



## RESEARCH ARTICLE

High-Pressure Geophysical Properties of  $Fcc$  Phase  $FeH_x$ 

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## Key Points:

- X-ray diffraction and nuclear resonant inelastic X-ray scattering were performed on  $fcc$   $FeH_x$  to determine densities and sound velocities to 82 GPa
- The Earth's outer core may contain up to 0.8–1.3 wt % hydrogen based on matching the density and velocities of variable stoichiometry iron hydrides to PREM
- The hydrogen content of Earth's core is highly dependent on the influence of temperature on the Birch's law relationship in iron alloys

## Supporting Information:

- Supporting Information S1

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**Abstract** Face centered cubic ( $fcc$ )  $FeH_x$  was synthesized at pressures of 18–68 GPa and temperatures exceeding 1,500 K. Thermally quenched samples were evaluated using synchrotron X-ray diffraction (XRD) and nuclear resonant inelastic X-ray scattering (NRIXS) to determine sample composition and sound velocities to 82 GPa. To aid in the interpretation of nonideal ( $X \neq 1$ ) stoichiometries, two equations of state for  $fcc$   $FeH_x$  were developed, combining an empirical equation of state for iron with two distinct synthetic compression curves for interstitial hydrogen. Matching the density deficit of the Earth's core using these equations of state requires 0.8–1.1 wt % hydrogen at the core-mantle boundary and 0.2–0.3 wt % hydrogen at the interface of the inner and outer cores. Furthermore, a comparison of Preliminary Reference Earth Model (PREM) to a Birch's law extrapolation of our experimental results suggests that an iron alloy containing ~0.8–1.3 wt % hydrogen could reproduce both the density and compressional velocity ( $V_p$ ) of the Earth's outer core.

## 1. Introduction

Earth's core is composed of an iron-rich alloy with the inclusion of light elements necessary to compensate for the 5–10% difference between seismically determined core densities and the density of pure iron at relevant pressure and temperature ( $P$ - $T$ ) conditions (Birch, 1952). As the most abundant and lightest element in the solar system, hydrogen is a plausible contributor to this core density deficit (e.g., Williams & Hemley, 2001). Iron hydride formation at Earth's surface is unlikely because the equilibrium hydrogen solubility in iron at atmospheric conditions is prohibitively low. However, as hydrogen solubility increases with pressure, so does the likelihood of  $FeH_x$  formation within the Earth's interior (Fukai & Akimoto, 1983). Nearly stoichiometric iron hydride ( $FeH_x$ ,  $X \sim 1$ ) has been shown to result from either the reaction of Fe and hydrous silicates (Yagi & Hishinuma, 1995) or the reaction of Fe and water at lower mantle conditions (Ohtani et al., 2005). Within the known iron hydride phase diagram, the face-centered cubic ( $fcc$ ) structure is considered the most stable structure at high temperatures, rendering it more important for extrapolation to core  $P$ - $T$  conditions than the  $bcc$  or  $hcp$  structures (Pépin et al., 2014). Despite its importance, experimental and *ab initio* efforts have yet to agree on the equation of state parameters needed to describe the compressional behavior of  $FeH_x$  (Badding et al., 1991; Fukai et al., 2003; Hirao et al., 2004; Pépin et al., 2014). To constrain the extent to which hydrogen contributes to the density deficit of the Earth's core, it is necessary to establish the compressional wave velocity-density ( $V_p$ - $\rho$ ) relationship of iron hydrides. New experimentally determined sound velocities of  $fcc$   $FeH_x$  are reported here. These values are combined with literature values to determine, via Birch's law, the influence of the nonstoichiometric hydrogen on the  $V_p$ - $\rho$  relationship of iron.

## 2. Methods

## 2.1. Sample Synthesis

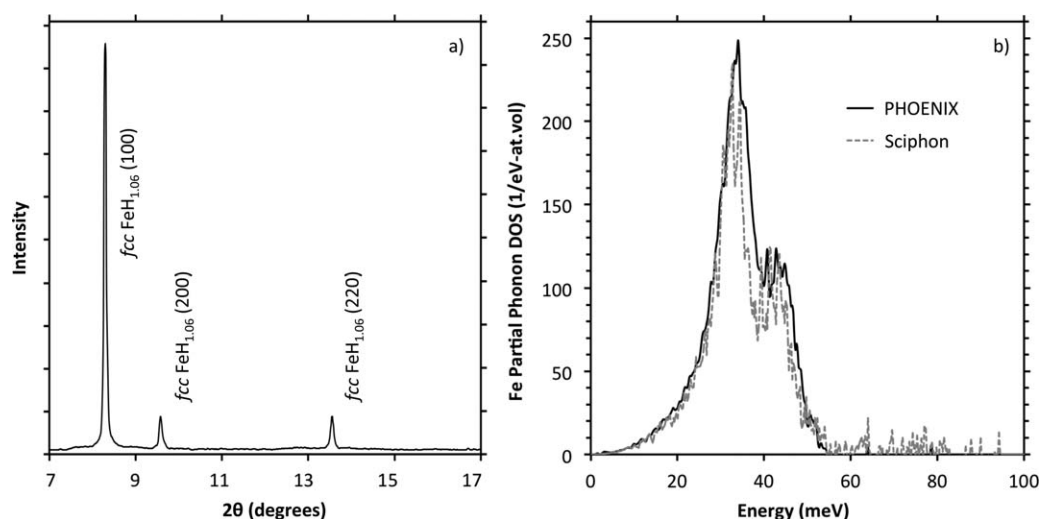
Two sample geometries were used in this study—one geometry for X-ray diffraction (XRD) experiments only (see section 2.2), and a second geometry for samples on which both Nuclear resonant inelastic X-ray scattering (NRIXS) and XRD experiments were performed (see section 2.3). XRD-only samples were composed of a 3–5  $\mu\text{m}$  thick, 30–50  $\mu\text{m}$  diameter natural iron foil (99.9% purity, Alfa Aesar) pressed between an

upper layer of  $C_nH_{2n+2}$  paraffin (100% purity, Candlewic), which served as the hydrogen source, and a lower layer of MgO, which served as pressure medium and secondary pressure standard. Paraffin was chosen as a hydrogen source based on the recent successful synthesis of *fcc* FeH demonstrated by Narygina et al. (2011). Additionally, we found no increased occurrence of diamond failure in these samples, presumably indicative of relatively low rates of hydrogen embrittlement. Sample pressures in this geometry were monitored using the Raman shift of the diamond peak (Akahama & Kawamura, 2007) and the equation of state for MgO (Matsui et al., 2000). These XRD-only samples were loaded into Re-gaskets pre-indented to  $\sim 27$  GPa. In the second geometry, samples were composed of individual 3–5  $\mu\text{m}$  thick, 30–50  $\mu\text{m}$  diameter iron foils of 20–95%  $^{57}\text{Fe}$  enrichment ( $>98\%$  purity, Cambridge Isotope Laboratories) pressed between two layers of  $C_nH_{2n+2}$  paraffin (100% purity, Candlewic) that served as both hydrogen source and pressure medium. A small ( $<10 \mu\text{m}$ ) ruby ball was included in the sample chamber adjacent to the iron foil, to enable pressure determination via the established pressure dependence of the ruby  $R_1$  luminescence line (Mao et al., 1986). These samples, prepared for both XRD and NRIXS experiments, were loaded into pre-indented Be-gaskets with boron-epoxy inserts. Samples of both configurations were loaded into  $\sim 70$  micron sample chambers in preindented gaskets, using panoramic or symmetric diamond anvil cells with 150–300  $\mu\text{m}$  culet anvils.

## 2.2. Synchrotron X-Ray Diffraction

Double-sided laser-heating synthesis was performed at beamline 13-ID-D (GSECARS) at the Advanced Photon Source (APS) of Argonne National Laboratory, where the formation of *fcc*  $\text{FeH}_x$  was monitored using in situ angle-dispersive XRD. Samples were simultaneously laser-heated on both sides using a flat-top profile laser, and laser power was adjusted upstream and downstream throughout heating to minimize axial temperature gradients, such that upstream/downstream differences were  $\sim 4\%$  of the sample temperature. Temperatures were determined via spectroradiometry using the greybody approximation (Prakapenka et al., 2008). Diffraction measurements utilized a monochromatic incident X-ray beam ( $\lambda = 0.3344 \text{ \AA}$  or  $0.2952 \text{ \AA}$ ) with a 3  $\mu\text{m}$  by 4  $\mu\text{m}$  focus size at full-width at half-maximum. Additional details of sample synthesis including  $P$ – $T$ – $V$  information can be found in supporting information Table S1. Sample-to-detector distances and tilt were calibrated using 1-bar diffraction of  $\text{LaB}_6$ . DIOPTAS was used to produce  $2\theta$  plots (Prescher & Prakapenka, 2015), and PeakFit [*Systat Software*] was used to fit individual Gaussian peaks in the resultant integrated patterns to determine lattice parameters as a function of pressure.

Preheating XRD confirmed that initial sample foil composition at high pressure was *hcp* iron, and in situ high-temperature diffraction established the formation of *fcc*  $\text{FeH}_x$  at temperatures of, or exceeding, 1,500 K (supporting information Table S1). Although the peak synthesis temperatures of this study at times exceeded the melting



**Figure 1.** (a) Measurements of quenched nonstoichiometric ( $X \sim 1.06$ ) *fcc*  $\text{FeH}_x$  at 64 GPa, including (a) Integrated X-ray diffraction with  $\text{FeH}_x$  peaks are labeled with their respective Miller indices, and (b) Fe partial phonon density of states (DOS). The DOS indicated by the solid black line was obtained using the PHOENIX program (Sturhahn, 2000), and dotted grey line is the DOS obtained from Sciphon 1.0.3 (Dauphas et al., 2014).

curve reported by Sakamaki et al. (2009), this discrepancy may be attributed to the different eutectic melting systems in these studies, which were on opposite sides of the FeH composition. High  $P$ - $T$  conditions were held until all *hcp* iron peaks diminished, at which point the sample was thermally quenched by shutting off laser power. Postheating room-temperature patterns were evaluated to confirm quenching of *fcc* FeH<sub>x</sub> (Figure 1). Preheating and postheating sample pressures determined using the Raman shift of the diamond peak revealed a postheating pressure decrease ( $\sim 0.5$  GPa), consistent with the transition to a higher density phase. The reaction sequence previously described by Narygina et al. (2011) ( $\text{Fe} + \text{C}_n\text{H}_{2n+2} \rightarrow 2\text{Fe}_3\text{C} + 3\text{H}_2 \rightarrow 6\text{FeH} + 2\text{C}$ ) was not consistently observed, as no attempt was made to evaluate this transformation with low temperature ( $< 1,500$  K) diffraction. Additionally, the obtained phase assemblage (supporting information Table S1) did not consistently indicate the presence of diamond, likely due to diamond's poor diffraction properties, particularly when synthesized at low temperatures (Zeng et al., 2017). Though the formation of *fcc* FeH<sub>x</sub> could be confirmed using at minimum the (111) and (200) peaks, the presence of iron carbide was not detected via XRD.

### 2.3. Nuclear Resonant Inelastic X-Ray Scattering

Sample synthesis for NRIXS experiments relied on the sample geometry described previously in 2.1 in panoramic-type diamond anvil cells. After starting materials were loaded, FeH<sub>x</sub> was synthesized at the University of Chicago via single-sided laser heating with a 1,064 nm Yb-doped fiber laser. Temperatures were determined by multispectral imaging radiometry (Campbell, 2008) and reported uncertainties reflect the temperature gradient typical of one-sided laser heating of a thin foil sample. To homogenize the synthesized sample the laser, producing a  $\sim 15$   $\mu\text{m}$  diameter heated spot, was slowly rastered across the sample chamber, avoiding the outermost edges nearest the gasket. Post-synthesis synchrotron XRD to confirm the conversion of iron to *fcc* FeH<sub>x</sub> and evaluate sample stoichiometry was performed at 13-ID-D (as previously described) or at 13-BM-C using a monochromatic incident X-ray beam ( $\lambda = 0.434$  Å). Initially, diffraction patterns were obtained at each postsynthesis pressure step to monitor stoichiometric changes in the quenched sample. In the final sample this was deemed unnecessary as the stoichiometry of each sample was found to depend on the  $P$ - $T$  conditions of formation and not post-quench pressure changes.

Ambient temperature NRIXS experiments on thermally quenched *fcc* FeH<sub>x</sub> were performed at Sector 3 of APS, Argonne National Laboratory. NRIXS spectra were obtained using an incident X-ray energy tuned within  $\pm 100$  meV around the nuclear transition energy of <sup>57</sup>Fe (14.4125 keV), an X-ray beam of approximately 15  $\mu\text{m}$  diameter (FWHM) and an energy resolution of 1 meV in the first experimental run and 2 meV in the second run. Three avalanche photodiode detectors, positioned equidistant around the panoramic DAC, collected time-delayed  $K_{\alpha, \beta}$ -fluorescence emitted from the excitation of the enriched iron sublattice due to the incident X-ray beam. The storage ring was operated in top-up mode with 24 bunches separated by 153 ns, allowing for the detection of nuclear resonant scattering during the time window following initial excitation. Multiple  $\sim 45$  minute NRIXS scans were collected at each pressure step and stacked to maximize counts with total per sample accumulation times of 10–21 h, increasing the signal to noise ratio. The collected *fcc* FeH<sub>x</sub> spectral form was found to be distinct from that of pure Fe or *dhcp* FeH<sub>x</sub> (Mao et al., 2004). Stacked spectra were analyzed using both PHOENIX (Sturhahn, 2000) and Sciphon 1.0.3 (Dauphas et al., 2014) to extract the partial phonon density of states (pDoS) from the iron sublattice using a quasiharmonic model (Figure 1b).

### 2.4. Synchrotron Mössbauer Spectroscopy

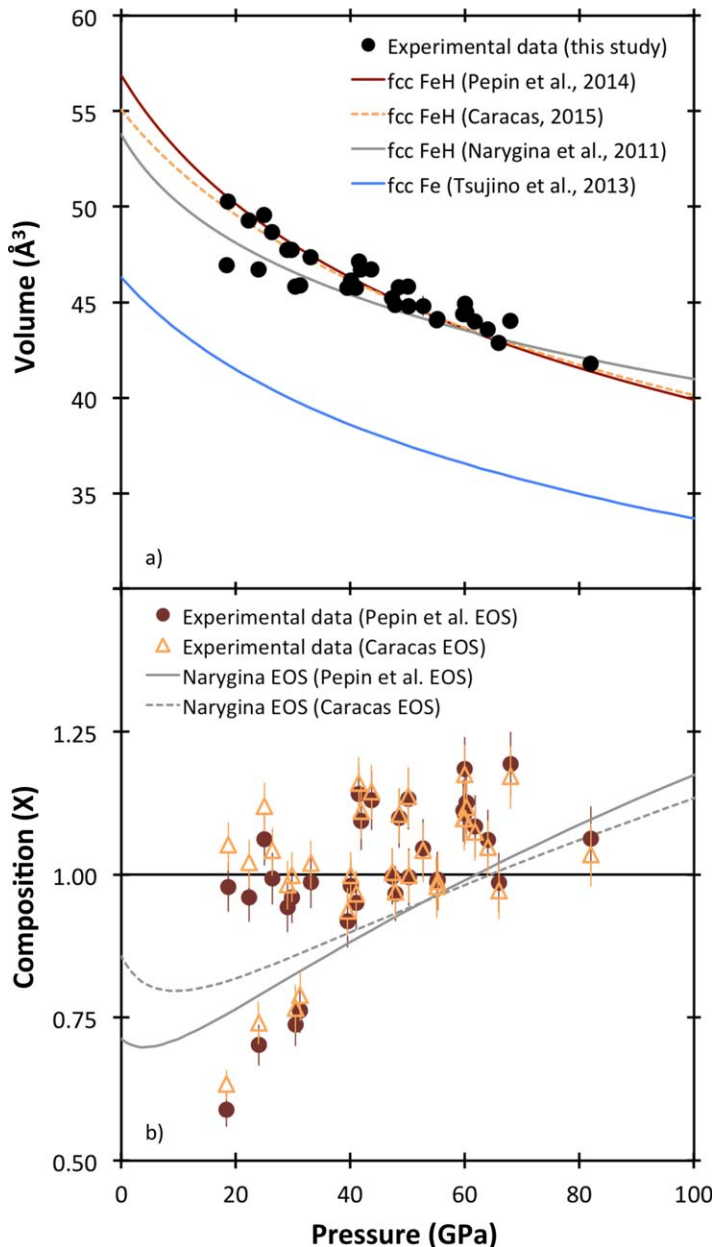
Room-temperature forward scattering synchrotron Mössbauer spectra of thermally quenched *fcc* FeH<sub>x</sub> samples were collected at beamline 3-ID-B of the Advanced Photon Source, Argonne National Laboratory using a fourth detector in line with the incident X-ray beam path. These experiments were performed contemporaneously to the 64 and 82 GPa NRIXS measurements using the same samples. A thin plate of FeSO<sub>4</sub> · 7H<sub>2</sub>O<sub>4</sub> (IS = 1.34 mm/s, QS = 3.16 mm/s) introduced into the beam path was used as a reference to obtain the isomer (central) shift. Resultant SMS spectra were evaluated using the CONUSS program (Sturhahn, 2000) to determine the magnetic properties, isomer shift,

**Table 1**

Third-Order Birch-Murnaghan Equation of State Parameters for Interstitial Hydrogen in Iron Hydride, Including Ambient-Pressure Volume ( $V_0$ ), Ambient-Pressure Bulk Modulus ( $K_0$ ), and Its Pressure Derivative ( $K_0'$ )

EoS	$V_0$ (Å <sup>3</sup> )	$K_0$ (GPa)	$K_0'$
Based on Caracas (2015)	2.232(0)	181.3(1)	3.18(1)
Based on Pépin et al. (2014)	2.684(3)	63.14(5)	3.82(1)

Note. Values in parentheses are uncertainties in the last digit.



**Figure 2.** (a) Experimental  $P$ - $V$  data from this study (black circles) compared to an  $fcc$  iron equation of state (blue), a previously reported  $fcc$  FeH equation of state (grey), and the two new synthetic  $fcc$  FeH <sub>$x$</sub>  equations of state reported in this study, based on Pépin et al. (2014) (red) and Caracas (2015) (orange). Error bars show uncertainty of experimental data points, and when not evident reflect errors not exceeding the size of the symbol itself. (b) Calculated sample stoichiometries of FeH <sub>$x$</sub>  as a function of pressure calculated using the hydrogen equation of state based on Pépin et al. (2014) (red solid circles) and Caracas (2015) (open orange triangles). The equation of state for stoichiometric ( $X = 1$ )  $fcc$  FeH reported by Narygina et al. (2011) has been re-evaluated using the both synthetic equations of state reported here. Both experimental data and equations of state are plotted at room temperature (300 K).

and quadrupole splitting of  $fcc$  FeH <sub>$x$</sub>  as a function of pressure (supporting information Figure S2).

### 3. Results

#### 3.1. Equation of State and Sample Stoichiometry

Determining the stoichiometry of metal hydrides is difficult owing to the small X-ray cross-section of hydrogen. However, it is possible to make informed estimates of the amount of hydrogen dissolved in the phase based on cell volumes and the well-established behavior of pure  $fcc$  iron. Hydrogen content of FeH <sub>$x$</sub>  can be estimated using the formula:

$$x = (V_{FeHx} - V_{Fe}) / \Delta V_H \quad (1)$$

in which  $V_{FeHx}$  and  $V_{Fe}$  are unit cell volumes of iron hydride and pure iron metal, respectively, and  $\Delta V_H$  is a predetermined volume expansion due to a single formula unit of interstitial hydrogen. The value of  $\Delta V_H$  is not precisely known for iron hydrides, and previous studies have utilized fixed values ranging from 1.8 to 2.6 Å<sup>3</sup> (Antonov et al., 1998; Badding et al., 1991; Fukai, 2005; Narygina et al., 2011). The basis for these approximations is the interstitial volumes associated with other 3d-transition metal hydrides or deuterides (e.g., CoH; Fukai, 2005) at ambient pressure. Variations in  $\Delta V_H$  can substantially alter the assumed stoichiometry of a sample, and the assumption that this value is fixed across all pressures may result in erroneous equations of state.

This study instead leverages more realistic interstitial hydrogen volumes that vary as a function of pressure. We utilize two different interstitial hydrogen equations of state, one based on  $hcp$  FeH <sub>$x$</sub>  calculations of Caracas (2015) and one based on the experimental  $dhcp$  FeH results of Pépin et al. (2014). No comparable work on the equation of state of  $fcc$  FeH is available, so we rely on the interstitial H volume in these closely related structures. In both cases, the  $V$ - $P$  relationship of interstitial hydrogen in FeH <sub>$x$</sub>  was determined by evaluating the difference in volume between the volumes of iron hydride and pure  $hcp$  iron at the same pressure. The reference volume of pure iron used with the Caracas (2015) data set was the iron curve presented in that same work, while an empirical  $hcp$  iron equation of state by Dewaele et al. (2006) was used for the Pépin et al. (2014) dataset. This synthetic  $V$ - $P$  data for hydrogen in FeH <sub>$x$</sub>  was fit to a third-order Birch-Murnaghan (BM) equation of state (Birch, 1978):

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

which relates pressure ( $P$ ), volume ( $V$ ), ambient pressure bulk modulus ( $K_0$ ), and its pressure derivative ( $K'_0$ ) in terms of finite Eulerian strain ( $f_E$ ):

$$f_E = \frac{1}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \quad (3)$$

which is a measure of the volume compression of a solid relative to its initial volume ( $V_0$ ). The resultant equation of state parameters for interstitial hydrogen in iron hydrides are reported in Table 1. A known trade-off exists between reference volume ( $V_0$ ) and bulk modulus ( $K_0$ ), such that both experimentally and

**Table 2**

Geophysically Relevant Parameters of Sample at Time of NRIXS Measurement Including Pressure (P), Stoichiometry in Formula Units Hydrogen (X), Density ( $\rho$ ), Bulk Modulus (K), Shear Modulus ( $\mu$ ), Compressional Wave Velocity ( $V_P$ ), Debye Velocity ( $V_D$ ), and Shear Wave Velocity ( $V_S$ )

P (GPa)	EoS	X	$\rho$ (kg·m <sup>-3</sup> )	K (GPa)	$\mu$ (GPa)	$V_P$ (km·s <sup>-1</sup> )	$V_D$ (km·s <sup>-1</sup> )	$V_S$ (km·s <sup>-1</sup> )
18.4(2)	C	0.63(4)	8.14(1)	232(1)	83(1)	6.49(5)	3.59(7)	3.20(7)
18.4(2)	P	0.59(3)	8.14(1)	212(1)	84(1)	6.30(5)	3.59(7)	3.20(7)
29.0(3)	C	0.98(4)	7.94(1)	277(1)	136.5(8)	7.61(2)	4.63(3)	4.15(3)
29.0(3)	P	0.94(4)	7.93(1)	250(1)	137.1(9)	7.39(2)	4.63(3)	4.16(3)
41.0(4)	C	0.97(5)	8.28(1)	326(1)	148.2(9)	7.96(3)	4.73(4)	4.23(4)
41.0(4)	P	0.95(5)	8.28(1)	300(1)	149(1)	7.76(3)	4.73(4)	4.24(4)
64.0(6)	C	1.05(5)	8.83(1)	416(1)	172(1)	8.55(3)	4.94(5)	4.42(5)
64.0(6)	P	1.06(5)	8.83(1)	390(1)	173(1)	8.38(3)	4.94(5)	4.42(5)
82.0(8)	C	1.04(6)	9.21(1)	484(1)	183(1)	8.90(3)	5.01(6)	4.46(5)
82.0(8)	P	1.06(6)	9.21(1)	460(1)	184(2)	8.75(4)	5.00(5)	4.47(5)

Note. Sound velocities below were determined using PHOENIX software (Sturhahn, 2000). Parameters are shown as calculated using both *fcc* FeH<sub>x</sub> equations of state rooted in the Caracas (2015) hydrogen values (denoted as "C" below) and the Pépin et al. (2014) hydrogen volumes (denoted "P"). Values in parentheses reflect uncertainties.

theoretically grounded equations of state provide reasonable, and not dissimilar, estimates of interstitial hydrogen compressibility.

The two interstitial hydrogen equations of state were combined with an experimental equation of state (EoS) for *fcc* iron (Tsuji et al., 2013) to enable the determination of sample stoichiometry in our experiments (Figure 2, supporting information Table S1), using equation (1) with  $\Delta V_H$  from the equations of state for interstitial H in FeH<sub>x</sub> (Table 1). These sample stoichiometries were subsequently used to interpret the resultant phonon density of states and Mössbauer hyperfine field parameters. Here it is assumed that  $\Delta V_H$  is identical in both *fcc* and *hcp* FeH, because of the similarity of interstitial sites in these structures. While the stoichiometries of our samples cluster around X = 1, there is scatter, particularly in at low pressures (<35 GPa). No systematic covariation was observed linking temperature of synthesis, heating duration, or sample geometry to stoichiometry. It is possible that local variation, at the scale of the laser heated spot, in the paraffin:Fe ratio of the sample led to reduced hydrogen enrichment at some P-V points. Based on the congruence of FeH<sub>x</sub> volumes and inferred stoichiometries (and velocities, described below) presented herein and earlier work in carbon-free (with respect to starting materials) Fe-H systems (e.g., Mao et al., 2004), we infer that during synthesis only negligible amounts of carbon entered the iron hydride.

In addition to evaluating the stoichiometry of our own samples, our synthetic FeH equations of state based on combining the EoS of pure *fcc* iron (Tsuji et al., 2013) with the addition of hydrogen

**Table 3**

Birch's Law Parameters Calculated Using both *fcc* FeH<sub>x</sub> Equations of State Rooted in the Caracas (2015) (Denoted "C") and the Pépin et al. (2014) (Denoted "P") Hydrogen Volumes

EoS	a (k·m·s <sup>-1</sup> )	b (m <sup>4</sup> ·kg <sup>-1</sup> ·s <sup>-1</sup> )	c (dimensionless)	Data included in fit
C	-4 (fixed)	1.206 (fixed)	1.72(8)	This study; Shibazaki et al. (2012); Mao et al. (2004)
C	-4 (fixed)	1.206 (fixed)	1.80(7)	This study
C	-5.1(7)	1.31(7)	2.0(2)	This study; Shibazaki et al. (2012); Mao et al. (2004); Antonangeli et al. (2012); Ohtani et al. (2013)
P	-4 (fixed)	1.206 (fixed)	1.73(9)	This study; Shibazaki et al. (2012); Mao et al. (2004)
P	-4 (fixed)	1.206 (fixed)	1.7(1)	This study
P	-4.9(8)	1.30(7)	1.9(2)	This study; Shibazaki et al. (2012); Mao et al. (2004); Antonangeli et al. (2012); Ohtani et al. (2013)

Note. Input sound velocities ( $V_P$ ) have been calculated from NRIXS data using PHOENIX (Sturhahn, 2000) software, while parameters determined using  $V_P$  determined using Sciphon are in supporting information Table S2. Values in parentheses are uncertainties in last digit



determined both theoretically and experimentally (Caracas, 2015; Pépin et al., 2014) were used to reevaluate the previously published EoS of *fcc* FeH<sub>x</sub> by Narygina et al. (2011) (Figure 2b). This comparison illuminates an important discrepancy as shown in Figure 2a, namely that the Narygina et al. (2011) EoS requires interstitial hydrogen to exhibit a negative bulk modulus, as the volume difference between their FeH isotherm and that of pure *fcc* iron increases with increasing pressure. The results of Narygina et al. (2011) might instead be better interpreted as a pressure-dependent evolution of stoichiometry, an interpretation that could also explain the unusually large bulk modulus pressure derivative ( $K' = 11.7$ ) reported in their study.

### 3.2. Nuclear Hyperfine Interactions

Synchrotron Mössbauer spectra of *fcc* FeH<sub>x</sub> at 64 and 82 GPa consist of a single broad feature (supporting information Figure S1). The 64 GPa hyperfine fields were best fit by model with a single iron sublattice site while the 82 GPa hyperfine fields were best fit by a model with a second site, consistent with a slightly distorted cubic system, possibly due to the room-temperature compression of the sample post-synthesis. The quadrupole splitting (QS) of a material using SMS is determined by fitting the experimental spectra to a model, and is indicative of the degree to which an electric field gradient has caused nuclear splitting in the iron sublattice, and to a lesser extent, the coordination of iron. If present, a pressure-induced spin transition (HS → LS) would lead to a dramatic increase in the value of QS (Bengtson et al., 2009; Catalli et al., 2011; Hsu et al., 2010; Li et al., 2006), but as no such change in the value of QS between

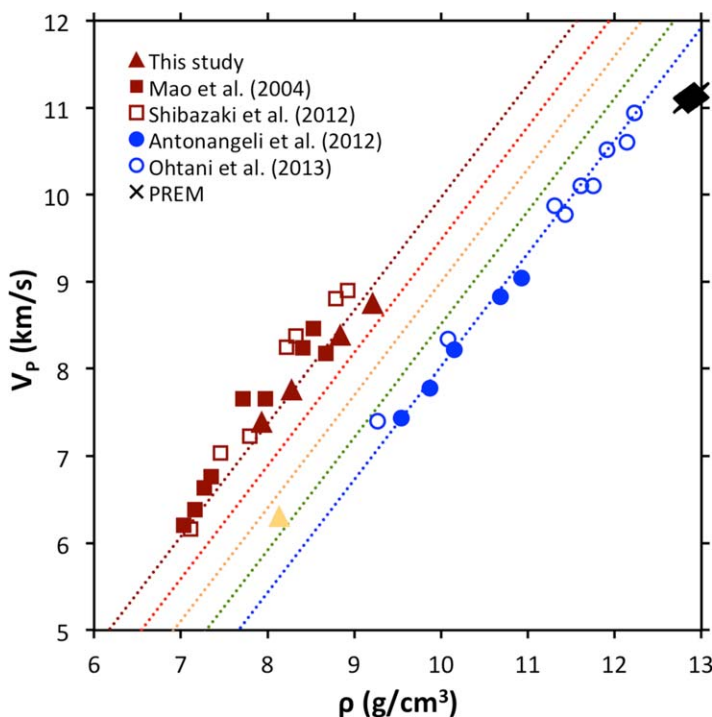
the 64 and 82 GPa spectra from this experiment (Table 1) a spin transition appears unlikely in *fcc* FeH<sub>x</sub> in this pressure range. Spectra at both pressures have similar (isomer) central shifts (CS) with respect to  $\alpha$ -iron at comparable pressure, are in reasonable agreement with the CS previously reported by Narygina et al. (2011) at 47 GPa, and are distinct from the central shift reported for either the *dhcp* or *hcp* phases (supporting information Table S2). In agreement with previous studies, the *fcc* phase of FeH<sub>x</sub> is not ferromagnetic, in contrast to that of the *dhcp* and *hcp* phases (Narygina et al., 2011; Tsumuraya et al., 2012), and as such SMS functions as a secondary confirmation of the structure of our samples, as there is no evidence of magnetic hyperfine field splitting in the measured spectra.

### 3.3. Sound Velocities and Geophysical Parameters

Coupled with quasihydrostatic XRD data and two *fcc* FeH equations of state to provide appropriate parameters, NRIXS provides velocity-density ( $V_{p-\rho}$ ) information for comparison against seismic measurements. The Debye velocity ( $V_D$ ) was determined from the calculated pDoS using both PHOENIX (Sturhahn, 2000) and Sciphon (Dauphas et al., 2014), assuming Debye-like behavior at low energies and fitting the low energy (~3.8–16.2 meV) region to a parabola (Table 2). Once a Debye velocity was obtained by fitting the partial phonon density of state curve, additional equation of state information was incorporated to extract compressional ( $V_p$ ) and shear velocities ( $V_s$ ) using the following equation (Mao et al., 2001):

$$\frac{3}{V_D^3} = \frac{1}{V_p^3} + \frac{2}{V_s^3} \quad (4)$$

In this study, the necessary input parameters ( $K$ ,  $\rho$ ), as well as stoichiometric information, were obtained from the two previously described FeH<sub>x</sub> equations of state. The shear moduli ( $\mu$ ) are fit using the sample density and shear velocity, based on the definition  $\mu = \rho V_s^2$ . Sound velocities determined from PHOENIX software are reported in Table 2; and comparable values determined using Sciphon, as well as the mean interatomic force constants ( $\Phi$ ) and Lamb-Mössbauer factor ( $f_{LM}$ ), are included in supporting information Table S2. These parameters



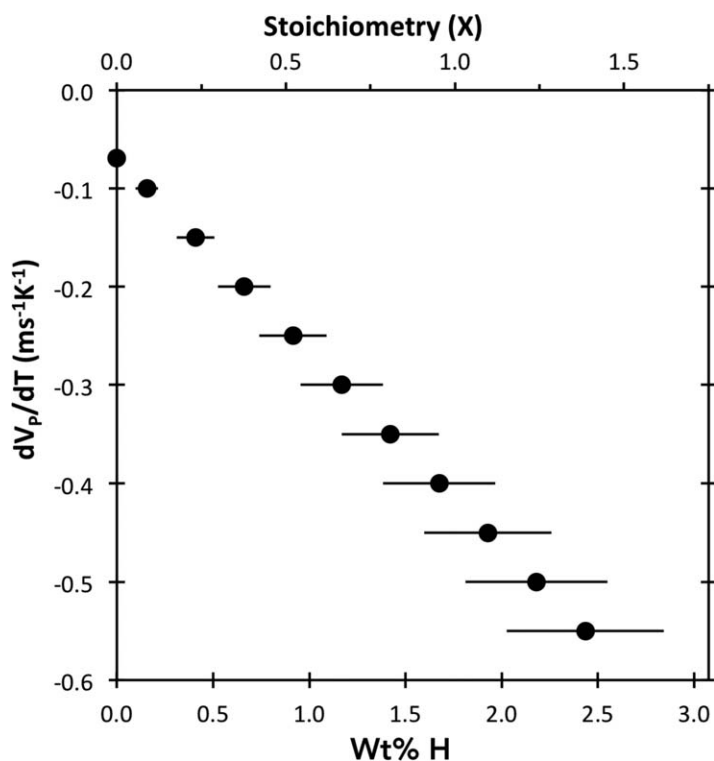
**Figure 3.** Birch's Law extrapolation of the influence of hydrogen stoichiometry on the velocity-density ( $V_{p-\rho}$ ) relationship in iron hydrides. Dotted lines indicate Birch's law parameterization for varying FeH<sub>x</sub> stoichiometries, including  $X = 0$  (blue),  $X = 0.25$  (green),  $X = 0.5$  (orange),  $X = 0.75$  (red), and  $X = 1$  (maroon). Experimental data include *fcc* FeH<sub>x</sub> (triangles), *dhcp* FeH<sub>x</sub> (squares), and *hcp* iron (circles) and individual data points have been color coded to reflect the approximate sample stoichiometry. Error bars do not exceed the size of the symbol itself. This should be edited to state, "This fit uses the hydrogen EoS based on Caracas (2015) and sound velocities were calculated using PHOENIX (Sturhahn, 2000) and equation (5). The PREM model for the inner core is represented by black crosses and all non-PREM data reflects ambient temperatures. Sample densities as plotted reflect some degree of isotopic variation (i.e., Fe<sup>57</sup> enrichment) owing to different sample preparation methods.

help to constrain the density, velocities, and moduli of *fcc* FeH<sub>x</sub> for comparison to seismic observations of Earth's core.

#### 4. Hydrogen in the Core

The Earth's core is known to be lighter than pure iron at the corresponding pressures and temperatures (Birch, 1952). The density deficit has been estimated to be 5–10% for the outer core (Anderson & Isaak, 2002; Stevenson, 1981) and 1–2% for the inner core (Jephcoat & Olson, 1987; Stixrude et al., 1997), attributable to the presence of one or more light element-bearing component(s) in the Earth's core. In addition to other elements (O, S, C, Si, etc.), hydrogen has long been considered a potentially major light component in the core (e.g., Stevenson, 1977). The amount of hydrogen needed to fulfill the density deficit can be estimated assuming an ideal mixture of pure iron and light element-bearing phases, and extrapolating the corresponding equations of state (EOSs) to core-mantle boundary (CMB) conditions (Poirier, 1994).

High-temperature Birch-Murnaghan EoSs for *fcc* iron (Tsujino et al., 2013) and *hcp* iron (Dewaele et al., 2006) were combined with our theoretically based interstitial hydrogen equations of state (Table 1) to determine the necessary hydrogen content required to match the density of the Preliminary Reference Earth Model (PREM) (Dziewonski & Anderson, 1981) at the CMB and at the inner core boundary (ICB) in *fcc* and *hcp* iron hydrides. While these synthetic equations of state reflect the thermal expansion of the iron component, no additional adjustment was made to mimic the potential thermal expansion of the interstitial hydrogen, as this relationship is unconstrained. To our knowledge no experimental measurements of the density of liquid FeH<sub>x</sub> exist, and approximations made on the basis of the known behavior of solids are the best available estimates. All CMB density calculations included a  $\delta V$  of +1.5% due to melting (Anderson & Isaak, 2000) and used CMB temperatures of  $4,000 \pm 500$  K (Anderson, 2003). Based on these calculations, the density at the CMB can be matched by an *hcp* iron hydride alloy of 1.0–1.3 wt % hydrogen or an *fcc* alloy containing 0.8–



**Figure 4.** Trade-off between the influence of increased temperature on the compression wave velocity ( $V_p$ ) of iron and the hydrogen content needed to match the  $V_p$  of the inner core boundary (ICB) based on equation (6). Modeled hydrogen contents are based on an ICB temperature of 5,500 K with error bars reflecting  $\pm 500$  K.

1.1 wt % hydrogen. A similar density calculation was made to determine the maximum hydrogen content of the Earth's inner core based on matching PREM ICB density, using an ICB temperature of  $5,500 \pm 500$  K (Anderson, 2003). This calculation indicated the ICB density can be matched an *hcp* iron hydride alloy of 0.4–0.6 wt % hydrogen or an *fcc* alloy containing 0.2–0.3 wt % hydrogen. Although the accuracy of the *fcc* iron equation of state is sufficient to determine the hydrogen contents in our FeH<sub>x</sub> samples, which are close in pressure to the stability range of *fcc* iron, the extrapolation of the *fcc* equation of state to Earth core conditions is significant. As such, hydrogen core-content estimates calculated using an *hcp* iron hydride alloy calculation to match PREM densities at the CMB and ICB (1.0–1.3 wt % and 0.4–0.6 wt %, respectively) are likely more accurate, as the *hcp* iron *P-V-T* relationship has been assessed up to inner core pressures.

Birch's law, effectively a linear extrapolation of the compressional wave velocity-density ( $V_p$ - $\rho$ ) relationship, has long been used to assess potential core constituent light elements (e.g., Badro et al., 2007). As hydrogen incorporation into the Earth's inner core is likely below 2 wt %, our sound velocities of nonstoichiometric *fcc* FeH<sub>x</sub>, as well as literature data for additional structures of FeH<sub>x</sub>, were used to extrapolate the effect of hydrogen incorporation of FeH<sub>x</sub>, using the relationship:

$$V_p = a + b\rho + cX \quad (5)$$

in which  $V_p$  is in units of  $\text{km}\cdot\text{s}^{-1}$ , density ( $\rho$ ) is in units of  $\text{kg}\cdot\text{m}^{-3}$ , and stoichiometry ( $X$ ) is in formula units. Two methods were used for this calculation. The first method fit experimental iron hydride data only (this study; Mao et al., 2004; Shibazaki et al., 2012), holding the values of  $a$  and  $b$  fixed to  $-4,000(11) \text{ m}\cdot\text{s}^{-1}$  and  $1.206(11) \text{ m}^4\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$  respectively, adopting values reported by Antonangeli and Ohtani

(2015) to describe the linear  $V_{p-\rho}$  relationship in pure iron which persists up to the pressure of Earth's inner core. In the second method, experimental iron hydride data (this study; Mao et al., 2004; Shibazaki et al., 2012), and *hcp* iron data (Antonangeli et al., 2012; Ohtani et al., 2013), were fitted together to the above equation, solving for all three parameters ( $a$ ,  $b$ , and  $c$ ). Literature data for  $\text{FeH}_x$  were reassessed using the equations of state presented herein for self-consistency within these Birch's law parameterizations, including adjustments to stoichiometry, density,  $V_S$  and, in the case of NRIXS data,  $V_p$ . These two methods were repeated using NRIXS  $V_p$  results determined using both interstitial hydrogen equations of states reported in Table 1, and results of these Birch Law calculations are reported in Table 3 and supporting information Table S3.

An example of the first method is shown in Figure 3, in which the influence of hydrogen incorporation is added to the previously determined ( $V_{p-\rho}$ ) relationship reported by Antonangeli and Ohtani (2015), and only the new variable hydrogen stoichiometry parameter ( $c$ ) is fit to equation (5). The resultant values of  $c$  reported herein reflect a significant influence of interstitial hydrogen on the  $V_{p-\rho}$  relationship of iron hydrides. The magnitude of this influence (i.e., values of  $c$ ) are indistinguishable to those reported by Umemoto and Hirose (2015) based on molecular dynamics calculations. Similarly, the experimentally determined shear wave velocities ( $V_S$ ) from this study were combined with literature values (Lin et al., 2005; Mao et al., 1998, 2004; Shibazaki et al., 2012) to parameterize the influence of interstitial hydrogen on the shear wave velocity-density ( $V_S-\rho$ ) relationship in iron hydrides (supporting information equation (S1), Table S4, and Figure S2). The differences in  $V_S$  of  $\text{FeH}_x$  between studies are much higher than for  $V_p$ , and furthermore the unknown temperature effect on  $V_S$  is likewise greater than for  $V_p$ ; consequently only the  $V_{p-\rho}$  parameterization is relied upon below to place limits on the inner core's hydrogen content.

Applying our Birch's Law parameterization (line 1 in Table 3) to ICB conditions suggests hydrogen incorporation is irreconcilable with attempts to simultaneously match the density and compressional sound velocity of Earth's inner core, as hydrogen leads to increased values of  $V_p$  relative to pure iron at a given density (Figure 3). However, this is an incomplete view, as increased temperature has been shown to have the opposite effect—i.e., pure iron ( $X = 0$ ) at high temperatures has reduced sound velocities relative to 300 K iron at a fixed density (Antonangeli et al., 2012; Decremps et al., 2014; Lin et al., 2005). Yet, although the literature reflects consensus on the general effect of temperature on the  $V_{p-\rho}$  relationship of iron, the magnitude and linearity of this effect remains contested (e.g., Antonangeli et al., 2012; Lin et al., 2005). Since there is no agreed upon temperature effect, here we evaluate the interplay between  $dV_p/dT$  and the amount of hydrogen needed to satisfy PREM. To quantify this, a linear temperature effect ( $d$ ), was added to the previously defined  $\text{FeH}_x$   $V_{p-\rho}$  relationship equation (5):

$$V_p = a + b\rho + cX + d(T - 300) \quad (6)$$

in which temperature ( $T$ ) is in kelvin. The utility of adding a temperature-dependence term to a 300 K Birch's Law fitting has been previously demonstrated (e.g., Ohtani et al., 2013). Using equation (6), we evaluated the amount of hydrogen needed to reproduce PREM ICB density and compressional velocity at an ICB temperature of  $5,500 \pm 500$  K (Figure 4). As shown in Figure 4, the greater the  $V_p$  reduction caused by high temperatures, the more hydrogen could be incorporated into the Earth's inner core while satisfying the density and velocity of PREM. It is unlikely that hydrogen could be the sole light element in Earth's core, because other candidate components (Si, O, S) are known to dissolve into the metal to varying degrees at high pressures and temperatures (Fischer et al., 2015). However, as shown in Figure 4, a hydrogen content of  $\sim 0.8\text{--}1.3$  wt %, which satisfies the core density deficit as described above, also matches the  $V_p$  profile of the inner core if the mean thermal reduction in velocity is from  $-0.22$  to  $-0.31$   $\text{m s}^{-1} \text{K}^{-1}$  for the Fe-H alloy. This further illustrates that additional high temperature sound velocity measurements of solid iron and iron alloys are greatly needed to more accurately predict the light element content of Earth's core.

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