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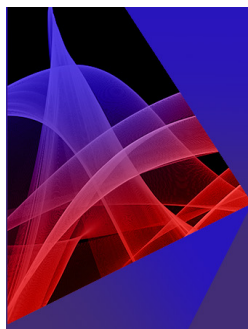
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# Direct hydrogen quantification in high-pressure metal hydrides

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## ABSTRACT

High-pressure metal hydride (MH) research evolved into a thriving field within condensed matter physics following the realization of metallic compounds showing phonon mediated near room-temperature superconductivity. However, severe limitations in determining the chemical formula of the reaction products, especially with regards to their hydrogen content, impedes a deep understanding of the synthesized phases and can lead to significantly erroneous conclusions. Here, we present a way to directly access the hydrogen content of MH solids synthesized at high pressures in (laser-heated) diamond anvil cells using nuclear magnetic resonance spectroscopy. We show that this method can be used to investigate MH compounds with a wide range of hydrogen content, from  $MH_x$  with  $x = 0.15$  ( $CuH_{0.15}$ ) to  $x \lesssim 6.4$  ( $H_{6\pm 0.4}S_5$ ).

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## I. INTRODUCTION

The theoretical prediction of high-temperature superconductivity in pressure-stabilized hydrogen-rich metal hydrides,<sup>1–3</sup> and their subsequent experimental confirmation,<sup>4–7</sup> can be considered to represent the dawn of one of the most prolific research fields within the high-pressure community in recent decades.<sup>8</sup>

The fruitful synergy between *ab initio* structure search methods<sup>9–11</sup> and electronic calculations,<sup>12,13</sup> with experimental characterization by synchrotron-based x-ray diffraction (XRD) and transport methods, provides a well-established framework for the search for novel binary or ternary metal hydride compounds with superconducting transition temperatures  $T_c$  now rapidly approaching 300 K.<sup>14</sup>

The hydrogen subsystems play a crucial role in the realization of high superconducting transition temperatures in pressure-formed metallic hydride solids,<sup>15,16</sup> and therefore precise knowledge of the content, atomic position, and electronic and vibrational properties of the H-sublattice of a metal hydride is of the utmost importance for detailed understanding of the underlying physical phenomena governing this new class of materials.

Direct access to the hydrogen subsystem via standard high-pressure methods has unfortunately turned out to be unfeasible. Indeed, hydrogen atoms are essentially invisible to XRD methods<sup>17,18</sup> owing to their possessing of just a single electron. While neutron diffraction does not suffer from this problem, it cannot routinely be used at the pressures required for stabilization of most high- $T_c$  materials.<sup>19</sup> Moreover, methods such as Raman and infrared spectroscopy struggle greatly with metallic samples.

Thus, characterization of metallic hydrides is often limited to structural investigation of the much heavier parent metal lattices, and their actual hydrogen content can only be approximately inferred from the expansion of their unit cell upon hydrogen uptake. The hydrogen positions can then be obtained by comparison with structures found to be stable in *ab initio* calculations.<sup>20–22</sup> However, there are various limitations to this approach: (i) The metal hydrides of interest cannot in most cases be synthesized in a phase-pure state. Therefore, unambiguous identification of the space group is usually difficult, especially from powder diffraction patterns. (ii) Relating the volume expansion of the unit cell to the hydrogen content relies on knowledge about volume per hydrogen as well as the other atoms at a certain pressure and (synthesis) temperature in the respective

chemical environment, which can only be approximated to a certain accuracy from analogue experiments or the respective equations of state. (iii) The calculated unit cell volumes as well as structural and dynamical stability can be influenced by a variety of parameters, and, especially for hydrides, thermal as well as nuclear quantum effects can be crucial for finding the correct structure,<sup>13</sup> but are widely not taken into account.

In summary, there is considerable potential for errors and therefore large deviations of the estimated values from the actual hydrogen content of synthesized hydride(s). Quantitative nuclear magnetic resonance (NMR) spectroscopic methods, on the other hand, are a well-established analytical tool in modern laboratories<sup>23–25</sup> and are especially suited for hydrogen-related experiments. Moreover, recent developments in *in situ* high-pressure NMR in diamond anvil cells (DACs) at pressures up to 200 GPa<sup>26–28</sup> present an outstanding opportunity for direct observation of hydrogen atoms under the relevant high-pressure conditions.

Here, we introduce a method suitable for the direct quantification of the hydrogen content in metal hydrides for a wide range of compositions and hydrogenations spanning an order of magnitude, based on the inherent relationship between signal intensity and number density of resonant nuclei<sup>29,30</sup> in *in situ* DAC NMR experiments at extreme pressures.

## II. EXPERIMENTAL DETAILS

We investigated seven metal hydrides with different hydrogen contents, namely, the copper hydrides CuH<sub>0.15</sub>, Cu<sub>2</sub>H, and CuH, iron monohydride, and the yttrium hydrides YH<sub>2</sub> and YH<sub>3</sub> as well as the tetragonal phase *t*I140 of sulfur polyhydride H<sub>6±δ</sub>S<sub>5</sub> ( $\delta \approx 0.4$ ) discovered recently by Laniel *et al.*<sup>31</sup>

DAC preparations of iron and copper hydrides are described elsewhere.<sup>28,32</sup> Pressure cells for sulfur (S-cell) and yttrium (Y-cell) hydrides were prepared in a similar fashion. Small pieces of elemental sulfur together with yttrium metal were loaded into a DAC set up for NMR experiments and loaded with paraffin oil as the pressure-transmitting medium as well as the hydrogen reservoir. The cells were precompressed to 45 GPa (Y-cell) and 65 GPa (S-cell), and their respective <sup>1</sup>H-NMR spectra were recorded using a magnetic field of 7.04 T, corresponding to a 300 MHz <sup>1</sup>H-NMR frequency. Pulse nutation experiments were used to determine optimal  $\pi/2$ -pulse excitation conditions, with long scan repetition times to allow for sufficient relaxation of the pressurized paraffin spin system (the spin–lattice relaxation time  $T_1 \approx 750$  ms). Both cells were then laser-heated with a double-sided laser heating system<sup>33</sup> to about 1500–2000 K. The corresponding <sup>1</sup>H-NMR spectra after laser heating featured additional signals, which were associated with the formation of YH<sub>3</sub> and YH<sub>2</sub> in the Y-cell (cf. Ref. 34) and H<sub>6±0.4</sub>S<sub>5</sub> [see Fig. 3(b) in Sec. III B 3] in the S-cell.

Data analysis was performed using the ONMR plugin in Origin 2019 Pro.

## III. QUANTIFICATION METHOD

The quantification method is illustrated schematically in Fig. 1(a).

### A. Background

To quantify the hydrogen content of the metal hydride compounds, we take advantage of the signal strengths in NMR

experiments being directly proportional to the amount of resonating spins contributing to the signal. The scan-normalized signal-to-noise ratio (SNR)  $\zeta$ , after single pulse excitation for infinitely short radio-frequency (RF) pulses, is given by<sup>35,36</sup>

$$\zeta = \frac{\text{SNR}}{\sqrt{N_{\text{scans}}}} = \frac{\eta N_{\text{coil}} A_{\text{coil}} \omega_0 \mu_0 M_0}{\sqrt{4 R_{\text{coil}} k_B T \Delta f}}, \quad (1)$$

where  $N_{\text{scans}}$  is the number of accumulations,  $\eta$  is the filling factor of the radio-frequency (RF) coils (i.e., the ratio between sample and resonator volumes), and  $N_{\text{coil}}$  and  $A_{\text{coil}}$  are the number of windings and the cross-section, respectively, of the resonators.  $\omega_0$  is the resonance frequency in angular units, which is directly related to the magnetic field strength via  $\omega_0 = \gamma_n B_0$ , with  $\gamma_n$  being the isotope-specific gyromagnetic ratio. The thermal Nyquist noise term [the denominator of Eq. (1)] is given by the resonator temperature  $T$ , the limiting bandwidth  $\Delta f$  (usually the inverse dwell time, or digitization frequency) and the AC resistance  $R_{\text{coil}}$  of the coil (corrected for limited penetration of the RF current in the conductive resonator structures), and the Boltzmann constant  $k_B$ .

The nuclear magnetization  $M_0$  in Eq. (1) is given by the Curie law for nuclear spins:<sup>37</sup>

$$M_0 = n \frac{\gamma_n^2 \hbar^2 I(I+1) B_0}{3 k_B T}, \quad (2)$$

where  $I$  is the nuclear spin quantum number,  $B_0$  is the external magnetic field, and the prefactor  $n = N/V$  represents the concentration of the nuclear spins contributing to the observed NMR signal.

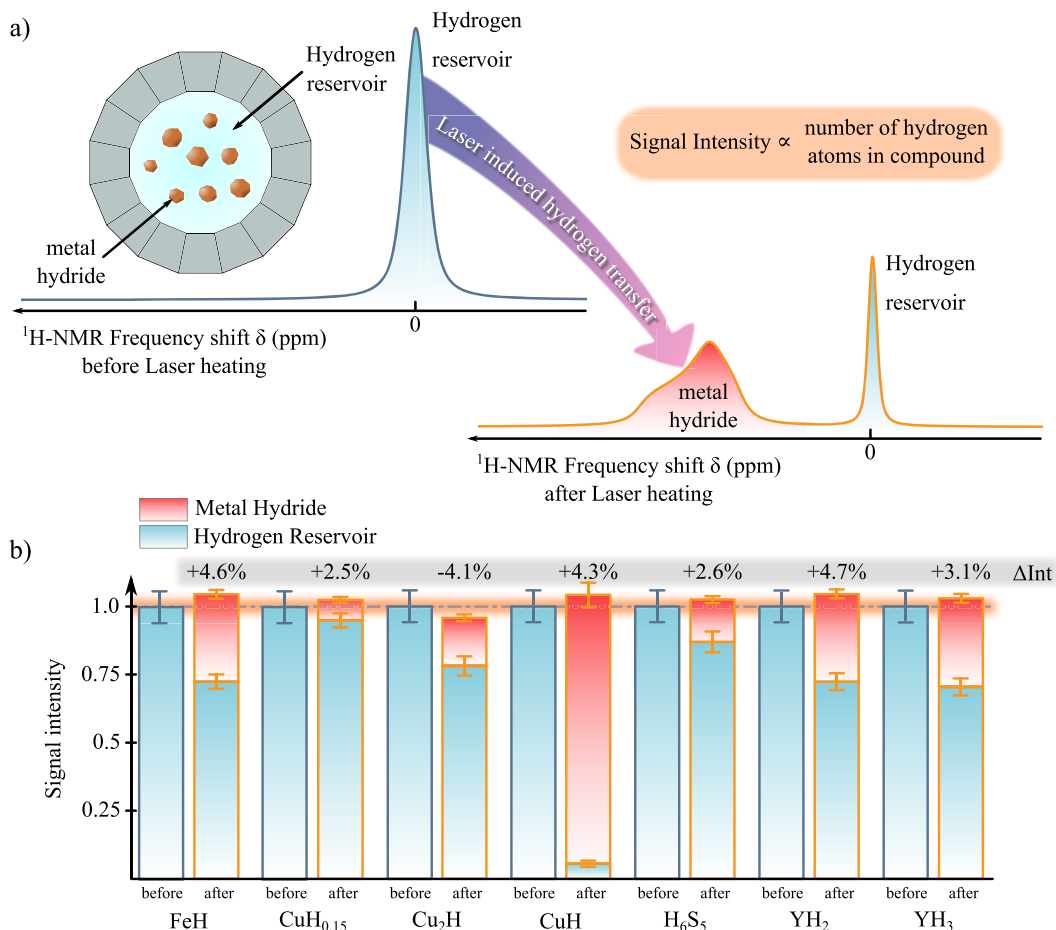
In special cases where other nuclei in the hydride possess nonzero spin (e.g., <sup>139</sup>La or <sup>89</sup>Y), it is possible to obtain the ratio of the signal contributed by each nuclei directly by comparing the resulting values of  $\zeta$ , as follows:

$$\frac{n_A}{n_B} = \frac{\zeta_A \omega_B}{\zeta_B \omega_A} \sqrt{\frac{R_B \Delta f_B}{R_A \Delta f_A}} \left( \frac{\gamma_B}{\gamma_A} \right)^2 \frac{I_B(I_B+1)}{I_A(I_A+1)}, \quad (3)$$

where the subscripts A and B indicate two separately observable nuclear species in the same sample or compound. This quantification method is akin to using an internal reference standard, in that knowledge of the relative amount of nucleus A, for example from diffraction experiments, determines the amount of nucleus B. In cases where no secondary information on nucleus A can be acquired, this method would still yield atomic ratios.

In the general case, however, only <sup>1</sup>H-NMR spectra can be acquired or hydrogen nuclei are the sole NMR-active nuclear species in the sample. In this case, for full quantification of the hydrogen content in the reaction products after laser heating, three assumptions have to be made, all of which are well justified given the experimental conditions:

1. Equation (1) is valid within the approximation of infinitely short RF pulses, i.e., partial spin relaxation within the RF excitation is negligible. This assumption is exceptionally well met in *in situ* high-pressure NMR experiments, where resonator structures are particularly small, leading to strong exciting RF magnetic fields and thus allowing excitation pulses of the order of 1  $\mu$ s or shorter.



**FIG. 1.** (a) Schematic representation of the quantification method. Before laser heating, the sample cavities are filled with powder or larger crystals of the parent metal (Cu, Fe, Y, S, etc.), as well as a suitable hydrogen reservoir such as molecular hydrogen, paraffin, or ammonia–borane. The resulting proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra contain solely signals stemming from the hydrogen-rich precursors. With thermal barriers being overcome via laser heating, hydrogen diffusion into the parent metals facilitates the formation of metal hydrides, whose <sup>1</sup>H-NMR signal intensity (i.e., signal-to-noise ratios) is proportional to the amount of hydrogen atoms in the hydride. (b) Summary of signal intensities of all recorded <sup>1</sup>H-NMR resonances before and after laser heating. Intensities are normalized with respect to the corresponding initial intensity of the hydrogen reservoir before laser heating. The sum of the intensities of metal hydride and remaining reservoir is equal to 1 within experimental error ranges for all samples. The system can therefore be considered as closed and the total amount of hydrogen nuclei in the DAC cavity as constant. The total deviation from 1 in percent is shown above the bars for the respective individual compounds.

- None of the geometric coil parameters given in Eq. (1) change significantly upon laser heating, and signal intensities are directly proportional to (a) the nuclear spin density  $n$ , (b) the filling factor of the compound  $\eta$ , and (c) the cavity volume of the DAC through the SNR:

$$\zeta \propto n\eta. \quad (4)$$

- The system is closed, i.e., the total hydrogen content in the sample chamber of the DAC remains constant, and the full experimental cavity is always probed, such that

$$N_{\text{Res}}^0 = N_{\text{Res}}^{\text{LH}} + \sum_i N_{\text{MH},i}^{\text{LH}}, \quad (5)$$

$$\eta_{\text{Res}}^0 = \eta_{\text{Res}}^{\text{LH}} + \sum_i \eta_{\text{MH},i}^{\text{LH}}, \quad (6)$$

where  $N_{\text{Res}}^0$  and  $\eta_{\text{Res}}^0$  denote the number of nuclei contributing to the respective signal and the filling factor of the signal-generating compound within the sample cavity of the DAC before laser heating.  $N_{\text{Res}}^{\text{LH}}$  and  $\eta_{\text{Res}}^{\text{LH}}$  denote the number of nuclei and the filling factor of the hydrogen reservoir (Res) and  $i$ th metal hydride (MH,  $i$ ) after laser heating, respectively.

Figure 1(b) compares normalized signal intensities before laser heating with those of the reaction products and remaining hydrogen reservoirs after heating. The sum of signal intensities and therefore the number of hydrogen nuclei can be considered

conserved, meaning that assumption 3 is valid within experimental accuracy.

Solving these equations for the hydrogen density in the reaction product,  $n_{\text{MH},i}^{\text{LH}}$ , yields (see the [supplementary material](#))

$$n_{\text{MH},i}^{\text{LH}} = n_{\text{Res}}^0 \frac{\zeta_{\text{MH},i}^{\text{LH}}}{\gamma_{\text{Res}}^0 - \zeta_{\text{Res}}^{\text{LH}} - \sum_{j \neq i} \zeta_{\text{MH},j}^{\text{LH}}} \quad (7)$$

To ensure reproducible results for these quantitative NMR experiments, it is necessary to ensure proper excitation of all contributing spin systems (using a well-defined RF excitation pulse), as well as sufficiently long pulse repetition times (to allow for full relaxation of all spin systems).

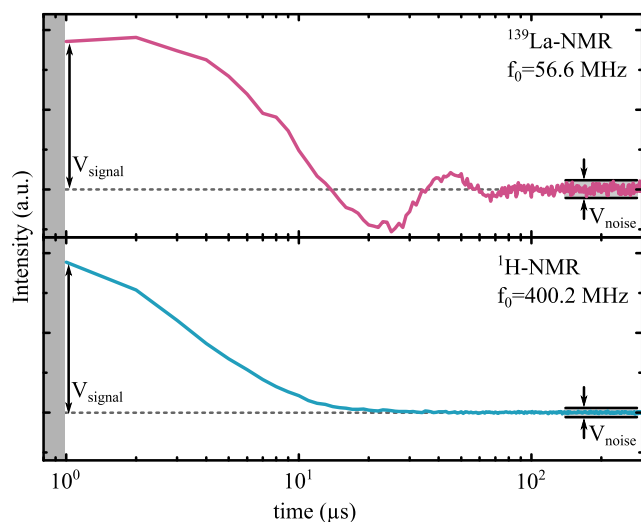
## B. Examples

We present here a detailed step-by-step procedure for hydrogen quantification experiments on three representative hydrides: lanthanum trihydride under ambient conditions and iron monohydride and sulfur polyhydride under pressure in DACs. The same steps were applied to all other investigated compounds, for which the necessary parameters for the calculation of  $n_{\text{MH}}^{\text{LH}}$  are given in the [supplementary material](#).

A detailed study of other NMR parameters (e.g., Knight shifts, linewidths, and relaxation times), as well as their physical interpretation, can be found in Refs. 28, 32, and 34.

### 1. Lanthanum trihydride

Figure 2 shows time-domain signals of both  $^{139}\text{La}$  and  $^1\text{H}$  from a commercially available sample of  $\text{LaH}_3$  (Sigma Aldrich, 4N



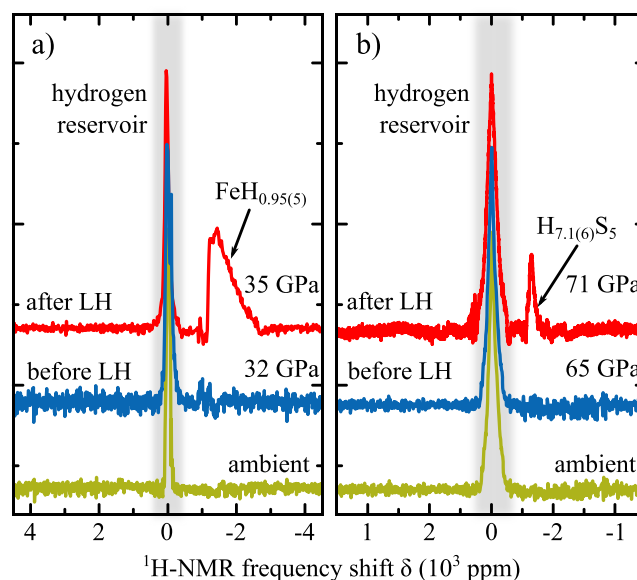
**FIG. 2.**  $^{139}\text{La}$ -NMR and  $^1\text{H}$ -NMR time-domain data acquired from a commercially available sample of  $\text{LaH}_3$  under ambient conditions. Both signals at 56.6 and 400.2 MHz were acquired using a well-defined single RF pulse with sufficiently low repetition time to allow full spin relaxation. The signal intensity  $V_{\text{signal}}$  in the time domain is given by the measured intensity at  $t = 0$ , and the root-mean-square noise voltage  $V_{\text{noise}}$  was acquired after total signal decay.

purity). The scan-normalized signal-to-noise ratios were found to be  $\zeta_{\text{La}} = 15.35(15) \times 10^4$  and  $\zeta_{\text{H}} = 3.23(9) \times 10^4$  at identical digitization frequencies  $\Delta f$ . Using Eq. (7), we find that the sample has a nuclear density ratio  $n_{\text{H}}/n_{\text{La}} = 2.95(7)$ , i.e., a threefold higher hydrogen than lanthanum content, matching the stoichiometry of the known lanthanum trihydride.

### 2. Iron monohydride

Figure 3(a) shows  $^1\text{H}$ -NMR spectra from a DAC using iron powder and paraffin oil as a hydrogen reservoir before laser heating (the yellow spectrum under ambient conditions and the blue spectrum at 32 GPa) and after laser heating (the red spectrum). All three spectra were recorded at a spectrometer frequency  $f_0 = 45.0831$  MHz ( $B_0 = 1059$  mT), with digitization frequencies of 1 and 3.33 MHz and with 1224 and 1988 scans for the spectra before and after laser heating, respectively.

The SNRs, corrected for differing numbers of scans and digitization frequencies [see Eq. (1)], of the paraffin oil signal before and after heating and the SNR of the hydride signal were found to be  $\zeta_{\text{Res}}^0 = 2.36(11) \times 10^4$ ,  $\zeta_{\text{Res}}^{\text{LH}} = 1.71(8) \times 10^4$ , and  $\zeta_{\text{FeH}_x}^{\text{LH}} = 0.77(4) \times 10^4$ , respectively. Assuming a hydrogen density of the precursor of  $n_{\text{Res}}^0 = 0.0729(73)$   $\text{H}/\text{\AA}^3$ ,<sup>38–40</sup> the hydrogen density of the hydride can be directly calculated to be  $n_{\text{FeH}_x}^{\text{LH}} = 0.086(18)$   $\text{H}/\text{\AA}^3$ . Using the equation of state from Narygina *et al.*,<sup>41</sup> the hydrogen concentration directly after the compound's synthesis at 35 GPa amounts to



**FIG. 3.** Representative  $^1\text{H}$ -NMR spectra used for quantification of the hydrogen content of metal hydrides. (a) Iron hydride. A strong additional resonance was found in the NMR spectra and was identified to be due to fcc iron hydride.<sup>28</sup> Comparison of signal-to-noise ratios gave a hydrogen content of  $x = 0.95(5)$  H atoms per formula unit, which is close to the inferred hydrogen concentration from XRD measurements. Spectra are taken from earlier studies.<sup>28</sup> (b) Sulfur hydride. Laser heating in the DAC was conducted at 65 GPa (blue spectrum), resulting in a weak additional signal at about  $-1750$  ppm at 71 GPa containing  $\sim 177$  H atoms per unit cell, corresponding to a hydrogenation of  $x = 7.1(9)$  H atoms per formula unit, which is in good agreement with the tetragonal  $I104$  phase of  $\text{H}_{6 \pm 0.4}\text{S}_5$  recently reported by Laniel *et al.*<sup>31</sup>

3.9(3) H/unit cell and thus gives rise to about 0.95(5) H/formula unit, which is reasonably close to the inferred hydrogen content from XRD experiments for the iron monohydride ( $x = 1$ ).

### 3. Sulfur polyhydride

Figure 3(b) shows recorded  $^1\text{H}$ -NMR spectra using sulfur and paraffin oil (yellow), pressurized to 65 GPa (blue) and laser-heated above 1500 K at  $\sim 71$  GPa (red). The spectrum before laser heating at ambient conditions was recorded at a magnetic field of 7.03 T using a digitization frequency of 2 MHz, yielding  $\zeta_{\text{Res}}^0 = 5.47(27) \times 10^4$ . After laser-assisted sample synthesis, a new spectrum was recorded at a 3.33 MHz digitization frequency, yielding renormalized values of  $\zeta_{\text{Res}}^{\text{LH}} = 4.76(24) \times 10^4$  and  $\zeta_{\text{H}_6\text{S}_5}^{\text{LH}} = 8.53 \times 10^3$ . The corresponding hydrogen density of the reaction product can be estimated to be  $n_{\text{H}_6\text{S}_5}^{\text{LH}} = 0.087(12) \text{ H}/\text{\AA}^3$ , yielding a stoichiometric hydrogen concentration of  $x = 7.1(9)$  H per formula unit.

## IV. RESULTS AND DISCUSSION

The combined data on the NMR-inferred hydrogen content are displayed in Fig. 4 in comparison with estimates from XRD and computations.<sup>6,20,31,41–43</sup> It can be clearly seen that direct measurements of the hydrogen concentration per formula unit using NMR coincide remarkably well with the hydrogenation inferred from XRD experiments for a wide range of stoichiometries.

Uncertainties in the obtained hydrogen content (Fig. 4) are primarily determined by the absolute SNR. Thus, sufficiently averaged noise patterns and strong signal intensities are desirable to

ensure the best possible accuracy in  $n_{\text{Res}}^{\text{LH}}$ . We assume an error of 5% for the integrated signal intensities, based on the small variation in the total number of hydrogen nuclei before and after laser heating [Fig. 1(b)].

Another possible source of inaccuracy is the hydrogen density of the precursor material. If a precursor with a known equation of state is used, it is sufficient to perform direct measurements before laser-heating-assisted sample synthesis in a precompressed DAC. In the case of an unknown or poorly constrained phase diagram, the initial measurements need to be conducted under almost ambient conditions for an accurate estimation of  $n_{\text{Res}}^0$ , or preliminary equation-of-state experiments or *ab initio* calculations must be performed beforehand.

Figure 1(b) shows that, on the one hand, the hydrogen content remains constant in the absence of leakage to within some percent of the initial hydrogen content before laser heating. On the other hand, it implies that all reaction products are observable in the first place. The latter point might be *a priori* not true. In cases where reaction products exhibit very long ( $>2$  s) or very short ( $<50$   $\mu\text{s}$ ) spin relaxation times or significantly broadened resonance spectra, a complete sampling of all reaction products will be challenging.

Considering these points, the NMR-based quantification method presented here is in very good agreement with estimates based on XRD and computations for a wide range of hydrogen content, and further improvements in the SNR of the NMR data will further improve the accuracy and enable the determination of previously unknown hydrogen contents, as well as re-evaluation of those that are at present ambiguous.

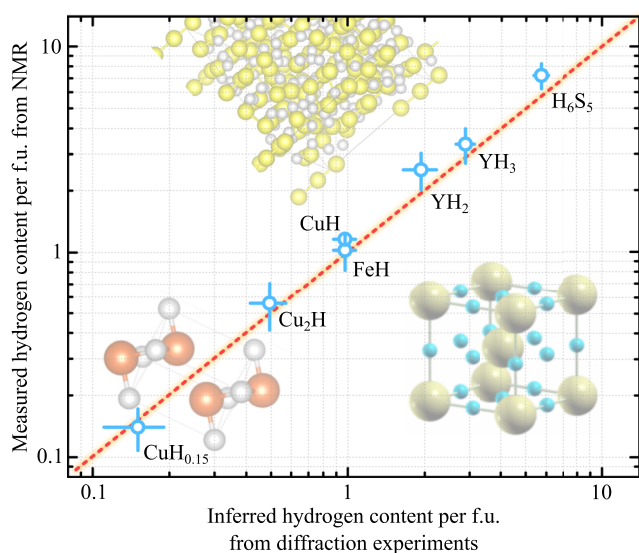
It is important to note that in the most general case, the approach presented here relies solely on knowledge of the H-atom density of the precursor material,  $n_{\text{Res}}^0$ , before laser heating. All other parameters are sufficiently determined by NMR. Knowledge of unit cell volumes or stoichiometries of the reaction products are not mandatory, and NMR-determined hydrogen concentrations are directly given in units of  $\text{H}/\text{\AA}^3$ .

In special cases, this method would also allow the direct estimation of total stoichiometries, if all components of the reaction products were observable. In this vein, hydrides of lanthanum, via  $^{139}\text{La}$ -NMR, and yttrium, via  $^{89}\text{Y}$ -NMR, in conjunction with  $^1\text{H}$ -NMR, could be chemically characterized directly upon their synthesis by conducting multinuclear NMR experiments. In these special instances, concentrations of metal atoms per  $\text{\AA}^3$  could be obtained using the same procedure as described above. This direct hydrogen quantification method using other, nonhydrogen nuclei, as internal standard is even superior to the indirect method using the NMR signal of the hydrogen precursor.

Moreover, since different spectral ranges would be employed (e.g.,  $\sim 400$  MHz for  $^1\text{H}$  and  $\sim 56.5$  MHz for  $^{139}\text{La}$ ), association of signals and their corresponding reaction products could be realized using two-dimensional NMR spectroscopy [e.g., heteronuclear correlation spectroscopy ( $^1\text{H}$ - $^{139}\text{La}$ -COSY)].

In fact, recent developments in *in situ* high-pressure NMR show that pressures well within the range of standard DAC experiments (i.e.,  $>150$  GPa) are possible, and therefore this method of hydrogen quantification can also be employed for potentially superconducting superhydrides, such as  $\text{LaH}_{10}$  or  $\text{YH}_9$ .

This independent method provides an opportunity to identify metal hydride systems on the fly with *in situ* NMR experiments



**FIG. 4.** Comparison between hydrogen content inferred from diffraction methods and that from direct measurements using NMR spectroscopy in DACs. The described method has been used to investigate several hydride systems, with hydrogen contents ranging from  $x = 0.15$  to  $x = 7.1$ . The red dotted line is a guide to the eye of a 1:1 correlation between the two quantification methods. The structures in the background depict the low-pressure trigonal  $\text{Cu}_2\text{H}$ , the face-centered cubic  $\text{FeH}$ , and the tetragonal  $\#140$  phase of  $\text{H}_{6\pm 0.4}\text{S}_5$ .  $\text{LaH}_3$  is not included, since the stoichiometry is known under ambient conditions and there would be a strong overlap with  $\text{YH}_3$ .

under high pressure, enabling the quantification of hydrogen uptake with or without laser heating, and it should also enable novel characterization experiments on this new class of high-temperature superconductors.

Moreover, this and similar methods might be applicable to other high-pressure problems, such as water transport in the deep interior regions of the Earth<sup>44</sup> using *in situ* high-pressure NMR experiments.<sup>45–47</sup>

## SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for tables of the data used to compute the hydrogen concentrations  $n_1^1$  and the derivation of Eq. (7).

## ACKNOWLEDGMENTS

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## Author Contributions

**Thomas Meier:** Conceptualization (equal); Formal analysis (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Dominique Laniel:** Data curation (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Florian Trybel:** Data curation (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data supporting the findings of this study are publicly available from the corresponding author upon request.

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