the proposed structural assignment is expected to be quite limited. Undoubtedly MS is currently the best and perhaps only method to investigate the Fe ions' electronic properties at very high pressures. This method allows distinguishing between ferric and ferrous ions, high and low spin states, and their relative abundance, and obtain some indication regarding their respective coordination numbers.[9] And as will be seen, the present detailed MS studies deduced structural information completely different from that of Ref. 8.

In the present paper we report combined Mössbauer spectroscopy and electrical conductivity studies up to 140 GPa and in the 5–573 K temperature range of *h*-Fe_3O_4. The purpose is to provide a comprehensive description of magnetite upon its transformation from a spinel to orthorhombic structure and the relationship between the magnetic, electronic, and structural properties of the high-pressure phase. Special emphasis was given to the *local*, *atomic scale* structural aspects obtained from the ^{57}Fe MS.

II. EXPERIMENT

The Fe_3O_4 sample used for MS was synthesized by direct solid-solid reaction of stoichiometric amounts of spectroscopical pure iron metal and Fe_2O_3 heated at 1100 °C in an evacuated quartz tube. The Fe content was enriched to 25% with ^{57}Fe. This sample quality was checked by powder x-ray diffraction and MS carried out at room temperature (RT) and at 80 K. Pressure and temperature studies of the resistance $[R(P,T)]$ were performed on single crystals of well defined stoichiometry; $Fe_{3(1-\delta)}O_4$ ($\delta=0.0006$), see Ref. 8 and references therein.

Pressure was generated using the TAU-diamond-anvils-cell (DAC) miniature piston cylinder diamond anvil cell[10] with diamond anvils having 200–400-μm-diam culet sizes. Samples were loaded together with ruby chips (for pressure calibration) into cylindrical cavities of 100–200 μm diameter and 25 μm height drilled in Re gaskets which also served as collimators for the ^{57}Co 14.4 keV γ radiation. Argon was used as pressure medium for MS studies and pressure gradient in the samples was $\leqslant 5$ GPa. For resistance measurements $CaSO_4$ was pre-pressed into the cavity to help ensure a quasi-hydrostatic environment.

Mössbauer measurements were carried out using a ^{57}Co (Rh) point source on a top-loaded LHe cryostat in the 5–300 K temperature range and pressures up to ~120 GPa. Measurements were also performed at 573 K using a home-made furnace. All spectra were analyzed using appropriate MS fitting programs from which the hyperfine interaction parameters of the various spectral components and their respective relative abundance were derived. The isomer shift (IS) cited is relative to iron metal at ambient temperature.

Four-probe dc resistance measurements were carried out up to 140 GPa with 5–7-μm-thick Pt foil electrodes placed on the culet of one of the anvils and insulated from the metallic gasket with a mixture of $Al_2O_3/NaCl$ combined mixed with epoxy. A chip of a magnetite single crystal was ground from which microcrystals of dimensions $\sim 70\times 70\times 25$ μm were loaded together with $CaSO_4$ powder at the center of the gasket hole. The pressure gradient in the region between contacts overlapping the sample area during resistance study was typically 5%–10%. The $R(T)$ measurements were carried out in the range 4.2–300 K using a dipstick sample holder immersed in helium vapor inside a helium storage Dewar.

III. RESULTS

A. Mössbauer Spectroscopy

Several sets of MS runs were carried out, each to test the various ranges of pressure and temperature treatments of magnetite.

In the first set of measurements Mössbauer spectra were recorded within an isothermal mode ($T=300$ K) in the 0–120 GPa range (see Fig. 1). The high-pressure, nonmagnetic component h-Fe_3O_4 phase is first detected at ~30 GPa and its relative abundance increases with further compression reaching 100% at $P>60$ GPa.

Following previous XRD experiments (Fei *et al.*,[4] Dubrovinsky *et al.*[6]) which clearly showed that the spinel $\rightarrow h$-Fe_3O_4 phase transition is both *pressure* and *temperature* sensitive, a second set of MS experiments was carried out to examine this feature. The following (P,T) cycle was pursued:

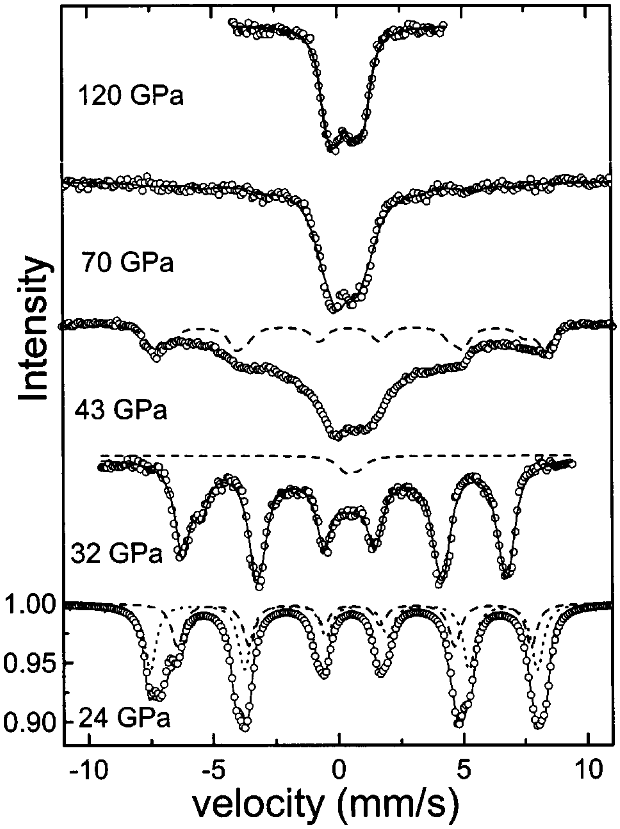

FIG. 1. Mössbauer spectra of magnetite recorded at RT and various pressures: 24 GPa, a spectrum characteristic of the normal spinel phase. The dashed line corresponds to Fe^{3+} at the B site and the dotted line to Fe^{2+} at the A site. 32 GPa, a paramagnetic component of h-Fe_3O_4 is first observed (near $v\sim 0$ mm/s). 43 GPa; the remnants of the spinel phase are shown by the dotted line, At $P>60$ GPa only the paramagnetic h-Fe_3O_4 phase remains.

$$\left[\frac{300\text{ K}}{0.004\text{ GPa}}\right]\xrightarrow[\text{isotherm}]{(a)}\left[\frac{300\text{ K}}{34\text{ GPa}}\right]\xrightarrow[\text{isobaric}]{(b)}\left[\frac{573\text{ K}}{34\text{ GPa}}\right]\xrightarrow[\text{isobaric}]{(c)}\left[\frac{300\text{ K}}{34\text{ GPa}}\right]\xrightarrow[\text{isotherm}]{(d)}\left[\frac{300\text{ K}}{7\text{GPa}}\right]. \qquad (1)$$

The sample was compressed to 34 GPa at RT [step (a)], kept at this pressure and gradually heated to 573 K [step (b)]. It was kept at this temperature for a few days and then gradually cooled to RT [step (c)]. A few days later it was decompressed to 7 GPa [step (d)].

Mössbauer spectra corresponding to this (P,T) cycle are shown in Fig. 2. The 300 K, 34 GPa spectrum [Fig. 2(a)] is the same as in Fig. 1(b), demonstrating the coexistence of the magnetic-ordered *normal* spinel[11] and a new, nonmagnetic high-pressure h-Fe_3O_4 phase (broad central line). The 573 K heat treatment results in a dramatic phase transformation [Fig. 2(b)]. The spinel phase[11] has completely disappeared and replaced by a new phase which spectrum constitutes *three* equal-abundant Fe components. Based on their respective hyperfine interaction parameters they can be assigned to two magnetic sublattices: (1) a magnetically ordered six-coordinated Fe^{3+} species, designated as Fe^{3+}(I), with

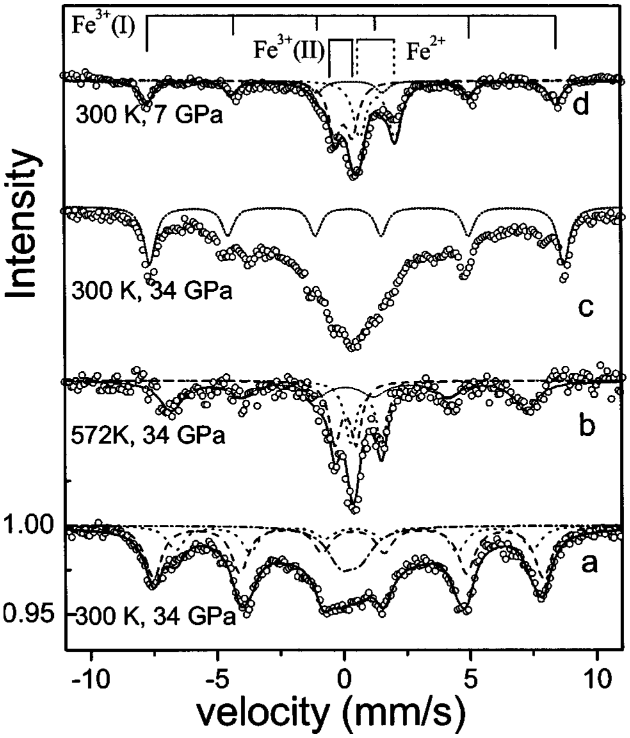

FIG. 2. Mössbauer spectra of magnetite recorded at 34 GPa and at various temperatures: (a) RT Mössbauer spectrum shows coexistence of the spinel and the h-Fe_3O_4 phase in form of a broad unresolved spectrum. The spinel spectrum was fitted assuming two Fe^{3+} in the octahedral and one Fe^{2+} in the tetrahedral sites (normal spinel), respectively (see Ref. 17). (b) At 573 K three Fe sites with equal abundance are observed, composed of two paramagnetic $[Fe^{3+}(II), Fe^{2+}]$ and one magnetically split Fe^{3+}(I) component. (c) The spectrum was recorded at 300 K following the sample annealing. The broad lines at the center correspond to magnetic relaxation signaling the onset of magnetic ordering of the $[Fe^{3+}(II), Fe^{2+}]$ species. (d) Spectrum recorded at 300 K after reducing pressure to 7 GPa [note its resemblance to (b)].

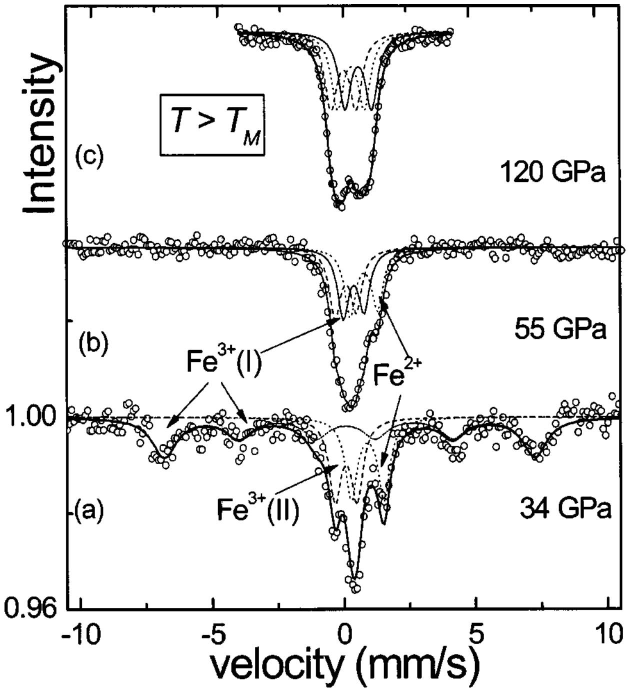

FIG. 3. High-temperature Mössbauer spectra of h-Fe_3O_4 recorded at $T > T_M$(II) at various pressures where "II" corresponds to the $[Fe^{3+}(II), Fe^{2+}]$ magnetic sublattice. At 58 GPa Fe^{3+}(I) loses its magnetic moment due to correlation breakdown (*Mott* transition). Spectra were fitted with three equal-abundant components.

$IS = 0.37$ mm/s, quadrupole splitting $(QS) = 0.42$ mm, hyperfine field $(H_{hf}) = 42$ T and magnetic ordering temperature $T_M(I) > 573$ K, (2) a Fe^{3+} nonmagnetic component, designated as Fe^{3+}(II) with $IS = 0.27$ mm/s and $QS = 0.6$ mm/s, typical of oxy-ferric compounds, and (3), a nonmagnetic Fe^{2+} component with $IS = 1.047$ mm/s and $QS = 1.01$ mm/s typical of oxy-ferrous species.[12] The spectrum shown in Fig. 2(c) is composed of a well defined, static hyperfine magnetic field H_{hf}(=51 T) corresponding to the Fe^{3+}(I) sublattice and a broad component suggestive of the onset of a magnetic ordering of another magnetic sublattice composed of Fe^{3+}(II) and Fe^{2+} moments, with T_M of Fe^{3+}(II) and Fe^{2+}, designated as $T_M(II) \leqslant 300$ K. By decompression to 7 GPa a spectrum similar to that observed at 34 GPa, 573 K is revealed, namely, a Fe^{3+}(I) magnetically ordered component with $H_{hf} = 51$ T[13] and two paramagnetic Fe^{3+}(II) and Fe^{2+} species. The corresponding magnetic and paramagnetic manifolds are shown in the upper part of the figure.

A third set of MS studies was carried out as follows: h-Fe_3O_4 was compressed to 55 GPa and spectra were recorded in the 50–573 K range. At this pressure and beyond no remnants of the spinel phase were ever detected. The high-temperature spectra of 34, 55 and 120 GPa measured at $T > T_M$(II), are shown in Fig. 3. As can be seen [Fig. 3(b)] at 55 GPa the Fe^{3+}(I) component is nonmagnetic with $IS = 0.1$ mm/s and $QS = 0.85$ mm/s. The spectrum could well be fitted with three paramagnetic equal-abundant components. The IS and QS of Fe^{3+}(II) and Fe^{2+} are the same, within the experimental errors, as for 34 GPa. The same fitting procedure was carried out at 120 GPa, 300 K [Fig. 3(c)]. At this pressure the QS of the Fe^{3+}(II) component has slightly increased but not much has changed concerning the MS parameters of the other species.

The pressure dependence of the low-temperature $[T < T_M(II)]$ regime is shown in Fig. 4. At 34 GPa [Fig. 4(a)] all components are fully magnetically split. The hyperfine features of the three components are not well resolved, yet the Fe^{3+}(I) subspectrum with its large H_{hf} (~50 T) is clearly distinguishable. At ~40 GPa a nonmagnetic component appears[14] and its abundance increases with further compression. At 82 GPa the spectrum can be fitted with three equal-abundant components, two fully magnetically split but one, the Fe^{3+}(I), which becomes nonmagnetic [Fig. 4(c)]. The relative abundance of this component which undergoes a sluggish magnetic → nonmagnetic transition reaches a value of 1/3 at ~80 GPa. The pressure variation of T_M(II) with pressure was determined by slowly cooling the sample, at each pressure, and observing the temperature at which the magnetic relaxation (see Fig. 5) first occurs.

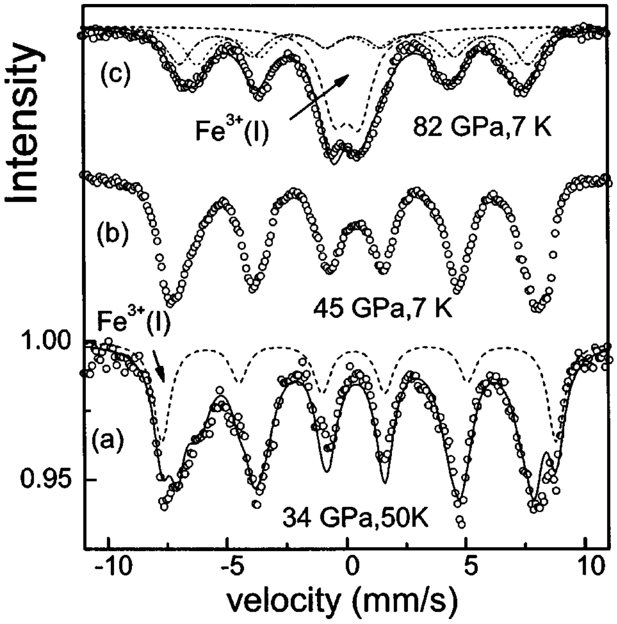

FIG. 4. Low-temperature Mössbauer spectra of h-Fe_3O_4 phase recorded at $T \ll T_M$(II). At 34 GPa and 50 K all components show full magnetic splitting. The dashed-line spectrum corresponds to the Fe^{3+}(I) component. At 45 GPa and 7 K, a nonmagnetic part corresponding to the Fe^{3+}(I) emerges at the center of the spectra reaching 1/3 abundance at 82 GPa and 7 K.

B. Resistance measurements

The pressure dependence of the resistance measured at RT with the highly stoichiometric sample obtained from a single crystal of $Fe_{3(1-\delta)}O_4$ (δ=0.0006)[15] is shown in Fig. 6. As can be seen with pressure increase, once the HP phase appears, $R(P)$ increases rapidly reaching a maximum at ~40 GPa after which it drops precipitously in the 50–60 GPa reaching a few ohms at 140 GPa, the largest pressure used. Unlike the MS samples, the one used for $R(P,T)$ studies was not *heat treated* resulting in a relatively large pressure range of spinel-$h$$Fe_3O_4$ phases coexistence (see Figs. 1 and 6). In the coexistence range the abundance of the spinel phase decreases, whereas that of h-Fe_3O_4 phase increases, reaching 100% at $P \sim 50$ GPa. The temperature dependence of the conductance in the pressure range 26–53 GPa is shown in Fig. 7. Thus, the electrical features in this region suggest that on inception, at ~25 GPa, h-Fe_3O_4 is a semiconductor with relatively strong carriers localization (see Fig. 7).[16] It is mentioning that $R(P)$ studies by Morris and Williams[7] resulted in a considerably lower peak for the incipient HP phase.

With pressure increase above 40 GPa an incipient metallic behavior (positive value of dR/dT) limited to the high-

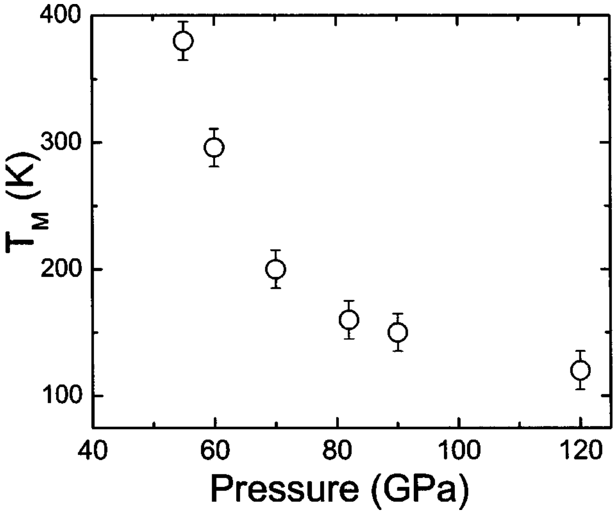

FIG. 5. The pressure dependence of the magnetic ordering temperature T_M(II) of the magnetic sublattice composed of Fe^{2+} and Fe^{3+}(II).

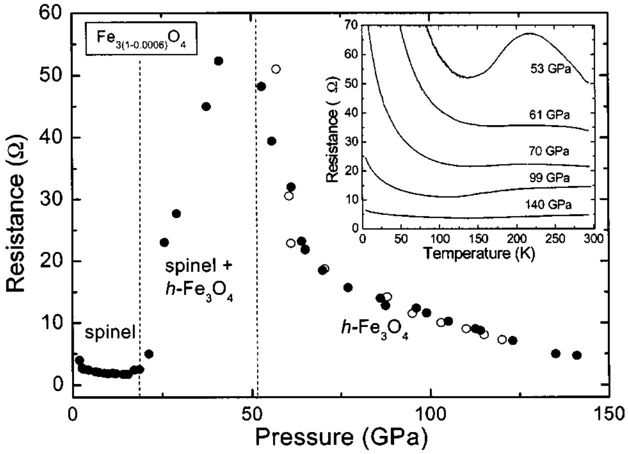

FIG. 6. The pressure dependence of the resistance of h-Fe_3O_4 recorded at 295 K. The open (○) and solid (●) circles are data points obtained during the cycles of compression and decompression, respectively, of the highly stoichiometric $Fe_{3(1-\delta)}O_4$ (δ=0.0006) sample. Note the impressive increase of R between 20 and 40 GPa. The sample did not go through temperature annealing. The vertical dot lines set the boundary of the coexistence between the spinel and h-Fe_3O_4 phases. The inset shows $R(T)$ of the sample with δ=0.0006 for $P \leqslant =53$ GPa. The incipient metallic behavior ($dR/dT > 0$) is observed starting at ~50 GPa.

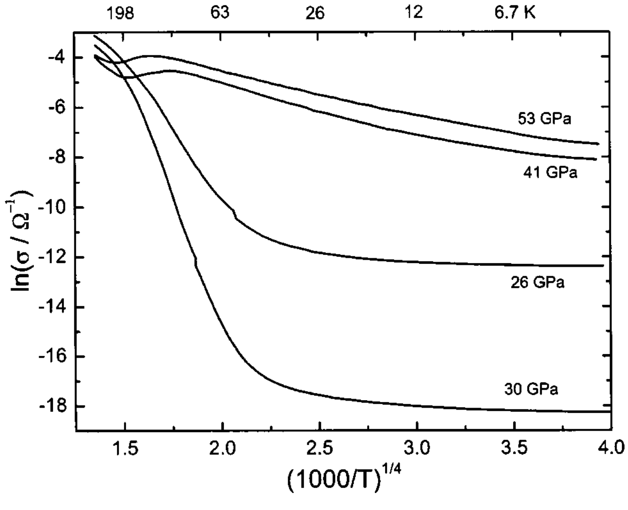

FIG. 7. Temperature dependence of $\ln \sigma$ vs $(1000/T)^{1/4}$ (σ is conductance) at pressures 25–53 GPa.

temperature range is observed (see inset in Fig. 6). Finally at $P>70$ GPa a metallic behavior in the 120–300 K range is clearly established. The smallest resistivity value obtained at 140 GPa was estimated to be $\sim 10^{-4}\ \Omega$ m, typical of a poor metal. Such resistivity values were obtained in ferric oxides and related compounds undergoing a *Mott* transition at elevated pressures.[17,18] Electrical resistance measurements under decompression show no hysteresis behavior down to ~50 GPa, suggesting that the transition above 50 GPa is of a pure electronic nature. Indeed no indications of new structural phases in this pressure range were observed either by Haavick *et al.*[5] or Dubrovinsky *et al.*[6]

IV. DISCUSSION AND CONCLUSIONS

According to recent XRD studies[4–6] h-Fe_3O_4 phase has an orthorhombic-type structure, $CaMn_2O_4$ or $CaTi_2O_4$. Fei *et al.*[4] suggested that in this structure Fe^{2+} ions are in eightfold sites and Fe^{3+} are in sixfold-coordinated sites. However, the present MS studies provide structural information at and surrounding the probing Fe-ions unambiguously show that the two ferric ions in h-Fe_3O_4 are not identical; they do not occupy the same crystallographic sites. The $H_{hf}(51\ \mathrm{T})$ of Fe^{3+}(I) is clearly consistent with a sixfold coordination site which is not the case of Fe^{3+}(II) with $H_{hf}=48.3$ T. Such a lower H_{hf} value for oxy-ferric ions could be associated with a four-coordination environment such as the case of Fe^{3+} in the *A* site within the inverse-spinel phase of magnetite.[11] But this option can be easily eradicated, considering the fact that a tetrahedral site in the high-pressure regime is unlikely. In principle higher than six coordination assignments could result in a smaller H_{hf} but this will be inconsistent with the phase assignment of h-Fe_3O_4 as an orthorhombic $CaMn_2O_4$ or $CaTi_2O_4$. Still, assigning a high-coordination number to Fe^{3+}(II) and to Fe^{2+} will be on par with the lack of high → low spin crossover and the unusual resilience of these iron cations to correlation breakdown (Mott–Hubbard transition) at such high pressures. One must conclude that the present Mössbauer studies are incompatible with the proposed h-Fe_3O_4 structures based on XRD data. Furthermore, the additional, most important information, obtained with low-temperature MS overrules the proposed structural model based on MS studies carried by Pasternak *et al.*[8] at ambient temperature and within the paramagnetic state of h-Fe_3O_4.

The incongruity between the structure modeled from XRD data in which two identical Fe^{3+} sites and one Fe^{2+} are derived, and the two Fe^{3+} and one Fe^{2+} electronic states obtained from the present Mössbauer studies can be attributed to the following:

(1) The h-Fe_3O_4 phase could be intimately related to specific temperature/pressure conditions upon which it was created. The present h-Fe_3O_4 species was created at 34 GPa and annealed at relatively low temperature, whereas those studied by XRD and reported in Refs. 5 and 6 were annealed at $T>820$ K. It is possible that XRD carried out with HP magnetite phase annealed at relatively low temperatures could result in a minor modification of the HP structures that could accommodate two dissimilar ferric sites, compatible with the MS results. Indeed, recent preliminary XRD studies carried with samples heat treated under similar conditions as the present studies[19] confirm this assumption results in a different and distinct crystallographic symmetry not compatible with the previous findings.

(2) The lack of resolution due to the intrinsic broad lines of the HP-XRD powder data may not provide sufficient information for a compatible structure assignment. In view of the present MS results a new structural assignment of the h-Fe_3O_4 could emerge which will take into account both the *macroscopic* (XRD) and *microscopic* (MS) information.

Finally, we discuss the fate of the magnetic state of Fe^{3+}(I) at $P>50$ GPa. The absence of magnetic splitting in Fe^{3+}(I) at $P>50$ GPa at the lowest temperature measured ($T<4.2$ K) suggests that this ferric species has undergone a correlation breakdown,[20] probably a closure of the “empty” Fe-*d* and the “filled” O-*p* gap, the so-called *charge-transfer* of (CT) gap.[21] Such correlation breakdown has been observed in Fe_2O_3.[22] The substantiation of such gap closure due to increase of carrier density resulting from the CT transition is corroborated by the sharp decrease of $R(P)$ and the onset of a gradual metallization process at $P<50$ GPa.

It should be pointed out that even at 140 GPa the resistivity of h-Fe_3O_4 is too high for a normal metal. Thus we can conclude that even at this pressure the transition is not completed and the system is still near a metal-insulator transition edge with only a small number of charge carriers contributing to the transport. It is expected that at higher pressure, once the Fe^{2+} and Fe^{3+}(II) Mott–Hubbard gap closes, we will witness the full metallization of h-Fe_3O_4.

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*Present address: Soreq Nuclear Research Center, 81500, Yavne, Israel.

[1] H. K. Mao, T. Takahashi, W. A. Basset, G. L. Kinsland, and L. Merrill, J. Geophys. Res. **79**, 1165 (1974).
[2] E. Huang and W. A. Basset, J. Geophys. Res. **91**, 46697 (1986).
[3] N. Nakagiri, H. M. Manghnani, M. C. Ming, and S. Kimura, Phys. Chem. Miner. **13**, 238 (1986).
[4] Y. Fei, D. J. Forst, H. K. Mao, C. T. Prewitt, and D. Hausermann, Am. Mineral. **84**, 203 (1999).
[5] C. Haavik, S. Stolen, H. Fjelivag, M. Hanfland, and D. Hausermann, Am. Mineral. **85**, 514 (2000).
[6] 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 (2003).

[7] E. R. Morris and Q. Williams, J. Geophys. Res. **102**, 18139 (1997).

[8] M. P. Pasternak, S. Nasu, K. Wada, and S. Endo, Phys. Rev. B **50**, 6446 (1994).

[9] M. P. Pasternak, W. M. Xu, G. Kh. Rozenberg, R. D. Taylor, G. R. Hearne, and E. Sterer, Phys. Rev. B **65**, 035106 (2001).

[10] G. Yu. Machavariani, M. P. Pasternak, G. R. Hearne, and G. Kh. Rozenberg, Rev. Sci. Instrum. **69**, 1423 (1998).

[11] The Mössbauer spectrum of the high-pressure RT normal spinel phase of Fe_3O_4 is composed of two spectral components with $2/1$ abundance ratio; the more intense, larger splitting component corresponds to six-coordinated Fe^{3+} and the second component to the four-coordinated Fe^{2+} [M. P. Pasternak, W. M. Xu, G. Kh. Rozenberg, R. D. Taylor, and R. Jeanloz, J. Magn. Magn. Mater. **265**, L107 (2003)].

[12] One should consider the pressure decrease of the IS caused by increase in $\rho(s)_0$ due to pressure and the negative sign of the nuclear $\Delta R/R$ parameter.

[13] The increase in H_{hf} at 300 K is due to increase of magnetization with reducing T.

[14] This component shows no magnetic splitting down to 4 K.

[15] G. Kh. Rozenberg, G. R. Hearne, M. P. Pasternak, P. A. Metcalf, and J. M. Honig, Phys. Rev. B **53**, 6482 (1996).

[16] We could not fit the conductance versus temperature dependence at this pressure range with a single universal law which could encompass the whole temperature range. However, in the $60 < T$, $160 <$ K range $\sigma(T)$ expressed as $A\exp(T_o/T)^{1/4}$ represented the experimental results quite well. This expression is commonly associated with the mechanism of *variable-range hopping* of carriers between localized states [N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1990)]. The extracted values of $k_B T_0$ range from 2×10^3 eV at $P = 25.7$ GPa to 2×10^4 eV for $P = 29.9$ GPa (k_B is Bolzmann's constant).

[17] G. Kh. Rozenberg, G. Yu. Machavariani, M. P. Pasternak, A. Milner, G. R. Hearne, R. D. Taylor, and P. Adler, Phys. Status Solidi B **211**, 351 (1999).

[18] W. M. Xu, O. Naaman, G. Kh. Rozenberg, M. P. Pasternak, and R. D. Taylor, Phys. Rev. B **64**, 094411 (2001); O. Naaman, G. Kh. Rozenberg, M. P. Pasternak, and K. Syassen, *Science and Technology of High Pressure*, *Proceeding AIRAPT-17* (Universities Press, Delhi, India), 2000, Vol. 1, 581.

[19] L. S. Dubrovinsky (private communication).

[20] It is worth noticing that a high to low spin state transition of Fe^{3+} $(S+1/2)$ will result in a decrease but not vanishing of the magnetic moment. See W. M. Xu, O. Naaman, G. Kh. Rozenberg, M. P. Pasternak, and R. D. Taylor, Phys. Rev. B **64**, 094411 (2001).

[21] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[22] M. P. Pasternak, G. Kh. Rozenberg, G. Yu. Machavariani, O. Naaman, R. D. Taylor, and R. Jeanloz, Phys. Rev. Lett. **82**, 4663 (1999).