

# Prediction and Synthesis of Dysprosium Hydride Phases at High Pressure

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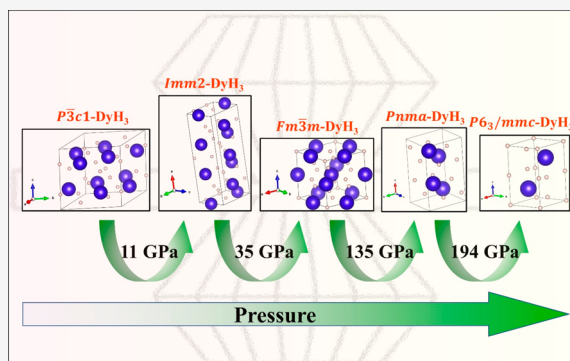
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**ABSTRACT:** Crystal structure prediction (CSP) methods recently proposed a series of new rare-earth (RE) hydrides at high pressures with novel crystal structures, unusual stoichiometries, and intriguing features such as high- $T_c$  superconductivity. RE trihydrides ( $\text{REH}_3$ ) generally undergo a phase transition from ambient  $P6_3/mmc$  or  $P\bar{3}c1$  to  $Fm\bar{3}m$  at high pressure. This cubic  $\text{REH}_3$  ( $Fm\bar{3}m$ ) was considered to be a precursor to further synthesize RE polyhydrides such as  $\text{YH}_4$ ,  $\text{YH}_6$ ,  $\text{YH}_9$ , and  $\text{CeH}_9$  with higher hydrogen contents at higher pressures. However, the structural stability and equation of state (EOS) of any of the  $\text{REH}_3$  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  $\text{DyH}_3$  up to 220 GPa. Experiments observed the  $Fm\bar{3}m$  phase of  $\text{DyH}_3$  to be stable at pressures from 17 to 100 GPa and temperatures up to  $\sim 2000$  K. After complete decompression, the  $P\bar{3}c1$  and  $Fm\bar{3}m$  phases of  $\text{DyH}_3$  recovered under ambient conditions. Our calculations predicted a series of phases for  $\text{DyH}_3$  at high pressures with the structural phase transition sequence  $P\bar{3}c1 \rightarrow Im\bar{m}2 \rightarrow Fm\bar{3}m \rightarrow Pnma \rightarrow P6_3/mmc$  at 11, 35, 135, and 194 GPa, respectively. The predicted  $P\bar{3}c1$  and  $Fm\bar{3}m$  phases are consistent with experimental observations. Furthermore, electronic band structure calculations were carried out for the predicted phases of  $\text{DyH}_3$ , including the  $4f$  states, within the DFT+U approach. The inclusion of  $4f$  states shows significant changes in electronic properties, as more Dy  $d$  states cross the Fermi level and overlap with H  $1s$  states. The structural phase transition from  $P\bar{3}c1$  to  $Fm\bar{3}m$  observed in  $\text{DyH}_3$  is systematically compared with other  $\text{REH}_3$  compounds at high pressures. The phase transition pressure in  $\text{REH}_3$  shows an inverse relation with the ionic radius of RE atoms.



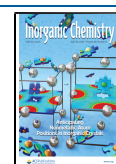
## INTRODUCTION

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.<sup>1–3</sup> Hydrogen reacts with most metals to form an interstitial hydrides with variable hydrogen concentrations.<sup>4</sup> Among them, rare-earth hydrides ( $\text{REH}_x$ ) have been of particular research interest lately, as RE atoms possess partially filled  $f$  orbitals<sup>5</sup> while hydrogen with one electron can accept or donate one electron or form covalent bonds.<sup>6</sup> Several experimental works have been recently carried out on RE hydrides due to the interesting electronic states predicted.<sup>7–13</sup> Under ambient conditions, RE elements react with hydrogen to form dihydrides,  $\text{REH}_2$ , with metallic conductivity. Further absorption of hydrogen results in the formation of RE trihydrides ( $\text{REH}_3$ ), with an electrically insulating character. These lead to the possibility of engineering the composition-dependent switching of electrical and optical properties in  $\text{REH}_x$ .<sup>1</sup>

Applied pressure on RE with hydrogen can provide a tremendous amount of internal energy and induce metalization, electronic, magnetic, and structural transitions, exotic physical properties, or formation of new compounds with unusual stoichiometries.  $\text{REH}_3$  species are known for their interesting high-pressure behavior.<sup>7–9,14–16</sup> In this respect, many  $\text{REH}_3$  species (RE = Sc, Y, Sm, Gd, Tb, Ho, Er, Lu, Dy) have been studied experimentally<sup>7,8,14–16</sup> and theoretically<sup>9</sup> under pressure. However, most of these studies are limited to  $\sim 35$  GPa or below. Under ambient conditions,  $\text{REH}_3$  species generally crystallize into a  $P6_3/mmc$  or  $P\bar{3}c1$  structure.<sup>9</sup> With further pressurization, they undergo a structural transition into a  $Fm\bar{3}m$  structure via an intermediate mixed phase or complex

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phase region.<sup>7,8,14–16</sup> The high-pressure phase transition sequence, from  $P6_3/mmc$  or  $P3c1$  to  $Fm\bar{3}m$ , appears to be prevalent in  $REH_3$  systems.<sup>7,8,14–16</sup> Theoretical investigations of  $REH_3$  compounds have focused on their structural stability, phase transitions, equation of state (EOS), electronic/electrical and phonon properties.<sup>9</sup> 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.<sup>13,17–19</sup> Hence, the high pressure–temperature ( $P$ – $T$ ) phase stability and physical properties of the  $Fm\bar{3}m$  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.<sup>10,11</sup> Many hydrogen-rich RE polyhydrides/superhydrides have been predicted to become stable under pressure.<sup>10,17,20</sup> 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.<sup>10,17,18,20</sup> Extensive efforts are taken by theorists and experimentalists to discover hydride-based superconductors.<sup>10,17,18,20–22</sup> 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.<sup>10,11,13,17,20</sup> RE superhydrides ( $REH_x$ ,  $x > 5$ ) 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.<sup>10,17,20</sup> 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  $Im\bar{3}m$  structure,<sup>17</sup>  $YH_{10}$  and  $LaH_{10}$  are predicted to crystallize in the cubic  $Fm\bar{3}m$  structure,<sup>10,20</sup> and  $YH_9$  and  $CeH_9$  predicted to have a hexagonal  $P6_3/mmc$  structure.<sup>10,13</sup> Experimentally synthesized and characterized  $YH_6$ ,  $YH_9$ ,  $CeH_9$ ,  $PrH_9$ , and  $LaH_{10}$  were consistent with their theoretically predicted structures and high-pressure phase stability.<sup>13,18,19,23,24</sup> Most of these clathrate-structured RE superhydrides were predicted to have a superconducting  $T_c$  value close to room temperature.<sup>10,17,19,20</sup> 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.<sup>18</sup>

The high-pressure  $Fm\bar{3}m$  phase of  $YH_3$  was also predicted to be a conventional superconductor under pressure.<sup>25</sup> In recent studies on the Ce–H system,  $CeH_3$  with a  $\beta$ - $UH_3$  type structure (space group  $Pm\bar{3}n$ ,  $\beta$ - $CeH_3$ ) was synthesized at 33 GPa after laser heating.<sup>13</sup> After further compression and reheating of  $\beta$ - $CeH_3$  and  $H_2$ ,  $CeH_9$  was formed at pressures of 80–100 GPa.<sup>13</sup> In the Pr–H system,  $PrH_3$  phases with  $Fm\bar{3}m$  and  $P4/nmm$  structures were synthesized at 10 and 40 GPa, respectively.<sup>24</sup> The point to be noted here is that the Ce–H and Pr–H systems were studied in the environment with

excess hydrogen.<sup>13,24</sup> Studies on RE in excess hydrogen under a megabar pressure regime and with laser heating resulted in discoveries of  $\beta$ - $UH_3$ -type  $CeH_3$ ,  $P4/nmm$ - $PrH_3$ ,  $LaH_{10}$ ,  $CeH_9$ , and  $PrH_9$  phases.<sup>12,13,24</sup> 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.<sup>11</sup>

Dysprosium (Dy), one of the heavy, normally trivalent lanthanoids, is known to form di- and trihydrides under ambient conditions.<sup>16,26</sup> 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.<sup>16</sup> Recently, Peng et al.<sup>10</sup> and Semenok et al.<sup>11</sup> predicted rich chemistry of the Dy–H system e.g.,  $DyH$ ,  $DyH_2$ ,  $DyH_3$ ,  $DyH_4$ ,  $DyH_6$ ,  $DyH_7$ ,  $Dy_5H_{14}$ , and  $DyH_9$ . It would be interesting to investigate Dy–H chemistry under extreme conditions.<sup>10,11</sup> The structural stability of the  $Fm\bar{3}m$  phase of  $DyH_3$  under high  $P$ – $T$  conditions has not 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  $\sim 100$  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  $Fm\bar{3}m$   $DyH_3$  phase, which remains stable up to  $\sim 100$  GPa and  $\sim 2000$  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  $REH_3$  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  $\sim 18$   $\mu m$ . Subsequently, a hole of  $\sim 45$   $\mu m$  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  $\sim 5$   $\mu m$  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  $\sim 1.7$  kilobar pressure at the Center for High Pressure Science & Technology Advanced Research (HPSTAR). Hydrogen served as a starting material as well as a hydrostatic medium. A tiny piece of gold ( $\sim 5$   $\mu m$  in diameter) was also placed next to the dysprosium sample and used as a pressure calibrant. Angle-dispersive XRD patterns were recorded on a

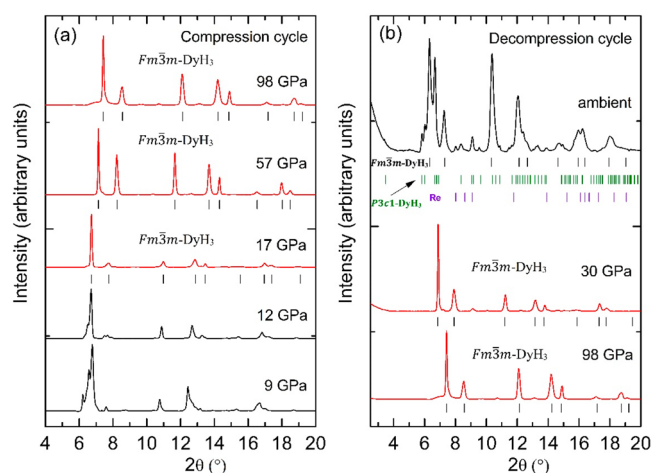
PILATUS CdTe 1M detector at beamline 13-IDD of GeoSoilEnviroCARS (GSECARS) at the Advanced Photon Source (APS) of Argonne National Laboratory, USA. An incident X-ray with a wavelength of 0.3344 Å was focused onto a spot size of  $\sim 3 \times 4$   $\mu\text{m}$  (fwhm) at the sample position, and a pinhole of 8  $\mu\text{m}$  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  $\mu\text{m}$  in diameter for single-sided laser heating.<sup>27</sup> 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.<sup>28</sup> The uncertainty in temperature measurements was typically less than  $\pm 100$  K. The obtained raw images of XRD were integrated with DIOPTAS software.<sup>29</sup> Le Bail refinements were carried out using the FullProf and Jana programs.

## COMPUTATIONAL DETAILS

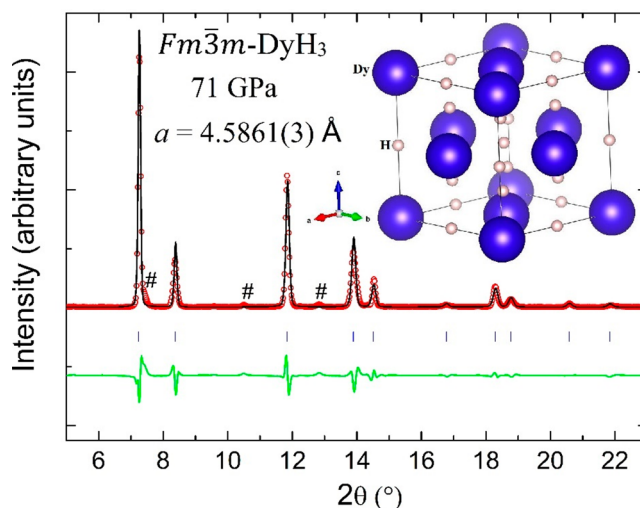
We performed a systematic fixed-composition crystal structure search using the *ab initio* evolutionary algorithm USPEX,<sup>30–32</sup> which is capable of simultaneously searching for a stable structure with different numbers of formula units (fu) for a given composition. Here, we carried out crystal structure prediction calculations at 0, 50, 100, 150, 200 GPa for DyH<sub>3</sub> with up to 6 fu in the primitive cell. The first generation was produced randomly (using random symmetric<sup>32</sup> and topological<sup>33</sup> 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 60% of the population as parents. Structure relaxation was performed using the all-electron projector augmented wave (PAW) method<sup>34</sup> implemented in the VASP package<sup>35</sup> in the framework of DFT. Valence electron configurations  $5p^6 5d^1 6s^2$  and  $1s^1$  were used for dysprosium and hydrogen, respectively. The Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) was used.<sup>36</sup> A plane-wave kinetic-energy cutoff of 1000 eV, hard PAW potentials, and dense  $\Gamma$ -centered  $k$ -point grids with reciprocal space resolution  $2\pi \times 0.05 \text{ \AA}^{-1}$  were employed to sample the Brillouin zone. To construct the phase diagram of DyH<sub>3</sub>, 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<sub>3</sub> were performed with the full-potential augmented-plane-wave + local orbital (APW +lo) approach as implemented in the Elk code.<sup>37</sup> The  $5s^2 5p^6 4f^{10} 6s^2$  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).<sup>38</sup> 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<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub> compounds,<sup>7,8,14,39–41</sup> and



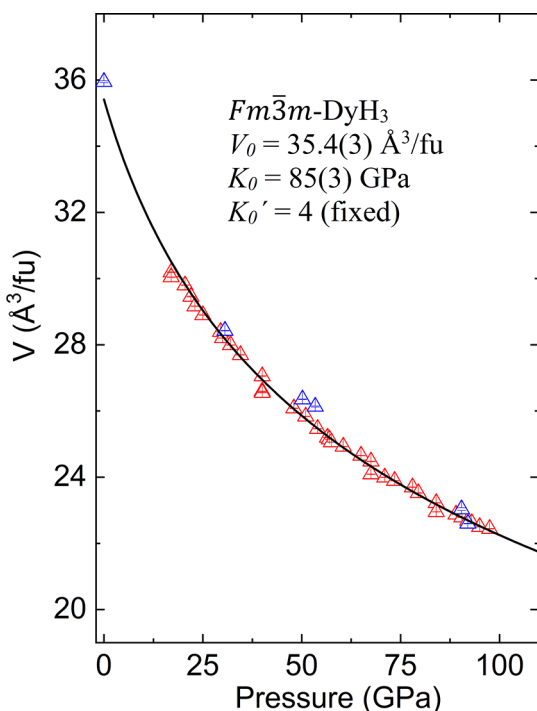
**Figure 1.** Representative integrated XRD patterns of the Dy–H system at high pressure and temperature. (a) In a compression cycle, a long-period polytype phase was observed at 9 GPa. Above 17 GPa, it transforms into  $Fm\bar{3}m$  phase of DyH<sub>3</sub>, which remains stable up to 98 GPa. (b) In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



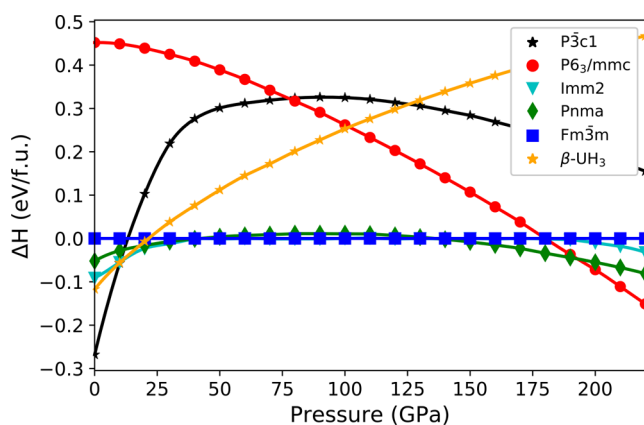
**Figure 2.** Refinement of the XRD pattern at 71 GPa. The inset shows crystal structure of the  $Fm\bar{3}m$  phase of DyH<sub>3</sub> with hydrogen atoms midway between the Dy atoms. The black hash symbol denotes the unknown peaks.

in most cases, it was mixed with hexagonal and cubic phases. In the case of YH<sub>3</sub>, the intermediate phase was observed with a long-period polytype structure.<sup>8,42</sup> In addition to an intermediate phase, the presence of bixbyite-type (i.e., fluorite-type with O vacancies) Dy<sub>2</sub>O<sub>3</sub> 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 DyH<sub>3</sub> was observed above 17 GPa. Previous high-pressure studies of DyH<sub>3</sub> also reported a sluggish hexagonal to cubic transition between 7 and 17 GPa.<sup>16</sup> The lattice parameter of the  $Fm\bar{3}m$  phase of DyH<sub>3</sub> at 17 GPa is refined to be  $a = 4.9423(2) \text{ \AA}$ . Further, DyH<sub>3</sub> and H<sub>2</sub> were pressurized up to  $\sim 100$  GPa and laser-heated up to 2000 K at





**Figure 3.** Unit cell volume of the  $Fm\bar{3}m$  phase of  $DyH_3$  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  $Fm\bar{3}m$  phase of  $DyH_3$  in the compression and decompression cycles, respectively. The black line represents the EOS fit.



**Figure 4.** Calculated enthalpies of various predicted structures of  $DyH_3$  as a function of pressure (relative to the cubic  $Fm\bar{3}m$  phase). The  $P\bar{3}c1$ ,  $Imm2$ ,  $Fm\bar{3}m$ ,  $Pnma$ , and  $P6_3/mmc$  phases of  $DyH_3$  became stable at 0, 11, 35, 135, and 194 GPa, respectively.

pressures of 25, 40, 54, 68, 84, and 98 GPa. Analysis of the XRD patterns for these  $P$ – $T$  conditions shows that the  $Fm\bar{3}m$  phase of  $DyH_3$  is the stable phase in the Dy–H system up to  $\sim 100$  GPa and  $\sim 2000$  K (Figure 1a). We did not observe the formation of any other phase with different stoichiometry or with a hydrogen content higher than that of the  $DyH_3$  phase. The lattice parameter of the  $Fm\bar{3}m$  phase of  $DyH_3$  at 98 GPa is  $a = 4.4775(2)$  Å. Figure 2 shows the Le Bail refinement plot and crystal structure of  $DyH_3$  at 71 GPa ( $R_p = 22.4\%$ ,  $R_{wp} = 28.3\%$ ). During the decompression cycle, the  $Fm\bar{3}m$  phase of  $DyH_3$  was present down to 30 GPa. With further decompression, the  $P\bar{3}c1$  phase of  $DyH_3$  emerged after complete decompression and coexisted with the  $Fm\bar{3}m$  phase

of  $DyH_3$  at ambient pressure. The high-pressure  $Fm\bar{3}m$  phase has also been recovered previously in studies on  $SmH_3$  and  $DyH_3$ .<sup>40</sup> The lattice parameters of the  $P\bar{3}c1$  phase of  $DyH_3$  recovered at ambient pressure are  $a = 6.3849(8)$  Å and  $c = 6.596(1)$  Å and that for the  $Fm\bar{3}m$  phase of  $DyH_3$  is  $a = 5.239(1)$  Å. The EOS parameters of the  $Fm\bar{3}m$  phase of  $DyH_3$  obtained in the compression and decompression cycles are given in Figure 3. The unit cell volume of the  $Fm\bar{3}m$  phase of  $DyH_3$  as a function of pressure fitted using third-order Birch–Murnaghan EOS yielded the zero-pressure unit cell volume  $V_0 = 35.4(3)$  Å<sup>3</sup>/fu and bulk modulus  $K_0 = 85(3)$  GPa, with fixed  $K_0' = 4$ .

Experiments did not observe the formation of  $\beta$ - $UH_3$  type or  $P4/nmm$  phases of  $DyH_3$  even after simultaneous compression and heating in excess hydrogen, as reported for the Ce–H and Pr–H systems.<sup>13,24</sup> In our calculations this structure is not stable, but becomes close to stability at pressures around 10 GPa.

**Theoretical Prediction of Various  $DyH_3$  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  $DyH_3$ , 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  $DyH$ ,  $DyH_2$ ,  $DyH_3$ ,  $DyH_4$ ,  $DyH_7$ , and  $Dy_5H_{14}$ .<sup>11</sup> Among the stable Dy–H phases predicted, only the  $DyH_3$  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  $DyH_3$  as it undergoes a series of structural phase transitions within the studied pressure range of 0–220 GPa. In theoretical calculations, the  $P\bar{3}c1$ ,  $Imm2$ ,  $Fm\bar{3}m$ ,  $Pnma$ , and  $P6_3/mmc$  phases of  $DyH_3$  were predicted to become stable at 0, 11, 35, 135, and 194 GPa, respectively (see the phase diagram in Figure 4).

Most  $REH_3$  compounds crystallize in a hexagonal structure under ambient conditions with the possible space groups  $P6_3$ ,  $P6_3/mmc$ ,  $P\bar{3}c1$ , and  $P6_3cm$ .<sup>9,43–50</sup> Among them, the stable phase of  $DyH_3$  crystallizes in a  $P\bar{3}c1$  structure, similar to the other reported  $REH_3$  phases such as  $(Er/Ho)_H_3$ <sup>43,45,47</sup> and antiferromagnetic  $GdH_3$ .<sup>46</sup> Consistent with our predictions, the  $P\bar{3}c1$  phase of  $DyH_3$  was recovered under ambient conditions after complete decompression. Kong et al.<sup>9</sup> reported  $REH_3$  ( $RE = Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu$ ) compounds that were stable in  $P6_3cm$  symmetry under ambient conditions. Extensive studies have been devoted to understanding the structural transition sequences in  $REH_3$  compounds. The known structural transition trends in this class of compounds are from an ambient  $P6_3/mmc$  or  $P\bar{3}c1$  structure to the  $Fm\bar{3}m$  structure at high pressure. Kataoka et al.<sup>48</sup> were able to stabilize the high-pressure  $Fm\bar{3}m$  phase under ambient conditions by doping it with an alkali or alkaline-earth metals (Li, K and Mg) for  $REH_3$  ( $RE = Y, Gd, Dy$ ). Interestingly, three new phases ( $Imm2$ ,  $Pnma$ , and  $P6_3/mmc$ ) of  $DyH_3$  have been predicted in addition to the known phases ( $P\bar{3}c1$ ,  $Fm\bar{3}m$ ) in the studied pressure range of 0–220 GPa. The pressure-induced structural transition sequence in  $DyH_3$  is as follows:  $P\bar{3}c1 \rightarrow Imm2 \rightarrow Fm\bar{3}m \rightarrow Pnma \rightarrow P6_3/mmc$  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 ( $Imm2$ )

Table 1. Crystal Structures of the Predicted DyH<sub>3</sub> Phases<sup>a</sup>

phase	pressure range, GPa	volume, Å <sup>3</sup> /fu	$\rho$ , g/cm <sup>3</sup>	lattice constants, Å	atom (Wyckoff site)	<i>x</i>	<i>y</i>	<i>z</i>
<i>P3̄c1</i>	0–11	38.14	7.21	<i>a</i> = 6.328 <i>b</i> = 6.598	Dy (6f)	0.6631	0	0.25
					H <sub>1</sub> (12g)	0.6782	0.0289	−0.0921
					H <sub>2</sub> (2a)	0	0	0.25
					H <sub>3</sub> (4d)	0.3333	0.6667	0.8142
<i>Imm2</i>	11–35	29.67	9.26	<i>a</i> = 10.619 <i>b</i> = 4.628 <i>c</i> = 3.621	Dy <sub>1</sub> (2a)	0	0	0.4861
					Dy <sub>2</sub> (4c)	0.6669	0	0.4230
					H <sub>1</sub> (4c)	0.8334	0	0.8783
					H <sub>2</sub> (2b)	0	0.5	0.5502
					H <sub>3</sub> (8e)	0.8349	0.2542	0.4097
					H <sub>4</sub> (4d)	0	0.7479	0.0052
<i>Fm3̄m</i>	35–135	26.62	10.33	<i>a</i> = 4.740	Dy (4a)	0	0	0
					H <sub>1</sub> (8c)	0.25	0.25	0.25
					H <sub>2</sub> (4b)	0.5	0.5	0.5
<i>Pnma</i>	135–194	20.25	13.57	<i>a</i> = 6.277 <i>b</i> = 4.046 <i>c</i> = 3.189	Dy (4c)	0.6353	0.25	0.8034
					H <sub>1</sub> (4c)	0.8627	0.25	0.3163
					H <sub>2</sub> (8d)	0.1077	0.4979	0.1863
<i>P6<sub>3</sub>/mmc</i>	194–220	17.86	15.39	<i>a</i> = 2.773 <i>c</i> = 5.360	Dy (2d)	0.3333	0.6667	0.75
					H <sub>1</sub> (2a)	0	0	0
					H <sub>2</sub> (4f)	0.3333	0.6667	0.417

<sup>a</sup>Volumes, densities, lattice parameters, and atomic coordinates are given for different phases at the given pressures. Stability ranges are given for each phase.

Table 2. Theoretical Parameters of the Third-Order Birch–Murnaghan EOS<sup>a</sup>

structure	<i>V</i> <sub>0</sub> , Å <sup>3</sup> /fu	<i>K</i> <sub>0</sub> , GPa	<i>K</i> <sub>0</sub> '
<i>P3̄c1</i>	38.1	80.7	4.05
	39.0 <sup>9</sup>	79.8 <sup>9</sup>	3.18 <sup>9</sup>
<i>Imm2</i>	34.6	96.3	3.80
<i>Fm3̄m</i>	34.2	96	3.69
	34.6	90.2	4 (fixed)
	35.4(3) exptl	85(3) exptl	4 (fixed) exptl
<i>Pnma</i>	34.5	97	3.75
<i>P6<sub>3</sub>/mmc</i>	34.2	97	3.91

<sup>a</sup>Experimental data of this work are also added for the cubic phase.

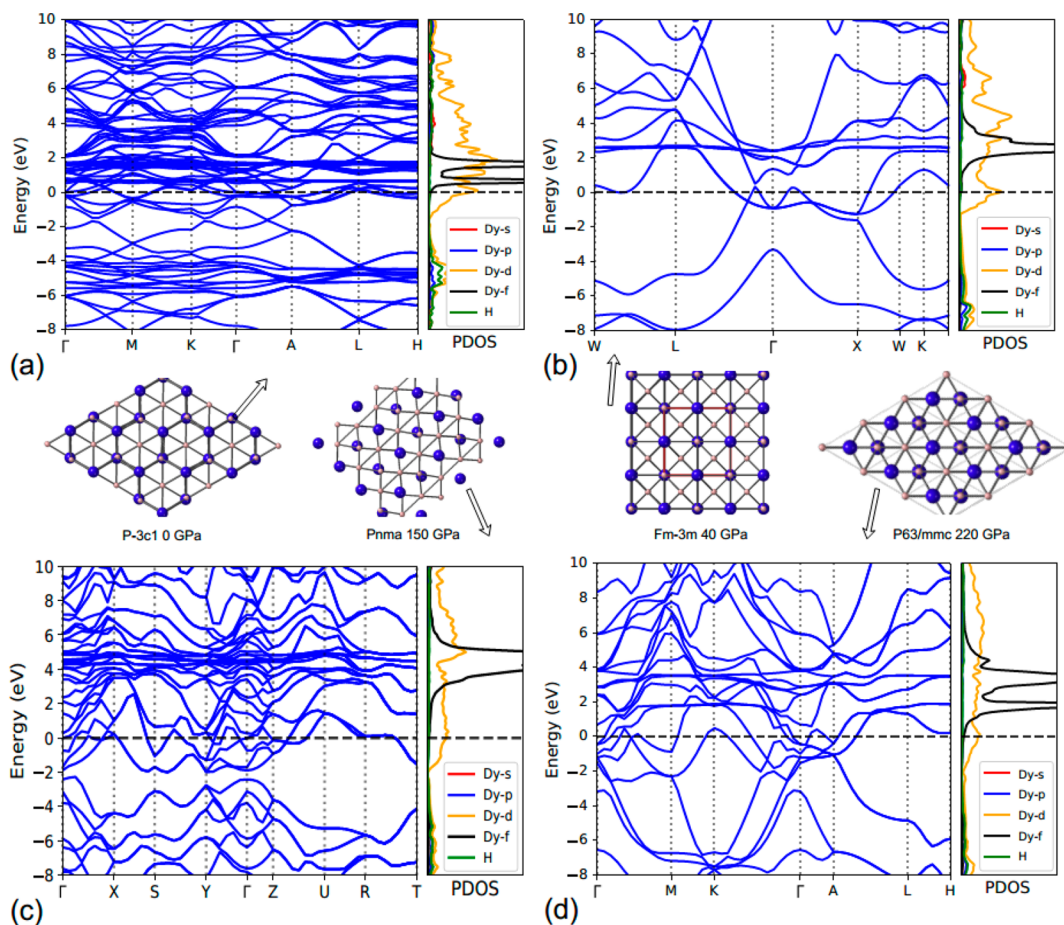
phase, which is stable in the pressure range of 11–35 GPa. The *Pnma* phase is also an energetically competitive for *Imm2* and *Fm3̄m* phases. The *Imm2*(*Pnma*) → *Fm3̄m* transition is a weakly first-order transition in nature, which is clearly seen from static enthalpy calculations in the pressure 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.<sup>51</sup> Detailed structural information on the predicted phases is given in Table 1. Moreover, the intermediate (*C2/m* and *Cmcm*) phases were also predicted for other REH<sub>3</sub> species such as ErH<sub>3</sub> and HoH<sub>3</sub> under high pressure.<sup>43</sup> The present study reveals the hidden intermediate phase (*Imm2*) for the investigated compound, DyH<sub>3</sub>. The EOS parameter values of DyH<sub>3</sub> 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 *Fm3̄m* DyH<sub>3</sub> are *V*<sub>0</sub> = 34.6 Å<sup>3</sup>/fu and *K*<sub>0</sub> = 90.21 GPa with *K*<sub>0</sub>' 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<sub>3</sub> stoichiometry. The experimental lattice parameter of the *Fm3̄m* phase at 30 GPa is *a* = 4.8319(1) Å (*a* = 4.812 Å theoretical). The theoretical EOS and fitted

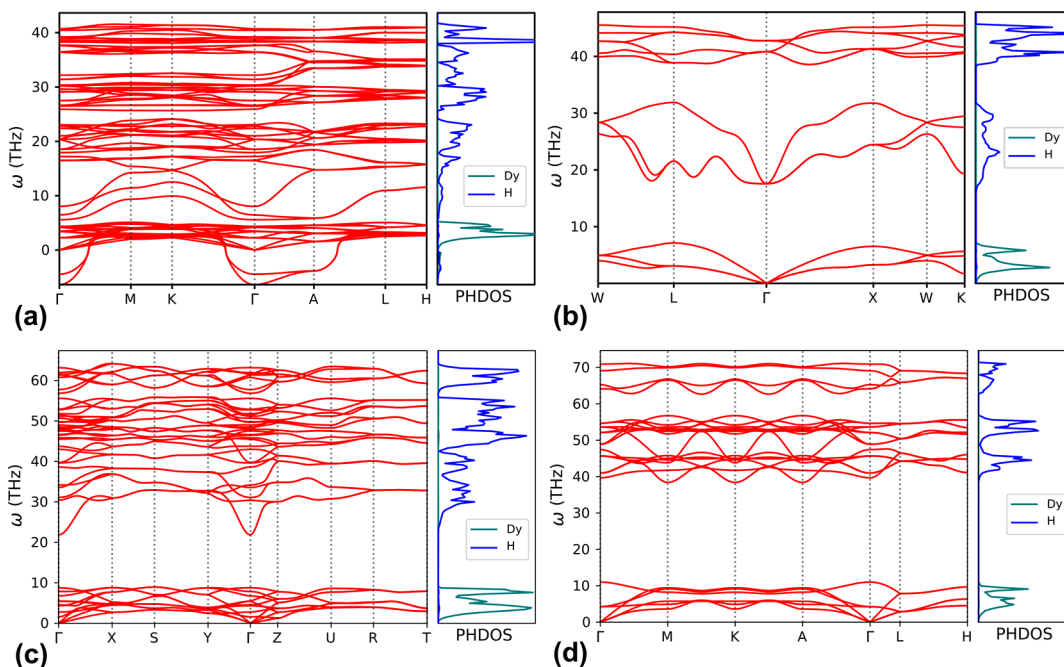
parameters in cubic DyH<sub>3</sub> are consistent with our experimental values (see Table 2). In the *Fm3̄m* phase of DyH<sub>3</sub>, dysprosium atoms occupy the 4a (0,0,0) Wyckoff position and hydrogen atoms occupy the 8c (1/4,1/4,1/4) and 4b (1/2,1/2,1/2) Wyckoff positions. The theoretical third-order Birch–Murnaghan EOS fit to the *P*–*V* data of DyH<sub>3</sub> along with experimental values are given in Table 2, which clearly shows *P3̄c1* has a lower bulk modulus of 80.7 GPa: i.e., higher compressibility in comparison with the high-pressure phase (*Fm3̄m* has a bulk modulus of 90.2 GPa) (see Table 2).

*P3̄c1*-DyH<sub>3</sub> has a hexagonal fluorite-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 *Fm3̄m* structure, the Dy–H bond distance is 2.12 Å at 20 GPa and 1.80 Å at 220 GPa. For DyH<sub>3</sub>, theoretical calculations obtained a complex phase diagram with four phase transitions between 0 and 220 GPa. DyH<sub>3</sub> transforms to a cubic phase with space group *Fm3̄m* with 4 fu/cell at 35 GPa. *Fm3̄m* 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<sub>3</sub> 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.<sup>9</sup> at ambient pressure shows consistency, in which the hexagonal fluorite-type phase (*P3̄c1*) 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<sub>3</sub> Phases.** Further, the electronic band structure and projected density of states (PDOS) were explored for the ambient- and high-pressure phases of DyH<sub>3</sub> with inclusion of 4*f* states for Dy as depicted in Figure 5. The inclusion of the 4*f* 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<sub>3</sub> (see Figure 5). As illustrated in Figure 5, the predicted ambient- and high-pressure phases of DyH<sub>3</sub> show



**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)  $P6_3/mmc$   $DyH_3$  at 0, 40, 150, and 220 GPa, respectively, including  $4f$  electrons using the GGA+ $U$  method ( $U = 6$  eV).

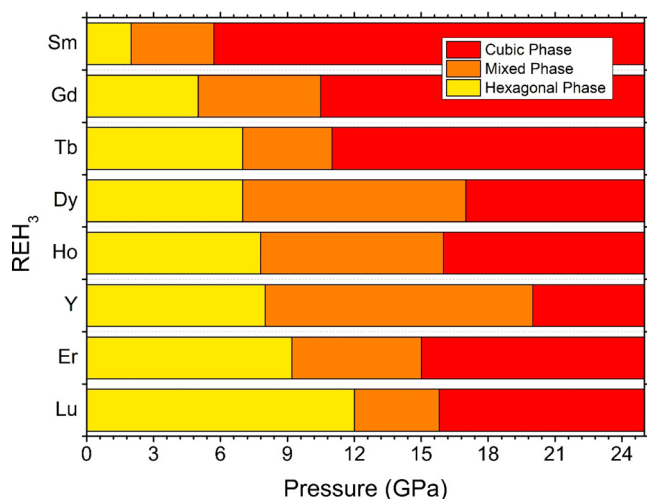


**Figure 6.** Calculated phonon dispersion curves and projected phonon density of states (PhDOS) of (a)  $P\bar{3}c1$ , (b)  $Fm\bar{3}m$ , (c)  $Pnma$ , and (d)  $P6_3/mmc$   $DyH_3$  at 0, 40, 150, and 220 GPa, respectively, without inclusion of  $4f$  states.

metallic character, and the Fermi level is mainly dominated by Dy  $d$  states for all of the predicted phases.

**Phonon Dispersion Curves of  $DyH_3$  Phases.** Phonon dispersion curves along with the projected phonon density of



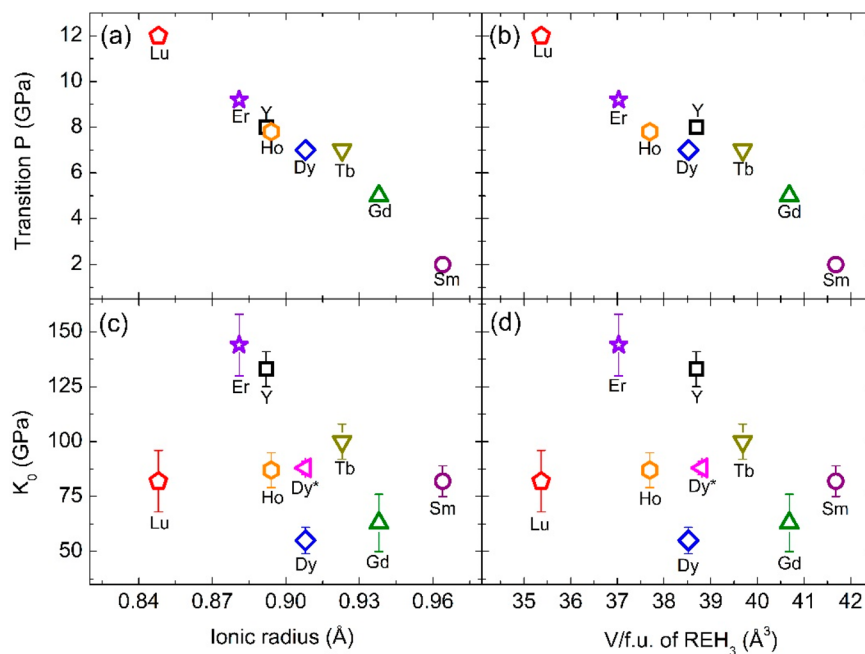


**Figure 7.** Phase diagram showing the ambient hexagonal  $P6_3/mmc$  or  $P\bar{3}c1$  phase, intermediate mixed phase region, and high-pressure cubic  $Fm\bar{3}m$  phase region for  $REH_3$  compounds. The  $REH_3$  compound is denoted by the respective RE on the vertical axis. The yellow, orange, and red regions represent the pressure ranges for the hexagonal  $P6_3/mmc$  or  $P\bar{3}c1$  phase, mixed phase, and cubic  $Fm\bar{3}m$  phase of  $REH_3$ , respectively.

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,<sup>52</sup> 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  $P\bar{3}c1$  phase to the cubic  $Fm\bar{3}m$  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  $P\bar{3}c1$  phase, intermediate mixed phase, and high-pressure cubic  $Fm\bar{3}m$  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  $P\bar{3}c1$  to  $Fm\bar{3}m$  phase in  $REH_3$  and the bulk modulus ( $K_0$ ) of the high-pressure  $Fm\bar{3}m$  phase of  $REH_3$  with respect to the ionic radius<sup>53</sup> of the RE atom and with respect to the volume per formula unit (V/fu) of the ambient  $P6_3/mmc$  or  $P\bar{3}c1$  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  $P\bar{3}c1$  phase. The reported bulk moduli of the high-pressure  $Fm\bar{3}m$  phases of  $REH_3$  were fitted with the Murnaghan EOS. For rational comparison, the reported V/fu data for the  $Fm\bar{3}m$  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



**Figure 8.**  $P6_3/mmc$  or  $P\bar{3}c1$  to  $Fm\bar{3}m$  transition pressure and bulk modulus of the  $Fm\bar{3}m$  phase of  $REH_3$  plotted as a function of the ionic radius<sup>53</sup> of the RE atom in (a) and (c), respectively, and as a function of volume per formula unit of hexagonal  $REH_3$  in (b) and (d), respectively. The bulk modulus was obtained by fitting the reported V/fu data of the  $Fm\bar{3}m$  phases of  $REH_3$  by a third-order Birch–Murnaghan EOS with fixed  $K_0' = 4$ . The name of the respective RE is mentioned in all the subfigures. (for references:  $YH_3$ ,<sup>8,14</sup>  $SmH_3$ ,<sup>40</sup>  $GdH_3$ ,<sup>39</sup>  $TbH_3$ ,<sup>41</sup>  $DyH_3$ ,<sup>16</sup>  $DyH_3$  (this study),  $HoH_3$ ,<sup>39</sup>  $ErH_3$ ,<sup>7</sup>  $LuH_3$ ,<sup>39</sup>).

modulus of DyH<sub>3</sub> between the earlier study and present study. Previous studies on DyH<sub>3</sub> 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 DyH<sub>3</sub> are  $K_0 = 119$  GPa and  $K'_0 = 1.9$ , and if they are fitted with a third-order Birch–Murnaghan EOS, then the values are  $K_0 = 55(6)$  GPa and  $K'_0 = 4$  fixed. In comparison to a previous study,<sup>16</sup> we studied DyH<sub>3</sub> in a larger pressure range, perhaps the largest experimental range in comparison with any other REH<sub>3</sub> studied so far. Most of the reported trihydrides were studied below about 35 GPa. Thus, our EOS for DyH<sub>3</sub> is more reliable than the earlier reported EOS for the *Fm* $\bar{3}$ *m* phase of DyH<sub>3</sub>. Most of the REH<sub>3</sub> phases studied in the past were with mineral oil as pressure-transmitting medium,<sup>40</sup> 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 DyH<sub>3</sub> under high pressures. Simultaneous compression and laser heating of elemental Dy with H<sub>2</sub> were performed inside a DAC to investigate the chemistry, *P*–*T* stability, and EOS parameters of the Dy–H system. The *Fm* $\bar{3}$ *m* phase of DyH<sub>3</sub> 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 DyH<sub>3</sub> at pressures up to 220 GPa. A series of structural transitions (*P* $\bar{3}$ *c*1  $\rightarrow$  *Imm*2  $\rightarrow$  *Fm* $\bar{3}$ *m*  $\rightarrow$  *Pnma*  $\rightarrow$  *P* $\bar{6}_3$ /*mmc* at 11, 35, 135, and 194 GPa, respectively) were theoretically predicted in DyH<sub>3</sub>. The calculated phonon dispersion curves reveal the dynamical stability of the predicted phases for DyH<sub>3</sub>. The predicted intermediate phases in the static calculations might change to the cubic *Fm* $\bar{3}$ *m* phase when anharmonic and quantum symmetrization effects are considered. In REH<sub>3</sub> compounds, the ionic radii of the RE elements are found to be inversely proportional to the transition pressures from *P* $\bar{6}_3$ /*mmc* (or *P* $\bar{3}$ *c*1) to *Fm* $\bar{3}$ *m*.

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### Notes

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