

# Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Enroute to Room-temperature Superconductivity

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Room-temperature superconductivity has been a long-held dream and an area of intensive research. Recent experimental findings of superconductivity at 200 K in highly compressed hydrogen (H) sulfides have demonstrated the potential for achieving room-temperature superconductivity in compressed H-rich materials. We report first-principles structure searches for stable H-rich clathrate structures in rare earth hydrides at high pressures. The peculiarity of these structures lies in the emergence of unusual H cages with stoichiometries  $H_{24}$ ,  $H_{29}$ , and  $H_{32}$ , in which H atoms are weakly covalently-bonded to one another, with rare earth atoms occupying the centers of the cages. We have found that high-temperature superconductivity is closely associated with H clathrate structures with large H-derived electronic densities of states at the Fermi level and strong electron-phonon coupling related to the stretching and rocking motions of H atoms within the cages. Strikingly, a Yttrium (Y)  $H_{32}$  clathrate structure of stoichiometry  $YH_{10}$  is predicted to be a potential room-temperature superconductor with an estimated  $T_c$  of up to 303 K at 400 GPa, as derived by direct solution of the Eliashberg equation.

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At high pressures the lightest element, H, is suggested to form metallic solids with the high Debye temperature and strong electron-phonon coupling necessary for high- $T_c$  phonon-mediated superconductivity [1, 2]. The superconductivity is supported by a number of calculations that have predicted a high  $T_c$  in the range 100-760 K in either molecular [3, 4] or atomic phases [5]. Unfortunately, low-temperature studies up to 388 GPa have not yet realized metallization of solid hydrogen [6]. Metallization of solid H at 495 GPa [7] has recently been reported, but additional experimental measurements are required to verify this claim. As an alternative, H-rich materials have been considered [8] since they can metallize at much lower pressures than are accessible to experiments. Extensive theoretical studies (e.g. Refs.[9–21]) have explored potential superconductivity in compressed H-rich materials. Encouragingly, the results suggest the possibility of high- $T_c$  superconductivity in hydrides with estimated  $T_c$  values in the range 50-264 K [9–21]. The subsequent experimental observation of high- $T_c$  superconductivity in the temperature ranges 30-150 K and 180-203 K for various temperature-annealed samples in highly compressed  $H_2S$  is remarkable [22]. These experiments were motivated by a theoretical prediction of high- $T_c$  super-

conductivity in compressed solid  $H_2S$  [23] which excluded the possibility of dissociation of  $H_2S$  into S and H and opened up the possibility of synthesizing superconducting  $H_3S$  via compression of  $H_2S$  [24–26].

Two properties of metallic hydrides are particularly beneficial for promoting high- $T_c$  superconductivity: (i) a large H-derived electronic density of states at the Fermi level, and (ii) large modifications of the electronic structure in response to the motion of the H atoms (electron-phonon coupling). It appears to be important to satisfy both of these criteria in hydrides with high H content in order to achieve high  $T_c$  values. However, the strategy of pursuing the highest possible H content may not always be the best solution. In reality, a number of hydrides with higher H content (e.g.,  $AsH_8$ ,  $MgH_{12}$ , and  $LiH_8$ , etc. Refs.[15, 27–29]) have been found not to exhibit higher  $T_c$  values than those containing relatively less H, such as  $CaH_6$  and  $YH_6$  [9, 10]. The key drawback of these H-rich structures lies in the appearance of  $H_2$ -like molecular units that attract many electrons from H atoms with low-lying energies away from the Fermi energy, which violates both criteria (i) and (ii). Another desirable property that is important for achieving high  $T_c$  superconductivity is that the structures should have

high symmetry. This appears to be a very general property that is not confined to metallic hydrides [30].

Synthesis of high- $T_c$  superconducting hydrides requires the elimination of  $H_2$ -like molecular units from the structures. One possible route is to introduce electrons that are accepted by  $H_2$  molecules which occupy the unfilled antibonding  $\sigma^*$  orbitals of the  $H_2$  molecules, which would weaken the intramolecular H-H bonds and result in dissociation of  $H_2$  [9, 30]. This is the physical origin of the stabilization of three-dimensional clathrate  $H_{24}$  cage structures, as first reported in  $CaH_6$  [9] and later in  $YH_6$  [10], where Ca and Y atoms occupy the center of the  $H_{24}$  cages and act as electron donors, while the H atoms are weakly covalently bonded to each other within the  $H_{24}$  cage. The  $H_{24}$  cage structure could be a useful compromise for achieving the largest possible number of H atoms, but without introducing molecular  $H_2$  units into the structure. The high- $T_c$  superconductivity arises from satisfying the above two criteria (i) and (ii) which has achieved theoretical  $T_c$  values of 235 K for  $CaH_6$ , and 264 K for  $YH_6$ , which is the highest theoretical  $T_c$  value achieved so far in a thermodynamically stable phase. Assuming  $MgH_6$  adopts the same structure as  $CaH_6$  does, an even higher  $T_c$  of 400 K was reported for  $MgH_6$  [31], however,  $MgH_6$  is known to be energetically unfavorable with respect to decomposition into  $MgH_4$  and  $MgH_{12}$  [29].

In this work we seek binary metal hydrides that have even higher H content than  $CaH_6$  and  $YH_6$ , while at the same time the structures should not contain  $H_2$  molecules. For this purpose, the H lattices of hydrides should involve more electrons from the metal elements than they do in  $CaH_6$  and  $YH_6$ . In this regard rare earth (RE) hydrides have come to our attention. On the one hand, RE elements such as Y in  $YH_6$  can easily lose electrons due to their small electronegativities in the range of 1.0-1.36 on the Pauli scale [32], which is comparable to the value of 1.0 for Ca. On the other hand, RE elements can readily accommodate higher oxidation states (e.g., in 3+ or 4+ charge states) than that of Ca/Y (2+) in  $Ca/YH_6$ , which enables donation of more electrons to the H lattice.

Here we report an extensive exploration of the high-pressure phase diagrams of RE (Sc, Y, La, Ce, and Pr, etc.) hydrides, focusing on H-rich species by performing swarm-intelligence based CALYPSO [33, 34] structure searches. Some of the key clathrate structures were subsequently confirmed using the Ab Initio Random Structure Searching (AIRSS) approach [35, 36]. Our structure searches revealed that H clathrate structures could be formed in all of the RE hydrides studied. Besides the known  $H_{24}$  cage structure in  $REH_6$ , H-rich  $H_{29}$  and  $H_{32}$  cage structures were predicted in  $REH_9$  and  $REH_{10}$  hydrides. Among them, the  $H_{32}$  cage structure in the temperature-stabilized  $YH_{10}$  clathrate is predicted to be a potential room-temperature superconductor with a  $T_c$

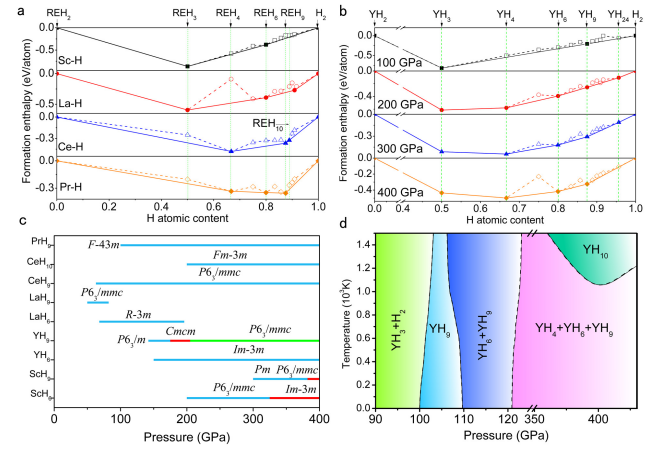


FIG. 1: (Color online) Phase stabilities of various H-rich RE hydrides (RE = Sc, Y, La, Ce, and Pr). (a) Enthalpies of formation of various H-rich RE hydrides at 200 GPa. (b) Enthalpies of formation of various H-rich Y hydrides under pressure. Dotted lines connect the data points, and solid lines denote the convex hull. (c) Predicted pressure-composition phase diagram of  $REH_6$ ,  $REH_9$ , and  $REH_{10}$  clathrate structures. (d) Temperature versus pressure phase diagram of Y-H system. Dashed lines show the proposed phase boundaries.

of up to 303 K at 400 GPa, as derived by direct solution of the Eliashberg equation [37].

Our main structure searching results are depicted in the convex hull diagrams of Fig. 1 (a and b) and Supplementary Figs. S1-S5. The energetic stabilities of a variety of RE hydrides were evaluated from their formation enthalpies relative to the dissociation products of mixtures of  $REH_2 + H_2$ , where  $REH_2$  is the known stable RE hydride at ambient pressure [38]. Fig. 1 (a and b) and Supplementary Figs. S1-S5 [39] show that the thermodynamically most stable stoichiometry varies with increasing atomic number of the RE metals. In the low-pressure regime ( $< 50$  GPa),  $REH_3$  (Figs. S1-S3) is the most stable species in the Sc-H, Y-H and La-H systems, while  $REH_4$  (Figs. S4-S5) is the most stable in the Ce-H and Pr-H systems. The change in stoichiometry with pressure might result from the distinct oxidation states (e.g., 3+ for Sc, Y, and La, and 3+/4+ for Ce and Pr at ambient pressure). Besides the known  $REH_3$  and  $REH_4$  hydrides, the predicted  $REH_6$  structures in the Sc-H and La-H systems adopt the same  $Im\bar{3}m$  clathrate structure as in  $CaH_6$  [9] and  $YH_6$  [10] that consists of  $H_{24}$  cages as depicted in Fig. 2a. Substantially H-richer  $REH_9$  and  $REH_{10}$  species exhibiting peculiar three-dimensional H clathrate structures of  $H_{29}$  and  $H_{32}$  cages were identified in most of the RE-H systems studied, as shown in Figs. 2b and 2c. The predicted stable pressure ranges at zero temperature for various clathrate structures are listed in Fig. 1c. We note that once temperature effects are included via quasi-harmonic free-energy calculations [55], the  $REH_{10}$  structure is also stabilized in Y-H systems at

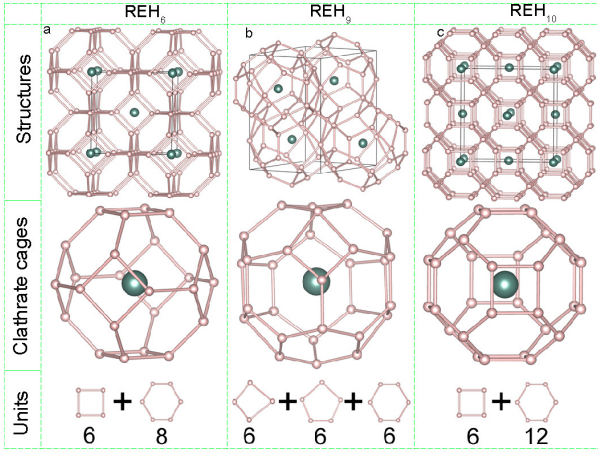


FIG. 2: (Color online) Clathrate structures of  $\text{REH}_6$  (a),  $\text{REH}_9$  (b), and  $\text{REH}_{10}$  (c). The small and large spheres represent H and RE atoms, respectively. The middle panel depicts the RE centered  $\text{H}_{24}$ ,  $\text{H}_{29}$ , and  $\text{H}_{32}$  cages of  $\text{REH}_6$ ,  $\text{REH}_9$ , and  $\text{REH}_{10}$ , respectively. Each  $\text{H}_{24}/\text{H}_{32}$  cage with  $O_h/D_{4h}$  symmetry contains six squares + eight hexagons/six squares + twelve hexagons. One  $\text{H}_{29}$  cage consists of six irregular squares + six pentagons + six hexagons.

temperatures  $> 1,000$  K, as shown in Fig. 1d. Interestingly, single  $\text{H}_{24}$  or  $\text{H}_{32}$  cages share a structural similarity with the  $\text{C}/\text{Si}_{24}$  [56, 57] or  $\text{C}_{32}$  [58] clusters that have been proposed theoretically for IVA group elements. In those cases C-C/Si-Si forms  $sp^3$  hybridized bonds, in contrast to H-H bonding which lacks  $p$  orbitals. In addition, our structure searches predict other stable stoichiometries of  $\text{REH}_8$  in Ce-H and Pr-H systems which have layered structures (Fig. S7) and  $\text{LaH}_{11}$  with a three-dimensional H net structure (Fig. S8). These structures are highly interesting and do not contain  $\text{H}_2$  molecules either, but we do not discuss their physical properties since they only show superconductivity that is much weaker than in the H clathrate structures that are the main focus of our work.

We examine the chemical bonding of the  $\text{REH}_6$ ,  $\text{REH}_9$  and  $\text{REH}_{10}$  clathrate structures by calculating the electron localization functions (ELF) [59] (Fig. S9). The RE-H bonding is purely ionic in view of the absence of charge localization between RE and H, while a weakly covalent H-H interaction is evident via the observation of charge localization between the nearest-neighbor H atoms. Note that within the  $\text{H}_{24}$ ,  $\text{H}_{29}$ , and  $\text{H}_{32}$  cages, the nearest H-H distances are very similar and are equal to 1.24 Å, 1.17 Å, and 1.08 Å at 200 GPa, respectively, which are much longer than in the  $\text{H}_2$  gas molecule (0.74 Å) and slightly longer than the H-H distance (0.98 Å) [60] in monatomic H at 500 GPa. Subsequent Crystalline Orbital Hamiltonian Population calculations [61] were performed to confirm the H-H covalent bonding in these clathrate structures. The results (Figs. S10a and S10b) clearly reveal the occupancy of the H-H bonding states, which lends

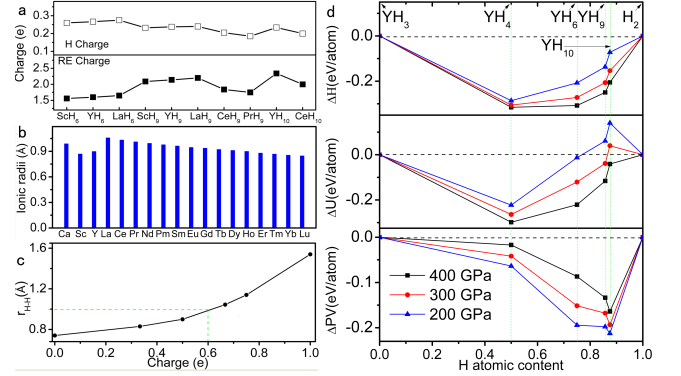


FIG. 3: (Color online) Formation mechanism of clathrate structures. (a) The anionic H and cationic RE charges are listed in the RE-H systems at 400 GPa. (b) Ionic radii for the RE elements are compared to those in Ca. (c) Variation of the H-H separation ( $r_{\text{H-H}}$ ) in a  $\text{H}_2$  molecule with the electrons accepted per  $\text{H}_2$  molecule (see computational details in the Supplementary Material). (d) Formation enthalpies (top panel), internal energies (middle panel), and PV energy terms (bottom panel) for Y hydrides relative to  $\text{YH}_3 + \text{H}_2$ .

strong support to the existence of H-H covalent bonding in the structure. There is significant charge transfer from RE to H as derived from a Mulliken population analysis [62] (Fig. 3a). The charges on the H atoms do not change much with increasing H content, but the RE charges increase significantly and provide additional electrons to the H atoms which stabilizes the clathrate structure. The strong anion-cation interaction increases the Madelung energy of the ionic component of the RE-H bonding, which increases the stability of these clathrate structures.

The clathrate structures are likely to be stable only if they contain a certain optimal numbers of H atoms and electrons accepted per  $\text{H}_2$  donated by the RE metals. Two H atoms readily form a chemical bond which reduces the energy, but once a  $\text{H}_2$  molecule is formed, the H-H  $\sigma$  bonding orbital is fully occupied and the  $\text{H}_2$  electrons accepted per  $\text{H}_2$  will reside in the antibonding  $\sigma^*$  orbitals, which weakens the H-H  $\sigma$  bond [9, 30, 63]. Indeed, the H-H  $\sigma$  bond-length increases with the number of electrons from the RE elements in an  $\text{H}_2$  molecule (Fig. 3c). If the number of electrons accepted per  $\text{H}_2$  molecule reaches about 0.6e, the  $\text{H}_2$  molecule dissociates as the H-H bond length increases to about 1.0 Å, which is similar to the H-H distance (0.98 Å) in monatomic H at 500 GPa [60]. This model calculation suggests that once an optimal compromise between the number of  $\text{H}_2$  molecules and electrons they accept is achieved, an alternative lower energy structure (e.g., clathrate structure) appears. Here, the nearest H-H distances for the  $\text{REH}_6$  and  $\text{REH}_9/\text{H}_{10}$  clathrate structures are  $\sim 1.2$  and 1.0 Å, corresponding to a number accepted electrons of 0.7e and 0.6e per  $\text{H}_2$ , respectively. Our structure searches have identified an

extremely H-rich species of  $\text{YH}_{24}$  (Fig. S11), however, the H atoms remains in a molecular form in which the electronic charge accepted of 0.13e per  $\text{H}_2$  is too small to destabilize the  $\text{H}_2$  molecule.

To probe the thermodynamical origins of the stabilization of these clathrate structures, we chose the Y-H system as an example and present data in Fig. 3d for the enthalpies  $\Delta H$ , the internal energies  $\Delta U$ , and the pressure-volume term  $\Delta PV$ . We see that  $\Delta U$  increases with increasing H content under pressure, while the  $\Delta PV$  term is reduced and the H-rich clathrate structures  $\text{YH}_6$  and  $\text{YH}_9$  tend to be stable and lie on the convex hull (see  $\Delta H$  in Fig. 3d). The substantial reduction in volume under pressure leads to the stability of H-rich clathrate structures. We further examined all the clathrate structures, and surprisingly found that the RE-H distances in  $\text{REH}_6$ ,  $\text{REH}_9$ , and  $\text{REH}_{10}$  are nearly equal, with a value of  $\sim 1.9$  Å, which is close to the sum of the atomic radius (0.79 Å) of H and the ionic radii of RE atoms (in the range 0.84-1.08 Å, Fig. 3b). This observation indicates that the atoms in these clathrate structures are densely packed, which gives a natural explanation of the much reduced  $\Delta PV$  term (bottom panel in Fig. 3d) once the clathrate structure is stabilized. Indeed, by careful inspection of 500 low-enthalpy structures generated by our searches for  $\text{YH}_9$  at 300 GPa (Fig. S12), we found that the clathrate  $\text{H}_{29}$  structure has the smallest volume ( $23.16$  Å<sup>3</sup> per formula unit) among those studied.

The H clathrate structures of  $\text{REH}_6$ ,  $\text{REH}_9$ , and  $\text{REH}_{10}$  are metallic as seen from the calculated electronic band structures and densities of states (Fig. S13 and S14). The electronic density of states at the Fermi level is typically large and is dominated by the contribution from H atoms. To examine potential superconductivity in the clathrate structures, lattice phonons and electron-phonon coupling (EPC) calculations were carried out using linear response theory [64]. Encouragingly, the resulting EPC parameters  $\lambda$ s of  $\text{YH}_9$  and  $\text{YH}_{10}$  are quite large and reach values of 4.42 and 2.41 at 150 and 400 GPa, respectively. Besides the H-derived high density of states at the Fermi level that is associated with a Van Hove singularity at the  $\Gamma$  point (Fig. S14), the large  $\lambda$  values are mainly associated with in-plane stretching, in-plane rocking, and out-of-plane rocking vibrations of H clathrate cages (Fig. S15). The Eliashberg equation [37] gives a better description of systems with strong electron-phonon coupling for  $\lambda > 1.5$ . We have therefore used the Eliashberg equation to predict superconductivity in the clathrate structures using the calculated logarithmic average frequency ( $\omega_{\log}$ ) and typical Coulomb pseudopotential parameters ( $\mu^*$ ) from 0.1 to 0.13. The resulting  $T_c$  values are 276 K (253 K for  $\mu^* = 0.13$ ) and 303 K (287 K for  $\mu^* = 0.13$ ) using  $\mu^* = 0.1$  for  $\text{YH}_9$  at 150 GPa and  $\text{YH}_{10}$  at 400 GPa, respectively. We also investigated potential superconductivity in other clathrate structures (Fig. 4) and predicted  $T_c$  values for  $\text{ScH}_6$  and  $\text{ScH}_9$  as

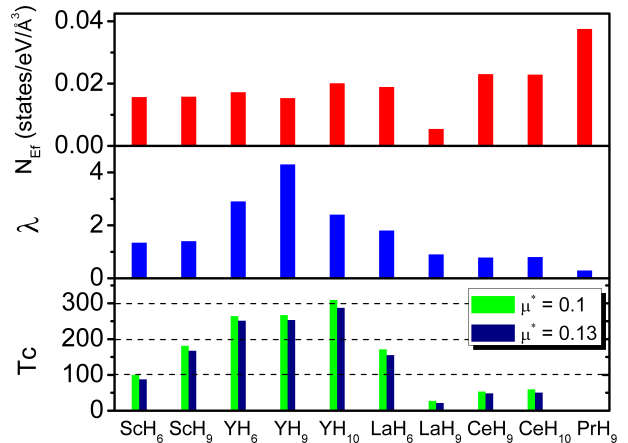


FIG. 4: (Color online) Calculated electronic DOS of H at the Fermi level ( $N_{Ef}$ ) per Å<sup>3</sup> (top panel), the EPC parameter  $\lambda$  (middle panel), and  $T_c$  (bottom panel) of various clathrate structures at high pressures. The pressure values chosen within their stable pressure ranges of the phases are 300, 400, 120, 150, 400, 100, 50, 100, 200, and 100 GPa for  $\text{ScH}_6$ ,  $\text{ScH}_9$ ,  $\text{YH}_6$ ,  $\text{YH}_9$ ,  $\text{YH}_{10}$ ,  $\text{LaH}_6$ ,  $\text{LaH}_9$ ,  $\text{CeH}_9$ ,  $\text{CeH}_{10}$  and  $\text{PrH}_9$ , respectively.

high as  $\sim 150$  K, although for  $\text{LaH}_9$ ,  $\text{CeH}_9$ ,  $\text{CeH}_{10}$  and  $\text{PrH}_9$  they are much lower at  $< 56$  K (Fig. 4) due to the introduction of much heavier elements which reduce BCS superconductivity.

Our extensive structure searches for RE (RE = Sc, Y, La, Ce, and Pr) hydrides have revealed the appearance of stable clathrate structures in  $\text{REH}_6$ ,  $\text{REH}_9$ , and  $\text{REH}_{10}$ . These structures have extended our searches into other RE (RE = Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) hydrides using density-functional-theory calculations and substituting the RE elements into the known  $\text{REH}_6$ ,  $\text{REH}_9$ , and  $\text{REH}_{10}$  structures (Supplementary Figs. S16-S27). Our results show that clathrate structures often emerge in these RE hydrides. Stabilization of clathrate structures using RE hydrides at high pressures might therefore be a widespread phenomenon.

Two families of binary hydrides (i.e., nonmetals with high electronegativity and metals hydrides) are promising candidates for high- $T_c$  superconductivity. For non-metal hydrides in which H is able to form covalent bonds with nonmetallic elements, the three-dimensional covalently-bonded H structure appears only in the high- $T_c$   $\text{H}_3\text{S}$  [14] and  $\text{H}_3\text{Se}$  [65] materials. For metal hydrides in which bonding between H and metallic elements is purely ionic, we emphasize that H-H bonding in three-dimensional clathrate structures established for RE hydrides are potential high- $T_c$  superconductors that present our greatest hope for achieving room- $T_c$  superconductivity. Future theoretical searches for high- $T_c$  superconductors are expected to investigate ternary or quaternary hydrides which have not been well-explored to date, although such structure searches can be challeng-

ing since their cost increases rapidly with the number of atoms and atomic species.

In conclusion, we have used extensive first-principles structure searches to establish the pressure-induced formation of H clathrate structures that contain  $H_{24}$ ,  $H_{29}$ , and  $H_{32}$  cages with RE atoms at the centre of the H-rich RE hydrides studied. The origin of the stabilization of these clathrate structures is related to their densely-packed structures via a much reduced PV energy term which achieves a near-optimal compromise between the number of H atoms and the electrons donated by RE atoms in the structure. The clathrate structures exhibit potential high- $T_c$  superconductivity that originates from the large H-derived electron density of states at the Fermi level and the strong electron-phonon coupling which is related to the motion of H atoms within the cages, among which  $YH_{10}$  is predicted to be a potential room temperature superconductor with a  $T_c$  of up to 303 K at 400 GPa. Our work will stimulate future high-pressure experimental work on synthesis of these clathrate structures to explore the high- $T_c$  superconductivity and the peculiar chemical bondings involved. Direct chemical reactions of RE metals and H in laser-heated diamond-anvil-cell experiments might be able to overcome the kinetic barriers and achieve synthesis of these interesting hydrides.

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