

# The investigation on exploring rare earth hydrides superconductors

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**Abstract.** This review provides a comprehensive overview of the challenges and potential solutions in the quest for high-temperature superconductivity using hydrogen-rich materials. Traditional superconductors often face limitations in terms of critical transition temperatures ( $T_c$ ) and stability under high pressures. However, hydrogen-rich compounds offer promising avenues due to their strong electron-phonon coupling, elevated Debye temperatures, and high electronic density. Recent discoveries, such as  $H_3S$ , have further invigorated the field. While an excess of  $H_2$ -like units can adversely affect  $T_c$ , clathrate structures like  $CaH_6$  and  $YH_6$  present viable alternatives by fostering high symmetry. Rare earth hydrides, notable for their electron-donating capabilities, have undergone extensive testing. Isotope effect studies, as exemplified by  $LaH_{10}$  and  $LaD_{10}$ , highlight the critical role of hydrogen vibrations in superconductivity. Ternary superhydrides incorporating dopant elements aim to reduce the pressure requirements for stability, with  $LaBeH_8$  emerging as a promising candidate, exhibiting a  $T_c$  of 110 K at 80 GPa. The review concludes by outlining future research directions, such as the incorporation of small-radius atoms to increase hydrogen content, a deeper understanding of the role of symmetry, and addressing challenges related to vibrational modes and structural stability.

**Keywords:** Superconductivity, Superhydrides, Room-Temperature Superconductivity.

## 1. Introduction

Superconductors were first discovered by Heike Kamerlingh Onnes in 1911, and since that seminal observation, their properties have been studied and introduced to global scientific communities. However, a significant limitation of superconductors is their exceedingly low critical transition temperatures ( $T_c$ ), which govern the onset of superconductivity. Moreover, achieving stable superconductive states often requires high pressure, further restricting their practical applications in daily life. A compelling avenue of research has emerged, focusing on the relationship between  $T_c$  and the Debye frequency, as well as the inverse correlation between the Debye frequency and atomic mass. Hydrogen, the lightest element in the universe, has been identified as a key factor in potentially achieving room-temperature superconductivity. Metal hydrides have been particularly promising, due to their strong electron coupling, elevated Debye temperatures during solidification, and a significant electronic density of states near the Fermi level, which largely originates from hydrogen atoms [1-3].

Furthermore, hydrogen-rich materials have garnered attention as strong candidates for achieving room-temperature superconductivity (RTS). These materials offer the advantage of becoming metallic at relatively low pressures, close to ambient conditions. Bolstering this line of inquiry, recent

experimental findings have reported a high  $T_c$  of 203 K for  $H_3S$ , achieved under a pressure of 155 GPa [4, 5]. These discoveries have invigorated the ongoing exploration of hydrogen-rich solid hydride superconductors.

## 2. Rare Earth elements

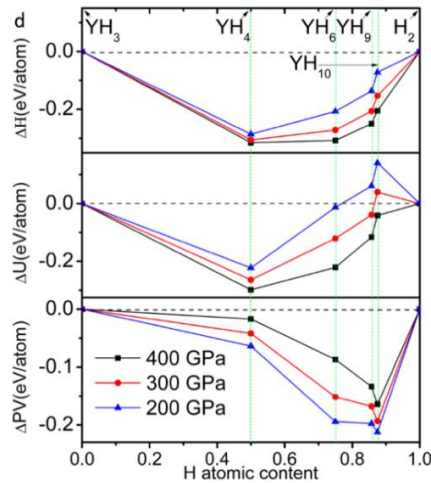
The use of sections to divide the text of the paper is optional and left as a decision for the author. Where the author wishes to divide the paper into sections the formatting shown in table 2 should be used. Although H atoms can contribute to strong electron-phonon coupling, the presence of abundant hydrogen in a material does not guarantee a higher critical temperature ( $T_c$ ). A large concentration of H atoms may not necessarily lead to an elevated  $T_c$ , owing to the formation of  $H_2$ -like molecular units. These units tend to attract electrons with Fermi energy, thereby interfering with the electron-phonon coupling and potentially leading to a lower  $T_c$  [3].

To achieve a high  $T_c$ , it is essential to eliminate these  $H_2$ -like molecular units. One approach to resolving this issue is to donate electrons that can be readily absorbed by the  $H_2$  molecules. In this scenario, the hydrogen atoms in the  $H_2$  units become occupied by the newly donated electrons, facilitating the easy dissolution of the  $H_2$  molecular units [6, 7]. This process also encourages the formation of stable clathrate structures. In a clathrate structure of hydrogen-rich materials, an atom is situated at the center while hydrogen atoms form a cage-like structure around it [3]. This arrangement is highly symmetrical, a crucial attribute for achieving a high  $T_c$ . The first molecules identified with this structure were  $CaH_6$  and  $YH_6$  [7, 8]. In these compounds, calcium (Ca) or yttrium (Y) resides at the center and donates electrons to the surrounding hydrogen atoms. As a result, the hydrogen atoms, now enriched with electrons from Ca or Y, no longer form  $H_2$ -like units. Instead, they are linked to each other through weak covalent bonds within the  $H_{24}$  cage. These two compounds exhibit the highest theoretical  $T_c$  values.

To identify potential clathrate structures in binary metal hydrides that contain a high number of hydrogen atoms without  $H_2$  molecular units, researchers have turned their attention to rare earth hydrides. Two key properties make rare earth elements particularly effective electron donors. First, their low electronegativities allow them to easily lose electrons [9]. Second, these elements are capable of sustaining higher oxidation states [3]. Through structural analysis of hydrides formed with rare earth (RE) elements, F. Peng et al. discovered that each of these RE-element hydrides can indeed form a clathrate structure. Notably, configurations exceeding  $H_{24}$  in  $REH_6$ , such as  $H_{29}$  in  $REH_9$  and  $H_{32}$  in  $REH_{10}$ , are also feasible and exhibit higher critical temperatures ( $T_c$ ) under elevated pressure [3].

The number of atoms involved is not selected arbitrarily. A critical balance exists between the number of hydrogen atoms in the clathrate structures and the electrons supplied by rare earth (RE) atoms. As the concentration of  $H_2$  molecules increases, there is enhanced electron acceptance by the hydrogen atoms. This dynamic affects the strength of the hydrogen-hydrogen bonds; the growing distance between hydrogen atoms leads to weakened bonds. Optimal stability is achieved when the number of  $H_2$  molecules and the electrons they can accommodate approach a state of near equilibrium. This culminates in the formation of a more stable configuration, such as a clathrate structure, distinguished by lower energy states [3].

The stability of RE binary hydrides is further enhanced by the properties of RE atoms. As the hydrogen content increases, the charge state of RE atoms is affected. Unlike hydrogen atoms, whose charge remains constant despite increasing H content, RE atoms acquire additional charge as the number of hydrogen atoms rises. Consequently, the RE-H structure becomes increasingly stable. Similarly, elevated pressure also serves to enhance the structural stability in the presence of increasing hydrogen content [3].

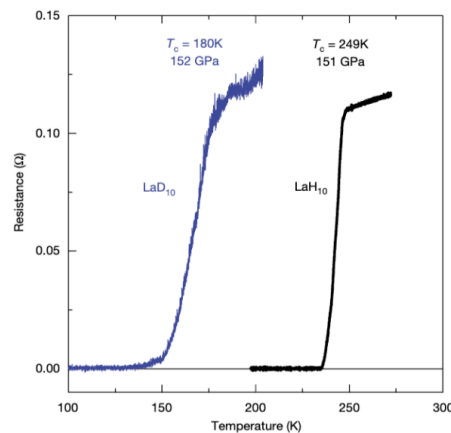


**Figure 1.** The change of enthalpy (top panel), the change of internal energy (mid panel), the change of PV energies terms (bottom panel) for Y hydrides relative to YH<sub>3</sub> + H<sub>2</sub>. Adapted from Ref [3].

The thermodynamic stability of the structure also necessitates high pressure. A key factor influencing this stability is the change in pressure-volume (PV) product. Referencing Figure 1, which analyzes the yttrium-hydrogen (Y-H) binary system, it is evident that energy fluctuations grow larger as H content increases. However, the change in PV becomes significantly lower with higher hydrogen content. This can be attributed to the densely packed structure that has been observed [3].

The following experiment work verified previous predictions. Russell J. Hemley et al. found that LaH<sub>10</sub> can display a highest  $T_c$  value of 260 K under pressure around 200 GPa. The highest  $T_c$  of LaH<sub>10</sub> will be lower when the pressure is around 170-180 GPa [10]. During the experiment, Russell J. Hemley et al. found that conductivity appear with higher  $T_c$  and higher synthesis pressure. They argue that this situation indicates that higher synthesis pressure related to higher H content. Moreover, under low pressure, the structure will become monoclinic when optimizing the H sublattice [11]. This breaks the high symmetric clathrate structure and make  $T_c$  lower (220K).

The subsequent experimental work corroborated earlier predictions. Russell J. Hemley et al. discovered that LaH<sub>10</sub> exhibits a highest  $T_c$  value of 260 K under pressures around 200 GPa. At reduced pressures of approximately 170-180 GPa, the highest  $T_c$  of LaH<sub>10</sub> diminishes [10]. During the experiments, Hemley's team observed that higher conductivity correlated with higher  $T_c$  and increased synthesis pressure. They suggested that this correlation indicates a relationship between higher synthesis pressure and higher hydrogen content. Furthermore, under low pressure, the structure transitions to a monoclinic form when optimizing the hydrogen sublattice. This transformation disrupts the highly symmetric clathrate structure, resulting in a lower  $T_c$  value of 220 K [11].



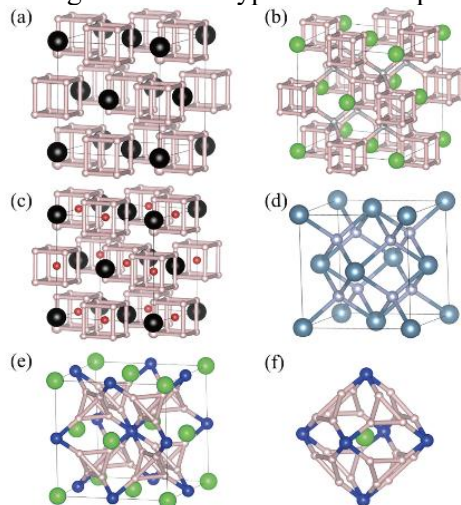
**Figure 2.** The superconducting phase transition of LaH<sub>10</sub> and LaD<sub>10</sub>. Adapted from Ref [4].

A. P. Drozdov et al. not only corroborate the high  $T_c$  of binary RE hydrides but also confirm the significance of hydrogen by isotope effect. The BCS and Migdal–Eliashberg theories indicate that possible room temperature superconductor requires a high frequency lattice vibration. The Density Functional Theory calculation states that the H atoms' high frequency vibrations are important to the electron-phonon interaction. A. P. Drozdov et al. observed isotope effect in lanthanum hydrides by substituting H atoms with D atoms [12]. From Figure 2, we can see that the  $T_c$  of  $\text{LaH}_{10}$  is higher than  $\text{LaD}_{10}$ . This implies that the phonon spectrum and the stability of the crystal lattice are impacted by the energy disparity between H and D isotopes. Understanding the isotope effect holds significance as it offers a window into the fundamental mechanisms driving superconductivity in lanthanum hydride. Additionally, it aids in comprehending how isotopes substitution can modify the superconducting characteristics of materials. Further exploration and dedicated theoretical or experimental studies might be necessary to fully comprehend the intricate aspects of the phonon spectrum and the role of hydrogen vibrations in the electron-phonon coupling within lanthanum hydride.

### 3. Road of Ternary Hydride

Footnotes should be avoided whenever possible. If required, they should be used only for brief notes that do not fit conveniently into the text. The instability of H-rich hydrides at relatively low pressures presents a significant challenge. To mitigate the pressure requirements for stable, high- $T_c$ , hydrogen-based superconductors, the concept of ternary superhydrides has been introduced. This involves incorporating dopant elements into existing hydrogen-rich binary systems [13]. The addition of these dopant elements can alter the electronic structure and bonding environment, potentially reducing the pressure needed for metallization and achieving high  $T_c$  in hydrogen-based superconductors. In this context, the hydride  $\text{AXH}_8$  has been introduced as a promising candidate. This compound features a fluorite-type structure, where 'A' serves as a 'pre-compressor' and 'X' is a small-radius atom ( $A = \text{Sc}, \text{Ca}, \text{Y}, \text{Sr}, \text{La}, \text{Ba}$ ;  $X = \text{Be}, \text{B}, \text{Al}$ ).

The fluorite-type structure is well-suited for maintaining the desired bonding environment and overall stability. This capability is attributed to the specific arrangement of atoms and the presence of voids within the crystal lattice, as illustrated in Figure 3[13]. In a fluorite structure, cations occupy the face-centered cubic lattice sites, while anions fill the tetrahedral voids. This arrangement enables precise bonding interactions among the atoms, thereby achieving the targeted bonding environment and enhancing structural stability [13]. In the case of  $\text{AXH}_8$ , the 'A' atoms serve as the cations that occupy the lattice sites, while hydrogen atoms fill the tetrahedral voids. The bonding environment facilitated by the fluorite-type structure allows hydrogen atoms to readily accept electrons. This, in turn, leads to an elongation of the H-H bonding length, a reduction in  $\text{H}_2$  molecular units, and a strengthening of the electron-phonon coupling. These features collectively contribute to the material's superconducting properties, making the fluorite-type structure a promising avenue for further research.



**Figure 3.** Atomic structure of  $\text{LaBeH}_8$  (e) and fluorite type  $\text{LaBeH}_8$  (f) [13].

Zhang, Z. et al. have attempted to modify the existing LaH<sub>10</sub> hydride structure, which exhibits a symmetry closely resembling that of UH<sub>8</sub> [14]., as shown in Figure 3 [13]. In LaH<sub>10</sub>, additional H atoms occupy the vacant positions found in the UH<sub>8</sub> structure. In the context of the AXH<sub>8</sub> structure, the 'X' atom can fill the vacancy located at the center of the cubic H<sub>8</sub> units [13]. Computational analyses of 18 different AXH<sub>8</sub> combinations revealed that LaBeH<sub>8</sub> requires the lowest pressure to maintain both dynamic and thermodynamic stability—20 GPa for dynamic stability and 98 GPa for thermodynamic stability [13]. Other combinations, however, require extremely high pressures to achieve stability, which contradicts the original design intent of AXH<sub>8</sub>.

Experimental work on LaBeH<sub>8</sub> has yielded intriguing results: the compound exhibits a T<sub>c</sub> of 110 K under a pressure of 80 GPa [15]. Unlike the fluorite-type structure, LaBeH<sub>8</sub> adopts a rocksalt-like structure. One advantage of LaBeH<sub>8</sub> over LaH<sub>10</sub> is its greater structural stability at lower pressures. Specifically, the symmetric structure of LaH<sub>10</sub> becomes distorted under pressures lower than 160 GPa due to phonon softening, which consequently lowers its T<sub>c</sub> [15]. In contrast, LaBeH<sub>8</sub> maintains a more stable structure under such conditions. The beryllium (Be) atom interacts weakly with hydrogen atoms, forming a BeH<sub>8</sub> unit that fills the empty spaces in the La sublattice, thereby contributing to its stability.

#### 4. Conclusion and prospects

In summary, RE superhydrides show promise as high-T<sub>c</sub> superconductors but require relatively high pressures to maintain stability. All RE hydrides tend to form highly symmetric clathrate structures. Binary RE hydrides exhibit relatively high T<sub>c</sub> values under the high pressures needed for thermodynamic stability. The ternary compound LaBeH<sub>8</sub>, on the other hand, can maintain stability under relatively lower pressures, although still far from ambient conditions. It has a T<sub>c</sub> of approximately 110 K under 80 GPa.

From my perspective, future research on room-temperature and pressure-stable superhydrides could focus on incorporating multiple small-radius atoms. This would allow for a higher hydrogen content in the structures. One of the primary reasons binary systems struggle to maintain stability at ambient pressure is the high change in the product of pressure and volume (PV) for hydrides with higher hydrogen content. Binary RE hydrides are densely packed, requiring a large initial volume due to the presence of more H<sub>2</sub> molecules, which results in a large PV value. Introducing more small-radius atoms that can donate electrons to H<sub>2</sub> molecular units could mitigate this issue by allowing hydrogen atoms to be less tightly bound to RE atoms. However, this strategy comes with potential drawbacks, such as changes in the high-vibration modes of hydrogen atoms, which could affect electron-phonon coupling. Additionally, the impact of these small-radius atoms on the symmetry of the structure remains uncertain.

Further investigation into the role of symmetry is warranted. High-symmetry structures are generally considered desirable for achieving high T<sub>c</sub>, but theoretical understanding of the underlying mechanisms needs to be expanded. If the reasons why high-symmetry structures benefit high T<sub>c</sub> can be identified, it may be possible to focus on those specific aspects and explore alternative materials that can maintain such properties under ambient pressure, especially since high-symmetry structures tend to distort under lower pressures.

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