

High pressure synthesis and stability of cobalt hydrides

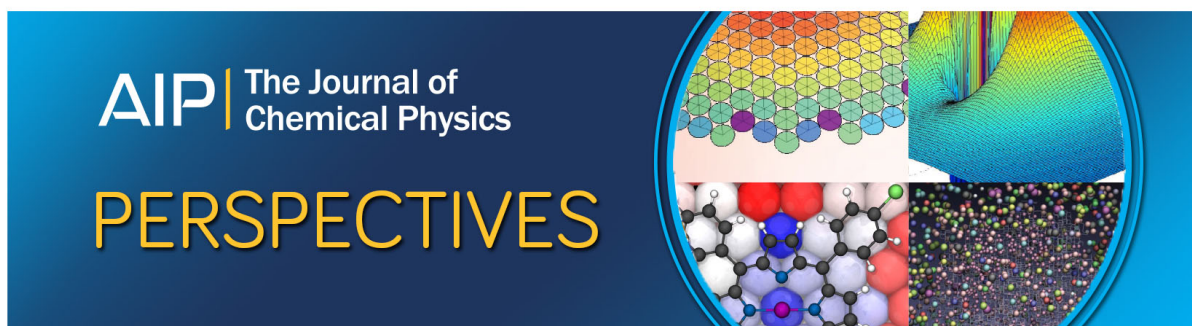
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High pressure synthesis and stability of cobalt hydrides

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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. Published by AIP Publishing. <https://doi.org/10.1063/1.5026535>

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 at 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 their 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 a 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 GPa.¹⁸ 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 K.¹⁶ 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 (DAC) 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 causes 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,

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below 10 GPa, CoH_2 decomposes to CoH , which subsequently decomposes to Co below 3 GPa. No evidence for the formation of the predicted CoH_3 was observed over the P - T conditions achieved in this study.

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 to 250 μm , with sample sizes ranging between 50 and 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 an energy of 37 keV ($\lambda = 0.3344$ Å). Two-dimensional image-plate data were integrated with DIOPTAS²⁴ to yield intensity vs. 2θ plots. Le Bail refinements²⁵ were carried out in JANA2006.²⁶ 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 H_2 . From 0.17 GPa up to 4 GPa, the observed X-ray diffraction pattern shows pure Co present in both the *hcp* phase and metastable *fcc* phase (Fig. 1). Closer examination shows

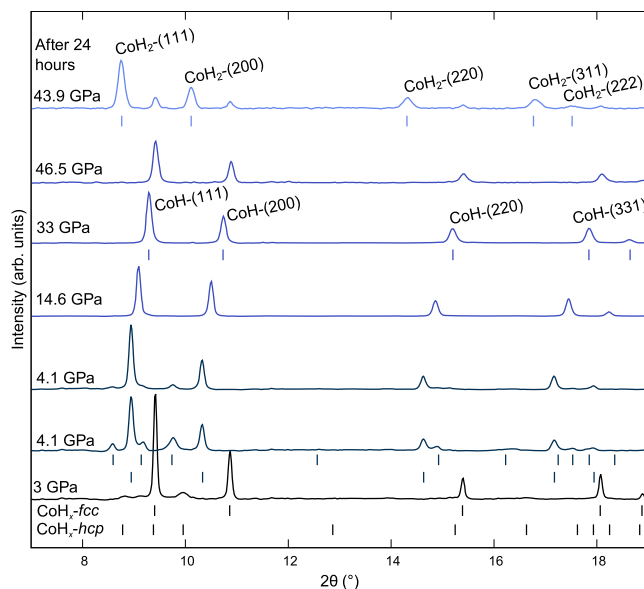


FIG. 1. High-pressure X-ray diffraction patterns ($\lambda = 0.3344$ Å) showing the stepwise synthesis of CoH (dark blue) from Co (black) with increasing pressure followed by the formation of CoH_2 (light blue) from CoH after 24 h at pressures greater than 45 GPa. Tick marks indicate the positions of Bragg reflections from the noted phases.

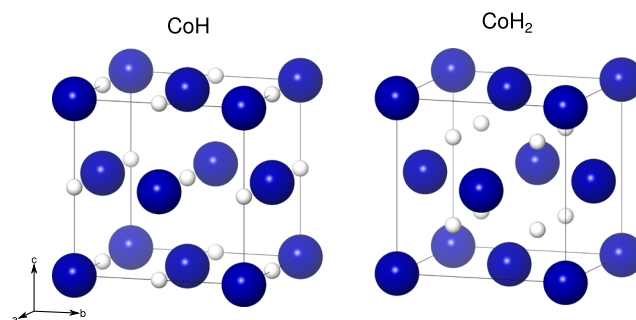


FIG. 2. Crystal structures of cobalt hydride (CoH) and cobalt dihydride (CoH_2). The cobalt atoms (blue) form a *fcc* lattice with hydrogen atoms (white) occupying the octahedral sites ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) in CoH . With increasing pressure hydrogen atoms occupy the tetrahedral sites ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), sharply increasing the unit-cell volume in the dihydride phase CoH_2 .

these unit-cell volumes to be greater than those of pure Co at these pressures, indicating that 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 (Figs. 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 time scale of 2 h, no further transformation to a hydride with $\text{H}/\text{Co} \geq 1$ was observed. On

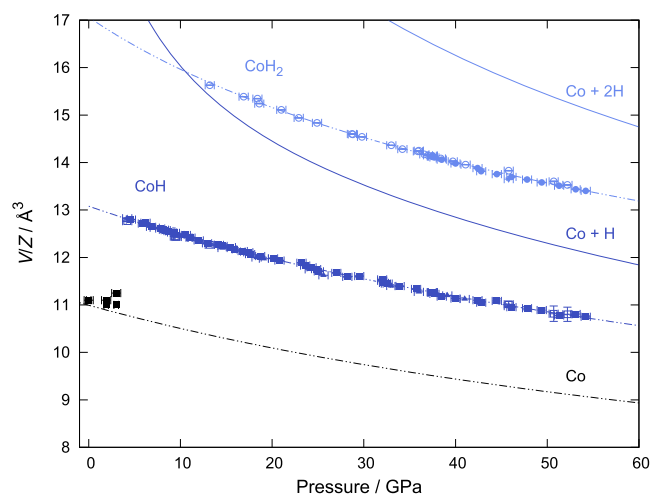


FIG. 3. Changes in volume per Co atom with pressure for CoH_x (black symbols), CoH (dark blue symbols), and CoH_2 (light blue symbols). Dashed lines correspond to fitted equations of state. Co equation of state given by Ref. 28. Closed and open symbols correspond to volumes observed under compression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

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 h, 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 are 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).

From this pressure, samples were compressed or decompressed to explore the stability range of the newly-synthesized CoH₂ 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 $I4/mmm$ CoH₂ phase.¹⁹ On decompression, we observe diffraction peaks from CoH₂ down to 13.2 GPa; below this pressure, CoH₂ decomposes to CoH and H₂. This is in close agreement with the predicted formation pressure of 10 GPa.¹⁹ The observed volumes per Co atom are shown in Fig. 3 for CoH_x, CoH, and CoH₂. 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 CoH₂ both show reasonable agreement with the equations of state predicted by Ref. 19. The pressure-volume behaviors of CoH and CoH₂ were fitted with third-order Birch-Murnaghan $P - V$ equations of state giving the following parameters: CoH $V_0 = 52.32(13)$ Å³, $K_0 = 194(11)$ GPa, $K'_0 = 3.5(4)$; and CoH₂ $V_0 = 68.3(11)$ Å³, $K_0 = 129(29)$ 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 CoH₂ and the possibility of synthesizing the predicted CoH₃. 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 concurrent instantaneous reduction in the intensity of the CoH diffraction peaks and appearance of peaks corresponding to CoH₂ (Fig. 4). The calculated lattice parameter after laser heating, $a = 3.8396(2)$ Å, is in excellent agreement

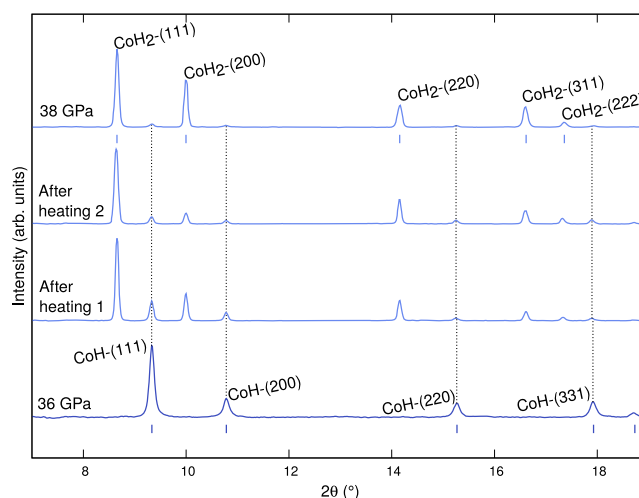


FIG. 4. High-pressure X-ray diffraction patterns ($\lambda = 0.3344$ Å) showing the synthesis of CoH₂ (light blue) from CoH (dark blue) + H₂ at 36 GPa by *in situ* laser heating. Repeated heating cycles show a reduction in intensities corresponding to CoH. CoH co-exists with CoH₂ even with further pressure increase (top pattern).

with our data from samples synthesized at room temperature. Repeated cycles of laser heating and quenching increases the relative concentration of CoH₂, although we continue to observe weak diffraction peaks from the CoH reactant. While it is possible that with higher pressure, temperature, and/or time complete transformation from CoH to CoH₂ could be achieved, we can conclude that the diffusion of H₂ into CoH is limited even at high pressure and temperature. Interestingly, we do not see any further transition to the predicted cobalt trihydride (CoH₃) 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 CoH₂ strongly suggests that these materials are stoichiometric hydrides. Similar behavior 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-H₂ system was a unique example of a two-step hydrogen absorption-desorption from metal (*M*) to *MH* to *MH*₂ by the stepwise 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-CoH₂ can be 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,

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> |

which 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 hydrogen content.

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 stepwise 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 and reducing the formation pressure to 35 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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