High Pressure Collapse of Magnetism in $Fe_{0.94}O$: Mössbauer Spectroscopy Beyond 100 GPa

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First studies of Mössbauer spectroscopy to pressures above 100 GPa are reported. The magnetic state of $Fe_{0.94}O$ was investigated to 120 GPa at $T \leq 300$ K. At 300 K a diamagnetic *low-spin* (LS) state of Fe^{2+} is detected at 90 GPa; its abundance increases with P. The gap between the $^5T_{2g}$ *high-spin* ground state and the $^1A_{1g}$ LS *excited state* decreases with increasing P and at 120 GPa the LS species, first observed at 70 K, is fully converted at ~450 K. The magnetic collapse of $Fe_{1-x}O$ is an isochoric, second-order transition resulting from a gradual increase in the crystal-field with increasing pressure. [S0031-9007(97)04690-5]

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Details of the state of matter at very high static densities is of fundamental significance to quantum mechanics, to the nature of magnetic ordering, and to band structure of narrow d-band materials. At the substantial high pressures that are now available with diamond anvil cells (DAC) and appropriate spectroscopical methods, new insights on magnetic properties are emerging. Magnetic properties are studied preferably in simple binary transition-metal (TM) compounds, the so-called *Mott insulators* [1] which, by virtue of the strong on-site electron-electron correlation within the d bands have localized moments, become antiferromagnetically ordered at temperatures below T_N, and are insulators with large optical gaps that persist at temperatures far above T_N. In the isostructural regime of density increase, the magnetic state will, in principle, eventually collapse as a result of one of the following mechanisms:

(i) Insulator-metal transition resulting from the closure of the Mott-Hubbard d-d gap (U) or of the Charge-Transfer p-d gap (Δ). Experimental verification of such a phenomenon is the concurrent metallization *and* collapse of magnetic moments within a narrow pressure range. The pressure-induced so-called *Mott transition* has been experimentally demonstrated in the case of NiI_2 by Pasternak *et al.* [2] and later on in CoI_2 (Ref. [3]) and FeI_2 (Ref. [4]) using the combined methods of Mössbauer spectroscopy (MS), x-ray diffraction (XRD), and electrical conductivity in DAC's.

(ii) High-spin (HS) to low-spin (LS) transition resulting from the breakdown of Hund's rule at very high density. In HS TM compounds a transition to LS will occur when the *crystal field* splitting exceeds the *exchange energy*, and the material will become diamagnetic resulting in the collapse of magnetic state, for the particular case of an even valence number n in a d^n configuration. In this Letter we report experimental proof for such an isostructural/isochoric HS $\rightarrow$ LS transition [5] in wüstite ($Fe_{1-x}O$). This has been observed with ^{57}Fe MS used as a probe of magnetism at pressures to 120 GPa. To our knowledge, this is the first report on Mössbauer spectroscopy beyond 100 GPa.

Wüstite is nonstoichiometric divalent (d^6) iron oxide invariably with a cation deficiency (x). Depending on x, T_N at ambient pressure may vary between 190–210 K in the $0.90 < x < 0.96$ range [6]. It crystallizes in a NaCl structure at ambient pressure and at ambient temperature distorts into rhombohedral cell above ~18 GPa. In both structures Fe is at the center of an oxygen octahedron.

The sample used in this experiment was prepared by sintering a pressed disk of Fe_2O_3 powder enriched to 20% ^{57}Fe, heating for one day at 900 °C in one atmosphere of CO/CO_2 gas mixture, and then quenching into ice water. The composition was established using both XRD and oxygen fugacity methods [7], and x was found to be 0.941(5). A modified piston/cylinder Mao-Bell type DAC was used with anvils having culet flats of 150 μm. A 75-μm hole was drilled in a Re gasket into which the sample was loaded in a 25 μm high cavity along with ruby chips for pressure determination. XRD using synchrotron radiation was also used for independent determination of pressure. We estimate the thickness of the absorber as 5 mg/cm^2 which in terms of Fe natural abundance is ~50 mg/cm^2. No pressurizing medium was used. A commercial 10 mCi $^{57}Co(Rh)$ point source (0.5×0.5 mm) was used. Typical data collection times were 24–48 hours. Most measurements were carried out using a top-loading cryostat with experiments conducted in the 4–300 K range. For details regarding HP-MS using the DAC, see Ref. [8].

Mössbauer spectroscopy studies of $Fe_{1-x}O$ at ambient pressure were carried out by several groups, and they are summarized in a recent review article by Long and Grandjean [9]. In both the paramagnetic and the ordered magnetic state the Mössbauer spectra are rather complex, reflecting distributions of magnetic and quadrupole interactions originating from a distribution of oxygen

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coordination numbers and other structural defects. However, ambient temperature MS studies by Nasu [10] to 66 GPa resulted in relatively simple magnetically split spectra at $P > 15$ GPa, composed of a single-site magnetic component corresponding to a hyperfine field (H_{hy}) of 47 T at 66 GPa and a small quadrupole shift. The Néel temperature at 13(2) GPa was found to be 300 K. Our measurements were carried out in the pressure range of 60–120 GPa. Typical spectra at 300 K obtained at 60, 90, 100, and 120 GPa are shown in Fig. 1. The solid line through the experimental points was obtained by a least-squares-fitting procedure. As can be seen from the relative intensities of the 60 GPa spectrum (see Fig. 1), the magnetic Mössbauer spectra show definite texture effects, resulting from orientation of the (111) planes axes preferentially lying parallel to the anvils' flats [11]. The Fe^{2+} moments are in the (111) direction perpendicular to the γ-ray direction [12]. Within experimental error the H_{hy} measured at 60 GPa agrees with that measured by Nasu [10] at 54 and 66 GPa.

The pressure dependencies of H_{hy} and isomer shift (IS) are shown in Fig. 2. In the 60–120 GPa range H_{hy} increases slightly with pressure; a similar trend was also observed in $^{57}FeI_2$ [Ref. 13]. The IS is proportional to $(\Delta R/R)\rho_s(0)$ where $\Delta R/R$ is the relative change in the excited and ground states nuclear radii, which in the case of ^{57}Fe is negative; $\rho_s(0)$ is the s–electron density at the nucleus. The negative slope in IS(P) reflects the increase in density with pressure.

With increasing pressure, at ambient temperature, a new nonmagnetic (nm) component evolves at ~90 GPa, and its abundance increases with pressure as shown in the inset of Fig. 1. At 120 GPa this spectral component is characterized by a quadrupole splitting (QS) and an IS of 0.85(7) mm/s and 0.75(10) mm/s, respectively. Those values are higher than those obtained for the magnetic component [QS = 0.2(2) mm/s and IS = 0.5(1) mm/s]. The nm abundance is also temperature dependent. A typical case is shown in the inset of Fig. 3 where the presence of the nm component at 120 GPa is first detected at $T > 70$ K, and its abundance increases with temperature. At this pressure full conversion is extrapolated to be ~450 K. These and all other measurements showed both temperature and pressure reversibility; no significant hysteresis was observed. We assign this nm spectral component to the $^1A_{1g}$ diamagnetic low-spin state of Fe^{2+}.

As mentioned earlier, isostructural magnetic collapse at high density has been observed in several TM-I_2 compounds and was shown to be of a Mott or CT transition type, the transformation being rather *sharp* at a given pressure [14]. Furthermore, all the observed pressure-induced Mott transitions caused by the decrease in $U/2w$ or $\Delta/2w$, where $2w$ stands for the bandwidth, were temperature independent. In the present studies the magnetic and the nm components coexist in a pressure range of 90–120 GPa at 300 K with complete conversion to the nm one at 140 GPa (see Fig. 3).

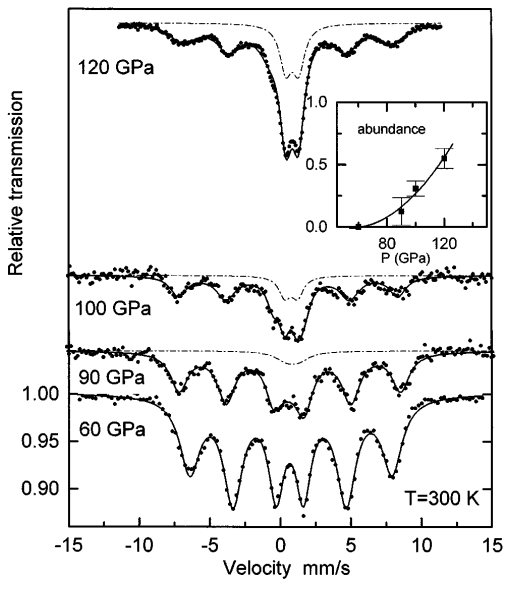

FIG. 1. Typical Mössbauer spectra of $Fe_{0.94}O$ measured at $P \geq 60$ GPa at 300 K. The solid line is a least-squares fit to the experimental points assuming magnetic- and quadrupole-split components with varying intensities. The inset depicts the variation of the relative abundance of the nonmagnetic component (the LS component, see text) with pressure. Note that by extrapolation the HS component will be fully converted to the LS at ~140 GPa.

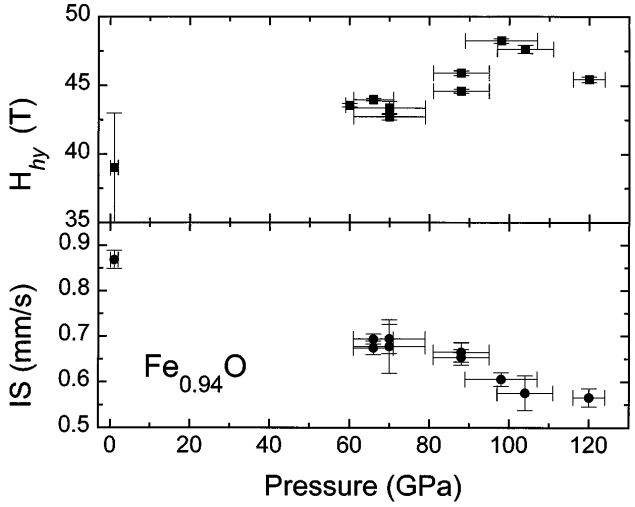

FIG. 2. The pressure dependence of H_{hy} and IS. The value of $H_{\mathrm{hy}}(0)$ is an average of three spectral sites [9] at $T \ll T_N$. The increase in H_{hy} with pressure can be accounted for by the increase in the s-electron density at the nucleus. The negative increase in IS is due to increases in $\rho_S(0)$ (see text) and should be related to the increase in density with pressure as measured by the EOS. Using the experimental values of $V(P)$ from Ref. [15] we calculate the relative change in density ρ in the 60–120 GPa range to be $d \ln \rho/d\mathrm{P} = 2.3 \times 10^{-3}$ GPa^{-1}, whereas the relative change of the IS for the same pressure range is $d \ln \mathrm{IS}/d\mathrm{P} = 3.3 \times 10^{-3}$ GPa^{-1}. IS values are with respect to a ^{57}Co(Rh) source.

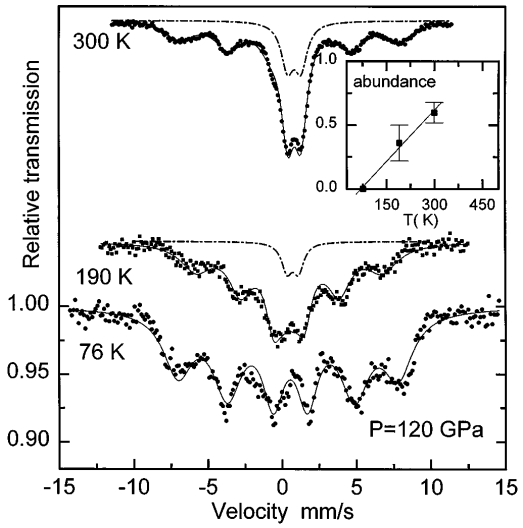

FIG. 3. Mössbauer spectra of $Fe_{0.94}O$ at 120 GPa measured as function of temperature. The inset shows the increase of the relative abundance of the LS, suggesting the completion of HS → LS conversion at ~450 K.

Static high pressure studies of XRD at 300 K carried out by Yagi *et al.* [15] to 120 GPa and by Mao [16] to 220 GPa showed no indication of a first-order phase transition involving change in structure or discontinuity in volume. This observation is consistent with our findings in which no hysteresis was detected upon decompression [17].

The prospect of a magnetic collapse in wüstite at high enough pressures has been theoretically treated by Isaak *et al.* [18], Cohen *et al.* [19], and Sherman [20]. Whereas Isaak *et al.* using *local density approximation* methods proposed a first-order magnetic collapse close to 100 GPa, recent studies by Cohen *et al.* using the *generalized gradient approximation* predicted a magnetic collapse at 200 GPa involving a first-order transition with a significant fractional volume change. As pointed out by Cohen *et al.*, the transition would not be due to changes in the crystal field ($10Dq$), which they assumed to be quite small, but rather due to w band widening with pressure increase [21]. On the other hand, Sherman considered the pressure dependence of $10Dq$ with its strong radial dependence ($\sim 1/R^5$) and suggested that at some pressure the crystal field energy will overcome the spin-spin exchange energy $U_{\text{ex-}}$ leading to a LS state.

Our experimental results at ambient temperature together with existing x-ray diffraction show unequivocally that the HS → LS transition in $Fe_{1-x}O$ is not related to a crystallographic phase transition [22]; it is not an isostructural first-order phase transition involving discontinuous volume change, but rather is an isochoric phenomenon where the $^5T_{2g}$ HS ground state and the $^1A_{1g}$ LS excited state separated by $\Delta U(P)$ coexist over a rather large range of pressure. With increasing pressure ΔU decreases, reaching values comparable to k_BT (a few tens of meV) at 120 GPa. Thus, the magnetic collapse of $Fe_{1-x}O$ is continuous; it can be inferred to be a second-order transition as a result of a pressure-induced monotonic increase in the crystal field with decreasing interatomic distances.

Since $\Delta U(P)$ increases with volume increase will the spin-crossover taking place at $P < 100$ GPa and elevated temperature also be an isochoric process? In recent XRD studies Fei and Mao [23] discovered a crystallographic transition into a denser phase, the NiAs ($B8$) structure, occurring upon uniformly heating the pressurized sample at 74 and 90 GPa. In the former case, the $B8$ diffraction lines were first detected at 900 K, becoming more intense with increasing T, and coexisting with the rhombohedral ($B1$) phase at temperatures beyond 1100 K. At 96 GPa the $B8$ phase was first detected at 600 K and fully converted at 800 K. At 70 and 90 GPa the molar volume decrease of $B8$ with respect to $B1$ phase is ~4% and ~3%, respectively [24] (see Fig. 2 in Ref. [23]). One may consider the sluggishness of the $B1 \rightarrow B8$ transition determined by XRD as similar to the wide pressure-temperature range over which the HS → LS observed by the magnetic hyperfine probe. We suggest that this structural transformation at 70–90 GPa range as driven by the spin crossover which at this pressure could not be accomodated within the $B1$ structure. However, with the decreasing Fe-O distances with increasing pressure, the LS and HS ionic radii of Fe^{2+} become equal (see Fig. 2, Ref. [23]) eventually resulting in the full collapse of Hund's rule in FeO beyond 120 GPa.

A proposed (P, T) magnetic phase diagram for $Fe_{0.94}O$ is depicted in Fig. 4. At low pressures, a linear $T_N(P)$ dependence is depicted to ~70 GPa separating the high-T paramagnetic with the low-T antiferromagnetic states. The slope determined from values of $T_N = 200$ K at

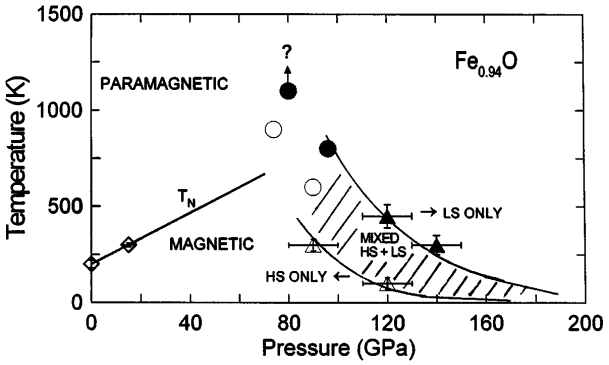

FIG. 4. Proposed P, T phase diagram for $Fe_{1-x}O$. The T_N line was calculated assuming $dT_N/dP = 7.6$ K/GPa (see text). The //// region encompasses the coexisting HS-LS states (see text). The ○ and ● symbols are data from XRD (Ref. [20]) corresponding to the (P, T) coordinates where the $B8$ phase was first observed and fully converted, respectively (see text). The "?" mark corresponds to a lower limit for the full $B8$ transformation. The full conversion according to Ref. [20] takes place at a higher temperature.

ambient pressure and $T_N = 300$ K at 13 GPa is $dT_N/dP = 7.6$ K/GPa, a slope which is quite similar to that of FeI_2 (Ref. [4]). The △ and ▲ symbols were deduced from the insets of Figs. 1 and 2 to determine the limits of the pure HS and LS regimes, respectively. In this diagram we also included the (P, T) points deduced from Ref. [23] where the ○ and ● symbols correspond to the first observation of the $B8$ phase (assumed to be LS) and the full conversion of $B1 \rightarrow B8$, respectively [25]. The ● with the "?" mark stands for the lowest T value of the full $B1 \rightarrow B8$ transformation at this pressure. As pointed out by the authors [23], the $B1$ lines were still present when the diamond anvils shattered.

In conclusion, this study is a manifestation of Mössbauer spectroscopy studies beyond 100 GPa using DAC's. We find that the collapse of the magnetic state in $Fe_{1-x}O$ is due to a constant-volume (probably second-order) HS → LS transition, where both species coexist over the pressure range of 90–140 GPa at $T \leq 300$ K. The energy gap separating the diamagnetic $^1A_{1g}$ and magnetic $^5T_{2g}$ states decreases with pressure, reaching values comparable to ambient temperature k_BT at ~100 GPa.

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[11] Lacking a hydrostatic medium, there is a preferential orientation of the elongated body diagonal perpendicular to directions of both the uniaxial stress and to the incoming photons. This effect has also been observed by Yagi *et al.* [15] in their XRD experiments. For a *thin* absorber a 90° orientation will result in a 3 : 4 : 1 : 1 : 4 : 3 intensity ratio. In the present case, because of a large effective thickness ($t_a > 20$), the intensity of the inner lines is preferentially enhanced with respect to the outer ones.
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[21] $H_{hy}(P)$ is a measure of the magnetic moment change with pressure. Since the moment is directly related the d-bandwidth w, namely, increase in w reduces the moment, we conclude that to the highest pressure there is not increase in w.
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[24] Densities of the B1 phase at several pressures were calculated by Mao and Fei [23] based on XRD data of Yagi *et al.* [15].
[25] We propose that the actual onset of the $B8$ phase at 70 and 90 GPa might be at lower temperatures considering the inherent experimental limitations of XRD in DACs. This will be in a better agreement with our extrapolated lower curves.