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### Structural Studies on the Cu–H System under Compression

**Citation for published version:**

Binns, J, Pena Alvarez, M, Donnelly, M-E, Gregoryanz, E, Howie, R & Dalladay-Simpson, P 2019, 'Structural Studies on the Cu–H System under Compression' Engineering. DOI: 10.1016/j.eng.2019.03.001

**Digital Object Identifier (DOI):**

[10.1016/j.eng.2019.03.001](https://doi.org/10.1016/j.eng.2019.03.001)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Engineering

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## Manuscript Details

<b>Manuscript number</b>	ENG_2018_853
<b>Title</b>	Structural studies on the Cu-H system under compression
<b>Article type</b>	Research Paper

### Abstract

Currently, hydrogen chemistry at extreme pressures is subject to extensive research due to the observed and predicted enhanced physical properties when it is incorporated in numerous binary systems. Despite hydrogen's high reactivity, the noble metals (Cu, Ag, and Au) display an outstanding resilience to hydride formation, with no reports of a stable compound with a hydrogen molar ratio  $\geq 1$  at room temperature. Here, through extreme compression and in-situ laser heating of pure copper in a hydrogen atmosphere, we explore their affinity to adopt binary compounds. We report on the phase behaviour and stabilities in the Cu-H system, analysed via synchrotron X-ray diffraction, up to pressures of 50 GPa. We confirm the existence of the previously reported,  $\epsilon$ -Cu<sub>2</sub>H,  $\gamma_0$ -CuH<sub>0.15</sub> and  $\gamma_1$ -CuH<sub>0.65</sub> phases. Most notably, we report the highest hydrogen content noble-metal hydride stable at room temperature to date,  $\gamma_2$ -CuH<sub>0.65</sub>, synthesised through laser heating. This study furthers our understanding of hydrogen-transition metal chemistry and could find applicability in future hydrogen-storage applications.

<b>Keywords</b>	Copper; Hydride; High-Pressure; Laser Heating; Hydrogen-storage; Noble metals; Diamond Anvil Cell; X-ray diffraction
<b>Manuscript category</b>	Materials Science and Engineering
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<b>Corresponding Author's Institution</b>	Center for High Pressure Science and Advanced Technology Research
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<b>Suggested reviewers</b>	Michael Hanfland, Yanming Ma, Helen Maynard-Casley, John Loveday, Jung-Fu Lin

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Dear Editor,

We are submitting our study entitled “Structural studies on the Cu-H system under compression” for your consideration. In this letter, we present a structural characterization of copper hydride formation using X-ray diffraction, laser heating and Diamond Anvil Cell (DAC) techniques.

Hydrogen chemistry is currently of intense interest, with hydrogen-bearing systems (hydrides) displaying remarkable properties, such as the H<sub>2</sub>S system with reports of high critical temperatures for superconductivity. Hydrides could also find commercial application, proving to be volume-efficient tools for hydrogen-storage, with pressure acting as a mechanism to readily trap or release hydrogen gas. Despite this extensive research activity and also hydrogen’s reactivity there are still binary-systems which have not been explored, with the noble metals (group 11) making a notable gap in the periodic table.

In this work, with the use of high-pressures, in-situ laser heating and synchrotron x-ray diffraction we explore the Cu-H system up to pressures of 50 GPa and temperatures in excess of 1000 K. We report the previously identified  $\gamma_0$ -CuH<sub>0.15</sub>,  $\gamma_1$ -CuH<sub>0.5</sub> and  $\epsilon$ -Cu<sub>2</sub>H phases. Crucially, however we identify a new  $\gamma$ -phase,  $\gamma_2$ -CuH<sub>0.65</sub>, synthesised via laser heating. This discovery is the highest reported hydrogen content for a group-11 system and strongly suggestive that a fully stoichiometric might be stable at higher pressures.

This work will motivate the re-examination and thorough exploration of many other metal-hydrogen systems and perhaps encourage the realisation of the other elusive group-11 hydrides, Au-H and Ag-H.

My best regards,

Phil Dalladay-Simpson

## Structural studies on the Cu-H system under compression

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(Dated: 3 September 2018)

Currently, hydrogen chemistry at extreme pressures is subject to extensive research due to the observed and predicted enhanced physical properties when it is incorporated in numerous binary systems. Despite hydrogen's high reactivity, the noble metals (Cu, Ag, and Au) display an outstanding resilience to hydride formation, with no reports of a stable compound with a hydrogen molar ratio  $\geq 1$  at room temperature. Here, through extreme compression and *in-situ* laser heating of pure copper in a hydrogen atmosphere, we explore their affinity to adopt binary compounds. We report on the phase behaviour and stabilities in the Cu-H system, analysed via synchrotron X-ray diffraction, up to pressures of 50 GPa. We confirm the existence of the previously reported  $\gamma_0$ -CuH<sub>0.15</sub>,  $\gamma_1$ -CuH<sub>0.5</sub> and  $\epsilon$ -Cu<sub>2</sub>H phases. Most notably, we report the highest hydrogen content noble-metal hydride stable at room temperature to date,  $\gamma_2$ -CuH<sub>0.65</sub>, synthesised through laser heating. This study furthers our understanding of hydrogen-transition metal chemistry and could find applicability in future hydrogen-storage applications.

# I. INTRODUCTION

Hydrogen-bearing systems are currently of intense interest, due to their desirable physical properties and as possible hydrogen storage materials. Physical properties such as superconductivity at high temperatures have been reported in the hydrogen-sulfur system<sup>1</sup>, whilst their storage capabilities are best exemplified by the hydrogen amassed in methane-hydrogen,  $\text{CH}_4(\text{H}_2)_4$ <sup>2</sup>, and more recently in the hydrogen-iodane system,  $\text{HI}(\text{H}_2)_{13}$ <sup>3</sup>. Despite these prospects and intensive research activity in this field, there remain many systems which have not been explored with the noble metals making a notable hydride-gap in the periodic table.

The noble metals, Cu, Ag and Au are relatively inert under ambient conditions, as seen by their reluctance to form oxides under ambient conditions, an attractive quality for their usage in ancient coinage and electronics. High-pressure has become an indispensable tool in modifying chemical affinities and thereby creating exotic materials<sup>4-7</sup>. Typically for hydride formation in *d*-metals, the barrier for molecular dissociation is driven down by pressure, resulting in atomic hydrogen permeating freely through the metallic lattice, tending to reside at interstitial sites. The presence of atomic hydrogen in the metal can lead to changes in the crystalline structure ranging from simple lattice expansion to reconstructive phase transitions and changes in space-group symmetry<sup>8</sup>.

Despite numerous attempts using complex synthesis techniques such as high pressures coupled with resistive and laser heating<sup>9,10</sup>, the definitive formation of Au-H and Ag-H has remained elusive, likely due to their large reduction potentials. On the other hand, Cu, with a reduction potential approximately half that of Ag, has been known to form a binary system with hydrogen for over 100 years, making it the first metal hydride to be discovered<sup>11</sup>.

The Cu-H system is found to have an extensive chemistry with some very unusual chemical pathways, such as sonofication<sup>12</sup>. Copper's reactivity with hydrogen offers a testing bed for further experimental and theoretical studies of the group-11 hydrides. The first binary compound was formed by the reduction of copper sulphate with hypophosphorous acid to form the stoichiometric monohydride,  $\text{CuH}$ <sup>11</sup>.  $\text{CuH}$  was identified to have a Wurzite structure with a significantly modified mechanical response, a consequence of Cu-H bonding, a highly unusual characteristic in *d*-metal hydride systems<sup>13</sup>. However, Wurzite- $\text{CuH}$ , the only stoichiometric noble-metal hydride, is unstable at ambient temperatures and readily

decomposes above  $-60^{\circ}\text{C}^{14}$ , with calculations predicting that pressures in excess of 30 GPa are required to stabilize it at room temperature<sup>14</sup>.

Since this early pioneering work, high-pressure experimental campaigns have attempted to form new hydrogen-bearing Cu compounds. Direct compression of Cu in a  $\text{H}_2$  atmosphere results in the formation of a low-H content hydride, isostructural to Cu exhibiting a slightly expanded lattice, in accordance with the literature naming scheme this phase is  $\gamma_0\text{-CuH}_{0.15}$ . Compressing this phase above 10 GPa leads to further hydrogen entering the lattice forming the second  $\gamma_1\text{-CuH}_{0.5}$  phase<sup>9</sup>. In both phases the lattice expansion is a consequence of hydrogen filling the octahedral interstitial sites. A subsequent study, using synchrotron X-ray diffraction, identified an  $\epsilon\text{-Cu}_2\text{H}$  phase<sup>10</sup>, distinctly different from the previously reported Wurzite-CuH and  $\gamma$  phases, synthesised around 18.6 GPa. This phase adopts an anti- $\text{CdI}_2$  type structure and its stoichiometry was constrained from significantly reduced volumes when compared to the formerly identified phases. As Cu-H has the highest chemical affinity with hydrogen of all the group-11 metals, it is imperative that we endeavour to fully describe its chemistry and perhaps reveal higher hydrogen stoichiometries, as reported for other  $d$ -metal systems<sup>15,16</sup>.

Here, with the use of high-pressure, *in-situ* laser heating and synchrotron X-ray diffraction we explore the Cu-H system up to pressures of 50 GPa and temperatures in excess of 1000 K. We report the previously identified high-pressure phases,  $\gamma_0\text{-CuH}_{0.15}$ ,  $\gamma_1\text{-CuH}_{0.5}$ <sup>9</sup> and  $\text{Cu}_2\text{H}^{10}$ , and constrain their pressure evolution up to 50 GPa respectively. Crucially we identify a new  $\gamma$  phase synthesized by laser heating Cu in a dense hydrogen atmosphere. Unusually this phase decomposes into  $\gamma_1\text{-CuH}$  rather than the  $\epsilon\text{-Cu}_2\text{H}$  phase previously found to be stable at these pressures. This work illustrates the complexities that may be found in the noble-metal hydride phase diagrams when explored with the latest experimental techniques.

## II. EXPERIMENTAL METHODS

The diamond-anvil cell (DAC) is the workhorse in most static high-pressure experiments. Its compact and simple design has proven powerful and adaptable finding itself as a principal driving force in high-pressure science for the last 30 years. The concept is simple, by coupling very small sample chambers and the hardness of diamond, pressures can be generated that are orders of magnitude greater than what can be achieved with conventional mechan-

ical presses. In this study high-pressure measurements were conducted in symmetric-type DAC with Boehler-Almax cut diamonds on tungsten-carbide seats with large opening angles ( $\sim 50^\circ$ ). The diamond culets varied from 200-300 microns in diameter. Samples were loaded in a laser-milled rhenium-foil gasket chamber with initial dimensions of 20-30 microns in thickness and approximately 75% the culet size in diameter. No pressures higher than 50 GPa were probed, limited by the mechanical instability dictated by the geometry of the diamond anvils. Pressures were determined during the experiment via the known equation of state of a particulate of gold and/or the calibrated shift of the  $R_1$  florescence of a ruby sphere placed in the sample chamber<sup>17,18</sup>.

High-purity Cu-grains (Alfa Aesar 99.9 %), approximately 10  $\mu\text{m}$  in size, were placed so that they were centered on a diamond anvil. The DAC was calibrated such that it hermetically sealed in a 2 kbar hydrogen atmosphere (research grade 99.9995%). The loading procedure resulted in significant excess of hydrogen, to promote hydride formation, whilst also providing hydrostatic conditions for synthesised samples.

The Cu-sample was heated *in-situ* from both sides uniaxially by directly coupling to IR lasers. Powder X-ray diffraction data were collected at the GSECARS beamline at APS, USA . The diffraction from 0.3344 Å wavelength X-rays was recorded using a Pilatus 1M image-plate detector, after which it was integrated using DIOPTAS<sup>19</sup> software to a two-dimensional data set. The data were subsequently indexed and further underwent Le Bail refinement using Jana2006<sup>20</sup>.

### III. RESULTS AND DISCUSSION

Although now a mature field in its own right, modern high-pressure chemistry dates back to the invention of pressure devices built and used by Bridgman, earning him the Nobel prize for physics in 1946. Since, high pressure has been widely applied to the formation and study of *d*-metal hydrides, first by Baranowski *et al.* over 50 years ago up to 0.3 GPa<sup>21</sup> and was further extended by the work of Antonov in the 1980s up to 9 GPa<sup>8</sup>. In recent times, primarily due to the advent of new extreme condition techniques along with key developments in diagnostics, we are in a prime position to routinely investigate and expand our understanding of hydrogen chemistry at high densities. This study providing an important example, outlining the techniques, diagnostics and synthesis pathways in the

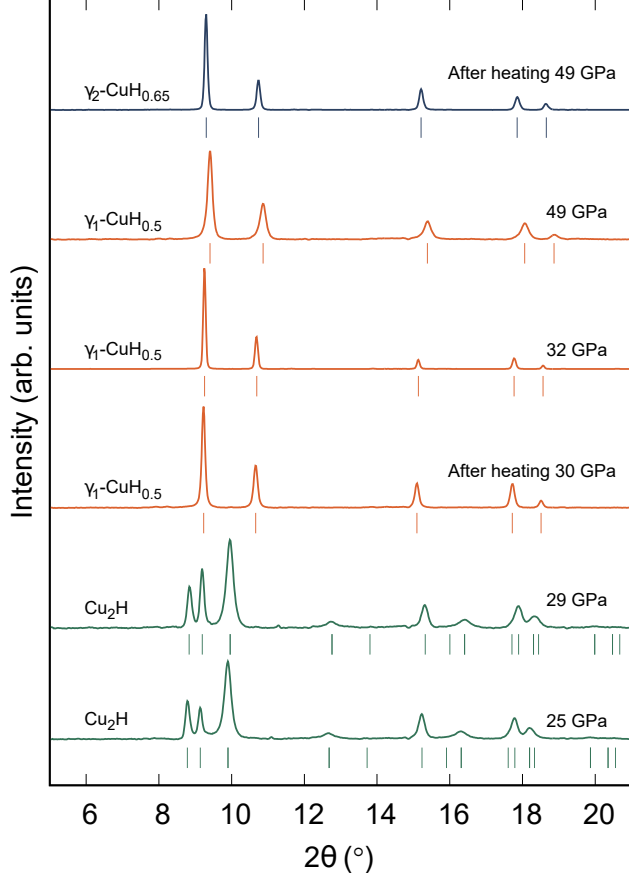


FIG. 1. High pressure X-ray diffraction patterns ( $\lambda = 0.3344 \text{ \AA}$ ) showing the stepwise synthesis of  $\gamma_1$ -CuH<sub>0.5</sub> (orange) and  $\gamma_2$ -CuH<sub>0.65</sub> (blue) by sequential laser heating at 30 GPa and 49 GPa. Tick marks indicate the positions of Bragg reflections from the noted phases.

Cu-H system, in doing so reporting a noble metal-hydride material with the highest reported hydrogen stoichiometry at ambient temperature.

The use of synchrotron radiation has greatly expedited the exploration of high-pressure systems, with their brilliance and tight focus finding great applicability with sample sizes on the order of tens of microns. In this study, harnessing synchrotron generated light, we have ascertained structural insight in the Cu-H system using conventional powder X-ray diffraction, as these studies only require a fraction of accumulation time when compared with conventional in-house sources<sup>9</sup> we present a thorough mapping of phases in the Cu-H system. Through the high-quality spectra obtained, which can be readily seen in Figures 1 and 3, we have identified the appearance of four phases in the Cu-H system:  $\gamma_0$ -CuH<sub>0.15</sub>, Cu<sub>2</sub>H,  $\gamma_1$ -CuH<sub>0.5</sub> and  $\gamma_2$ -CuH<sub>0.65</sub>, the latter two requiring high-temperatures (discussed later). As



discussed previously, the Cu-H system has been well characterised at ambient temperatures up to 50 GPa in previous studies<sup>9,10</sup> and our data up to 25 GPa at room temperature are in agreement, observing the direct reaction between Cu and its surrounding H<sub>2</sub> atmosphere. The reaction product is readily seen by the appearance of diffraction peaks, Figure 1, corresponding to previously reported  $\epsilon$ -Cu<sub>2</sub>H crystallising in space group  $P\bar{3}m1$ ,  $a = 2.5229(2)$ ,  $c = 4.1984(8)$  Å at 25 GPa.

Temperature has always been an essential parameter in chemistry, where in particular high-temperatures serve as a pathway to overcome potential energy barriers thereby promoting reactivity. In diamond-anvil cell work specialist heating techniques are required, where large amounts of thermal energy need to be deposited typically over very small surface areas. Laser heating provides an optimum solution<sup>22</sup>, where high-powered IR lasers ( $\sim 100$  W) can be tightly focused, consequently having roughly an energy density of 20 W/ $\mu\text{m}^2$  and, if incident on strongly coupling metallic foils, temperatures in excess of 3000 K can be produced. Therefore, to promote further reactions, samples that were first compressed to 30 GPa were further subjected to laser heating to temperatures in excess of 1000 K. A treatment that resulted in radical changes to the observed diffraction patterns. Peaks due to aforementioned  $\epsilon$ -Cu<sub>2</sub>H phase disappeared to be replaced by a new phase,  $\gamma_1$ -CuH<sub>0.5</sub>, that was readily indexed to a face-centered cubic structure with  $a = 3.5976(1)$  Å at 30.1 GPa. Once transformed, the sample was further compressed to explore the possible synthesis of other Cu-H compounds. After heating at 50 GPa we observe another abrupt increase in unit-cell volume consistent with the formation of an isostructural phase with greater hydrogen content,  $\gamma_2$ -CuH<sub>0.65</sub>.

Unfortunately, despite the brilliance of synchrotron light, hydrogen has a weak X-ray scattering cross-section and is therefore essentially invisible to the X-ray diffraction technique. Although this makes it impossible to directly infer the stoichiometry of synthesised hydrides, it is still possible to ascertain the content in interstitial hydrogen systems as the presence of hydrogen distorts the structure of the metallic host, often observed as a volume expansion. Therefore, examination of the atomic volume per Cu atom with pressure allows us to understand the relationship and estimate the hydrogen contents of these new copper hydride phases. Figure 2 illustrates the observed volumes for Cu<sub>2</sub>H, and the two new phases induced through laser heating  $\gamma_1$ -CuH<sub>0.5</sub> and  $\gamma_2$ -CuH<sub>0.65</sub> previously discussed. In *fcc* metal hydrides ( $\gamma$  phases), hydrogen atoms occupy the octahedral vacancies and result in a vol-

umetric expansion proportional to the hydrogen content with  $\Delta V = 2.9 \text{ \AA}^3$  per hydrogen atom for the stoichiometric  $n = 1.0$  and in the absence of neutron diffraction data this provides the assigned estimate of the hydrogen content in a metallic hydride<sup>23</sup>.

As is common with interstitial hydrides, none of the high-pressure phases in the Cu-H system,  $\gamma_0$ -CuH<sub>0.15</sub>,  $\gamma_1$ -CuH<sub>0.5</sub> and  $\gamma_2$ -CuH<sub>0.65</sub>, display modified mechanical properties when compared with the host material, Cu. As can be seen in Figure 2 both synthesised  $\gamma$  phases show similar compressibility as pure Cu over this pressure range, the average increase in volume versus pure Cu for ‘ $\gamma_1$ -CuH’ is  $1.44(10)\text{\AA}^3$  per Cu atom which establishes our stoichiometric assignment of  $\gamma_1$ -CuH<sub>0.5</sub>. The second isostructural  $\gamma$  phase formed after laser heating  $\gamma_1$ -CuH<sub>0.5</sub> shows an average  $\Delta V = 1.85(5) \text{ \AA}^3$  implying a formula  $\gamma_2$ -CuH<sub>0.65</sub>. Therefore, despite revealing CuH<sub>0.65</sub> with a marked 30% molar increase in hydrogen content, the mechanical properties remain largely unchanged. However, although there is not a marked change in their mechanical properties, these materials’ electronic properties can be altered profoundly. As reported for the Pd-H system, the absorption of hydrogen to form the monohydride PdH, results in an enhanced critical temperature for superconductivity when compared with elemental Pd (greater than 3 orders of magnitude)<sup>24</sup>. The same has also been proposed for other transition metal hydrides, such as PtH<sup>25,26</sup>. Studying the impact on the electrical properties of noble metal-hydrides through the incorporation of hydrogen would be of particular interest, as these materials find widespread industrial and commercial application due to their desirable conductive properties.

From the highest pressure point of 50 GPa samples were decompressed to determine the stability range of the newly formed hydride phases.  $\gamma_2$ -CuH<sub>0.65</sub> was found to be stable to 32 GPa (Figure 3) where interestingly it decomposed to  $\gamma_1$ -CuH<sub>0.5</sub>, rather than the  $\epsilon$ -Cu<sub>2</sub>H phase which is the favoured phase under room temperature compression<sup>10</sup>. This phase in turn was stable down to 19 GPa where weak peaks due to  $\epsilon$ -Cu<sub>2</sub>H could be observed, and below this pressure the sample transformed to the known  $\epsilon$ -Cu<sub>2</sub>H phase.

Laser-heating is a powerful technique to synthesise new phases particularly with unreactive metals. The observation of two new stable phases, with increasing hydrogen content, in the pressure range up to 50 GPa and the known existence of analogous d-metal monohydrides, CoH<sup>16</sup> and NiH<sup>21</sup>, it is strongly suggestive that further pressurization and high temperatures a true copper monohydride species could be stable. These results should encourage the reexamination of many metal-hydrogen systems, particularly in light of the

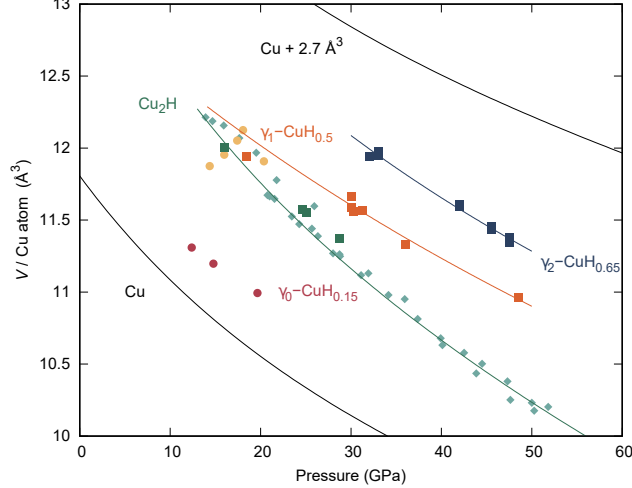


FIG. 2. Atomic volume as a function of pressure for Cu-H compounds. Data from this study are shown with squares, data on  $\text{Cu}_2\text{H}$  from Ref.<sup>10</sup> shown with diamonds,  $\gamma_0\text{-CuH}_{0.15}$  and  $\gamma_1\text{-CuH}_{0.5}$  from Ref.<sup>9</sup> shown with circles. Equations of state shown with solid lines.

moderate pressures used here. This method is applicable to any metal-hydrogen system and may be of interest in the study of high-performance alloys under extreme conditions.

#### IV. CONCLUSIONS

In summary, using high-pressure powder X-ray diffraction, we have explored the Cu- $\text{H}_2$  system up to pressures of 50 GPa. In agreement with previous studies we have verified the synthesis of  $\epsilon\text{-Cu}_2\text{H}$ ,  $\gamma_0\text{-CuH}_{0.15}$  and  $\gamma_1\text{-CuH}_{0.5}$  compounds, further constraining their structural evolution with pressure. We find that a second, more hydrogen-rich,  $\gamma_2\text{-CuH}_{0.65}$  phase is formed after laser heating above 30 GPa, and is the highest hydrogen content system known to exist for the noble metals stable at room temperatures. This study and its incorporated understanding will reinvigorate interest in H-rich hydrogen bearing materials and the realisation of the other noble metal hydrides, Au-H and Ag-H.

#### ACKNOWLEDGMENTS

PD-S and RTH acknowledge their respective “1000 talents” awards. MP-A acknowledges the support of the European Research Council (ERC) Grant Hecate reference No. 695527. Parts of this research were conducted at the APS facility under proposal No. 51037 at the

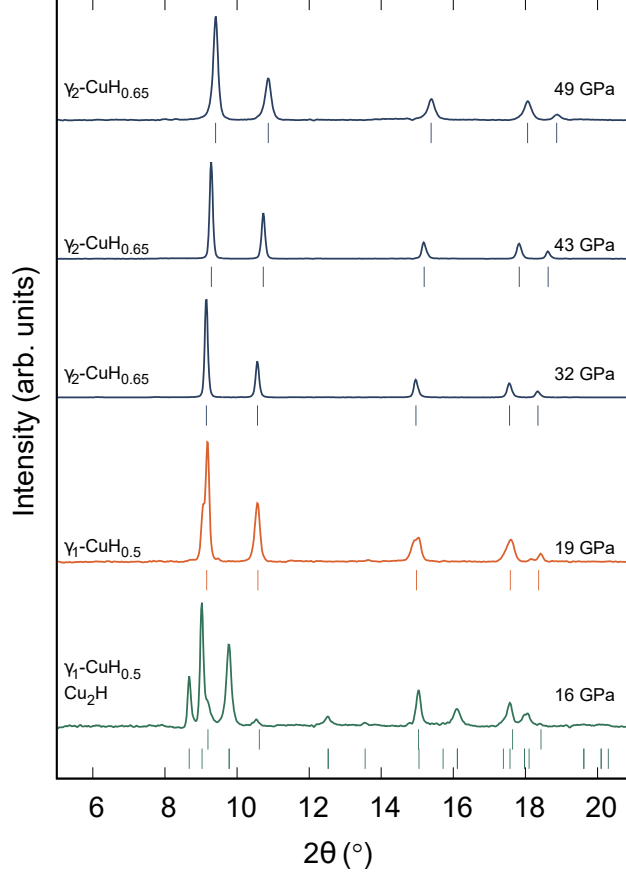


FIG. 3. High pressure X-ray diffraction patterns ( $\lambda = 0.3344 \text{ \AA}$ ) taken on decompression showing the step-wise decomposition of  $\gamma_2$ -CuH<sub>0.65</sub> into  $\gamma_1$ -CuH<sub>0.5</sub> and Cu<sub>2</sub>H. Tick marks indicate the positions of Bragg reflections from the noted phases.

GSECARS beamline, we would like to thank Eran Greenberg and Vitali Prakapenka for their assistance during the course of the data collection.

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