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# **Vibrational spectroscopy of Fe(OH)<sub>2</sub> at high pressure: Behavior of the O-H bond**

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Infrared and Raman spectra of Fe(OH)<sub>2</sub>, “white rust”, were measured between 7 GPa and 21 GPa at ambient temperature. The frequency of the infrared-active A<sub>2u</sub> and of the Raman-active A<sub>1g</sub> stretching modes of the O-H group decrease linearly with pressure with slopes of  $-1.3 \pm 0.1 \text{ cm}^{-1}/\text{GPa}$  and  $-4.9 \pm 0.2 \text{ cm}^{-1}/\text{GPa}$ , respectively. The peak widths of both the infrared-active and Raman-active modes increase non-linearly with pressure, with a discontinuous increase of in broadening between 10 and 12.5 GPa. The overall broadening of the A<sub>2u</sub> and of the A<sub>1g</sub> stretching modes is approximately four-fold in the examined pressure range. The results of this spectroscopic study are compatible

with the trends observed in recent neutron diffraction studies in the isostructural  $\text{Co}(\text{OH})_2$ . Progressive pressure-induced H disordering could be a viable model to interpret both the broadening of the OH stretching mode and the changes in oxidation state of Fe recently observed by Mössbauer spectroscopy.

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## Introduction

Brucite-type hydroxides with the general formula  $\text{M}^{2+}(\text{OH})_2$  ( $\text{M}^{2+}$  is a divalent cation) present a layered structure with hydrogen atoms isolated between sheets of  $\text{M}^{2+}\text{O}_6$  octahedra, and are widely considered a model system for characterizing hydrogen bonding in oxides. Extensive high-pressure experimental and theoretical studies have been carried out on  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$  and  $\beta\text{-Ni}(\text{OH})_2$ <sup>1 2 3 4 5 6 7 8 9 10</sup>, whereas information available for the Mn, Fe, Cd members of this isomorphous family is restricted to ambient pressure<sup>11 12</sup>.

The application of pressure on these apparently simple materials has revealed a range of important effects, such as progressive softening and broadening of the OH stretching-vibration mode detected in all the studied compositions, and the loss of X-ray diffraction peaks at 11 GPa in  $\text{Ca}(\text{OH})_2$ <sup>1</sup>. Interpretations of the different observations encompass pressure-induced amorphization in the case of  $\text{Ca}(\text{OH})_2$ , O-H sublattice disordering in the

case of  $\text{Co}(\text{OH})_2$  and progressive structural changes in the case of  $\text{Mg}(\text{OH})_2$ <sup>1 3 4 5 7</sup>, modeled as structural frustration and dynamic hydrogen disordering. The role and even the presence of hydrogen bonding in this class of minerals are still open to question, however<sup>1 2 7 8</sup>.

The different electronic structures of transition-metal and alkaline-earths cations make it possible to test the role of ionic size and bonding on the stability of the brucite-type hydroxides. In particular, studying the high-pressure behavior of O-H bonding in  $\text{Fe}(\text{OH})_2$  is important to better understand the irreversible oxidation of Fe ( $\text{Fe}^{2+} \xrightarrow{P} \text{Fe}^{3+} + e^-$ ) that has been recently documented at pressures above 8 GPa<sup>13</sup>. No clear evidence of structural transformation has been detected by x-ray diffraction, however, and the “internal” oxidation has been associated with the disordering of H ions caused by  $\text{H}\cdots\text{H}$  repulsion enhanced by compression<sup>13</sup>, in agreement with the results of high-pressure neutron diffraction on  $\text{Co}(\text{OD})_2$ <sup>7</sup>. The purpose of the present study is to test the validity of this hypothesis by vibrational spectroscopy. Finally, layered hydroxides are considered appropriate analogs for understanding dense hydrous silicates, which play a key role in the retention and transport of hydrogen (“water”) in the Earth interior<sup>14</sup>.

## **Material synthesis and experimental methods**

$\text{Fe}(\text{OH})_2$  powder was synthesized by dissolving  $\text{FeCl}_2$  and  $\text{KOH}$  in deoxidized water. The precipitated hydroxide was dried and loaded in a miniature diamond-anvil cell in a controlled atmosphere of 99.999% pure Ar. The sample was loaded together with several

ruby grains in a 200  $\mu\text{m}$ -wide chamber drilled in a Re gasket preindented to 30  $\mu\text{m}$  thickness. Argon was used as a pressure-transmitting medium. The sample was compressed between two 480  $\mu\text{m}$  diamond culets.

IR absorption was measured between 1000 and 4500  $\text{cm}^{-1}$  using a Bruker Optics Vector-33 interferometer, with a globar source and liquid-nitrogen cooled CdTe detector. Data were collected at 4  $\text{cm}^{-1}$  resolution. The spectra were corrected for diamond absorption and instrument response, and the relative absorption peaks were fitted to pseudo-Voigt line shapes after background subtraction.

Raman scattering measurements were performed using the 488 nm line of an Ar-ion laser. Data were collected using a 1800 groove/mm grating spectrometer and a CCD detector. The data collection times ranged between 25 and 1000 s. Raman spectral features were fitted to pseudo-Voigt line shapes after background subtraction.

Pressure was determined by the ruby  $R_1$  fluorescence line shift, using the hydrostatic calibration by Mao et al.<sup>15</sup>. Ten different ruby grains were measured at each pressure, and the scatter never exceeded 0.5 GPa.

## **Results and discussion**

$\text{Fe}(\text{OH})_2$ , “white rust”, crystallizes in the hexagonal system (space group  $P\bar{3}m1$ , Fig.1). It is isostructural with brucite,  $\text{Mg}(\text{OH})_2$ , and the simple hydroxides  $\text{Ca}(\text{OH})_2$ ,  $\text{Mn}(\text{OH})_2$ ,  $\beta\text{-Co}(\text{OH})_2$  and  $\beta\text{-Ni}(\text{OH})_2$ .

Factor group analysis at the Brillouin zone-center determines that there are two internal stretching OH vibrations, the symmetric  $A_{1g}(\text{OH})$  and the antisymmetric  $A_{2u}(\text{OH})$  modes, and six lattice modes,  $A_{1g}(\text{T})$ ,  $A_{2u}(\text{T})$ ,  $E_g(\text{T})$ ,  $E_u(\text{T})$ ,  $E_g(\text{R})$ ,  $E_u(\text{R})$  (Fig. 2).

The present study focused on the behavior of the Raman-active  $A_{1g}(\text{OH})$  mode and the IR-active  $A_{2u}(\text{OH})$  mode between 7 and 21 GPa (Fig. 3). In the range between 690 and 750  $\text{cm}^{-1}$  we have also observed a Raman spectral feature which does not correspond to any of the Raman-active lattice modes observed for  $\text{Fe}(\text{OH})_2$  at ambient conditions<sup>11</sup>. We assigned this feature to the rotation  $E_g(\text{R})$ . This lattice vibration is often not detected in studies of transition-metal hydroxides<sup>11</sup> and it has been only observed in one high-pressure Raman study of  $\beta\text{-Ni}(\text{OH})_2$ <sup>9</sup>. The spectral line assigned to  $E_g(\text{R})$  has a positive linear pressure dependence,  $\partial\nu/\partial P = 4.0 \pm 0.2 \text{ cm}^{-1}/\text{GPa}$ . The extrapolated ambient-pressure frequency is  $664 \pm 3 \text{ cm}^{-1}$ , substantially lower than in  $\text{Mg}(\text{OH})_2$  ( $724 \text{ cm}^{-1}$ )<sup>5</sup> and  $\beta\text{-Ni}(\text{OH})_2$  ( $880 \text{ cm}^{-1}$ )<sup>9</sup>.

The frequencies of the OH stretching modes,  $A_{1g}$  and  $A_{2u}$ , decrease almost linearly with increasing pressure, and do not exhibit hysteresis (outside estimated errors) on decompression (Fig. 4). A linear fit to the frequencies yields zero-pressure values of  $3628 \pm 1 \text{ cm}^{-1}$  for  $A_{2u}$  and  $3572 \pm 3 \text{ cm}^{-1}$  for  $A_{1g}$ , in good agreement with the extant data<sup>11</sup>. The corresponding pressure derivatives are  $\partial\nu/\partial P = -1.3 \pm 0.1 \text{ cm}^{-1}/\text{GPa}$  and  $-4.9 \pm 0.2 \text{ cm}^{-1}/\text{GPa}$ , respectively. The frequencies of the internal OH stretching modes in brucite-type hydroxides are influenced by the nature of the octahedral cation. They are correlated to

both metal-oxygen distance and to the inverse-root metal-OH mass (Table 1). The influence of the cation is modeled by a harmonic-oscillator with metal–OH vibrational frequency (e.g.<sup>16</sup>):

$$\nu \propto \sqrt{\frac{k}{\mu}}, \quad (1)$$

where  $k \propto r^{-3}$  is a force constant for a coulombic interaction, and  $r$  is the metal-oxygen distance and  $\mu$  is the reduced mass. The behavior of alkaline-earth and transition-metal hydroxides frequencies is visibly different (Fig. 5). Table 2 shows that the rate of pressure-induced softening of  $A_{2u}$  in  $\text{Fe}(\text{OH})_2$  is intermediate between that of  $\text{Mg}(\text{OH})_2$ , which does not show evidences of pressure-induced loss of structural order at pressures below 30 GPa<sup>5 8</sup>, and that of  $\text{Ca}(\text{OH})_2$  that instead exhibits broadening (interpreted as amorphization) above 11 GPa<sup>1 17 18</sup>. The rate of softening of  $A_{1g}$  is smaller in absolute magnitude than that of  $\text{Mg}(\text{OH})_2$ , and also of  $\beta\text{-Co}(\text{OH})_2$  and  $\beta\text{-Ni}(\text{OH})_2$ . Nevertheless, the difference between the two stretching-mode frequencies increases with pressure, as is observed for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  (Table 2).

Pressure-induced softening of the OH stretching modes is accompanied by peak broadening and loss of intensity for the isostructural  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$ <sup>1 3 4 5 9</sup>. Analysis of the pressure dependence of the linewidth of the two stretching modes gives us insight concerning local structural disordering. Both  $A_{2u}$  and  $A_{1g}$  vibrations of  $\text{Fe}(\text{OH})_2$  show non-linear pressure-induced broadening, with an approximately 4-fold increase in full width at half maximum (FWHM) through the experimental pressure range (Fig. 6). The widths of both spectral lines show an increase in pressure dependence between 10 and 12.5 GPa, similar to the enhanced broadening observed for  $\text{Co}(\text{OH})_2$ <sup>3 4</sup>



<sup>10</sup>. However, we do not observe, to the limit of our experimental resolution, a clear discontinuity in the pressure dependence of the broadening of  $A_{2u}$ . In the case of  $\text{Co}(\text{OH})_2$ , pressure-induced hydrogen disordering has been quantitatively determined through neutron diffraction experiments and interpreted as an effect of  $\text{H}\cdots\text{H}$  coulombic repulsion<sup>7</sup>.

We interpret the observed pressure dependence of the stretching-mode frequencies and line widths for  $\text{Fe}(\text{OH})_2$ , by comparison with the behavior of the closely similar  $\text{Co}(\text{OH})_2$ <sup>3 4 10</sup>, as a confirmation of the hypothesis that newly observed electronic effects induced by pressure on  $\text{Fe}(\text{OH})_2$  are indeed linked to hydrogen disordering driven by pressure-enhanced  $\text{H}\cdots\text{H}$  repulsion<sup>13</sup>. In detail, the change above 10 GPa in the pressure dependence of the line widths of the OH stretching modes of  $\text{Fe}(\text{OH})_2$  can be interpreted in terms of a disordering of H around the crystallographic position occupied at ambient pressure, toward a range of positions occupied in response to  $\text{H}\cdots\text{H}$  repulsions: this caused by pressure-induced compression of the crystalline structure along the  $c$ -axis<sup>7</sup>. Displacement (and disordering) of H alters the Coulomb potential at the Fe site, which is interpreted as furnishing the driving force for the delocalization of the weakly bonded 3d electron of Fe. This explains the pressure-induced change of Fe oxidation state in  $\text{Fe}(\text{OH})_2$  documented by Mössbauer spectroscopy<sup>13</sup>. However, the reversibility of the vibrational-line width does not match the electronic transition of Fe, which is irreversible, perhaps due to the affinity of Fe for the  $3^+$  oxidation state. Analogous mechanisms of hydrogen disordering in dense hydrous silicates could potentially cause pressure-induced self-oxidation of Fe, which in turn would affect the phase stability<sup>19</sup>, minor and trace

elements partitioning and the transport properties of “water”-bearing mineral minerals in the Earth’s mantle.

## **Conclusions**

A combined Raman and infrared-absorption study of the OH stretching vibrations of  $\text{Fe}(\text{OH})_2$  up to 21 GPa demonstrates that structural disordering of the hydrogen sublattice occurs above 10 - 12.5 GPa. The new observations support the hypothesis that the pressure induced self-oxidation of Fe in  $\text{Fe}(\text{OH})_2$  is causally linked to a progressive increase of H··H coulombic repulsion, and loss of long range order of the hydrogen ions. This effect could, in principle, be a general mechanism of Fe self-oxidation in high-density hydrous silicates of the Earth’s mantle, and affect both phase stability and element partitioning, as well as the electrical conductivity of mantle rocks. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

**Table 1. Frequencies (in  $\text{cm}^{-1}$ ) of Raman- and infrared-active stretching modes of OH, and M-O distances (in  $\text{\AA}$ ) in brucite-type hydroxides at ambient conditions**

Compound	$A_{1g}$	$A_{2u}$	$\frac{1}{m_{\text{M-OH}}}$ *	M-O	References
Mg(OH) <sub>2</sub>	3652 3661.3	3688 3700	10.006	2.099	<sup>1 20</sup> <sup>5</sup>
Ca(OH) <sub>2</sub>	3620	3640 3646	11.941	2.369	<sup>1 20</sup>
Mn(OH) <sub>2</sub>	3578	3625	12.987	2.186	<sup>11</sup>
Fe(OH) <sub>2</sub>	3576 3572 $\pm$ 3	3624 3627 $\pm$ 1	13.037	2.139	<sup>11</sup> This study
$\beta$ -Co(OH) <sub>2</sub>	3569 3572	3630	13.198	2.115	<sup>10 11</sup>
$\beta$ -Ni(OH) <sub>2</sub>	3580	3639	13.186	2.073	<sup>9 11</sup>
$\beta$ -Cd(OH) <sub>2</sub>	3566	3607	14.772	2.314	<sup>11</sup>

\*  $(m_{\text{M}}^{-1} + (m_{\text{OH}})^{-1})^{-1}$  where m is the atomic mass in amu.

**Table 2. Pressure dependence  $\partial\nu/\partial P$  (in  $\text{cm}^{-1}/\text{GPa}$ ) of Raman- and infrared-active stretching modes of OH in brucite-type hydroxides at ambient conditions**

Compound	$A_{1g}$	$A_{2u}$	$ A_{1g} - A_{2u} $	References
Mg(OH) <sub>2</sub>	-7.68	-0.6	7.08	<sup>15</sup>
Ca(OH) <sub>2</sub>	-6.8*	-3.5	---	<sup>1 18*</sup>
Fe(OH) <sub>2</sub>	-4.9 $\pm$ 0.2	-1.3 $\pm$ 0.1	3.6	This study
$\beta$ -Co(OH) <sub>2</sub>	-9.6 <sup>†</sup>	---	---	<sup>10</sup>
$\beta$ -Ni(OH) <sub>2</sub>	-6.8	---	---	<sup>9</sup>

\*Linear fit of the data below 9GPa.

<sup>†</sup>Second order fit  $\partial\nu/\partial P = -9.6 + 0.15 P$  ( $\text{cm}^{-1}/\text{GPa}$ ).

## Figure captions

**Figure 1. Crystal structure of  $\text{Fe}(\text{OH})_2$ . The  $\text{MO}_6$  octahedral layers are drawn in grey, and the isolated hydrogen ions are represented as black spheres.**

**Figure 2. Vibrational modes of  $\text{Fe}(\text{OH})_2$ , from Ref. 11.**

**Figure 3. Representative spectra of (a)  $A_{2u}$ , and (b)  $A_{1g}$  OH stretching modes of  $\text{Fe}(\text{OH})_2$  up to 21 GPa.**

**Figure 4. Pressure dependence of the OH stretching vibrations of  $\text{Fe}(\text{OH})_2$ . Solid symbols are for data collected during compression, and open symbols for data collected on decompression.**

**Figure 5. Frequencies of the OH stretching modes of brucite type hydroxides as a function of the model vibrational frequency for the system metal-OH considered as a harmonic oscillator (Equation 1).**

**Figure 6. Full width at half maximum (FWHM) of (a)  $A_{1g}$ , and (b)  $A_{2u}$  OH stretching modes of  $\text{Fe}(\text{OH})_2$  up to 21 GPa. Data for  $\text{Ca}(\text{OH})_2$ <sup>3 4 10</sup> and  $\beta\text{-Ni}(\text{OH})_2$ <sup>9</sup> are shown for comparison.**

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