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High pressure synthesis and stability of cobalt hydrides

Mengnan Wang,¹ Jack Binns,¹ Mary-Ellen Donnelly,¹ Miriam Peña-Alvarez,² Philip Dalladay-Simpson,¹ and Ross T. Howie*¹

¹Center for High Pressure Science & Technology Advanced Research, 1690 Cailun Rd, Bldg 6, Pudong, Shanghai, 201203, P.R. China

²School of Physics & Astronomy and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh EH9 3FD, UK

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In-situ high-pressure high-temperature X-ray powder diffraction studies of the cobalt-hydrogen system reveal the direct synthesis of both the binary cobalt hydride (CoH), and a novel cobalt dihydride (CoH₂). We observe the formation of *fcc* CoH at pressures of 4 GPa, which persists to pressures of 45 GPa. At this pressure, we see the emergence with time of a further expanded *fcc* lattice, which we identify as CoH₂, where the hydrogen atoms occupy the tetrahedral vacancies. We have explored alternative synthesis routes of CoH₂, and can lower the synthesis pressure to 35 GPa by the application of high temperature. CoH₂ is stable to at least 55 GPa, and decomposes into CoH below 10 GPa, releasing molecular hydrogen before further decomposing completely into its constituent elements below 3 GPa. As a first-row transition metal, cobalt has a relatively lower mass than other hydride-forming transition metals, and as a result CoH₂ has a high hydrogen content of 3.3 wt% and a volumetric hydrogen density of 214 g/L.

Keywords: High pressure, cobalt, hydrogen, cobalt hydride, X-ray diffraction

I. INTRODUCTION

Studies of metal hydrides are often driven by the pursuit to produce a hydrogen-storage material that has high volumetric hydrogen density and high gravimetric content.¹ Although there are many recent examples of materials with such properties, the challenge still remains to produce such a material with hydrogen absorption and discharge conditions that could be achieved industrially. Despite the high reactivity of hydrogen, none of the group-VI to group-XI transition metals form hydrides at ambient conditions.² High pressure has been an effective and clean route to producing stoichiometric and non-stoichiometric hydrides with extremely high hydrogen contents.^{3–10} This is due to the chemical potential of hydrogen rising steeply with pressure, resulting in the ability to synthesize novel metal hydrides.

Rhodium dihydride (RhH₂), with a high volumetric hydrogen density of 163.7 g/L, was discovered at 8 GPa on compression at ambient temperature.³ Remarkably, this binary hydride was quenched to ambient pressure at low temperatures. The combined effect of both high pressure and high temperature would seem to increase the metal to hydrogen ratio, this can be exemplified by the Ir - H and Fe - H systems, whereby IrH₃ was synthesised at 65 GPa, whilst FeH₂, FeH₃ and FeH₅ were synthesised 67 GPa, 86 GPa and 130 GPa, respectively.^{5,6,10–12} Given that the other heavier members of group VIIIb, rhodium (Rh) and iridium (Ir), and its period neighbor, Fe, all form hydrides with hydrogen-to-metal ratios ≥ 1 , it is highly probable that cobalt could also form such a compound.

At ambient conditions, cobalt adopts an *hcp* crystal structure, however with the application of either temperature (above 700 K) or moderate pressure (0.17 GPa) a metastable *fcc* structure exists.¹³ Early studies of the

cobalt-hydrogen system have concentrated on the high temperature hydrogenation of *hcp* cobalt to form non-stoichiometric hydrides.^{14–17} These studies revealed that at 523 K, the hydrogen concentration increases monotonically with pressure up to 7 GPa, after which a *fcc* monohydride (CoH) is formed. A subsequent study reported the synthesis of the *fcc* monohydride from a solid-solid solution at ambient temperature and at pressures above 4.5 GPa¹⁸. Remarkably, both the non-stoichiometric *hcp* hydride and the *fcc* monohydride can be quenched in a metastable state at ambient pressure and temperatures below 200 K¹⁶. Recent theoretical predictions have investigated the cobalt-hydrogen system revealing novel structures with hydrogen-to-metal ratios ≥ 1 . Two new cubic polyhydrides, CoH₂ and CoH₃, emerge at pressures of 10 GPa and 30 GPa, respectively.¹⁹ These structures are predicted to be stable over a large pressure regime and both possess high volumetric hydrogen density.

In this study, we report the synthesis of two cobalt-hydrogen compounds in a laser heated diamond-anvil cell and confirmed through synchrotron X-ray diffraction. At pressures of 3 GPa and ambient temperature, we find that the known binary compound, CoH, is stable to at least 54 GPa. By compressing CoH to 35 GPa, we observe the formation of cobalt dihydride (CoH₂) with time, which is stable between 10 and 55 GPa. Laser heating CoH above 35 GPa and 2000 K cause the reaction to occur instantaneously. The structure of CoH₂ is also found to adopt a *fcc* structure with an expanded volume compared with the binary hydride. On decompression, below 10 GPa, CoH₂ decomposes to CoH, which subsequently decomposes to Co below 3 GPa. No evidence for the formation of the predicted CoH₃ was observed over the *P-T* conditions achieved in this study.

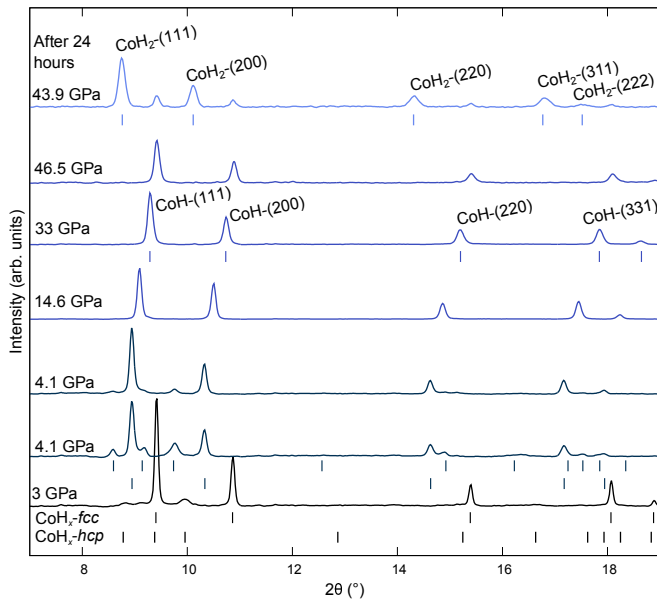


FIG. 1. High-pressure X-ray diffraction patterns ($\lambda = 0.3344$ Å) showing the stepwise synthesis of CoH (dark blue) from Co (black) with increasing pressure followed by the formation of CoH₂ (light blue) from CoH after 24 hours at pressures greater than 45 GPa. Tick marks indicate the positions of Bragg reflections from the noted phases.

II. EXPERIMENTAL DETAILS

High purity cobalt powder (99.8%, 1.6 μm particle size) from Alfa Aesar was loaded into a diamond-anvil cell (DAC), together with gold and/or ruby as a pressure marker and subsequently gas loaded with research grade hydrogen gas (99.9999%) at 0.17 GPa.^{20,21} Loading of hydrogen was confirmed by the observation of the hydrogen vibrational mode using a custom-built micro-focused Raman system.^{22,23} Rhenium gaskets were used to form the sample chamber in all experimental runs, diamond anvil culets ranged from 200 - 250 μm , with sample sizes ranging between 50 to 125 μm once hydrogen was in the solid state.

Angle-dispersive X-ray diffraction patterns were recorded on a Pilatus 1M image-plate detector at the GSECARS 13-IDD beamline (Advanced Photon Source, USA) with energy of 37 keV ($\lambda = 0.3344$ Å). Two-dimensional image-plate data were integrated with DIOP-TAS²⁴ to yield intensity *vs.* 2θ plots. Le Bail refinements²⁵ were carried out in JANA2006²⁶. Equation of state data were determined using EOSFIT 7.²⁷

III. RESULTS AND DISCUSSION

In our first series of experiments we have investigated the synthesis conditions of CoH from the direct reaction between Co and H₂. From 0.17 GPa up to 4 GPa, the observed X-ray diffraction pattern shows pure Co present

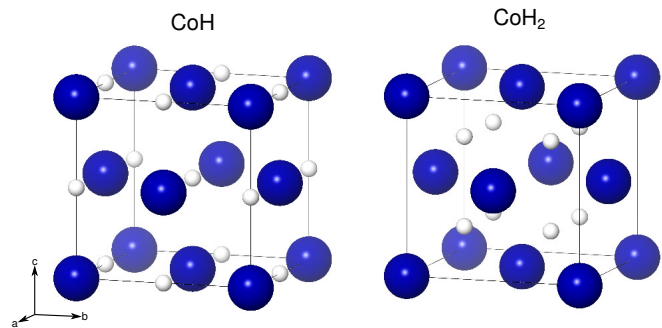


FIG. 2. Crystal structures of cobalt hydride (CoH) and cobalt dihydride (CoH₂). The cobalt atoms (blue) form an *fcc* lattice with hydrogen atoms (white) occupying the octahedral sites ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) in CoH. With increasing pressure hydrogen atoms occupy the tetrahedral sites ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), sharply increasing the unit-cell volume in the dihydride phase CoH₂.

in both the *hcp* phase and metastable *fcc* phase (Fig. 1). Closer examination shows these unit-cell volumes to be greater than those of pure Co at these pressures, indicating hydrogen has diffused into the lattices of both phases forming non-stoichiometric CoH_{*x*}, $x < 1$. It is interesting to note that the diffusion of hydrogen appears to favour the formation of the *fcc* phase. Further compression above 4 GPa leads to an expansion of both the *hcp* and *fcc* lattices as hydrogen is absorbed. With time the *hcp* phase gradually disappears leaving an expanded *fcc* structure. This phase, cobalt hydride (CoH), has space group symmetry *Fm* $\bar{3}$ *m*, with unit-cell length $a = 3.7132(2)$ Å (at 4.6(5) GPa). The volume per Co atom increases by 2.061(5) Å³ (+19.2%) compared to pure Co due to H atoms occupying the octahedral vacancies in the structure (Fig. 2 and 3). This transition and associated volume change are in agreement with previous observations of the formation of CoH and other transition metal monohydrides.^{7,8,18} One sample of CoH was compressed up to 54 GPa, into the predicted stability range of the cobalt polyhydrides. Over a timescale of 2 hr, no further transformation to a hydride with H/Co \geq was observed. On decompression, the sample was observed to decompose to Co and H₂ below 4.2 GPa, showing no hysteresis.

In a second experimental run, we compressed CoH to pressures of 46 GPa. After a period of 24 hr we see marked reduction of intensity of the diffraction peaks corresponding to CoH, substituted with new, intense and well defined diffraction lines (see Fig. 1). These peaks could be easily indexed to another face-centered cubic lattice, $a = 3.7946(2)$ Å, at 46 GPa, showing another abrupt volume increase of 2.675(1) Å³ (+24.4%) per Co atom compared to CoH at the same pressure. This volume increase and observed crystal symmetry is in agreement with the predicted fluorite-type structure of cobalt dihydride (CoH₂).¹⁹ In this structure H atoms fill each tetrahedral vacancy in the *fcc* lattice of Co atoms (Fig. 2).

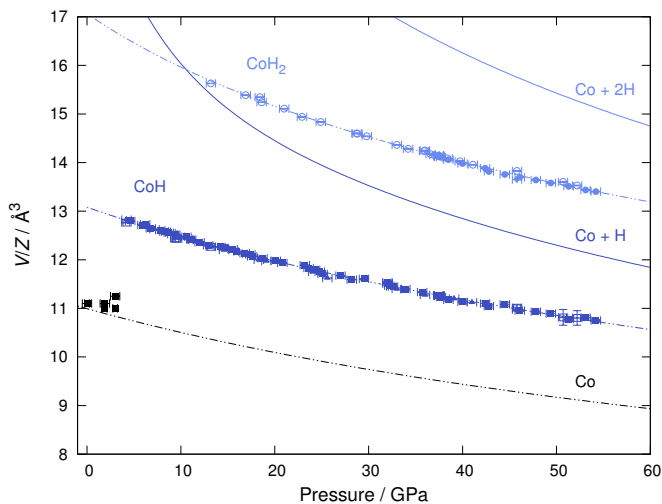


FIG. 3. Changes in volume per Co atom with pressure for CoH_x (black symbols), CoH (dark blue symbols), and CoH_2 (light blue symbols). Dashed lines correspond to fitted equations of state. Co equation of state given by Ref.²⁸. Closed and open symbols correspond to volumes observed under compression and decompression runs, respectively. Solid lines show equations of state derived from the atomic volumes of Co and H.^{28,29}

From this pressure samples were compressed or decompressed to explore the stability range of the newly-synthesized CoH_2 phase (Fig. 3). Cobalt dihydride remains stable to at least 55 GPa and adopts the same structure throughout this pressure range. We observe no sign of the predicted $I4/mmm$ CoH_2 phase.¹⁹ On decompression we observe diffraction peaks from CoH_2 down to 13.2 GPa, below this pressure CoH_2 decomposes to CoH and H_2 . This is in close agreement with the predicted formation pressure of 10 GPa.¹⁹ The observed volumes per Co atom are shown in Figure 3 for CoH_x , CoH , and CoH_2 . As expected for the non-stoichiometric hydrides, the data for CoH_x -*hcp* and CoH_x -*fcc* phases lie slightly above the equation of state for pure Co. The volumes of CoH and CoH_2 both show reasonable agreement with the equations of state predicted by Ref.¹⁹. The pressure-volume behaviors of CoH and CoH_2 were fitted with third-order Birch-Murnaghan P - V equations of state giving the following parameters: CoH $V_0 = 52.32(13) \text{ \AA}^3$, $K_0 = 194(11) \text{ GPa}$, $K'_0 = 3.5(4)$; and CoH_2 $V_0 = 68.3(11) \text{ \AA}^3$, $K_0 = 129(29) \text{ GPa}$, $K'_0 = 4.6(11)$ which results in good agreement between predicted and observed volumes (see Table I and Fig. 3).

In subsequent experimental runs, we investigated alternative synthesis routes of CoH_2 and the possibility of synthesizing the predicted CoH_3 . High-temperature laser heating is an effective route to form new hydrogen-containing compounds, often with unusual stoichiometries.^{5,6,10,30} Through *in-situ* laser heating X-ray diffraction measurements at pressures ≥ 36 GPa, we observe the thermal expansion of the CoH lattice and

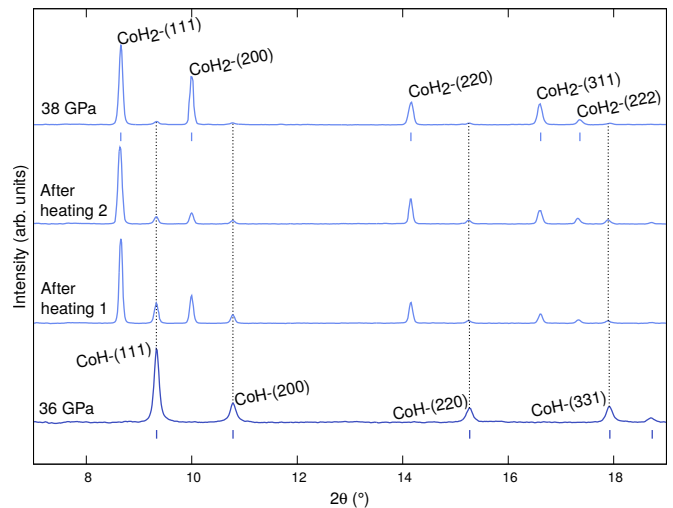


FIG. 4. High-pressure X-ray diffraction patterns ($\lambda = 0.3344 \text{ \AA}$) showing the synthesis of CoH_2 (light blue) from CoH (dark blue) + H_2 at 36 GPa by *in situ* laser heating. Repeated heating cycles show a reduction in intensities corresponding to CoH . CoH co-exists with CoH_2 even with further pressure increase (top pattern).

concurrent instantaneous reduction in intensity of the CoH diffraction peaks and appearance of peaks corresponding to CoH_2 (Fig. 4). The calculated lattice parameter after laser heating, $a = 3.8396(2) \text{ \AA}$, is in excellent agreement with our data from samples synthesized at room temperature. Repeated cycles of laser heating and quenching increases the relative concentration of CoH_2 , although we continue to observe weak diffraction peaks from the CoH reactant. While it is not impossible that with higher pressure, temperature and/or time that complete transformation from CoH to CoH_2 could be achieved, we can conclude that the diffusion of H_2 into CoH is limited even at high pressure and temperature. Interestingly, we do not see any further transition to the predicted cobalt trihydride (CoH_3) despite being within the calculated stability regime. However, it could be that higher pressure and longer reaction times are required for synthesis. In the case of iridium trihydride, pressures greater than 55 GPa were required for synthesis, however this formed a non-interstitial hydride directly from elemental Ir, compared with the step-wise interstitial filling of the cobalt hydrides.⁵ The step-wise nature of the transitions between CoH and CoH_2 strongly suggest these materials are stoichiometric hydrides. Similar behaviour is observed in the Ta-H and Rh-H systems, however this should be further explored with high-pressure neutron diffraction.^{3,8}

It was previously thought that the Rh- H_2 system was a unique example of a two-step hydrogen absorption-desorption from metal (M) to $M\text{H}$ to $M\text{H}_2$ by the step-wise filling of octahedral and tetrahedral sites whilst maintaining the *fcc* lattice.³ Our study shows that this is not the case, and synthesis of Co- CoH - CoH_2 can be

TABLE I. Equation of state parameters for Co, CoH, and CoH₂. Predicted values are given in italics.¹⁹

Phase	V_0 (Å ³ /Z)	B_0 (GPa)	B'_0
Co	10.87	224.6	4.08
CoH	13.08(13)	194(11)	3.5(4)
	<i>12.72</i>	<i>211.3</i>	<i>4.48</i>
CoH ₂	17.1(11)	129(29)	4.6(11)
	<i>16.03</i>	<i>194.4</i>	<i>4.03</i>

achieved on both compression and the application of high temperature. As a first-row transition metal, cobalt has a much lower mass than the analogous rhodium and as a result CoH₂ has a much higher gravimetric hydrogen content of 3.3 wt% as compared to 1.9 wt% for RhH₂. Extrapolation of the unit cell volume data to ambient pressure at room temperature results in cobalt dihydride also possessing a much higher volumetric hydrogen density of 196 g/L versus 163.7 g/L for RhH₂.³ Interestingly, it was reported that RhH₂ was recoverable to ambient pressure by cooling the sample to 6.1 K and on heating to 150 K, releases hydrogen over the time scale of minutes. Similarly, CoH has been shown previously to be recoverable in a metastable state below 200 K.¹⁴ Given the recoverability of the monohydride, and the strong similarities with the analogous RhH₂, it seems likely that CoH₂ could also be stabilized at low temperatures down to atmospheric pressure.³ Recovering to ambient pressure could open up the possibilities to conduct further diagnostic measurements, such as neutron diffraction to definitively determine the atomic positions of hydrogen.

IV. CONCLUSIONS

In conclusion, we have explored the cobalt-hydrogen system at pressures up to 55 GPa through X-ray diffraction and *in situ* laser heating. We have shown the step-wise formation of CoH and a new dihydride, CoH₂, from the pure elements. Cobalt dihydride forms with time from a mixture of CoH and H₂ at pressures above 45 GPa. The reaction can be expedited at lower pressures by laser heating the sample, reducing the formation pressure to 36 GPa. This newly observed dihydride is stable on decompression down to *ca.* 10 GPa, where it decomposes to CoH, before further decomposing completely below 3 GPa. The possibility of recovering both compounds to ambient pressure should be explored with further experiments at low temperatures. Owing to its relatively low mass compared to second and third-row transition metals, cobalt hydrides have a high hydrogen density compared to analogous transition metal hydrides.

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* ross.howie@hpstar.ac.cn

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