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The formation of hydride phases in the noble metals copper, silver, and gold was investigated by *in situ* x-ray diffraction at high hydrogen pressures. In the case of copper, a novel hexagonal hydride phase, Cu_2H, was synthesised at pressures above 18.6 GPa. This compound exhibits an anti-CdI_2-type structure, where hydrogen atoms occupy every second layer of octahedral interstitial sites. In contrast to chemically produced CuH, this phase does not show a change in compressibility compared to pure copper. Furthermore, repeated compression (after decomposition of Cu_2H) led to the formation of cubic copper hydride at 12.5 GPa, a phenomenon attributed to an alteration of the microstructure during dehydrogenation. No hydrides of silver (up to 87 GPa) or gold (up to 113 GPa) were found at both room and high temperatures. © *2013 American Institute of Physics.*
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I. INTRODUCTION

Despite hydrogen being highly reactive, none of the group-6 to group-11 transition metals react with it at ambient conditions.[1–3] However, at elevated pressures, the chemical potential of hydrogen rises steeply and reactions, usually leading to the formation of a binary metal hydride, are induced.[3–5] The group-11 noble metals play an interesting role in this context. While the formation of gold hydride was reported more than 30 years ago,[6] it has not been confirmed since. In fact, recent *ab initio* calculations found no evidence for a reaction between gold and hydrogen, due to a large energy barrier preventing the dissociation of hydrogen molecules at the gold surface.[7] For silver, to the best of our knowledge, no bulk hydride phase has ever been found. Theoretical studies predict that *fcc*-silver hydride stabilises at pressures above 50 GPa.[8]

In contrast, copper hydride was one of the very first *d*-metal hydrides to be discovered. It was first synthesised in 1844 by reacting hypophosphorous acid with copper sulphate (known as Wurtz method).[9] Forming a stoichiometric monohydride,[10] it adopts a hexagonal wurtzite-type structure ($P6_3mc$ space group).[11] This is unusual compared to other transition metal hydrides, many of which exist in NiAs-type or NaCl-type structure. Often, the metal atoms form a closed-packed host lattice in which hydrogen atoms occupy interstitial sites[4] and participate in metallic bonds. As a result, the presence of hydrogen atoms does not influence the mechanical properties of its host lattice, except for a measurable volume expansion. However, in wurtzite CuH, the bulk modulus was measured to be 72(2) GPa,[12] significantly lower than the bulk modulus of pure copper (137.4 GPa).[13] This can be attributed to the hydrogen-copper bond which has been described as partly covalent and ionic.[14, 15] Chemically produced CuH is unstable at ambient conditions, but at temperatures below −5 °C, it can be stored permanently.[16] At room temperature it decomposes at pressures below 8.4(6) GPa.[17] Copper hydride is widely used as a reagent for reduction reactions in organic synthesis[18] and can also be used to obtain extremely reactive catalysts.[19] Most recently, a facile synthesis of CuH through sonochemistry was reported.[20]

However, the direct synthesis of hexagonal CuH from elements under thermodynamic equilibrium (i.e., at high pressures and temperatures) has never been reported. Through Gibbs free energy calculations, based on the decomposition pressure, a formation pressure of 30 GPa was predicted.[17] Interestingly, a different form of copper hydride has been synthesised at pressures above 14.4 GPa, the only high pressure study of copper hydride formation we are aware of.[21] This hydride retains the *fcc* lattice of copper, where hydrogen atoms occupy interstitial sites at a hydrogen-to-metal atomic ratio of ∼0.4. In accordance with the notation for other hydrides,[4] this cubic phase will be referred to as the γ-phase of CuH here. It was suggested that this phase *could only be observed* in a reaction of hydrogen with *dehydrogenated* copper, obtained from decomposing hexagonal wurtzite-type CuH (i.e., copper mono hydride synthesised by the Wurtz method). Conversely, pristine copper foil remained inert and no other hydride phase was observed at pressures up to 20 GPa.[21]

In this study, we present results of synchrotron-based powder x-ray diffraction (XRD) experiments on copper, silver, and gold in a dense hydrogen medium. In the copper-hydrogen system, we identified a novel hexagonal hydride phase, distinctly different from wurtzite-type CuH and γ-Cu-H. This phase formed at 18.6 GPa and remained stable up to 51 GPa in an anti-CdI_2 type structure, with a stoichiometric composition of Cu_2H. It decomposes at pressures below 10 GPa. On repeated compression a volume expansion in *fcc*-Cu was measured, indicating the formation of cubic copper hydride, although with a lower hydrogen content than previously reported.[21] No hydride phases were observed upon pressurization of silver and gold.

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II. EXPERIMENTAL DETAILS

We conducted six independent high-pressure experiments, two each for copper, silver, and gold. Metal samples from commercial thin foils (Alfa Aesar, 10 μm thickness, 99.8% purity) were loaded into symmetrical diamond anvil cells (DACs). Hydrogen was subsequently gas-loaded to pressures between 1600 and 2000 bar and thus also acted as the pressure transmitting medium. The samples were always surrounded by excess hydrogen (monitored visually and by Raman spectroscopy), even at the highest pressures. The gasket material was rhenium, with a hole drilled to a diameter of ~50% of the culet diameter. Pressure was measured *in situ* using the revised ruby fluorescence pressure scale.[22] The diffraction patterns were recorded on MAR345 or MAR555 detectors and integrated using the Fit2D[23] software.

III. RESULTS AND DISCUSSION

In the first experimental run on copper, the metal remained unchanged in its *fcc* phase ($Fm\bar{3}m$ spacegroup) up to 21.1 GPa. At this pressure, over time, new reflections started to emerge (see Fig. 1). Although the new reflections gained intensity at higher pressures, the *fcc* signature remained visible up to 51 GPa, the highest pressure achieved in this run. Initially, this new phase was indexed in the $P6_3/mmc$ spacegroup (*hcp* lattice), an increased volume per formula unit compared to *fcc*-Cu indicates the formation of a hydride. The
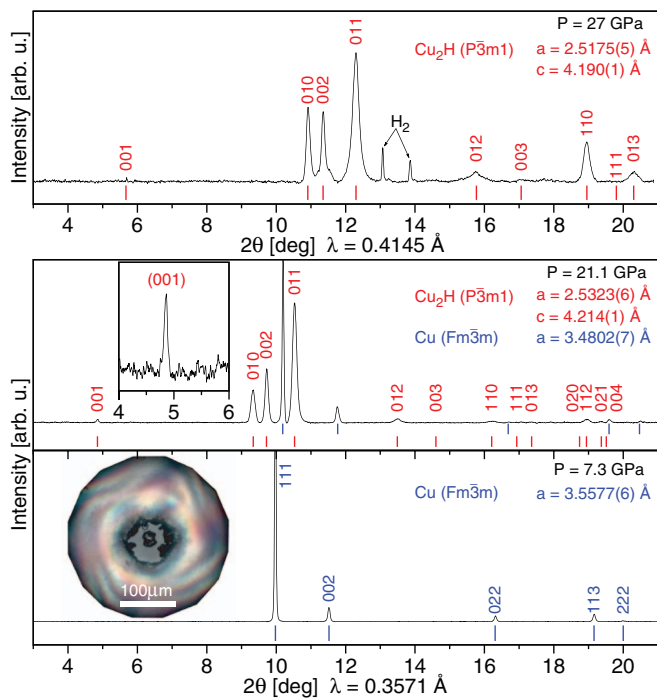

FIG. 1. Integrated XRD spectra of pure Cu at 7.3 GPa (bottom panel); Cu_2H along with remaining Cu at 21.1 GPa (middle panel); the fully converted Cu_2H along with reflections from excess H_2 at 27 GPa (upper panel). Tick marks indicate calculated peak positions of Cu (blue) in the bottom panel, Cu (top row, blue), and Cu_2H (bottom row, red) in the middle panel and Cu_2H (red) in the upper panel. The inset shows the (001) superstructure peak of the layered anti-CdI$_2$ structure of Cu_2H. The optical micrograph in the bottom panel shows the sample at 50 GPa.
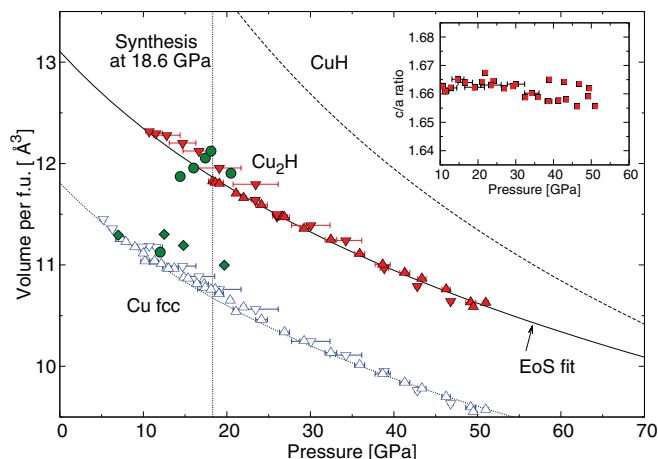

FIG. 2. Equation of state of copper and its hydrides. Blue open triangles denote *fcc*-Cu, red solid triangles ϵ-Cu_2H, and green diamonds γ-$CuH_{\sim 0.15}$. Triangles pointing upwards are data points from compression, triangles pointing down are from decompression. For comparison, green circles are data points belonging to γ-$CuH_{\sim 0.4}$, taken from Ref. 21. Dotted and dashed lines are literature equations of state for *fcc*-Cu and wurtzite-type CuH, respectively (Refs. 13 and 12). The solid line is a Vinet-type fit to the observed equation of state of ϵ-Cu_2H. The inset shows the pressure variation of the c/a-ratio for ϵ-Cu_2H.

new diffraction pattern is also easily distinguishable from rhenium hydride which forms at the inner gasket rim and also exhibits an *hcp*-like structure.[24] Apart from a smaller unit-cell volume compared to ReH, the c/a-ratio of the new hexagonal phase remained at a constant 1.661(3) throughout the experiment (see inset Fig. 2) whereas it is between 1.61 and 1.58 for rhenium hydride.[25] In the second run, the new phase appeared at 18.6 GPa. In contrast to the first run, the sample converted completely within 2 h, leaving no signal from *fcc*-Cu. The only difference between the two experiments was the size of the loaded copper sample: The volume of the sample in the second run was an order of magnitude smaller than in the first run. While it is not impossible that with time a larger sample would fully convert, it can be concluded that, even at very high pressures, the penetration depth of hydrogen into bulk copper is limited. A similar behaviour is known from platinum nitride[26] where only a thin surface layer reacted even at pressures above 50 GPa and temperatures exceeding 2000 K.

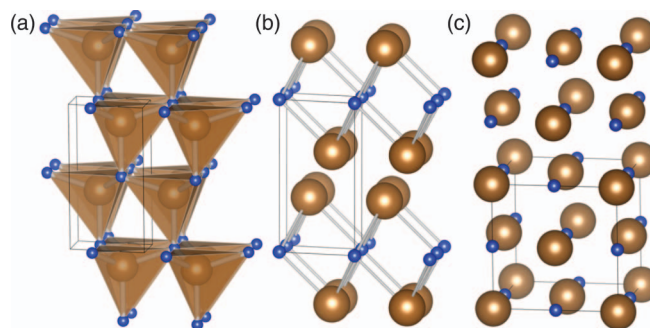
FIG. 3. Ordering of hydrogen (small, blue) and copper (large, copper) atoms showing (a) wurtzite-type CuH ($P6_3/mc$ space group), (b) anti-CdI$_2$ structure ϵ-Cu_2H ($P\bar{3}m1$ space group, the displacement of copper atoms is exaggerated), and (c) cubic γ-Cu-H ($Fm\bar{3}m$ space group) (visualised via VESTA[30]).

We therefore assume a synthesis pressure of 18.6 GPa for the hexagonal phase. Decomposition occurred at pressures below 10.5 GPa, close to the decomposition pressure of wurtzite-type CuH (8.4(6) GPa[17]). However, the new hexagonal phase is distinctly different: Over the entire experimental pressure range, the volume difference compared to pure Cu remained between 1.23(1) and 1.05(1) Å^3 per atom, much lower than for wurtzite-type CuH (see Fig. 2). In fact, volume considerations allow to estimate the hydrogen content (see, e.g., Refs. 3, 24, and 27). It has been found empirically that hydrogen atoms occupying the octahedral interstitial sites of an *hcp* metal expand the lattice by ∼2.1 Å^3 per hydrogen atom.[27] As the lattice expansion scales linearly with hydrogen content,[27] it can be inferred that the new hexagonal phase exhibits a Cu_2H composition. After platinum,[28] copper is the second *fcc* metal known to transform into an *hcp* hydride. Both possess significantly larger *c/a* ratios (1.66–1.7) than all other *hcp* *d*-metal hydrides,[4] providing a signature for this transformation. The hexagonal Cu_2H phase will be referred to as the ϵ-phase of copper hydride.

A Vinet equation of state was fitted to the data, yielding a zero-pressure volume of $V_0 = 13.10(1)$ Å^3 and bulk modulus of $K_0 = 145(5)$ GPa ($K' = 4.8(3)$) for ϵ-Cu_2H (compared to $K_0 = 137.4$ GPa for *fcc*-Cu).[13] This is in agreement with the widely accepted concept that interstitial hydrogen does not influence the mechanical properties of its host metal, but in stark contrast to the mechanical properties of wurtzite-type CuH (see Table I). This can be attributed to the different bonding of hydrogen atoms in the chemically synthesised hydride, which causes a significant increase in compressibility and volume ($V_0 = 16.75$ Å^3, $K_0 = 72(2)$ GPa).[12] Optical observations of our samples during hydrogenation and at higher pressures did not show a change in appearance. In addition to the absence of changes in the compressibility and the typical volume expansion, this led to the conclusion that the interstitial hydrogen atom donates its electron partly to the *s*- and *d*-bands of the surrounding metal (as found for many other hydrides[3]), such that the hydride retains a metallic character.

It is often assumed that the hydrogen sublattice in metal hydrides with hydrogen:metal ratios below 1 would form a disordered solid.[3] With a hydrogen:metal ratio of 0.5 in ϵ-Cu_2H, hydrogen atoms would be randomly distributed over the available sites, leaving 50% vacant. However, in our data, an additional weak reflection can be seen, matching the forbidden (001) reflection of the *hcp* lattice. Such reflections (00*l*, with odd *l*) appear when the *c*/2 translational symmetry is absent in the hexagonal lattice, through atoms being dis-

placed from their equilibrium hexagonal positions. This suggests an anti-CdI_2 type superstructure ($P\bar{3}m1$ space group) for Cu_2H: In this structure, instead of occupying random sites, hydrogen atoms fill every second layer of octahedral interstices. This periodic vacancy and filling of sites along the c-axis causes the displacement of the metal atoms. The anti-CdI_2 type structure is also observed in the hydrides of other metals, such as technetium,[29] cobalt,[27] and rhenium.[24,25] A comparison between wurtzite, anti-CdI_2 and cubic copper hydride structures is shown in Fig. 3.

The new positions of the metal atoms in the unit-cell are thus given by $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4} + \delta)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4} - \delta)$. The displacement δ can be determined by comparing calculated with observed intensities. Throughout both experiments, the relative intensity of the (001) reflection, $I_{(001)}/I_{(011)}$, remained at a constant 2.3(3)%, corresponding to a fractional displacement of $\delta = 0.016(2)$, larger than for $CoD_{0.5}$ ($\delta = 0.012$) and $TcH_{0.5}$ ($\delta = 0.01$). This may be due to imperfect hydrogen ordering in the latter hydrides: For $CoD_{0.5}$, neutron diffraction showed that ∼4% of hydrogen atoms occupy 1b sites of the lattice, forming a second sublayer that should be vacant in an ideal anti-CdI_2 structure.[27] Generally, a lower hydrogen content seems to manifest in smaller displacements, as $\delta = 0.007$ for $CoD_{0.38}$ and 0.009 for $ReH_{0.36}$.[25] From the larger displacement in Cu_2H it can be inferred that the intermediate layers are indeed completely vacant and that the structure is of perfect or nearly perfect anti-CdI_2-type.

In order to test the hypothesis that γ-Cu-H only forms with dehydrogenated copper, we decompressed the sample in the ϵ-phase to below decomposition pressure. After the sample fully separated into Cu and H_2, pressure was increased in steps up to ∼20 GPa. At 12.5 GPa, an increase in unit-cell volume of *fcc*-Cu was measured, indicating the formation of γ-Cu-H. Multiple hydride phases have also been observed in other metal-hydrogen systems, such as manganese hydride, which forms both γ- and ϵ-phases, depending on the temperature during compression.[31]

In the case of γ-Cu-H, the volume difference per atom increased from 0.338(6) Å^3 at 12.5 GPa to 0.386(6) Å^3 at 19.7 GPa. For *fcc* metals, hydrogen atoms typically occupy octahedral interstices in the γ-phase, leading to a volume expansion of ∼2.9 Å^3 per hydrogen atom.[32] Assuming that this is the case for γ-Cu-H, a hydrogen:metal ratio of ∼0.15 is found. Compared to the results reported by Burtovyy *et al.*,[21] we find the same synthesis pressure of 12.5 GPa, but a smaller volume increase of the host lattice (3.45(5)% vs 8%–11%) and thus hydrogen content (∼0.15 compared to ∼0.4 in Ref. 21). If the formation of γ-Cu-H does indeed depend on the history of the individual copper sample, the difference in hydrogen content in the γ-phase may be accounted for by different initial hydrogenation conditions: Burtovyy *et al.* used commercial wurtzite-type copper hydride to prepare their samples, whereas we used pristine copper foil which was hydrogenated under thermodynamic equilibrium. Furthermore, it was speculated[21] that small crystallites of copper, created through the decomposition of CuH, may show higher reactivity and could thus form the γ-phase more easily. An alteration of the microstructure during hydrogenation/dehydrogenation cycles is common in metals. This

TABLE I. Equation of state parameters for Cu, wurtzite-type CuH, and hexagonal Cu_2H. The bulk modulus of the chemically obtained CuH is significantly lower than for pure copper, in contrast to Cu_2H, where the mechanical properties are unchanged.

	Reference	EoS type	B_0 (GPa)	B_0'	V_0 (Å^3)
Cu	13	Birch-Murnaghan	137.4	5.52	11.81
CuH	12	Murnaghan	72(2)	2.7(3)	16.75
Cu_2H	This work	Vinet	145(5)	4.8(3)	13.10(1)

process could be more effective in the decomposition of wurtzite-type CuH than of ϵ-Cu$_2$H, leading to favourable conditions for hydrogen uptake in the γ-phase. A different explanation is that the lower hydrogen content seen in our data originates from slow kinetics, impeding the hydrogenation of the sample. It is not uncommon that kinetic effects play an important role in the formation of isomorphous metal hydrides (i.e., the incorporation of hydrogen into the metal matrix without it undergoing a structural phase transition, see, e.g., rhenium hydride[24]). In the present case, the time difference between crossing synthesis conditions and reaching maximum pressure for the γ-phase was only 1 h, in contrast to 20 h between individual data points in the study by Burtovyy *et al*. At room temperature, higher hydrogen concentrations in the γ-phase may only be achieved after a certain time.

It is interesting to note that wurtzite-type CuH could not be synthesised under thermodynamic equilibrium at pressures up to 51 GPa. Extrapolation of the equations of state of wurtzite-type CuH and ϵ-Cu$_2$H shows that both acquire the same volume at approximately 95 GPa, due to the larger compressibility of the first hydride. It can be argued that at this pressure the ϵ phase might undergo a transition to the wurtzite phase.

We compressed silver to 87 GPa and gold to 113 GPa at room temperature without observing any signs of hydrogenation (i.e., volume increase or phase transition). For silver, single-sided laser heating to well above 1000 °C was applied at 40 GPa while the gold-hydrogen mixture was externally heated to ~300 °C at pressures up to 45 GPa, to no effect in both cases. Figure 4 shows the measured pressure-volume data for silver and gold. No significant deviation from the known equations of state for both metals can be seen. It was predicted that *fcc*-silver hydride stabilises at pressures above 50 GPa,[8] which could not be confirmed. More recently, a theoretical study reported that pressures in excess of 180 GPa might be necessary.[7] In the same paper, the authors find that the formation of a gold hydride is impeded by a large energy barrier preventing the dissociation of hydrogen molecules at the metal surface. However, hydrogen undergoes a structural

phase transition into a mixed atomic and molecular state at 220 GPa (phase IV, see Ref. 33). At this point, a direct reaction of gold (and also silver) with hydrogen is very likely.

IV. CONCLUSION

In conclusion, we synthesised a novel hexagonal copper hydride from elements at pressures above 18.6 GPa. This ϵ-Cu$_2$H phase is the third known copper hydride, along with wurtzite-type CuH and cubic γ-Cu-H. The presence of superstructure peaks allowed to identify the structure as anti-CdI$_2$-type, where the hydrogen atoms are arranged in layers instead of being randomly oriented. Furthermore, we were able to reproduce the synthesis of γ-Cu-H, albeit with a lower hydrogen concentration. It remains uncertain whether the formation of γ-Cu-H is promoted by the hydrogenation history or the particular grain size and microstructure of the copper sample. However, it can be concluded that wurtzite-type copper hydride is in fact not the thermodynamically favourable structure of this hydride, despite having the highest hydrogen content and being the easiest to synthesise under non-equilibrium conditions.

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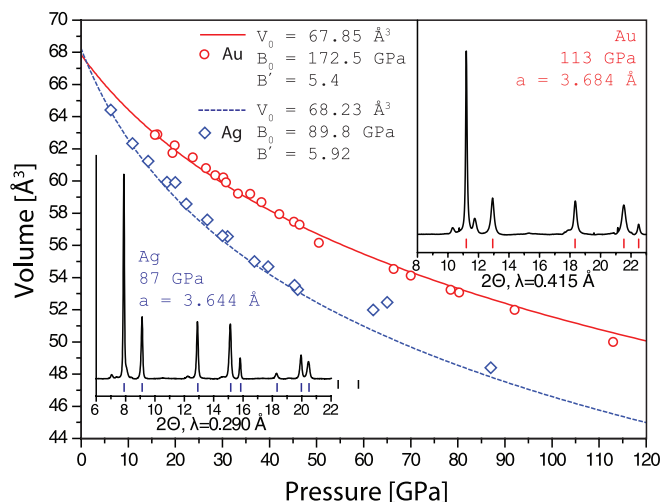[25]H. Kawamura, M. Harada, Y. Akahama, and K. Takemura, Solid State Commun. **130**, 59 (2004).

FIG. 4. Equation of state of silver (blue diamonds) and gold (red circles) measured in a hydrogen medium. The lines are literature EoS for *fcc*-silver[34] and *fcc*-gold.[35]

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