1	Phase transitions in <i>ɛ</i> -FeOOH at high pressure and ambient temperature
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20 Abstract

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Constraining the accommodation, distribution, and circulation of hydrogen in the Earth's interior 22 is vital to our broader understanding of the deep Earth due to the significant influence of 23 hydrogen on the material and rheological properties of minerals. Recently, a great deal of 24 attention has been paid to the high-pressure polymorphs of FeOOH (space groups $P2_1nm$ and 25 *Pnnm*). These structures potentially form a hydrogen-bearing solid solution with AlOOH and 26 27 phase H (MgSiO₄H₂) that may transport water (OH⁻) deep into the Earth's lower mantle. Additionally, the pyrite-type polymorph (space group $Pa\overline{3}$ of FeOOH), and its potential 28 dehvdration have been linked to phenomena as diverse as the introduction of hydrogen into the 29 outer core (Nishi et al. 2017), the formation of Ultra Low Velocity Zones (ULVZs) (Liu et al. 30 2017), and the Great Oxidation Event (Hu et al. 2016). In this study, the high-pressure evolution 31 of FeOOH was re-evaluated up to ~75 GPa using a combination of synchrotron-based X-ray 32 diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and optical absorption 33 spectroscopy. Based on these measurements, we report three principal findings: (1) pressure-34 induced changes in hydrogen bonding (proton disordering or hydrogen bond symmetrization) 35 occur at substantially lower pressures in ϵ -FeOOH than previously reported and are unlikely to 36 be linked to the high-spin to low-spin transition, (2) ε -FeOOH undergoes a 10% volume collapse 37 coincident with an isostructural *Pnnm* \rightarrow *Pnnm* structural transition at approximately 45 GPa, 38 and (3) a pressure-induced band gap reduction is observed in FeOOH at pressures consistent with 39 the previously reported spin transition (40 to 50 GPa). 40 41 42 43 44 45 **Keywords:** Phase transitions, infrared-spectroscopy, optical absorption spectroscopy, X-ray 46 diffraction, spin transition 47 48 49 50

51 Introduction

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The accommodation, distribution, and circulation of hydrogen in the deep Earth is key to 53 54 understanding the evolution of Earth's interior due to the significant influence of hydrogen on the material and rheological properties of high-pressure phases (e.g., Sarafian et al. 2017; Karato 55 2010). Geophysical observations indicate that the Earth's upper mantle and transition zone, at 56 least locally, host significant quantities of hydrogen (van der Meijde et al. 2003; Dixon et al. 57 58 2004, Pearson et al. 2014; Palot et al. 2016; Tschauner et al. 2018). Additionally, tomographic evidence supports the idea that subducting lithospheric plates pierce the transition zone, 59 potentially ushering water into the Earth's lower mantle (van der Hilst et al. 1997). Yet while 60 hydrogen in the upper mantle and transition zone is hosted primarily in nominally anhydrous 61 62 phases, these phases are not stable at the high pressure and temperature conditions of the lower mantle (Hirschmann 2006). If hydrogen introduced into the lower mantle remains in the lower 63 mantle, it is almost certainly accommodated primarily in minor hydrous phases, because the 64 dominant lower mantle minerals (bridgmanite, ferropericlase, calcium silicate perovskite) do not 65 have the same capacity for water storage (Bolfan-Casanova et al., 2002, 2003; Panero et al., 66 2015). A plausible lower mantle host is the isostructural FeOOH–AlOOH–MgSiO₄H₂ system. 67 At moderate pressures (>6 GPa) goethite (α -FeOOH, space group *Pbnm*), a widespread 68 iron oxy-hydroxide, transforms into ε -FeOOH, an orthorhombic (space group $P2_1nm$, Z = 2) 69 phase composed of edge-sharing FeO₆ units that are close-packed along the *c*-axis, with 70 hydrogen atoms occupying the channels between these close-packed octahedra (Bendeliani et al. 71 1972; Pernet et al. 1975; Bolotina et al. 2008) (Figure 1a). At increased pressure, ε-FeOOH 72 undergoes pressure-induced hydrogen bond symmetrization resulting in a second-order phase 73 transition (space group Pnnm, Z = 2) (Figure 1c). However, the pressure at which this hydrogen 74 bond symmetrization induced $P2_1nm \rightarrow Pnnm$ transition occurs remains contested (Gleason et 75 al. 2008; Xu et al. 2013; Thompson et al. 2017; Ikeda et al. 2019). At the pressures of the 76 Earth's lower mantle, ε -FeOOH forms a solid solution with δ -AlOOH and phase H (MgSiH₂O₄), 77 creating a viable hydrogen reservoir with *P*-*T* stability extending from lower mantle conditions 78 to those of the core-mantle boundary (Sano et al. 2008; Nishi et al. 2015; Xu et al. 2019). 79 Hydrogen bond symmetrization is the process by which the hydrogen in an asymmetrical 80 O—H…O bonding unit becomes centered with respect to the two oxygens with increased 81

pressure, as the longer hydrogen bridge bond $(H \cdots O)$ compresses more rapidly than the shorter 82 but stiffer hydroxyl bond (O-H) (Holzapfel 1972). Once the hydrogen bond is 'symmetrized', 83 the two donor-acceptor distances are equivalent, and this shift in charge balance can lead to 84 additional subtle structural changes (Figure 1c). In ɛ-FeOOH and other isostructural MOOH 85 phases, the MO₆ octahedra shift from a slightly offset position to one centered along the two-fold 86 axis, leading to the increase in symmetry from $P2_1nm$ to Pnnm (e.g., Sano-Furukawa *et al.* 2009, 87 2012). Alternatively, proton disorder in which both hydrogen and iron atoms are disordered over 88 89 symmetric positions on the two-fold axis may also produce MOOH with *Pnnm* symmetry (Bolotina et al. 2008) with the resulting diffraction patterns nearly indistinguishable from 90 91 symmetrized H-bond structures (e.g., Fujihara et al. 2002) (Figure 1b). Importantly, a recent neutron diffraction study by Sano-Furukawa *et al.* (2018), found that in δ -AlOOH, which is 92 93 isostructural to ε -FeOOH, proton disordering is a precursor to hydrogen bond symmetrization. Accurately determining the pressure at which hydrogen bond symmetrization occurs is important 94 95 because the phenomenon is linked to changes in compressibility (Vanpeteghem et al. 2003; Tsuchiya et al. 2005; Hushur et al. 2011) and due to isotopic effects may influence H/D 96 97 fractionation in the deep Earth (e.g., Sano-Furukawa et al. 2009). In addition to the previously described $P2_1nm \rightarrow Pnnm$ transition, ε -FeOOH reportedly 98 undergoes a high-spin to low-spin transition, determined on the basis of X-ray diffraction (XRD) 99 and X-ray emission spectroscopy (XES) experiments (Gleason et al. 2013). The XES results 100 from Gleason et al. (2013) are indicative of a high-spin to low-spin transition initiated at ~40 101 GPa and completed at ~60 GPa. However, that study did not use a pressure-transmitting 102 medium, which introduced significant deviatoric stress into the sample, inhibiting the detection 103 of a sharp transition. A contemporary study by Xu et al. (2013), which used a pressure-104 transmitting medium, pinpointed this electronic transition more closely to ~45 GPa using a 105 combination of Mössbauer spectroscopy, single-crystal diffraction, and resistivity measurements. 106 In both studies, the authors propose causality between the hydrogen bond symmetrization and 107 spin transition in E-FeOOH, although Gleason et al. (2013) report that hydrogen bond 108 symmetrization induces the spin transition, whereas Xu et al. (2013) conclude the spin transition 109 induces hydrogen bond symmetrization. However, both studies agree that a large (~11%) volume 110 111 collapse occurs coincident with the high-spin to low-spin transition, attributable to an isostructural phase transition. Significant volume reductions have been previously reported due 112

to high-spin to low-spin transitions without invoking hydrogen bond symmetrization, although a 113 volume reduction of $\sim 11\%$ is higher than the volume reductions reported for either ferropericlase 114 ((Mg,Fe)O) (1-3%) or ferromagnesite ((Mg,Fe)CO₃) (6-10%) (Lin et al. 2013), possibly due to 115 116 the larger relative volume occupied by iron atoms in FeOOH compared to these phases. In this study, we present experimental evidence of two distinct transitions in ε -FeOOH in 117 the explored pressure range (0-70 GPa): a low-pressure (~18 GPa) second-order transition 118 connected to hydrogen bond symmetrization and an independent first-order transition at ~45 119 120 GPa. Additionally, we report evidence of a rapid reduction in the bandgap of ε -FeOOH at pressures consistent with the previously reported spin transition. 121

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- 123 Methods

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Synthesis of ε -FeOOH for this study was performed by Akio Suzuki and is described in 125 Suzuki (2010). The high pressures necessary for this study were achieved by compressing ε -126 FeOOH samples using symmetric-type diamond anvil cells (DACs) with 250 µm culet type II 127 diamond anvils. Seventy-micron diameter sample chambers were laser ablated into stainless steel 128 or rhenium gaskets pre-indented to 22 or 28 GPa, respectively. Powdered & FeOOH, kept in a 129 desiccator prior to loading, was pressed into platelets ~3-5 µm thick and ~30 microns in 130 diameter. Platelets of ε -FeOOH were loaded into the sample chamber, utilizing gas-loaded Ne or 131 132 $\sim 10 \,\mu m$ thick platelets of KBr as a pressure medium to reduce pressure gradients within the sample. Neon was loaded as a pressurized gas at the Advanced Photon Source using the 133 COMPRES/GSECARS gas loading system (Rivers et al. 2008) and acted as a secondary 134 pressure standard (Fei et al. 2007), with reported uncertainties based on the standard error of the 135 (111), (200), and (220) d-spacings. Pressures were independently determined via the in situ 136 monitoring of the R_1 luminescence line (Dewaele *et al.* 2008) of 2-3 ruby grains placed in the 137 sample chamber, with errors reflecting the larger of either the standard deviation or 3%. 138 Room-temperature X-ray diffraction experiments were performed at beamline 13-ID-D 139 (GSECARS) at the Advanced Photon Source, Argonne National Laboratory. A monochromatic 140 $(\lambda = 0.3344)$ incident X-ray beam was used, measuring 3 µm by 4 µm at full width at half 141 maximum of the focused spot. Sample-to-detector distances and tilt were calibrated using 1-bar 142

143 diffraction of LaB₆. Diffraction patterns were integrated to produce 2θ plots using DIOPTAS

(Prescher and Prakapenka 2015), positions of individual diffraction peaks were determined using 144 PeakFit (Systat Software), and lattice parameters were calculated from the fitted *d*-spacings 145 using the author's own Mathematica script. Individual peaks were fit to single Gaussian curves, 146 147 and unresolved overlapping peaks were not used in the calculation of lattice parameters. All samples prepared for X-ray diffraction experiments were loaded using Ne as a pressure medium. 148 Fourier transform infrared (FTIR) spectra in this study were collected using both 149 synchrotron and globar sources. Synchrotron experiments were performed at the 1.4.3 beamline 150 151 of the Advanced Light Source at Berkeley Laboratory using a Nicolet 760 FTIR spectrometer with a custom microscope and HgCdTe detectors. Offline experiments were performed at 152 Brookhaven National Laboratory using a Bruker Vertex 80v spectrometer and Hyperion 2000 153 microscope with a MCT detector. All FTIR spectra presented here reflect a spectral resolution of 154 4 cm⁻¹, measured wavelength ranges of 500 to 8000 cm⁻¹, and were recorded as 1024 or 512 155 scans. PeakFit was used for background subtraction and to obtain precise absorption peak 156 positions using a least-squares refinement, and interference fringes in absorbance spectra were 157 reduced mathematically in DatLab. Samples prepared for FTIR experiments used either Ne or 158 KBr as pressure medium, and the three samples that went to the highest pressures used KBr. 159 Optical absorption measurements were collected at the University of Chicago. Spectra 160 were recorded from 420 to 980 nm using a 0.3 meter focal length Princeton Instruments SP-161 2300i spectrograph. Transmitted light (I), generated with a tungsten filament bulb, was measured 162 through the pressure medium (KBr) only, while incident light (I_0) was collected through the 163 164 sample and pressure medium. Background measurements were collected both with the light source off and with the light source on but measured at the gasket, which is opaque, with 165 comparable results. Interference fringes in the absorbance spectra were removed mathematically 166 in DatLab. To account for variation in sample thickness (h), reported absorption values $\alpha = h^{-1}$ 167 168 $\ln(I_0/I)$ have been scaled such that I_0/I is equal for all samples at 10 GPa. Samples prepared for optical absorption measurements used KBr as pressure medium. 169

- 171 Results and Discussion
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- 173 X-ray Diffraction
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High-pressure, room-temperature X-ray diffraction (XRD) measurements were used to 175 re-evaluate the phase diagram of FeOOH up to 75 GPa, as the existing literature exhibits a 176 paucity of volume-pressure (V-P) data in the mid-pressure range (20-50 GPa) (Gleason et al. 177 2008, 2013; Suzuki 2010, 2016; Ikeda et al. 2019). Additionally, using a gas-membrane 178 diaphragm to remotely pressurize the DAC between diffraction measurements without manual 179 action, data could be collected with greater pressure resolution than in previous studies. As X-ray 180 diffraction inherently relies on electron density, the detection of hydrogen using powder XRD is 181 182 virtually impossible. The $P2_1nm \rightarrow Pnnm$ transition is primarily defined by the pressure-induced symmetrization of the hydrogen bonds, but associated with hydrogen bond disordering and 183 symmetrization are subtle changes in the structure and strain accommodation, which enable the 184 detection of these transitions indirectly (e.g., Sano-Furukawa et al. 2009, 2012; Kuribayashi et 185 al. 2014). 186

In the lower pressure interval (0.5-43 GPa) the lattice parameters of ε -FeOOH were 187 determined using at a minimum the (110), (101), (011), (020), (210), (211), (121), (220), (002), 188 and (301) *hkl* peaks. The resulting unit cell volumes and lattice parameters are plotted in Figures 189 190 2a and 2b and are reported in tabulated form in Table S.1. The measured lattice parameters and unit cell volumes of ε -FeOOH in this pressure interval are in excellent agreement with the results 191 of Suzuki (2010, 2016) and Ikeda et al. (2019), albeit slightly lower than those reported by the 192 Gleason et al. (2013). The diffraction data from Gleason et al. (2013) exhibit more scatter, likely 193 194 due to the lack of pressure medium in that study, which likely contributed to the slight offset in 195 measured P-V values.

Based on the Bragg peaks indexed in this study, the $P2_1nm$ and Pnnm structure cannot be 196 distinguished from one another, as even at the lowest pressures of this study no peaks were 197 observed that violated the additional systematic absences characteristic of the Pnnm symmetry (h 198 199 + l odd for h0l, k + l odd for 0kl). Additionally, based on the findings of Sano-Furukawa *et al*. (2009), who evaluated the $P2_1nm \rightarrow Pnnm$ transition in isostructural δ -AlOOH, the volume 200 reduction associated with this second-order transition is likely unresolvable, rendering 201 determinations of this phase boundary on this basis alone dubious. Thus, employing the approach 202 of Sano-Furukawa et al. (2009, 2012), we evaluated the ratios of lattice parameters as a means of 203 elucidating the subtle $P2_1nm \rightarrow Pnnm$ transition. 204

205 The evolution of the a/b and b/c lattice parameter ratios (Figure 2c) reveal a change in the

- axial compression of ε -FeOOH with pressure, and the inflection points evident at 18±1 GPa
- 207 indicate a shift in the accommodation of strain in this system. Similar changes in axial
- 208 compression have been used previously as an indicator of second-order phase changes in similar
- 209 materials (e.g., Sano-Furukawa et al. 2009, 2012; Kuribayashi et al. 2014). On the basis of these
- 210 lattice parameter ratios, we confirm that ε-FeOOH undergoes a second-order phase transition
- from the $P2_1nm$ to Pnnm structure at 18±1 GPa, in good agreement with previous predictions
- based on density functional theory-based calculations (Thompson et al. 2017) and recent
- 213 experiments (Ikeda et al. 2019). As any volume reduction across this presumed phase boundary
- is minimal (Figure 2a), the V–P data from the entire pressure interval (0 to 45 GPa) was fit to a
- 215 third-order Birch-Murnaghan equation of state (EoS) (Birch 1978):

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$$P(V,T) = 3K_0 f_E \left[(1+2f_E)^{\frac{5}{2}} \left(1 + \frac{3}{2} [K'_0 - 4] f_E \right) \right]$$

which relates pressure (*P*), volume (*V*), ambient pressure bulk modulus (K_0), and its pressure derivative (K_0') in terms of finite Eulerian strain (f_E):

219 $f_E = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^2 - 1 \right]$

which is a measure of the volume compression of a solid relative to its initial volume (V_0). Residuals from this fit are shown in Figure S1.

To obtain EoS parameters with the most comprehensive data set available, the V-P data 222 223 from this study and Suzuki (2010, 2016) were combined, and the resultant equation of state parameters are presented alongside parameters fit to the data from only this study. In addition to 224 fitting V–P data from the entire 0-45 GPa pressure range, we also report EoS parameters derived 225 from fitting the V-P data of the $P2_1nm$ and Pnnm structures separately. The resultant EoS 226 parameters, as well as previously published results, are reported in Table 1. We find that EoS 227 parameters derived from fitting the combined data set across the entire pressure range (0-45 GPa) 228 are in reasonable agreement with those reported by Gleason et al. (2008) and Suzuki (2010, 229 2016). However, fitting V-P data for the $P2_1nm$ and Pnnm structures independently (using a 230 fixed K_{θ} value of 4 because fewer fitted parameters are justified over the limited pressure 231 232 ranges), reveals that the Pnnm structure has a bulk modulus ~20% higher than that of the $P2_1nm$ ε-FeOOH, in good agreement with the ~19% predicted from DFT calculations (Thompson *et al.* 233

2017). These findings are also in good agreement with a prior study by Xu *et al.* (2013) that
identified a reduction in the compressibility of FeOOH at ~16 GPa but did not connect this
change in material properties to the onset of pressure-induced hydrogen bond symmetrization or
proton disordering. Similar increases in bulk modulus have been reported for other hydrous
phases due to the onset of pressure-induced hydrogen bond symmetrization or proton disordering
(Vanpeteghem *et al.* 2003; Tsuchiya *et al.* 2005; Hushur *et al.* 2011).

Additionally, XRD data from this study revealed a second, independent structural 240 241 transition in ε-FeOOH at ~45 GPa. The transition occurs over a small (<3 GPa) pressure interval and is evident in the appearance of multiple new Braggs peaks and a simultaneous reduction in 242 the intensity, and eventual disappearance, of the Braggs peaks of the high-spin *Pnnm* structure 243 (Figure 3). This high-pressure (> 45 GPa) structure of FeOOH is stable at ambient temperatures 244 and pressures exceeding 70 GPa. While an earlier study identified a potential unit cell volume 245 reduction in this pressure range (Gleason et al. 2013), the improved pressure resolution of the 246 current study clarifies the pressure at which this transition occurs. The sharpness of this phase 247 boundary and the significant volume reduction contrast with the gradual, displacive second-order 248 transition produced by the gradual change in charge density due to hydrogen bond 249 symmetrization. Conversely, the structural transition observed at ~45 GPa is within the pressure 250 range in which the high-spin to low-spin transition has been observed (Gleason et al. 2013), and 251 the contraction of the Fe³⁺ ionic radius across the high-spin to low-spin transition has been 252 reported to produce significant volume reductions in other iron-bearing minerals (e.g., Lin et al. 253 2013). Although the <3 GPa interval in which the first-order transition is observed in this study 254 is significantly narrower than the 20 GPa pressure interval across which the high-spin to low-255 spin transition was reported (Gleason *et al.* 2013), this discrepancy may be due to the lack of a 256 pressure medium in the earlier study, an omission that can produce pressure gradients that could 257 258 lead to significantly broader spin transitions.

High-pressure (>45 GPa) X-ray diffraction data from this study were indexed to a *Pnnm* (Z=2) unit cell, using at a minimum the (110), (200), (011), (121), (310), (301), and (112) *d*spacings. The resultant lattice parameters and unit cell volumes are consistent with a volume reduction of 10% without a loss of symmetry, in reasonable agreement with the isostructural, 11% volume collapse proposed by Gleason *et al.* (2013) (Figure 2a). However, a recent *ab initio* study has predicted an intermediate *Pbca* (Z=8) structure is stable between the *Pnnm* and the

pyrite ($Pa\bar{3}$) phases of AlOOH (Verma *et al.* 2018). The high-pressure (>45 GPa) XRD data 265 from this study was indexed to the proposed *Pbca* structure, but the reduction in volume across 266 this potential $Pnnm \rightarrow Pbca$ transition appears implausibly large (26%) and resulted in a reduced 267 quality of fit. An attempt was made to index the high-pressure Bragg peaks to the α -PbO₂ 268 structure (*Pbcn*), a structure adopted by $CaCl_2$ -type (*Pnnm*) oxides at high pressures, but this 269 failed to produce a reasonable fit to the data. Additionally, we can definitively state that this is 270 not the appearance of the high-pressure pyrite structure of FeOOH, to which ε -FeOOH is 271 272 expected to transition at comparable pressures and elevated temperatures (Nishi et al. 2017; Hu et al. 2016). Therefore, we interpret the first-order transition at 45 ± 2 GPa as an isostructural 273 274 volume collapse (i.e., $Pnnm \rightarrow Pnnm$), accompanied by an increase in the *a/b* ratio in the higherpressure structure (Figure 2d). The change in the a/b ratio may be due to a relaxation of the 275 276 distortion of the FeO₆ units, in agreement with Xu et al. (2013) and linked to the previously reported high-spin to low-spin transition (Gleason et al. 2013; Xu et al. 2013). In the future, 277 single crystal X-ray diffraction structure refinements might help elucidate the nature of this 278 structural transition (displacive versus reconstructive) and refine the symmetry of the high 279 pressure, low-spin structure. 280

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282 Infrared and Visible Absorption Spectroscopy

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Room temperature infrared absorption spectra of ϵ -FeOOH were collected at ambient 284 pressure and at regularly increasing pressure intervals of ~2 GPa up to ~50 GPa. Qualitatively, 285 the ambient pressure ε -FeOOH spectrum bears similarity to that of $P2_1nm$ β -CrOOH, with which 286 ε-FeOOH is isosymmetric (Jahn et al. 2012) (Figure 4). At ambient pressure, the O-H stretching 287 region presents as a broadband feature (2600-3100 cm⁻¹), consistent with previously reported 288 spectra of low-pressure polymorphs of FeOOH (e.g., Williams and Garnero 1996; Kagi et al. 289 290 2008), and with increased pressure, the broadband O-H stretching region further broadens and 291 shifts to lower wavenumbers. Unfortunately, the increased breadth of the O-H stretching feature and its increased proximity to the diamond absorption region prevents tracking the pressure 292 293 dependence of this feature above ~17 GPa. Although the O-H stretching band could only be 294 monitored over a limited pressure range, its negative frequency shift pressure dependence was clearly observable at low pressures (Figure S3). A linear fit of the pressure-frequency data of the 295

296 O-H stretching band results in an approximate pressure dependence of $-14 \text{ cm}^{-1}\text{GPa}^{-1}$,

297 demonstrative of a softening behavior consistent with eventual hydrogen bond symmetrization.

However, it isn't feasible to predict the pressure of eventual hydrogen bond symmetrization, as

299 the relationship between the 1-bar stretching frequency and O-H pressure dependence is poorly

300 understood in ε -FeOOH and similarly structured phases, and the pressure range of available ε -

301 FeOOH O-H stretching frequency data is limited.

The ambient pressure infrared spectrum of ε -FeOOH also contains three distinct 302 absorption bands at 965, 1145, 1175 cm⁻¹ that were identified as O-H bending vibrations based 303 on comparison to similar structures (Williams and Garnero, 1996; Mashino et al. 2016; Pinney 304 305 and Morgan 2013). Spectra at successive pressure steps were evaluated to determine the frequency shifts in the O-H bending as a function of pressure (Figure 5). As with the OH-306 307 stretching region, these features broaden with increased pressure, and the two higher frequency bands become indistinguishable above 17.5±1 GPa. The lowest-frequency bending band remains 308 309 distinct to higher pressures, but the pressure dependence of this band changes dramatically above 17.5 ± 1 GPa. The sudden change in the pressure dependence of this band suggests a reorientation 310 of the O-H bonds, suggestive of the onset of pressure-induced hydrogen bond symmetrization or 311 proton disordering. A similar shift in the pressure dependence of the OH-absorption bands in 312 isostructural δ -AlOOH was observed by Kagi *et al.* (2010) at approximately 10 GPa, consistent 313 with the onset of proton disordering in that phase (Sano-Furukawa et al. 2018). 314

During the course of these IR measurements, a reduction in the transmitted IR signal was 315 316 observed in ε-FeOOH samples compressed above ~40 GPa (Figure S4). In addition to the changes in IR transmission properties, changes in the optical properties of FeOOH were 317 observed upon compression. The samples were translucent orange at ambient and low pressures, 318 319 but reddened with increased pressure and became opaque to transmitted visible light at 45 GPa, slightly preceding the loss of IR transmission (Figure S4). To quantify these observations, visible 320 321 to near-infrared absorption measurements of ε -FeOOH were collected up to pressures exceeding 322 70 GPa, to track the pressure dependence of the absorption edge. Representative high-pressure optical absorption spectra of ϵ -FeOOH are shown in Figure 6a and indicate a systematic 323 pressure-induced increase in absorption concordant with qualitative observations. Normalized 324 data for five samples are plotted in Figure 6b, in which there are two key features. First, each 325 sample underwent a transient minimum in optical transmission between 15-20 GPa before 326

327 gradually recovering to previous values over the subsequent ~5 GPa. Second, all five samples 328 became opaque in the light range probed (1.45 eV to 2.05 eV) above 50 GPa (Figure 6b), above 329 which the ratio of transmitted light (I) to incident light (I_0) that can propagate through the sample 330 decreases to zero. These vis/NIR absorption findings suggest a significant reduction in the 331 bandgap in this pressure interval.

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333 Implications

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Close evaluation of the high-pressure behavior of ε -FeOOH at ambient temperature 335 indicates two sequential, structural phase transitions in the 0-75 GPa pressure range. A second-336 337 order transition at 18 ± 1 GPa was determined on the basis of three observations: (1) a change in 338 axial compressibility evident in the lattice parameter ratios measured using powder XRD, (2) a change in the OH-bending modes observed with FTIR spectroscopy, and (3) a transient decrease 339 in optical absorption. In accordance with the previous work of Sano-Furukawa et al. (2009, 340 341 2012, 2018) that evaluated isostructural MOOH phases, this 18±1 GPa transition is the $P2_1nm \rightarrow$ 342 *Pnnm* transition produced by either pressure-induced hydrogen bond symmetrization or proton disordering, with future neutron diffraction work needed to differentiate between these 343 mechanisms. Furthermore, this transition is observed to lead to a $\sim 20\%$ increase in bulk modulus 344 and could be linked to the increase in compressional velocity (V_P) reported by Ikeda *et al.* 345 (2019). 346

At 45±2 GPa, *Pnnm* ε-FeOOH undergoes a first-order structural phase transition, 347 identifiable due to the appearance of new Bragg peaks coincident with the disappearance of the 348 high-spin Pnnm peaks. This high-pressure structure of FeOOH can also be indexed to Pnnm with 349 a ~10% volume reduction, in good agreement with previous studies (Gleason et al. 2013; Xu et 350 al. 2013). Therefore, we propose that the first-order transition at 45 ± 2 GPa is a nearly 351 isostructural volume collapse (i.e., $Pnnm \rightarrow Pnnm$), accompanied by a small (~1%) increase in 352 the *a/b* ratio in the higher-pressure structure (Figure 2d). As such, low-spin *Pnnm* FeOOH is 353 354 stable across a wide pressure range (more than 30 GPa). However, the phase diagram of FeOOH at high pressures and moderate temperatures should be assessed to determine the relevance of 355 low-spin *Pnnm* FeOOH to the Earth's interior, as the formation of the pyrite ($Pa\overline{3}$) structure is 356 357 reported at comparable pressures and high temperatures (Nishi et al. 2017; Hu et al. 2016). In the future, single crystal X-ray diffraction structure refinements may be beneficial in verifying the
 symmetry of this higher pressure, low-spin structure.

In addition to the first-order structural transition identified in FeOOH at ~45 GPa, a color 360 change (translucent orange to black) was observed at high pressure, and the optical opacity of 361 Pnnm E-FeOOH was quantified using visible/NIR transmission and infrared absorption. Visible 362 to near-infrared absorption measurements of ɛ-FeOOH also identified a systematic pressure-363 induced increase in absorption consistent with band gap reduction in the high-spin *Pnnm* phase, 364 365 although complete band gap collapse (i.e., metallization) of this phase cannot be established on the basis of these experiments alone. FeOOH becomes opaque in the 1.45-2.05 eV range and 366 also in the mid-IR at 45 GPa, indicating a change in optical properties along with the high-spin to 367 low-spin transition in this material, as both phenomena are tied to changes in the d orbitals of the 368 369 iron atoms. In fact, a similar increase in optical opacity has been previously linked to the highspin to low-spin transition in siderite (Lobanov et al. 2015) and ferropericlase (Keppler et al. 370 2007). The apparent width of this transition, when compared to the sharpness of the structural 371 transition observed using diffraction, may be attributable to the difference in the hydrostaticity of 372 the pressure medium (KBr and Ne, respectively). 373

These results demonstrate that bandgap reduction, the previously observed high-spin to 374 low-spin spin transition (Gleason et al. 2013; Xu et al. 2013), and the first-order phase transition 375 in ε -FeOOH all occur at a pressure (45±2 GPa) greatly exceeding the $P2_1nm \rightarrow Pnnm$ symmetry 376 transition associated with a change in hydrogen bonding (18±1 GPa). Therefore, hydrogen-bond 377 378 symmetrization is not the driver of spin transition in ε -FeOOH or vice versa. Rather, FeOOH undergoes a second-order $P2_1nm \rightarrow Pnnm$ symmetry change caused by a shift in hydrogen 379 bonding at 18 GPa, and a subsequent, unrelated first-order transition at 45 GPa that involves a 380 significant volume change, spin transition, and optical opacity. Furthermore, although 381 endmember ε -FeOOH is expected to transition to the pyrite ($Pa\overline{3}$) structure at the concurrent 382 pressures and high temperatures of the Earth's mantle (Nishi et al. 2017; Hu et al. 2016), 383 384 aluminum substitution is expected to increase the thermodynamic stability of (Fe,Al)OOH such that the low-spin *Pnnm* structure may be stable at the conditions of the deep Earth (e.g., Nishi et 385 386 al. 2015; Xu et al. 2019). We anticipate that the high-spin to low-spin spin transition and associated volume collapse in intermediate compositions in the FeOOH-AlOOH-MgSiH₂O₄ 387 system are likely to occur at lower pressures than in the Fe-endmember, as has been observed in 388

ferropericlase (Fei *et al.* 2007). Additional experiments are needed to assess the influence of

390 cation substitution on the phase boundaries of the FeOOH–AlOOH–MgSiO₄H₂ system, as this

391 may play a pivotal role in the transport of water (OH⁻) deep into the Earth's lower mantle (Ohira

- *et al.* 2014, Xu *et al.* 2019) and may contribute to geophysical heterogeneities observed in the
- deep Earth (Thompson *et al.* 2017; Ohira *et al.* 2019).
- 394

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594 Tables

595

596 **Table 1.** Birch-Murnaghan equation of state (EoS) parameters of ε-FeOOH, including ambient-

597 pressure unit volume (V_0), bulk modulus (K_0), and the pressure derivative of the bulk modulus

598 (K_0) . Also included is the pressure range of the included room-temperature XRD data and the

number of V-P data points included in each EoS fitting. The first and second lines are

600 parameters obtained from fitting the same data to second- and third-order BM EOSs,

respectively. Values in parentheses are uncertainties on the last digit. Residuals from the fit to a

602 third-order Birch-Murnaghan equation of state are shown in Figure S1.

	Pressures (GPa)	# Data points	V_{θ} (Å ³)	K ₀ (GPa)	K_{0}'
This study	0 to 45	59	65.87(3)	152(4)	4.9(2)
This study	0 to 45	59	65.57(6)	170(1)	4 (fixed)
This study, Suzuki	0 to 45	80	66.15(5)	141(3)	5.4(2)
2010, 2016					
This study, Suzuki	0 to 45	80	65.88(4)	163(1)	4 (fixed)
2010, 2016					
This study, Suzuki	0 to 16	29	66.14(4)	146(2)	4 (fixed)
2010, 2016 (<i>P2</i> ₁ <i>nm</i>)					
This study (Pnnm)	18 to 45	50	65.3(1)	176(3)	4 (fixed)
Gleason et al. 2008	8 to 17	9	66.3(5)	158(5)	4 (fixed)
Suzuki 2010	0 to 9	8	66.20(3)	126(3)	10(1)
Suzuki 2016	0 to 11	13	66.278(6)	135(3)	6.1(9)

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Figure 1. Low and moderate pressure structures of ε -FeOOH including the (**a**) *P*2₁*nm* structure with ordered hydrogen occupation and asymmetric hydrogen bonds, (**b**) *Pnnm* structure with disordered hydrogen (hydrogen positions are 50% occupied), and (**c**) *Pnnm* structure with symmetric hydrogen bonds. Dashed lines indicate unit cells, oxygen atoms are red spheres, hydrogen atoms are grey spheres, and FeO₆ units are tan polyhedra, which are stacked in edgesharing chains parallel to the *c*-axis. Image generated in VESTA [Momma and Izumi, 2008]

Figure 2. (a) Unit cell volume, (b) lattice parameters, (c) a/b and (d) b/c lattice parameter ratios 611 of FeOOH as a function of pressure, including this study (solid symbols), Suzuki 2010 (black 612 crosses), Suzuki 2016 (black X's), Gleason et al., 2008 (open diamonds), Gleason et al. 2013 613 (open triangles), and Ikeda et al. 2019 (open circles). Different solid symbols (circles, diamonds, 614 squares) are used to show replicate samples in this study. Green, purple, and yellow symbols 615 indicate that Braggs peaks have been indexed to the $P2_1nm$ (green), high-spin Pnnm (purple), 616 and low-spin *Pnnm* (yellow) structures. Light green and light purple lines in (a) represent the 617 618 equations of state using the parameters from lines 3 and 4 of Table 1, respectively. Error bars reflect uncertainties in the lattice parameters from this study, and when not visible reflect that 619 620 errors are smaller than the symbols. 621 Figure 3. Integrated X-ray diffraction patterns of FeOOH at five increasing pressure steps from 622 bottom to top: 44.3 GPa (red), 44.6 GPa, 45.0 GPa, 45.9 GPa, and 46.6 GPa (black), illustrating 623 the structural transition in this pressure interval. Miller indices of ε -FeOOH are shown in red for 624 the lower-pressure *Pnnm* structure, and in black for the higher-pressure, presumably low-spin, 625 structure that is approximately 10% smaller. The Miller indices for the pressure medium (Ne) 626 and gasket material (Re) are shown in grey. 627 628 **Figure 4.** Ambient pressure infrared spectra of $P2_1nm \varepsilon$ -FeOOH in the (a) lattice and OH-629

630 bending vibrations region and (b) OH-stretching region.

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Figure 5. Evolution of the O-H bending frequencies of FeOOH as a function of pressure. The
pressure of the P2₁nm → Pnnm transition is indicated by a black dashed line. Different colors are
used to distinguish the five replicate samples from this study using either Ne as a pressure
medium (red, orange) or KBr as a pressure medium (green, blue, purple).
Figure 6. Optical absorption data, including (a) representative optical transmission spectra,

638 indicating the pressure dependent increase in the absorption of ε -FeOOH, and (b) data from five 639 samples of ε -FeOOH, each indicated with a different symbol (diamonds, squares, circles,

640 triangles, and horizontal dashes), showing the change in the ratio of transmitted light (I) to

incident light (I_{θ}) as a function of pressure (X-axis) and the wavelength of the incident light, 641 which is indicated by color. 642 643 **Supplemental Information** 644 645 **Table S1.** Lattice parameters and unit cell volumes of ε -FeOOH based on X-ray diffraction 646 measurements. Values in parentheses reflect uncertainties. (ATTACHED CSV FILE) 647 648 Figure S1. Residuals from the third-order Birch-Murnaghan equation of state fit to ε -FeOOH 649 volume-pressure data from 0 to 45 GPa (Table 1, line 1). Closed black symbols show data 650 collected during compression and open symbols show data collected during decompression. 651 652 **Figure S2.** Eulerian strain (f) versus the normalized pressure (F) of ε -FeOOH, using a V_0 of 653 65.87 Å³ (Table 1, line 1). Closed black symbols show data collected during compression and 654 open symbols show data collected during decompression. 655 656 Figure S3. Stacked high-pressure IR spectra of ε -FeOOH including (a) lattice and OH-bending 657 658 vibrations region and (b) OH-stretching region. Spectra are color coded according to pressure, which are indicated (in GPa) in the legend. 659 660 Figure S4. The % maximum FTIR signal intensity collected through the FeOOH sample as a 661 662 function of pressure. Filled and open symbols are use to indicate duplicate samples used in this study. Dashed red line indicates the predicted pressure of the HS \rightarrow LS transition from Gleason 663 et al. 2013. 664

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a) $P2_1 nm$, ordered hydrogen



b) Pnnm, disordered hydrogen



c) *Pnnm*, symmetric hydrogen



Figure 2





Figure 3





Figure 6

