Pressure Induced Self-Oxidation of $Fe(OH)_2$

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Mössbauer spectroscopy, x-ray diffraction, and electrical resistance [$R(P,T)$] studies in $Fe(OH)_2$ to 40 GPa revealed an unforeseen process by which a gradual Fe^{2+} oxidation takes place, starting at ~8 GPa reaching 70% Fe^{3+} abundance at 40 GPa. The nonreversible process $Fe^{2+} \rightarrow Fe^{3+} + e^-$ occurs with no structural transition. The "ejected" electrons form a deep band within the high-pressure electronic manifold becoming weakly localized at $P > 50$ GPa. This process is attributed to an effective ionization potential created by the pressure induced orientationally deformed (OH) dipoles and the unusual small binding energy of the valence electron in $Fe^{2+}(OH)_2$.

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With the advent and development of diamond anvil pressure cells (DAC) during the past two decades [1], we have witnessed many new discoveries in the state of matter at ever higher densities. An insulator-metal transition of wide-gap insulators, breakdown of the *d-d* Mott-Hubbard correlation in transition metal compounds, new and unusual structural phase transitions, pressure induced amorphization, order-disorder transformations, etc. are but a few examples of the important forefront topics. One of the most interesting subjects has been the *in situ* formation of new materials resulting from chemical reactions taking place in the cell chamber such as polymerization [2] or dissociation [3,4] of molecular crystals and chemical reaction of the type $A + B \xrightarrow{P} C$ [5], where heating was often needed as a catalyst [6]. In this Letter we report a rather unusual phenomenon, a static pressure induced oxidation of $Fe^{2+}(OH)_2$ ($Fe^{2+} \xrightarrow{P} Fe^{3+} + e^-$) taking place at ambient temperature. As will be shown this unique process is irreversible upon decompression, and it seems to be intimately related to the (O-H) orientation disorder.

Structural properties of $M(OH)_2$ under static pressure have been the subject of numerous studies during the last few years. The main motivation was an early experimental discovery by Kruger *et al.* [7] of a pressure induced broadening of the O-H vibrational A_{2u} modes in both $Mg(OH)_2$ and $Ca(OH)_2$, observed by way of infrared spectroscopy. The broadening phenomenon was later confirmed by Duffy *et al.* [8] from high-pressure Raman studies in $Mg(OH)_2$. A similar phenomena was later observed by Nguyen *et al.* [9] in $Co(OH)_2$ using both Raman and IR spectroscopy. From x-ray diffraction (XRD) studies in the $Co(OH)_2$ case, the authors attributed the broadening to a local "hydrogen sublattice amorphization, "with no effect on the long-range ordering of the Co-O lattice. Several studies have shown that the O-H vibrational broadening first appears at ~11–14 GPa, increases monotonically with pressure, and is reversible upon decompression.

The CdI_2 related hydroxides (space group $P\bar{3}m1$) have a rather unique structure with hydrogen atoms isolated between layers of metal ions in octahedral coordination with oxygen (see Fig. 1, 0.01 GPa). By applying pressure one may follow a series of controlled O-H—H and O-H—O stages of repulsion and attraction, respectively. And indeed, a recent systematic high-pressure (HP) study by Parise *et al.* [10] in $Co(OD)_2$ using neutron powder diffraction has shown that the hydrogen atoms become continuously disordered with increasing pressure as a result of structural frustration due to interlayer H-H repulsion. In the CdI_2-related structure, at ambient pressure, M is located at (0,0,0) and O and H at (1/3, 2/3, z) with $z \sim 0.2$ for O and ~0.4 for H (Ref. [10]). At ambient pressure the O-H axis is aligned along the threefold symmetry c axis of the crystal, but because of the pressure induced repulsion, the $(O\text{-}H)^-$ dipole axis "splays" with respect to the c-axis direction with the bending angle increasing with pressure (see Fig. 1). According to Ref. [10], the H position is continuously laterally displaced from its original threefold axis, reaching

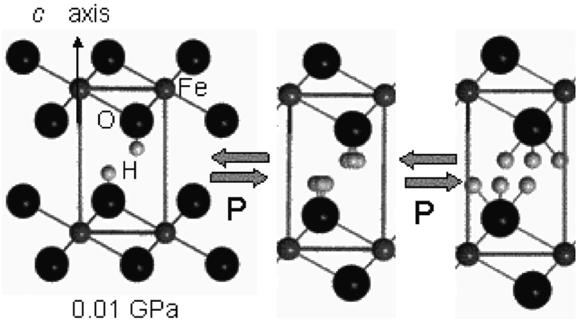

FIG. 1. A schematic showing the pressure induced lateral displacement of the H atom caused by interlayer O-H—H-O repulsion. The structural changes with pressure caused by the H displacement are continuous (Ref. [10]). It is assumed that this pressure induced phenomenon is common to all $M(OH)_2$ species.

$D = 0.4$ Å at 16 GPa. The pressure induced H displacement or (O-H)$^{-1}$ dipole bending is responsible for the vibrational broadening as observed by optical spectroscopy in all $M(\mathrm{OH})_2$ HP studies. As will be shown this dipole orientation mechanism is also responsible for the continuous self-oxidation, or ionization, of the ferrous ion in $\mathrm{Fe(OH)_2}$ (Ref. [11]).

We carried out HP studies in $\mathrm{Fe(OH)_2}$ using x-ray diffraction, ^{57}Fe Mössbauer spectroscopy (MS), and electrical conductivity with diamond anvil cells to pressures up to ~80 GPa. $\mathrm{Fe(OH)_2}$, a material extremely sensitive to oxygen, was synthesized by dissolving $\mathrm{FeCl_2}$ and KOH in deoxidized water at room temperature [12]. The precipitated white hydroxide was dried in a glove box in a continuous flow of 99.999% pure Ar and then immediately loaded together with ruby chips, used for pressure calibration, into a 200-μm diam. by 25-μm height cavity drilled in the preformed Re gasket of a DAC and immediately sealed. All elements in contact with the sample were thoroughly cleaned and dried prior to loading to eliminate any residual $\mathrm{O_2}$. The quality of the sample was tested in the DAC by MS, a sensitive method to distinguish between $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$. Argon was used as a pressurizing medium. X-ray diffraction studies were performed up to 30 GPa at room temperature in the angle-dispersive mode at the ID30 beam line of the European Synchrotron Research Facility. Mössbauer studies at pressure were carried out using a top-loading He cryostat (5–100 K) with a ^{57}Co(Rh) point source. Resistance studies to 90 GPa and various temperatures were done with the four-point method using Pt electrodes.

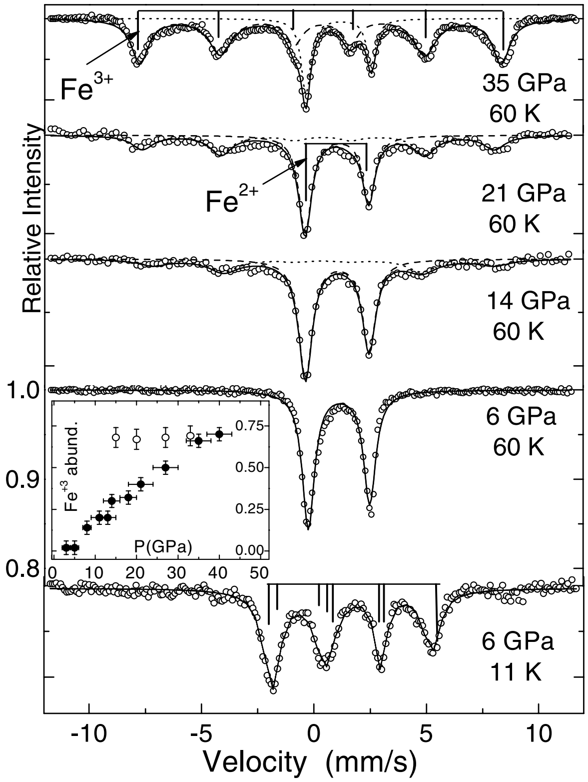

FIG. 2. Mössbauer spectra of $^{57}\mathrm{Fe(OH)_2}$. The spectrum at 6 GPa and 11 K shows the magnetically ordered state hyperfine splitting. The solid line is the theoretical spectrum calculated from the full spin Hamiltonian. The paramagnetic state spectrum at 6 GPa and 60 K is characterized by QS = 2.7 mm/s and IS = 1.0 mm, typical of ferrous compounds. At $P > 6$ GPa the Mössbauer spectra reveal the onset of a ferric species. The pressure dependence of the $\mathrm{Fe^{3+}}$ abundance is shown in the inset.

Typical Mössbauer spectra measured at 6 GPa, 11 K ($T < T_N$) and at 60 K ($> T_N$) at various pressures are shown in Fig. 2. Below ~8 GPa the spectra are composed of a single $\mathrm{Fe^{2+}}$ component characterized by quadrupole splitting $\mathrm{QS}(e^2 q_{zz} Q) = 2.95(2)$ mm/s and isomer shift IS = 1.00(1) mm/s, with values barely changing to 40 GPa. The asymmetry in intensity of the QS doublet which increases with P is attributed to a sample texture effect. The hyperfine field H_{hf} obtained from the least-squares fitting at 11 K is $H_{\mathrm{hf}} = 19.5(2)$ T oriented at 90° (270°) relative to the principal axis of the electric-field gradient, eq_{zz}. In the 0–40 GPa range T_N increases monotonically, reaching 63 K at 40 GPa. Spectra taken at $P > 8$ GPa show the presence of a new, additional component whose relative abundance increases with pressure. The hyperfine parameters of this new component are IS = 0.3(1) mm, QS = 0.3(1) mm/s, and $H_{\mathrm{hf}} = 51(1)$ T values characteristic of $\mathrm{Fe^{3+}}$ in an oxygen sixfold coordination configuration. The relative abundance of the $\mathrm{Fe^{3+}}$ component was evaluated using the appropriate areas A of the respective absorption spectra components:

$$\mathrm{Fe^{3+}}\ \text{abundance} = \frac{A(\mathrm{Fe^{3+}})}{A(\mathrm{Fe^{3+}}) + A(\mathrm{Fe^{2+}})} = \frac{f_{\mathrm{Fe^{3+}}} n_{\mathrm{Fe^{3+}}}}{f_{\mathrm{Fe^{3+}}} n_{\mathrm{Fe^{3+}}} + f_{\mathrm{Fe^{2+}}} n_{\mathrm{Fe^{2+}}}},$$

where n stands for the concentration of ^{57}Fe nuclei and f stands for the nuclear recoil-free fraction of the respective $\mathrm{Fe^{3+}}$ and $\mathrm{Fe^{2+}}$. Considering the fact that both iron cations have the same oxygen coordination numbers we may assume that for a first approximation $f_{\mathrm{Fe^{3+}}} \approx f_{\mathrm{Fe^{2+}}}$ [13]. The inset in Fig. 2 shows the pressure dependence of the $\mathrm{Fe^{3+}}$ abundance to 40 GPa. Starting at ~8 GPa, the first pressure point where the ferric component is observed, the $\mathrm{Fe^{3+}}$ abundance increases monotonically with pressure reaching ~0.7 at 40 GPa. With decompression (inset Fig. 2, open circles), down to ambient pressure that $\mathrm{Fe^{3+}}$ abundance remains constant, i.e., the $\mathrm{Fe^{2+}} \xrightarrow{P} \mathrm{Fe^{3+}}$ process is irreversible despite the reversibility of the O-H bending and the vibrational broadening (Refs. [1–3]).

We now proceed to examine the nature of the self-oxidation [14] taking place in the pressurized $\mathrm{Fe(OH)_2}$ sample, pondering whether the gradual decrease of the interatomic distances between the layers is a mechanism that could induce such a self-oxidation. As far as we know no such plausible physical mechanism has ever been reported. In fact, recent Mössbauer studies in the isostructural layered compounds FeI_2 (Ref. [15]) and $FeCl_2$ (Ref. [16]), taken to a pressure range similar to that studied here, showed no indication of Fe^{2+} oxidation even at the highest pressure studied. We assert that the onset of the orientation disorder of the O-H dipoles in concert with the relatively weak binding energy of the last valence electron in $Fe^{2+}(OH)_2$ is responsible for the oxidation. The continuous increase of H disorder resulting in the formation of splayed dipoles and possibly multipoles of O-H units would no doubt produce a finite electric field at the Fe site. And such an induced potential must be sufficient to remove this weakly bonded electron creating either a new ferric hydroxide $Fe^{3+}O(OH)$,

$$Fe^{2+}(OH)_2 \xrightarrow{P} Fe^{3+}OOH + \tfrac{1}{2}H_2, \qquad (1)$$

or a new electronic band within the high-pressure band structure,

$$Fe^{2+}(OH)_2 \xrightarrow{P} Fe^{3+}(OH)_2 + e^-. \qquad (2)$$

To show whether a new ferric compound is created [expression (1)], coexisting with the ferrous hydroxide (and a free H_2), we carried out a series of HP-XRD to 30 GPa. Typical diffraction patterns recorded at several pressures at RT are shown in Fig. 3. The vertical arrows indicate the positions of the strongest peaks of two of the most common derivatives of FeO(OH), α-FeO(OH) (Goethite) and γ-FeO(OH) (Lepidocrocite) [17,18]. As can be seen the indices of $Fe(OH)_2$ persist to 30 GPa. Some weak new peaks that we attribute to a distortion of the original structure appear even at low pressures (5 GPa).

Thus, process (2) seems more likely, namely, within the original ferrous-hydroxide structure Fe^{2+} transforms gradually into Fe^{3+} (probably within a Fe-O length reduction) resulting in a new electronic valence band that is progressively filled with electrons as the pressure increases. What is the nature of this ejected electronic band? Is it at or close to the Fermi level resulting in metallization at ~8 GPa or is it a deep-lying, "localized," band? To address this point we looked for supporting evidence in the transport properties through a series of HP electrical conductivity studies. The resistance versus pressure plot is shown in Fig. 4. The first $R(P, 300\ \mathrm{K})$ point measured at 5.2 GPa has a resistance value close to a megohm. With increasing pressure R decreases gradually by 2 orders of magnitude in the 5–50 GPa range. Temperature dependence of the conductance (see inset) in this pressure range is that typical of an insulator. This behavior is indicative of the fact that the ejected electrons are trapped in a low-lying valence band and play no role in the conductivity mechanism in the 0–40 GPa range. However, in the 50–60 GPa range we witness a sharp discontinuous decrease in R, by about 2.5 orders of magnitude, reaching R values of a few ohms at $P > 70$ GPa. This and the temperature dependence of the conductance (see inset) for $P > 50$ GPa is a strong indication of a first-order electronic transition in which the new electronic phase is characteristic of a weak localization brought about by further disordering associated with increasing pressure [19].

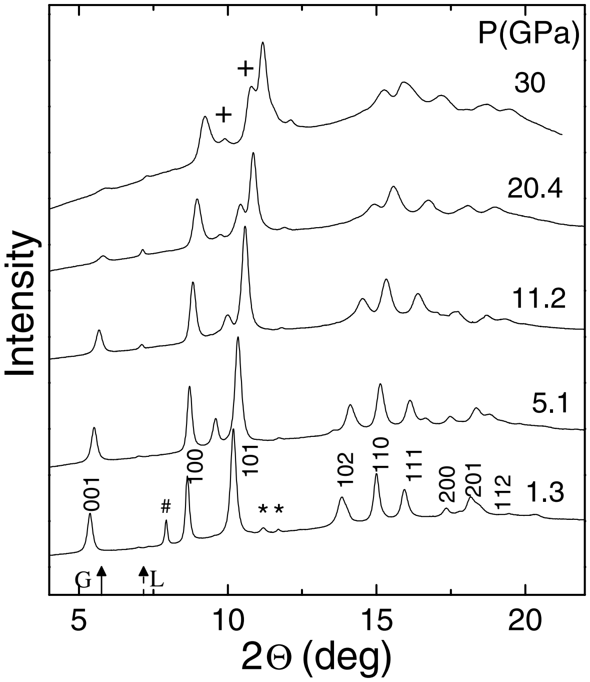

FIG. 3. X-ray powder diffraction patterns of $Fe(OH)_2$ at 298 K and various pressures. Indices correspond to the diffraction peaks of the original CdI_2 type structure. Weak peaks corresponding to ruby and Ar (111) are marked with (*) and (#), respectively. Peaks marked with (+) which appear at ~5 GPa can be accounted for as a consequence of distortion of the original structure. Positions of the most intense peak of α-FeO(OH) (G) and γ-FeO(OH) (L) are marked with arrows.

In conclusion, the present series of experimental data, using XRD, MS, and R measurements at various pressures and temperatures determines unequivocally the gradual pressure induced oxidation of Fe^{2+} to Fe^{3+}. This phenomenon of "self-oxidation" in $Fe(OH)_2$ is attributed to the gradual lateral displacement of the H atom, due to Coulomb repulsion, that culminates in the formation of splayed (O-H) dipoles. The breakdown of the (O-H) axial symmetry creates an effective dipole potential at the iron site in addition to the relatively weak binding energy of the last valence electron that contributes to the ionization of the Fe^{2+}. This self-oxidation does not lead to a new ferric hydroxide species, e.g., $Fe^{3+}O(OH)$, but rather to the creation of a new electron band within the HP band structure of $Fe(OH)_2$. Up to ~50 GPa this band is positioned rather deep below the Fermi level but at $P > 50$ GPa a first-order electronic phase transition takes place in which the electrons become weakly delocalized and the resistivity decreases discontinuously by ~2.5

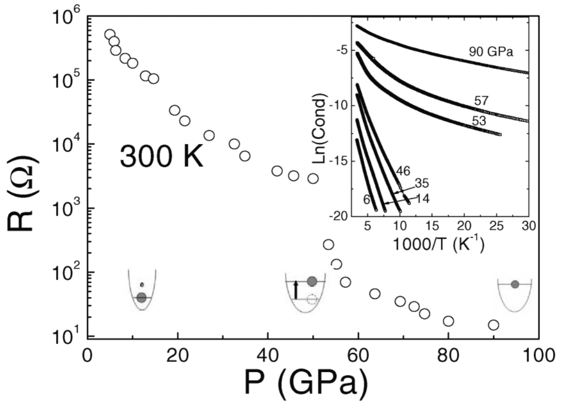

FIG. 4. Pressure dependence of the resistance. Up to 50 GPa the HP phase is an insulator whose gap decreases gradually with pressure. At $P > 50$ GPa a discontinuous decrease in $R(P)$ is observed leading to a narrow-gap semiconductor behavior (see inset). This electronic phase transition is attributed to a broadening of the "ejected" electrons (from the oxidation process: $Fe^{2+} \rightarrow Fe^{3+} + e^-$) sufficient to overlap with the conduction band.

orders of magnitude. Because of the extremely low affinity of Fe^{3+} reduction to Fe^{2+} the oxidation process is not reversible by decompression. Finally, it should be noted that based on MS data obtained at RT, a self-reduction process of $Fe^{3+} \rightarrow Fe^{2+}$ had been reported by Drickamer *et al.* [20] in some inorganic ferric compounds.

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[12] $FeCl_2$ was prepared by direct Fe-Cl_2 reaction in an evacuated quartz tube at 800 °C. Spectroscopic pure iron metal was enriched to 25% ^{57}Fe, and dry pure Cl_2 was obtained by decomposing $PdCl_2$. Oxygen-free distilled water was used, and all procedures were done in a 99.999% pure Ar atmosphere. $Fe(OH_2)$ is extremely sensitive to oxygen. At atmospheric conditions it oxidizes rapidly to $Fe^{3+}OOH$.

[13] The f values for ferric/ferrous oxides at low temperatures and particularly at high pressure can be safely assumed to be similar. The inequality of their values, if any, will introduce a small error in the abundance which is reflected in the error bars. Errors in pressure are ±1 GPa and ±0.5 K in temperature.

[14] One differentiates between pressure induced self- and external oxidation processes. The latter takes place following a chemical reaction between two substances present in the pressurized sample chamber, say, $A^{2+} + B^{-1} \rightarrow A^{3+} + B^{-2}$, where B can be another species in the sample chamber or a substantial large ligand such as an organic species with sufficient charge-transfer bands that allows such a process. A self-oxidation process is described as $A^{2+} \xrightarrow{P} A^{3+} + e^-$ where the ejected electrons will form a new valence band.

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[18] All ferric-hydroxide derivatives have the orthorhombic structure whereas the $M(OH)_2$ have the trigonal structure.

[19] Preliminary Mössbauer studies to 100 GPa show no indication of a Mott-Hubbard transition (characterized by a collapse of magnetism and the onset of an insulator-metal transition) at ~50 GPa. Similarly, IS data from MS studies show no indication of a volume collapse in the vicinity of 50–60 GPa.

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