Prediction and Synthesis of Dysprosium Hydride Phases at High Pressure

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ABSTRACT: Crystal structure prediction (CSP) methods recently proposed a series of new rare-earth (RE) hydrides at high pressures with novel crystal structures, unusual stoichiometries, and intriguing features such as high-$T_c$ superconductivity. RE trihydrides (REH$_3$) generally undergo a phase transition from ambient $P6_3/mmc$ or $P3c1$ to $Fm3m$ at high pressure. This cubic REH$_3$ ($Fm3m$) was considered to be a precursor to further synthesize RE polyhydrides such as YH$_4$, YH$_6$, YH$_9$, and CeH$_9$ with higher hydrogen contents at higher pressures. However, the structural stability and equation of state (EOS) of any of the REH$_3$ have not been fully investigated at sufficiently high pressures. This work presents high-pressure X-ray diffraction (XRD) measurements in a laser-heated diamond anvil cell up to 100 GPa and ab initio evolutionary CSP of stable phases of DyH$_3$ up to 220 GPa. Experiments observed the $Fm3m$ phase of DyH$_3$ to be stable at pressures from 17 to 100 GPa and temperatures up to $\sim$2000 K. After complete decompression, the $P3c1$ and $Fm3m$ phases of DyH$_3$ recovered under ambient conditions. Our calculations predicted a series of phases for DyH$_3$ at high pressures with the structural phase transition sequence $P3c1 \rightarrow $Imm2 $\rightarrow Fm3m \rightarrow$ Pnma $\rightarrow P6_3/mmc$ at 11, 35, 135, and 194 GPa, respectively. The predicted $P3c1$ and $Fm3m$ phases are consistent with experimental observations. Furthermore, electronic band structure calculations were carried out for the predicted phases of DyH$_3$, including the 4$f$ states, within the DFT+U approach. The inclusion of 4$f$ states shows significant changes in electronic properties, as more Dy $d$ states cross the Fermi level and overlap with H 1$s$ states. The structural phase transition from $P3c1$ to $Fm3m$ observed in DyH$_3$ is systematically compared with other REH$_3$ compounds at high pressures. The phase transition pressure in REH$_3$ shows an inverse relation with the ionic radius of RE atoms.

INTRODUCTION

Metal hydride formation has been of huge scientific interest, as hydrides are known for their unique optical and superconducting properties as well as for potential hydrogen storage applications. Hydrogen reacts with most metals to form an interstitial hydrides with variable hydrogen concentrations. Among them, rare-earth hydrides (REH$_3$) have been of particular research interest lately, as RE atoms possess partially filled $f$ orbitals while hydrogen with one electron can accept or donate one electron or form covalent bonds.

Several experimental works have been recently carried out on RE hydrides due to the interesting electronic states predicted. Under ambient conditions, RE elements react with hydrogen to form dihydrides, REH$_2$, with metallic conductivity. Further absorption of hydrogen results in the formation of RE trihydrides (REH$_3$), with an electrically insulating character. These lead to the possibility of engineering the composition-dependent switching of electrical and optical properties in REH$_3$. Applied pressure on RE with hydrogen can provide a tremendous amount of internal energy and induce metallization, electronic, magnetic, and structural transitions, exotic physical properties, or formation of new compounds with unusual stoichiometries. REH$_3$ species are known for their interesting high-pressure behavior. In this respect, many REH$_3$ species (RE = Sc, Y, Sm, Gd, Tb, Ho, Er, Lu, Dy) have been studied experimentally and theoretically under pressure. However, most of these studies are limited to $\sim$35 GPa or below. Under ambient conditions, REH$_3$ species generally crystallize into a $P6_3/mmc$ or $P3c1$ structure. With further pressurization, they undergo a structural transition into a $Fm3m$ structure via an intermediate mixed phase or complex
phase region. The high-pressure phase transition sequence, from $P_6_{3}/mmc$ or $P3\_1$ to $Fm\_3m$, appears to be prevalent in $REH_3$ systems. Theoretical investigations of $REH_3$ compounds have focused on their structural stability, phase transitions, equation of state (EOS), electronic/ electrical and phonon properties. For some studies at pressures above 35 GPa, $REH_3$ species have been reported to be the precursor phase for $RE$ hydrides with higher hydrogen contents. Hence, the high pressure–temperature ($P$–$T$) phase stability and physical properties of the $Fm\_3m$ phase above 35 GPa have greatly inspired our recent pursuit of $RE$ polyhydrides with high hydrogen contents and/or superconductivity at high pressures.

Crystal structure prediction (CSP) has become a powerful research tool to predict materials at ambient as well as at high pressure. Many hydrogen-rich $RE$ polyhydrides/superhydrides have been predicted to become stable under pressure. Those hydrides have hydrogen contents greater than what would follow from atomic valencies. Experimentally the concentration of hydrogen can be implied through the expansion of the unit cell volume with changes in the bonding nature between the $RE$ atom and hydrogen. The hydrogen content also has a significant effect on the structural, electronic, and magnetic properties of $RE$ hydrides. $RE$ hydrides are also very interesting systems to investigate theoretically, as a variety of electronic states are expected to change at high pressure. Many of them are expected to exhibit superconductivity close to room temperature. Extensive efforts are taken by theorists and experimentalists to discover hydride-based superconductors. Superconductivity is governed by the interactions between hydrogen and metal atoms in certain crystal structures, which can be seen from the very distinct $T_c$ values for various hydrides of different $RE$ atoms. RE superhydrides ($REH_x$, $x > S$) with stoichiometries $REH_6$, $REH_9$, and $REH_{10}$ are predicted to form novel clathrate structures. These clathrate-structured $RE$ superhydrides possess a three-dimensional dense hydrogen sublattice which encapsulates $RE$ atoms. Interestingly, these superconducting $RE$ superhydrides were predicted to crystallize in highly symmetric crystal structures at high pressures. For example, $YH_6$ is predicted to crystallize in the cubic $Im\_3m$ structure, $YH_{10}$ and $LaH_{10}$ are predicted to crystallize in the cubic $Fm\_3m$ structure, and $YH_9$ and $CeH_9$ predicted to have a hexagonal $P6_{3}/mmc$ structure. Experiments confirmed and characterized $YH_{6o}$ $YH_{9p}$, $CeH_{9p}$, $PrH_{9p}$, and $LaH_{10}$, were consistent with their theoretically predicted structures and high-pressure phase stability. Most of these clathrate-structured RE superhydrides were predicted to have a superconducting $T_c$ value close to room temperature. Notably, following recent theoretical predictions, high-temperature superconductivity was experimentally observed in $LaH_{10}$ with a record high $T_c$ of 250 K at 170 GPa.

The high-pressure $Fm\_3m$ phase of $YH_3$ was also predicted to be a conventional superconductor under pressure. In recent studies on the $Ce$–$H$ system, $CeH_x$ with a $\beta$-UH$_3$ type structure (space group $Pm\_3m$, $\beta$-$CeH_7$) was synthesized at 33 GPa after heating. After further compression and reheating of $\beta$-$CeH_7$ and $H_2$, $CeH_7$ was formed at pressures of 80–100 GPa. In the $Pr$–$H$ system, $PrH_x$ phases with $Fm\_3m$ and $P4/nmm$ structures were synthesized at 10 and 40 GPa, respectively. The point to be noted here is that the $Ce$–$H$ and $Pr$–$H$ systems were studied in the environment with excess hydrogen. Studies on RE in excess hydrogen under a megabar pressure regime and with laser heating resulted in discoveries of $\beta$-UH$_3$-type $CeH_x$, $P4/nmm$-$PrH_y$, $LaH_{10}$, $CeH_9$, and $PrH_x$ phases. However, the $RE$–$H$ binary systems that produced new $RE$ hydrides with stoichiometries and structures were light lanthanoids. Importantly, they have been investigated at pressures over the megabar range. For other $RE$ elements, particularly heavy lanthanoids such as Dy, Ho, and Er, their possible hydride phases have not been explored experimentally at megabar pressures, at high-temperatures and in excess of hydrogen. In a recent report, heavy lanthanoids were reported to possibly be low $T_c$ superconductors.

Dysprosium ($Dy$), one of the heavy, normally trivalent lanthanoids, is known to form di- and trihydrides under ambient conditions. High-pressure X-ray diffraction (XRD) studies on $DyH_3$ reported up to 35 GPa found the HCP to FCC transition, as for other $REH_3$ compounds. Recently, Peng et al. and Semenok et al. predicted rich chemistry of the $Dy$–$H$ system e.g., $DyH_4$, $DyH_5$, $DyH_6$, $DyH_9$, $DyH_{14}$, and $DyH_{16}$. It would be interesting to investigate $Dy$–$H$ chemistry under extreme conditions.

The structural stability of the $Fm\_3m$ phase of $DyH_3$ under high $P$–$T$ conditions has been studied; hence, its experimental and theoretical investigations would be very intriguing.

Here we conducted a systematic investigation of the $Dy$–$H$ system theoretically and experimentally focusing on $DyH_3$. CSP methods were used to predict new structures of $DyH_3$ at high pressure up to 220 GPa. In experiments, the $Dy$–$H$ system was studied in an excess hydrogen environment at pressures up to ~100 GPa in laser-heated diamond anvil cells (DACs). The direct chemical reaction between elemental dysprosium and hydrogen was carried inside DACs, coupled with synchrotron XRD. Our experimental results show that dysprosium reacts with hydrogen to form the $Fm\_3m$ $DyH_3$ phase, which remains stable up to ~100 GPa and ~2000 K. Further theoretical calculations were used to verify the dynamical stability of the cubic $DyH_3$ phase in the experimental pressure range. A detailed ab initio investigation of the structural stability and electronic structure of the new high-pressure phases predicted for $DyH_3$ are presented here. Our results on the phase stability and EOS parameters of the $DyH_3$ phase are compared with other previously reported $REH_x$ phases to provide us with a better understanding of the thermodynamic and physical behavior of $RE$–$H$ systems at high pressures.

**EXPERIMENTAL DETAILS**

High $P$–$T$ XRD experiments on the $Dy$–$H$ system were carried out using laser-heated DACs. Pairs of beveled diamond anvils with 75–300 $\mu$m culets were used to reach the desired pressures. Rhenium gaskets were used to preindent from the initial thickness of 250 $\mu$m to ~18 $\mu$m. Subsequently, a hole of ~45 $\mu$m was drilled and served as a sample chamber. Dysprosium samples were prepared in a glovebox filled with argon, where both $H_2O$ and $O_2$ concentrations were maintained below 0.1 ppm. The polycrystalline dysprosium sample was slightly pressed to ~5 $\mu$m in thickness and 10 $\times$ 10 $\mu$m in size and then loaded into the sample chamber. High-purity hydrogen gas was loaded into the sample chamber using a high-pressure gas compressor by pumping hydrogen gas to ~1.7 kilobar pressure at the Center for High Pressure Science & Technology Advanced Research (HPSTAR). Hydrogen served as a starting material as well as a calibrant. Angle-dispersive XRD patterns were recorded on a
PILATUS CdTe 1M detector at beamline 13-IDD of GeoSoilEnviroCARS (GSECARS) at the Advanced Photon Source (APS) of Argonne National Laboratory, USA. An incident X-ray with a wavelength of 0.3344 Å was focused onto a spot size of \( \sim 3 \times 4 \) μm (fwhm) at the sample position, and a pinhole of 8 μm size was used as a cleanup slit, which helped in the collection on cleaner XRD patterns from the smallest area possible by cutting down the tails of the incident X-ray beam. An infrared pulsed laser with a wavelength of 1064 nm at beamline 13-IDD was focused onto the sample as a flat top of the laser heating spot size at around 10 μm in diameter for single-sided laser heating. Several cycles of laser heating were carried out at each given pressure of 25, 40, 54, 68, 84, and 98 GPa, respectively. Laser pulses of a microsecond width at a rate of 10 kHz and accumulation of 200–300k frequency were used to heat the sample to 1000–2000 K. We intentionally limited laser heating to less than 2000 K to avoid a parasitic reaction with the Re gasket and to protect the diamonds from reacting with hydrogen under high \( P–T \) conditions. In situ temperature measurements were carried out by fitting the slope of the measured thermal radiation spectra to a Planck radiation function. The uncertainty in temperature measurements was typically less than ±100 K. The obtained raw images of XRD were integrated with DIOPTAS software. Le Bail refinements were carried out using the FullProf and Jana programs.

## COMPUTATIONAL DETAILS

We performed a systematic fixed-composition crystal structure search using the \textit{ab initio} evolutionary algorithm USPEX,	extsuperscript{30–32} which is capable of simultaneously searching for a stable structure with different numbers of formula units (fu) for a given composition. Here, we carried out crystal structure prediction calculations at 0, 50, 100, 150, 200 GPa for DyH\textsubscript{3} with up to 6 fu in the primitive cell. The first generation was produced randomly (using random symmetric	extsuperscript{32} and topological	extsuperscript{33} structure generators), while USPEX made subsequent generations with 20% random structures and 80% using heredity, soft mutation, and lattice mutation operators using the lowest enthalpy of the on-site Coulomb interaction among the \( 4f \) orbitals of H were treated as valence states. The \( 5s^2 \), \( 5p^6 \) and \( 1s^1 \) were used for dysprosium and hydrogen, respectively. The Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) was used.

A plane-wave kinetic-energy cutoff of 1000 eV, hard PAW potentials, and dense \( \Gamma \)-centered \( k \)-point grids with reciprocal space resolution \( 2\pi \times 0.05 \) Å\(^{-1}\) were employed to sample the Brillouin zone. To construct the phase diagram of DyH\textsubscript{3}, the enthalpies were recalculated with increased precision at various pressures with a smaller pressure increment of 10 GPa. Electronic structure calculations for all of the predicted phases of DyH\textsubscript{3} were performed with the full-potential augmented-plane wave + local orbital (APW +lo) approach as implemented in the Elk code.

The \( 5s^{2} 5p^{6} 4f^{13} \) orbitals of Dy and \( 1s^{1} \) orbitals of H were treated as valence states. The exchange and correlation effects were treated with the PBE-GGA functional. The effect of the on-site Coulomb interaction among the \( 4f \) states of Dy was also considered within GGA+U (\( U = 6 \) eV).

The obtained electronic band structure and density of states with inclusion of the \( 4f \) states expectedly showed significant changes at the Fermi level for the predicted phases of DyH\textsubscript{3} within the studied pressure range.

## RESULTS AND DISCUSSION

### Synthesis of High-Pressure Phases in the Dy–H System in a DAC

Parts a and b of Figure 1 show the XRD patterns observed in our experiments in the compression and decompression cycles, respectively. After elemental Dy and H\textsubscript{2} were loaded in the sample chamber, an intermediate phase was observed at 9 GPa at ambient temperature (see Figure 1a). Similarly, the intermediate phase between hexagonal and cubic was also observed for other REH\textsubscript{3} compounds,	extsuperscript{7,8,14,39–41} and in most cases, it was mixed with hexagonal and cubic phases. In the case of YH\textsubscript{3}, the intermediate phase was observed with a long-period polytype structure.\textsuperscript{8,42} In addition to an intermediate phase, the presence of bixbyte-type (i.e., fluorite-type with O vacancies) Dy\textsubscript{2}O\textsubscript{3} was noticed in XRD patterns at 9 GPa, but on the basis of its XRD intensities it should minimally affect the experiments as a minor impurity phase. With further pressurization, a complete transformation into the \( Fm\bar{3}m \) phase of Dy\textsubscript{3}H\textsubscript{10} was observed above 17 GPa. Previous high-pressure studies of DyH\textsubscript{3} also reported a sluggish hexagonal to cubic transition between 7 and 17 GPa.16 The obtained raw images of XRD were integrated with DIOPTAS software. Le Bail refinements were carried out using the FullProf and Jana programs.

### Figure 1. Representative integrated XRD patterns of the Dy–H system at high pressure and temperature. (a) In a compression cycle, a long-period polytype phase was observed at 9 GPa. Above 17 GPa, it transforms into \( Fm\bar{3}m \) phase of Dy\textsubscript{3}H\textsubscript{10} which remains stable up to 98 GPa. (b) In a decompression cycle the \( Fm\bar{3}m \) phase of Dy\textsubscript{3}H\textsubscript{10} was decompressed down to approximately 30 GPa. Under ambient conditions, the recovered sample was the \( P\bar{3}c1 \) phase of Dy\textsubscript{3}H\textsubscript{10} that coexisted with the \( Fm\bar{3}m \) phase. The wavelength of the incident X-rays (\( \lambda \)) was 0.3344 Å.

### Figure 2. Refinement of the XRD pattern at 71 GPa. The inset shows crystal structure of the \( Fm\bar{3}m \) phase of Dy\textsubscript{3}H\textsubscript{10} with hydrogen atoms midway between the Dy atoms. The black hash symbol denotes the unknown peaks.
of DyH₃ at ambient pressure. The high-pressure Fm̅3m phase has also been recovered previously in studies on SmH₃ and DyH₃.⁴⁰ The lattice parameters of the P̅3c1 phase of DyH₃ recovered at ambient pressure are a = 6.3849(8) Å and c = 6.596(1) Å and that for the Fm̅3m phase of DyH₃ is a = 5.239(1) Å. The EOS parameters of the Fm̅3m phase of DyH₃ obtained in the compression and decompression cycles are given in Figure 3. The unit cell volume of the Fm̅3m phase of DyH₃ as a function of pressure fitted using third-order Birch–Murnaghan EOS yielded the zero-pressure unit cell volume \( V_0 = 35.4(3) \text{ Å}^3/\text{fu} \) and bulk modulus \( K_0 = 85(3) \text{ GPa} \), with fixed \( K_0' = 4 \).

Experiments did not observe the formation of \( \beta \)-UH₃ type or \( P4/nmm \) phases of DyH₃ even after simultaneous compression and heating in excess hydrogen, as reported for the Ce–H and Pr–H systems.¹³,²⁴ In our calculations this structure is not stable, but becomes close to stability at pressures around 10 GPa.

**Theoretical Prediction of Various DyH₃ Phases at High Pressures.** First-principles calculations were performed to understand the chemistry of the Dy–H system at high pressure, along with the electronic structure, dynamical stability, and structural properties. Here, the focus was on the theoretical study of DyH₃, a compound that has been successfully synthesized. In previous theoretical studies, various compositions of the Dy–H system were predicted at high pressure, such as DyH, DyH₂, DyH₃, DyH₄, DyH₇, and Dy₅H₁₄.¹¹ Among the stable Dy–H phases predicted, only the DyH₃ phase was obtained in our experiment. Therefore, various fixed-composition calculations were performed at different pressures, to find the stable phases and clarify the phase diagram of DyH₃ as it undergoes a series of structural phase transitions within the studied pressure range of 0–220 GPa. In theoretical calculations, the P̅3c1, Imm2, Fm̅3m, Pnma, and P6₃/mmc phases of DyH₃ were predicted to become stable at 0, 11, 35, 135, and 194 GPa, respectively (see the phase diagram in Figure 4).

Most REH₃ compounds crystallize in a hexagonal structure under ambient conditions with the possible space groups P6₃, P6₃/mmc, P3c1, and P6₃/mm. From the space groups, the stable phase of DyH₃ was recovered under ambient pressure after complete decompression. Kong et al.⁹ reported REH₃ (RE = Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds that were stable in P6₃/mmc symmetry under ambient conditions. Extensive studies have been devoted to understanding the structural transition sequences in REH₃ compounds. The known structural transition trends in this class of compounds are from an ambient P6₃/mmc or P3c1 structure to the Fm̅3m structure at high pressure. Kataoka et al.⁴⁶ were able to stabilize the high-pressure Fm̅3m phase under ambient conditions by doping it with an alkali or alkaline-earth metals (Li, K and Mg) for REH₃ (RE = Y, Gd, Dy). Interestingly, three new phases (Imm2, Pnma, and P6₃/mmc) of DyH₃ have been predicted in addition to the known phases (P̅3c1, Fm̅3m) in the studied pressure range of 0–220 GPa. The pressure-induced structural transition sequence in DyH₃ is as follows: P̅3c1 \( \rightarrow \) Imm2 \( \rightarrow \) Fm̅3m \( \rightarrow \) Pnma \( \rightarrow \) P6₃/mmc at 11, 35, 135, and 194 GPa, respectively. The hexagonal to cubic transition is observed experimentally at 17 GPa and predicted the same transition at 35 GPa via an intermediate (Imm2).

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Figure 3. Unit cell volume of the Fm̅3m phase of DyH₃ as a function of pressure. The experimental volume per formula unit is plotted as a function of pressure. Red and blue open triangles represent the Fm̅3m phase of DyH₃ in the compression and decompression cycles, respectively. The black line represents the EOS fit.

Figure 4. Calculated enthalpies of various predicted structures of DyH₃ as a function of pressure (relative to the cubic Fm̅3m phase). The P̅3c1, Imm2, Fm̅3m, Pnma, and P6₃/mmc phases of DyH₃ became stable at 0, 11, 35, 135, and 194 GPa, respectively.
parameter values of DyH$_3$ phases were calculated and other REH$_3$ species such as ErH$_3$ and HoH$_3$ under high pressure. The present study reveals the hidden intermediate phase, which is stable in the pressure range of 11–35 GPa. The Pnma phase is also an energetically competitive for Imm2 and Fm$\bar{3}$m phases. The Imm2(Pnma) → Fm$\bar{3}$m transition is a weakly first-order transition in nature, which is clearly seen from static enthalpy calculations in the pressure range of 20–35 GPa (see Figure 4). The predicted intermediate phases were not observed in our experiment at room temperature, which might be due to the anharmonic and quantum symmetrization effects. Detailed structural information on the predicted phases is given in Table 1. Moreover, the intermediate (C$\bar{2}$m and Cmcm) phases were also predicted for other REH$_3$ species such as ErH$_3$ and HoH$_3$ under high pressure. The present study reveals the hidden intermediate phase (Imm2) for the investigated compound, DyH$_3$. The EOS parameter values of DyH$_3$ phases were calculated and fitted using a third-order Birch–Murnaghan EOS. The fitted parameters, such as the volume at zero pressure, bulk modulus, and first pressure derivative of bulk modulus for Fm$\bar{3}$m DyH$_3$ are $V_0 = 34.6$ Å$^3$/fu and $K_0 = 90.21$ GPa with $K_0’$ fixed at 4.

From our calculated phase diagram and EOS parameters, it is apparent that the cubic phase observed above 17 GPa with laser heating has DyH$_3$ stoichiometry. The experimental lattice parameter of the Fm$\bar{3}$m phase at 30 GPa is $a = 6.328$ Å ($a = 4.812$ Å theoretical). The theoretical EOS and fitted parameters in cubic DyH$_3$ are consistent with our experimental values (see Table 2). In the Fm$\bar{3}$m phase of DyH$_3$, dysprosium atoms occupy the 4a (0,0,0) Wyckoff position and hydrogen atoms occupy the 8c (1/4,1/4,1/4) and 4b (1/2,1/2,1/2) Wyckoﬀ positions. The theoretical third-order Birch–Murnaghan EOS fits to the P–V data of DyH$_3$ along with experimental values are given in Table 2, which clearly shows P$\bar{3}$c1 has a lower bulk modulus of 80.7 GPa: i.e., higher compressibility in comparison with the high-pressure phase (Fm$\bar{3}$m) has a bulk modulus of 90.2 GPa) (see Table 2).

P$\bar{3}$c1-DyH$_3$ has a hexagonal fluorocite-type structure, with the nearest H–H distance of 2.10 Å and Dy–H distance of 2.13 Å at 0 GPa. In the Fm$\bar{3}$m structure, the Dy–H bond distance is 2.12 Å at 20 GPa and 1.80 Å at 220 GPa. For DyH$_3$, theoretical calculations obtained a complex phase diagram with four phase transitions between 0 and 220 GPa. DyH$_3$ transforms to a cubic phase with space group Fm$\bar{3}$m with 4 fu/cell at 35 GPa. Fm$\bar{3}$m remains the most stable phase until 135 GPa and then transforms to a Pnma phase. Finally, at pressures above 194 GPa, a hexagonal phase with 6 fu/cell becomes stable. Predicted stable phases of DyH$_3$ at different pressures are shown in Figure 5 (detailed structural information is provided in Table 1). A comparison of our results with the results obtained by Kong et al. at ambient pressure shows consistency, in which the hexagonal fluorocite-type phase (P$\bar{3}$c1) has lattice parameters $a = 6.328$ Å and $c = 6.598$ Å (in comparison with the experimental values $a = 6.3849(8)$ Å and $c = 6.596(1)$ Å) recovered at ambient pressure.

**Electronic Structure of DyH$_3$ Phases.** Further, the electronic band structure and projected density of states (PDOS) were explored for the ambient- and high-pressure phases of DyH$_3$ with inclusion of 4f states for Dy as depicted in Figure 5. The inclusion of the 4f states for Dy along with Hubbard $U (=6)$ parameter shows a significant change in the electronic properties at the Fermi level for all of the predicted phases of DyH$_3$ (see Figure 5). As illustrated in Figure 5, the predicted ambient- and high-pressure phases of DyH$_3$ show

### Table 1. Crystal Structures of the Predicted DyH$_3$ Phases

<table>
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<tr>
<th>Phase</th>
<th>Pressure Range, GPa</th>
<th>Volume, Å$^3$/fu</th>
<th>ρ, g/cm$^3$</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
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<td>P$\bar{3}$c1</td>
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<td>38.14</td>
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<td>$b = 6.598$</td>
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<td>$a = 10.619$</td>
<td>$b = 4.628$</td>
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<td>P6$_3$/mmc</td>
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<td>17.86</td>
<td>15.39</td>
<td>$a = 2.773$</td>
<td>$b = 5.360$</td>
<td>$c = 4.207$</td>
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</table>

### Table 2. Theoretical Parameters of the Third-Order Birch–Murnaghan EOS

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<th>Structure</th>
<th>$V_0$, Å$^3$/fu</th>
<th>$K_0$, GPa</th>
<th>$K_0’$</th>
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<td>79.8$^a$</td>
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<td>Fm$\bar{3}$m</td>
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<td>P6$_3$/mmc</td>
<td>34.2</td>
<td>97</td>
<td>3.91</td>
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</table>

$^a$Experimental data of this work are also added for the cubic phase.
metallic character, and the Fermi level is mainly dominated by Dy d states for all of the predicted phases.

**Phonon Dispersion Curves of DyH₃ Phases.** Phonon dispersion curves along with the projected phonon density of states.

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Figure 5. Electronic band structure and projected electronic density of states of (a) $P\bar{3}c1$, (b) $Fm\bar{3}m$, (c) $Pnma$, and (d) $P6_3/mmc$ DyH₃ at 0, 40, 150, and 220 GPa, respectively, including 4f electrons using the GGA+U method ($U = 6$ eV).

Figure 6. Calculated phonon dispersion curves and projected phonon density of states (PhDOS) of (a) $P\bar{3}c1$, (b) $Fm\bar{3}m$, (c) $Pnma$, and (d) $P6_3/mmc$ DyH₃ at 0, 40, 150, and 220 GPa, respectively, without inclusion of 4f states.
states for the predicted ambient- and high-pressure phases of DyH$_3$ were calculated using a finite-displacement method as implemented in the PHONOPY code, without inclusion of 4f states. As shown in Figure 6, the absence of any imaginary frequencies in the whole Brillouin zone indicates dynamical stability of the predicted phases, except for the ambient phase, and anharmonic effects might play a role in stabilizing the ambient phase. As illustrated in the phonon density of states, the phonon bands are well separated due to the large difference in atomic mass between the Dy and H atoms (Figure 6). The low-frequency bands below 10 THz are mainly from the vibrations of Dy atoms, whereas modes between 20 and 70 THz are from the vibrations of H atoms.

**Phase Transition Sequence and Systematics in REH$_3$ Compounds.** In REH$_3$ systems, the high-pressure phase transition from ambient hexagonal P6$_3$/mmc or P3c1 phase to the cubic Fm$ar{3}$m phase through an intermediate mixed-phase region is a commonly observed sequence. Figure 7 shows the phase diagram of various REH$_3$ compounds, denoting the pressure range for the ambient hexagonal P6$_3$/mmc or P3c1 phase, intermediate mixed phase, and high-pressure cubic Fm$ar{3}$m phase region. RE elements and compounds bearing REs are known for their systematic trends in physical properties. Therefore, we plotted the phase transition pressure from the P6$_3$/mmc or P3c1 to Fm$ar{3}$m phase in REH$_3$ and the bulk modulus ($K_0$) of the high-pressure Fm$ar{3}$m phase of REH$_3$ with respect to the ionic radius of the RE atom and with respect to the volume per formula unit (V/fu) of the ambient P6$_3$/mmc or P3c1 phase of REH$_3$ under ambient conditions, as shown in Figure 8. We can clearly see that the transition pressure decreases with the increasing ionic radius as well as with ambient V/fu of the P6$_3$/mmc or P3c1 phase. The reported bulk moduli of the high-pressure Fm$ar{3}$m phases of REH$_3$ were fitted with the Murnaghan EOS. For rational comparison, the reported V/fu data for the Fm$ar{3}$m phase of REH$_3$ compounds is fitted with the most frequently used third-order Birch–Murnaghan EOS with $K_0' = 4$ fixed. In Figure 8c,d, it can be seen that bulk modulus values for various REH$_3$ phases show a great deal of variation without any definite trend, which is probably due to the limited data range available for the previous studies. There is a huge difference in the bulk
modulus of DyH₃ between the earlier study and present study. Previous studies on DyH₃ were only up to 31 GPa; hence, they could fit the pressure–volume data in the 17–31 GPa range with limited data points. The reported bulk modulus and its derivative fitted by the Murnaghan equation for DyH₃ are K₀ = 119 GPa and K’₀ = 1.9, and if they are fitted with a third-order Birch–Murnaghan EOS, then the values are K₀ = 55(6) GPa and K’₀ = 4 fixed. In comparison to a previous study,¹⁶ we studied DyH₃ in a larger pressure range, perhaps the largest experimental range in comparison with any other REH₃ studied so far. Most of the reported trihydrides were studied below about 35 GPa. Thus, our EOS for DyH₃ is more reliable than the earlier reported EOS for the Fm3m phase of DyH₃. Most of the REH₃ phases studied in the past were with mineral oil as pressure-transmitting medium,⁴⁰ which likely can contaminate the sample. Hence, it is essential to revisit those studies with a better hydrostatic and inert medium in a higher pressure range.

■ SUMMARY

To summarize, experimental and theoretical studies were conducted to understand the Dy–H system, particularly the stability of DyH₃ under high pressures. Simultaneous compression and laser heating of elemental Dy with H₂ were performed inside a DAC to investigate the chemistry, P–T stability, and EOS parameters of the Dy–H system. The Fm3m phase of DyH₃ was synthesized at 17 GPa and ambient temperature and remained stable up to at least 100 GPa and 2000 K. The ab initio CSP using the evolutionary USPEX method were used to explore the crystal structures, their stability, and electronic band structures to understand the structural transitions of DyH₃ at pressures up to 220 GPa. A series of structural transitions (P3c1 → Imm2 → Fm3m → P6₃/mmc at 11, 35, 135, and 194 GPa, respectively) were theoretically predicted in DyH₃. The calculated phonon dispersion curves reveal the dynamical stability of the predicted phases for DyH₃. The predicted intermediate phases in the static calculations might change to the cubic Fm3m phase when anharmonic and quantum symmetrization effects are considered. In REH₃ compounds, the ionic radii of the RE elements are found to be inversely proportional to the transition pressures from P6₃/mmc (or P3c1) to Fm3m.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

N.P.S. thanks HPSTAR for support. M.M.D.E. and N.Y. thank the National Science Foundation (EAR-1723160) for supporting this work. N.Y. thanks SERB/IUSSTF for providing financial support through a SERB Indo-US postdoctoral fellowship. J.Z. and J.-F.L. acknowledge support by the US Army (grant W911NF-16-1-0559). J.L. acknowledges support by the National Natural Science Foundation of China (U1930401). Y.Z. acknowledges support by the National Natural Science Foundation of China (No. 11872077) and the Fundamental Research Funds for the central universities (No. YJ201809). Portions of this work were performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1634415) and Department of Energy-GeoSciences (DE-FG02-94ER14466). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

REFERENCES


(37) Computer code Elk, ver. 5.2.14; http://elk.sourceforge.net.


(45) Computer code Elk, ver. 5.2.14; http://elk.sourceforge.net.


(50) Zeng, T.-X.; Kong, B.; Diao, X.-F. First principles studies of the structural stability and lattice dynamics for rare earth hydrides REH$_3$ (RE = Sm, Gd, Tb, Dy, Ho, Tm, x = 2, 3) under pressure. *J. Phys. Chem. Solids* 2019, **126**, 196–208.

