

## Compressed hydrides as metallic hydrogen superconductors

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The 2014–2015 prediction, discovery, and confirmation of record high-temperature superconductivity above 200 K in compressed H<sub>3</sub>S, followed by the 2018 extension to superconductivity in the 250–260 K range in lanthanum hydride, mark a new era in the long-standing quest for room-temperature superconductivity: quest achieved, at the cost of supplying 1.5–2 Mbar pressure. Predictions of numerous high-temperature superconducting metal hydrides XH<sub>n</sub> (X=metal atom) have appeared but are providing limited understanding of why some transition temperatures  $T_c$  are high while others are low. We make use of the small mass ratio  $M_H/M_X$  to obtain an atomic decomposition of the coupling strength to reveal that although the X atom provides coupling strength via  $\lambda_X$  as commonly calculated, it is irrelevant for  $T_c$  because the resulting lowering of frequency moments compensates (and sometimes overcompensates) for the increase in  $\lambda$ . It is important for analysis and for understanding that the X atom contribution is *neglected* because  $T_c$  depends more transparently on  $\lambda_H$ . Five XH<sub>n</sub> compounds, predicted in harmonic approximation to have  $T_c$  in the 150–300 K range, are analyzed consistently for their relevant properties, revealing some aspects that confront conventional wisdom. A phonon frequency–critical temperature ( $\omega_2$ - $T_c$ ) phase diagram is obtained that reveals a common structural phase instability boundary limiting  $T_c$  at the *low-pressure* range of each compound. The hydrogen scattering matrix elements are obtained and found to differ strongly over the hydrides. A quantity directly proportional to  $T_c$  in these hydrides is identified, indicating that (in common notation)  $N_H(0)I_H^2/\omega_H = \eta_H/\omega_H$  is the parameter combination to be maximized in hydrides.

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### I. BACKGROUND

The disruptive discovery of record high-temperature superconductivity (HTS) in SH<sub>3</sub> above 200 K [1–4] has now been superseded by reports from two groups of critical temperatures  $T_c$  in the 250–260 K range in lanthanum hydride [5–7], both requiring pressure in the 160–190-GPa range. Even more recently,  $T_c$  up to 240 K has been report in yttrium hydrides [8]. The mechanism of pairing is convincingly electron-phonon coupling (EPC) in these hydrides [1,9–15], and several predictions of HTS in dozens of other metal hydrides at high pressure have appeared (see, for example, [4,9,16–23]). For prediction of new superconductors it is essential to identify the energetically favorable structures, and there has been an emphasis on this issue in several of these studies [1,4,9,11,12,14,16–22]. However, relatively little has been decided about the relative importance of the few underlying characteristics that determine  $T_c$ . This issue of analysis and understanding of the microscopic mechanisms is the topic of this paper.

For EPC superconductivity, the critical temperature  $T_c$  is determined by a retarded Coulomb repulsion  $\mu^*$ , a minor property that varies only within the range 0.10–0.15, and the function of primary interest, the Eliashberg EPC spectral function  $\alpha^2F(\omega) = \alpha^2(\omega)F(\omega)$ , where  $F(\omega)$  is the phonon density of states and  $\alpha^2(\omega)$  gives the coupling strength from phonons of frequency  $\omega$ . While calculating (or measuring)

$\alpha^2F$  is essential for any basic understanding of the coupling,  $T_c$  itself can be obtained sufficiently accurately from the Allen-Dynes equation [24]  $T_c = T_c^{AD}(\lambda, \omega_{\log}, \omega_2; \mu^*)$  in terms of the EPC coupling strength  $\lambda$  and two frequency moments obtained from  $\alpha^2F$ , the logarithmic ( $\omega_{\log}$ ) and second ( $\omega_2$ ) frequency moments. Specific expressions are provided in the Supplemental Material (SM) [25]. For all aspects of the EPC formalism and implementation, the review of Giustino can be consulted [26]. A useful review of methods and materials for conventional high-temperature superconductors was provided by Flores-Livas *et al.* [27].

Compounds present challenges in obtaining the relative importance of the various constituent atoms. With  $\lambda$  given by

$$\lambda = \int \frac{2}{\omega} \alpha^2 F(\omega) d\omega \rightarrow \frac{N(0)I^2}{M\omega_2^2}, \quad (1)$$

individual atomic contributions are spread throughout  $\alpha^2(\omega)$  and  $F(\omega)$ . For an elemental metal, one has the exact decomposition given on the right side of Eq. (1) in terms of the Fermi level ( $E_F = 0$ ) density of states  $N(0)$ , the Fermi surface-averaged squared electron-ion matrix element  $I^2$ , the atomic mass  $M$ , and the second moment  $\omega_2$ . The scattering strength is given by the change in crystal potential  $V(\vec{r})$  due to the displacement of the atom at  $\vec{R}$ ,

$$I^2 = \left\langle \left\langle \left| \langle k | \frac{dV}{d\vec{R}} | k' \rangle \right|^2 \right\rangle \right\rangle_{FS}, \quad (2)$$

where the large brackets indicate a double average of  $\vec{k}, \vec{k}'$  over the Fermi surface.

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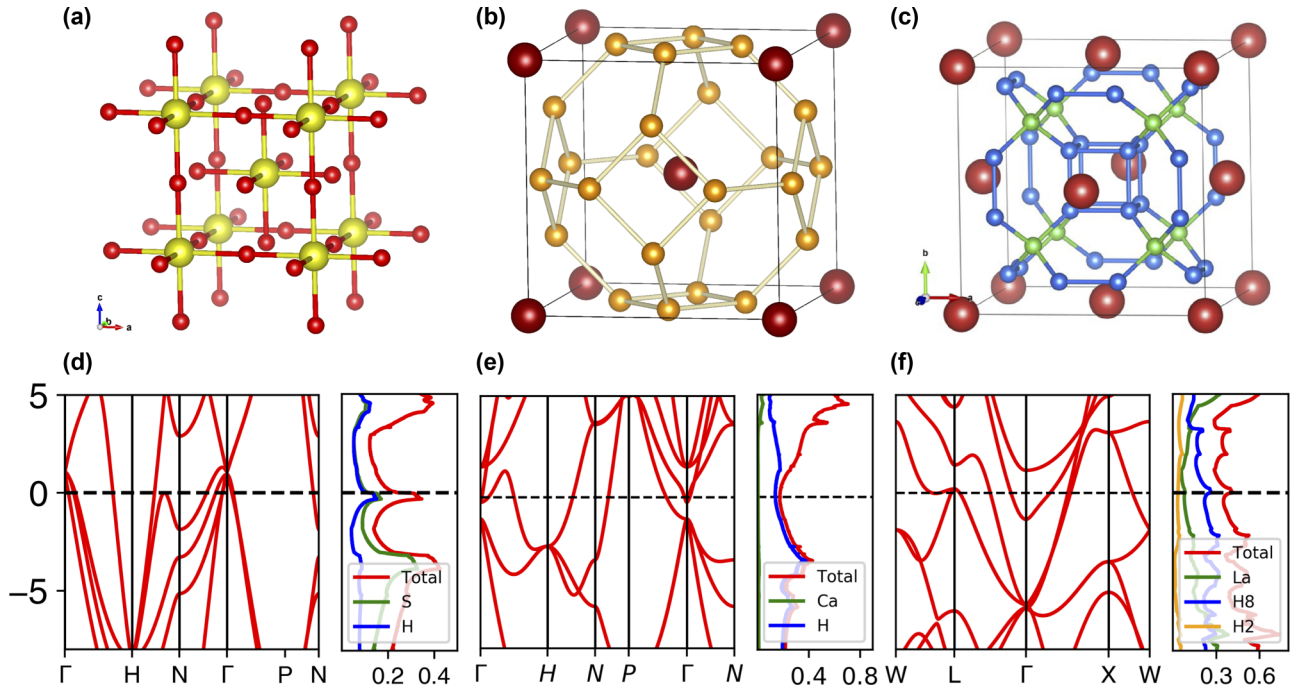


FIG. 1. Top: crystal structures of  $n = 3$  bcc  $\text{SH}_3$ ,  $n = 6$  bcc  $\text{CaH}_6$ , and  $n = 10$  fcc  $\text{LaH}_{10}$ . Bottom: corresponding band structures (in eV) and electronic densities of states (in states per eV unit cell). In each case several bands cross the Fermi level.

In generic compounds no such decomposition to atomic values is possible because the more general expression for the Fermi surface-averaged matrix elements in Eq. (2) depends on displacement of pairs of distinct atoms. A main point of this paper is that for binary hydrides  $\text{XH}_n$ , atom-specific (subscript  $j = X, \text{H}$ ) values

$$\lambda_j = N_j(0)I_j^2/M_j\omega_{2,j}^2, \quad \lambda = \lambda_X + \lambda_H, \quad (3)$$

can be obtained with accuracy and applied to great advantage to understand the origins and possible limits of  $T_c$ . The three crystal classes encompassing the five hydrides that we have studied and compared are illustrated in Fig. 1.

## II. ATOMIC ANALYSIS: H VERSUS METAL ATOM X

Binary hydrides provide a unique opportunity: the light mass of H results in separation of the phonon spectrum  $\omega_{q,v}$  and  $F(\omega)$  into disjoint metal atom low-frequency and H high-frequency regimes, with examples given below. One thus obtains separate  $\alpha^2F_j(\omega)$  functions for each atom type  $j = X$  or H from the associated frequency regime and, consequently, for  $\lambda = \lambda_X + \lambda_H$  as well. Reported predictions for  $\text{XH}_n$  compounds often quote the  $X$  and H contributions to  $\lambda$  separately.

This separation provides the extension to specific atomic contributions  $\lambda_j$  on the right side of Eq. (1). The subscript refers to each atom type  $j$ ;  $N_j(0)$  is the atom-type projected electronic density of states (DOS), and the other quantities are evident. Since  $\lambda$ , its denominator, and  $N_j(0)$  are all known after calculation, we can extract the atom-specific Fermi surface-averaged matrix elements  $I_j^2$  for each atom type in a compound because these squared matrix elements no longer contains cross terms from pairs of distinct atoms.

Specifically, we obtain  $I_H^2$  for each hydride for comparison. In addition, H frequency moments that are uncontaminated by X contributions are obtained for comparison across the hydrides.

We first note that from Eq. (3) it seems crucial for high-pressure superconductivity that  $I_j^2$  increases with pressure comparably to  $M_j\omega_{2,j}^2$  to maintain, if not to increase,  $\lambda_j$  and  $\lambda$ . The behavior of the atom-specific  $I^2$  in metals is almost unexplored in compounds, the exception being some insight obtained from the rigid atomic potential model [28–30], which has been applied successfully to close-packed medium-temperature (former high-temperature) superconductors. While all the contributions to  $I_j^2$  are available from modern EPC codes, the information has never been extracted and exploited for a deeper understanding of screening of the proton motion and its impact on high  $T_c$ .

The importance of  $I^2$  is evident as it is one of the three components of  $\lambda_j = \eta_j/\kappa_j$ :  $\eta_j = N_j(0)I_j^2$ , and  $M_j\omega_{2,j}^2 \equiv \kappa_j$ .  $\kappa_j$  is the effective harmonic lattice stiffness constant for atom  $j$ ; thus, the McMillan-Hopfield [31,32] parameter  $\eta_j = N_j(0)I_j^2$  is an effective electronic stiffness for atom  $j$ , and  $\lambda_j = \eta_j/\kappa_j$  is their ratio. The strong-coupling limit explored by Allen and Dynes [24] gives  $T_c \rightarrow 0.18\sqrt{\eta/M} = 0.18\sqrt{N(0)I^2/M}$ , further emphasizing the importance of  $I^2$  along with  $N(0)$  and  $M$ , also indicating the seeming irrelevance of frequencies. For these hydrides, we obtain a linear relation between  $T_c$  and hydrogen (not total) parameters, discussed later.

To extract these various quantities from published papers in which often only limited information is provided, we describe in the SM [25] a constrained model [10] of a piecewise constant  $\alpha^2F$  that enables extraction from published

figures, information of the type that we introduce in this paper.

### III. CRYSTAL STRUCTURE AND METHODS

In Fig. 1 the bcc  $Im\bar{3}m$  space group structure of  $\text{SH}_3$ ; the fcc  $Fm\bar{3}m$  structure of  $\text{LaH}_{10}$ , which has two hydrogen sites, H2 (green) and H8 (blue), with two and eight sites, respectively; and the bcc  $X\text{H}_6$  structure are shown. (For structural information see the SM [25].) An overview of the electronic band structure and atom-projected DOS are also shown. Several bands cross the Fermi energy (the zero of energy), so the detailed band structure *per se* provides little useful information about superconductivity. The  $\text{LaH}_{10}$  1:10 stoichiometry is calculated to be dynamically stable in the observed pressure range, and the La sublattice has been observed to be fcc [6], making it the candidate structure of choice for the recent signals of superconductivity in La-H samples in the 250–280 K range [5–7]. From one viewpoint, the La atom sits inside a hydrogen cage of 32 H atoms, as shown in Fig. 1, prompting the description as a clathrate structure.

Electronic structure calculations were carried out using the pseudopotential (PP) QUANTUM ESPRESSO (QE) code [33]. We have found that the results can be sensitive to the choice of PP, which partially accounts for the differing results that can be found in the literature for certain compounds. We have conservatively and consistently used Hamann's optimized norm-conserved Vanderbilt PPs identified as ONCV pseudopotentials [34]. The energy cutoffs for wave function and charge density expansion are 80 and 480 Ry, respectively.

For self-consistent calculations, a mesh of  $24 \times 24 \times 24$   $k$  points is used. The generalized gradient approximation [35] was adopted for the exchange-correlation functional. The optimized tetrahedron method, as implemented by Kawamura *et al.* in QE, is used for Brillouin zone integration [36]. The dense mesh that we have used provides accurate energy resolutions of  $N(E)$  when Van Hove singularities fall at  $E_F$ , which occurs in both  $\text{SH}_3$  and  $\text{LaH}_{10}$ . For phonon dispersion calculations, the  $6 \times 6 \times 6$   $q$  mesh includes the  $\Gamma$  point, while to obtain electron-phonon coupling from the optimized tetrahedron method, we used a similar mesh that is displaced from  $\Gamma$ . Since these compounds are three-dimensional, they do not display Kohn anomalies (rare in three dimensions). Also, they have strong metallic screening, so the interatomic force constants will be relatively short range. Because of these factors, the phonon dispersion curves are rather smooth, and dense  $q$  sampling is not required for the trends with pressure that we are exploring.

Anharmonic corrections are known to be important for phonons and thereby  $T_c$  in both  $\text{SH}_3$  and  $\text{LaH}_{10}$  and to stabilize them to lower pressures [11,37]. Quantum fluctuations of the H atom arise in  $\text{SH}_3$  [14] and can shift boundaries in the phase diagrams [38]. In this study we restrict ourselves to the harmonic approximation and neglect quantum fluctuations; these effects shift phase diagram boundaries but do not impact our conclusions. Only with these simplifications do the formal expressions for EPC apply. We calculate the electronic and phononic spectra, electron-phonon coupling, and  $\alpha^2F$

using the EPW (Electrons and Phonons with Wannier functions) code [39,40] and use the Coulomb repulsion constant  $\mu^* = 0.13$  throughout.

$T_c$  is calculated consistently for all compounds from the full Allen-Dynes equation, which is a refitting to dozens of calculations to an extension of the McMillan equation for  $T_c$  to include (very) strong coupling and phonon-spectrum-shape corrections. The full expression, which sports a prefactor of the logarithmic moment  $\omega_{\log}$  as a primary feature, is provided in the SM [25].

### IV. BEHAVIOR HOLDING ACROSS THE HYDRIDES

The compounds we discuss— $\text{SH}_3$ ;  $\text{CaH}_6$  and  $\text{MgH}_6$ ; and  $\text{LaH}_{10}$  and  $\text{YH}_{10}$ —share broad features: they have cubic symmetry, they have a single  $X$  atom per primitive cell, and many bands cross  $E_F$  (see Fig. 1 for crystal structures and band structures), giving a multisheet Fermi surface, the details of which do not seem to be important except for the possible occurrence of Van Hove singularities (VHSs) [15]. At the high pressures, lying variously across 160–400 GPa across this study, for which these structures have been reported (calculated) to be harmonically stable, the H vibrations dominate the optic modes with energies up to 220–250 meV, which are distinct from the  $X$ -dominated acoustic modes at 70 meV or lower, depending on the  $X$  atom mass. Tables I–III in the Appendix contain the material parameters obtained from our studies. The main results are as follows.

#### A. The dominance of hydrogen

The anticipated importance of H for  $T_c$  in hydrides is clouded by the observation that the  $X$  atom provides 15%–25% of  $\lambda$ , seemingly very important. An overriding feature in our results in Tables I–III in the Appendix is that coupling  $\lambda_X$  from the metal atom is useless in increasing  $T_c$ , at best enhancing  $T_c$  by only 3%, although the total  $\lambda$  is increased by the above-mentioned 15%–25%. More startlingly, including the  $X$  portion of  $\alpha^2F$  can *decrease*  $T_c$ . For example, for  $\text{LaH}_{10}$  at both 250 and 300 GPa, including  $\lambda_X$  increases  $\lambda$  by +14%, but this increased strength at low frequency *decreases*  $\omega_{\log}$  by 18%, producing a net *decrease* of  $T_c$  by 5%.  $\lambda_X$  thus becomes a source of misconceptions, and by being included in obtaining  $T_c$  as in previous calculations, it has resulted in the impression (incorrect) that it contributes proportionally to  $T_c$ .

This anti-intuitive behavior appears to contradict the result of Bergmann and Rainer [41] that any small increase in coupling increases  $T_c$ ; that is,  $\delta T_c / \delta \alpha^2 F(\omega)$  is non-negative. The resolution of this conundrum lies in effects that have been addressed before [42–44]: in physical materials (and in a self-consistent treatment) an increase in  $\alpha^2F$  at a given frequency will feed back into a softening of phonon modes. This mode softening always opposes the positive effect on  $T_c$  from the increase in  $\lambda$ . For  $X=\text{La}$  in  $\text{LaH}_{10}$  the softening dominates, and (as mentioned)  $T_c$  *drops* by 5% in spite of stronger coupling, just before the lattice instability sets in (see below).  $T_c$  in  $\text{CaH}_6$  and  $\text{MgH}_6$  is effectively unchanged under the 15%–20% increase from  $\lambda_X$ ;  $\text{SH}_3$  shows a small positive effect. The important message is that for  $T_c$ ,  $\lambda_X$  is ineffectual, and it should be disregarded for gaining knowledge about

increasing  $T_c$ . This option is included in Tables I–III in the Appendix.

### B. Our major results

Since it was just established that  $X$  atom coupling is ineffective at best and misleading in practice, henceforward, we focus on the H atom contributions alone: unless otherwise stated (sometimes the H subscript is included for emphasis), our comments apply only to the H atoms' contributions (the rows in Tables I–III in the Appendix labeled “H”). The following observations are drawn from the  $\omega_2$ - $T_c$  phase diagram and six other panels providing a variety of correlations in Fig. 2.

#### 1. High frequencies but not too high

Higher- $T_c$  compounds have higher-frequency moments [compare Fig. 2(a) with Fig. 2(e)]. Figure 2(a) provides an  $\omega_2$  vs  $T_c$  phase diagram, which identifies a boundary separating the high- $T_c$  region from an island of lattice instability. Interestingly, MgH<sub>6</sub> at the highest- $T_c$  end has frequencies very similar to those of SH<sub>3</sub>. Since the denominator  $M_H \omega_2^2$  in  $\lambda$  is the same for these two materials, the numerator  $\eta$  must be substantially larger. Figure 2(f) and Tables I–III in the Appendix indeed show that  $\eta$  is  $\sim 35\%$  larger, with *twice as large matrix elements*  $I_H^2$  [Fig. 2(g)], overcoming a somewhat lower value of  $N(0)$ . This is clear evidence of a strong material dependence of  $I_H^2$  in hydrides.

#### 2. Highest $T_c$ lies at the low-frequency end

Since pressure enhancement of hydride  $T_c$  has been a prevalent notion, we quantify that  $T_c$  *decreases with increasing pressure and increasing frequencies* within each class studied. Strong coupling is (unfortunately) associated with lower frequencies, within a region of stability. This result (noted previously in some individual materials) seems in opposition to conventional wisdom that higher pressure is better for  $T_c$ . Our results establish that  $T_c$  is maximum at the lower-pressure end of crystal stability where frequencies are softer, as shown in Fig. 2(a).  $T_c$  is ultimately limited in these systems, as in many strongly coupled but lower- $T_c$  analogs, by lattice instability [45–47] that depends on the details of the EPC of the material. The emerging picture is that while pressure stabilizes favorable structures with metallic *atomic H*, providing high  $T_c$  with high frequencies, *within each phase* additional pressure increases frequencies but lowers  $\lambda_H$  and  $T_c$ . To repeat, the essential role of pressure is simply to stabilize structures composed of atomic H; further pressure is detrimental for  $T_c$ . Less pressure, that is, the instability region, comprises insulating phases with H<sub>2</sub> and H<sup>−</sup> units or conducting structures with these units [19], which do not promote strong scattering and strong EPC.

#### 3. H matrix elements are not atomic properties

The derived squared H matrix element  $I_H^2$  has been suggested to be an “atomic quantity” [32,48], not varying much from material to material.  $I_H^2$  is highlighted in boldface in Tables I–III of the Appendix and plotted versus pressure in Fig. 2(g), facilitating the observation that it differs by a *factor of 5* for these compounds: from 24 for LaH<sub>10</sub> to 125 in MgH<sub>6</sub>

( $eV^2/\text{\AA}^2$ ). Evidently, the screening of the proton displacement is sensitive to the response of the environment, and  $I_H^2$  is not the atomic quantity as previously suggested.

#### 4. Impact of atomic fraction of H

Is the atomic fraction of H a crucial factor? By dividing  $N_H(0)$  in Tables I–III in the Appendix by the number of H atoms, the contribution per H atom is obtained. The values range from around 0.022 for CaH<sub>6</sub> and MgH<sub>6</sub> to 0.033 for the VHS compounds SH<sub>3</sub>, LaH<sub>10</sub>, and YH<sub>10</sub>; units are states per (eV atom spin). These values, which represent chemical differences and can be sensitive to the precision of the calculation and to decompositions into  $X$  and H contributions, do not scale well with  $T_c$ .

#### 5. Behavior of $\lambda(P)$

The variation of  $\lambda$  with pressure depends primarily on the strong variation with pressure of the lattice stiffness  $\kappa = M\omega_2^2$  [see Fig. 2(c)]. For example,  $\kappa$  decreases by 55% in CaH<sub>6</sub> from 300 to 150 GPa, beyond which the lattice becomes unstable. The minor variation of the electronic stiffness  $\eta = N(0)I^2$  is apparent from Fig. 2(f). Increasing  $\lambda$  by softening the lattice increases  $T_c$  for currently studied hydrides but encounters lattice instability for  $\lambda_H \approx 2.2$ .

#### 6. Achievement of “atomic hydrogen”

These alkaline-earth- and rare-earth-based compounds are effectively atomic hydrogen crystals with a charge carrier void (more precisely, a scattering strength void) in the volume consumed by the  $X$  atom: the  $X$  atom serves to compress and to provide electrons to destabilize H<sub>2</sub> units and produce atomic (versus diatomic) H, thereby enhancing scattering and producing HTS. This observation suggests that elements  $X$  that are most able to “break” H<sub>2</sub> molecules into atoms in a crystalline environment provide the most promise of providing Ashcroft’s “chemical precompression concept” [48], i.e., decreasing the pressure necessary to obtain HTS hydrides.

### V. PROSPECTS FOR HIGHER $T_c$ AND LIMITATIONS

We collect here some important characteristics by example from the various compounds.

#### A. Strong coupling and lattice instability

There have been many examples over several decades [45–47] in which pushing a superconducting system toward stronger coupling results in marginally higher  $T_c$ , accompanied by renormalization toward softer phonons, followed by lattice instability. The process is understood: EPC renormalizes phonon frequencies  $\omega_q$  downward from their bare values  $\Omega_q$ :

$$\omega_q^2 = \Omega_q^2 - 2\Omega_q \Pi_q(\omega_q), \quad (4)$$

where  $\Pi_q(\omega)$  is the phonon self-energy that increases with  $\lambda_q$ ; increasing coupling drives frequencies downward, as seen from Tables I–III in the Appendix. Then, lower frequencies increase the coupling strength measured by  $\lambda$  (other things

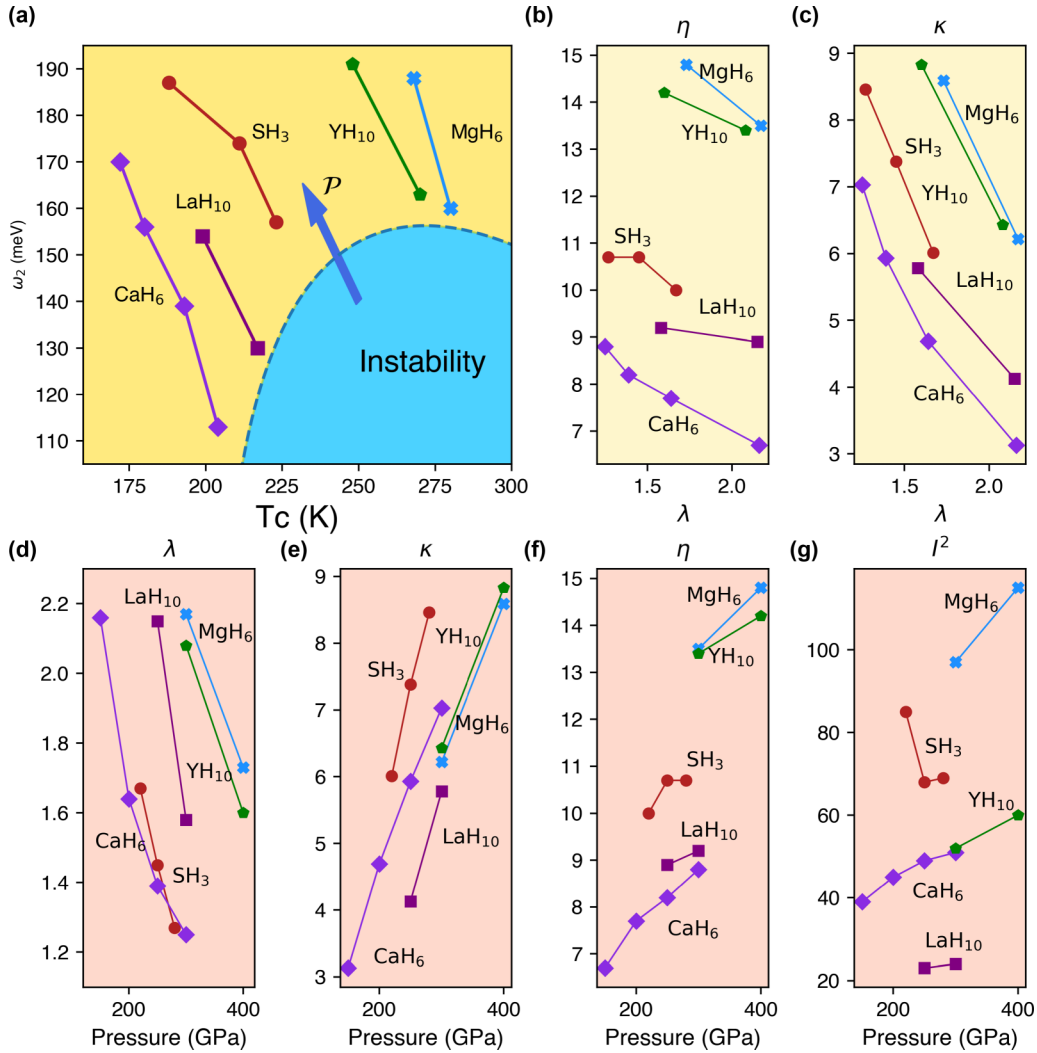


FIG. 2. Interrelationships between the various materials characteristics for the H atoms in the hydrides we discuss. (a) Schematic  $\omega_2$ - $T_c$  phase diagram, with blue indicating the island of lattice instability. The blue arrow denotes the direction of increasing pressure  $P$ . (b) and (c) Plots of  $\kappa$  and  $\eta$ , respectively, versus  $\lambda = \frac{\eta}{\kappa}$ . The increase of  $\lambda$  correlates strongly with the decrease in  $\kappa$  (frequencies). (d)–(g) Plots of  $\lambda = M\omega_2^2$  ( $\text{eV}/\text{\AA}^2$ ),  $\eta = N(0)I^2$  ( $\text{eV}/\text{\AA}^2$ ), and  $I^2$  ( $\text{eV}^2/\text{\AA}^2$ ), respectively, versus pressure. All panels show each of the five hydrides toward the lower end of their region of stability.

being equal): it is a cooperative process inviting vanishing frequencies and the accompanying lattice instability and material-dependent limitation of  $T_c$ .

The process is illustrated for  $\text{SH}_3$  in Fig. 3, where  $F(\omega)$ ,  $\alpha^2F(\omega)$ ,  $\alpha^2F(\omega)/\omega$ , and  $\alpha^2(\omega)$  are shown for a range of (harmonic) lattice stability above the instability around 140 GPa, from which distinct features can be identified. The differences with pressure in  $F(\omega)$  are unexceptional, with some hardening of the high-frequency H modes proceeding as expected. Differences in  $\alpha^2F$  begin to be more evident: peak values decrease from 170 to 150 to 130 meV as pressure is lowered. This shift downward of coupling strength is more striking in  $\alpha^2(\omega) = \alpha^2F(\omega)/F(\omega)$ , which reveals very strong coupling in the 80–120-meV region. These H-derived optic modes are reflected in the moments of  $\alpha^2F$  in Tables I–III in the Appendix:  $\omega_2$  decreases by a third before instability. Neither the moments, e.g.,  $\omega_{\log}$ , which

probably (over)emphasizes the low-frequency modes, nor  $\lambda$  dictate the instability of the lattice by vanishing or diverging, respectively.

Instead, a single branch (with small phase space) dips toward zero, and the structure becomes dynamically unstable. In these hydrides the lower-pressure, roomier structures tend to allow molecularlike dimerization of some of the H atoms into  $\text{H}_2$  units, which is unfavorable for metallicity and strong coupling. Figure 4 indicates the regions of the zone where instabilities in  $\text{SH}_3$  and  $\text{LaH}_{10}$  occur. In  $\text{SH}_3$  the instability lies along the  $H$ - $P$  symmetry line along the zone boundary, with another instability occurring at  $\Gamma$ . In  $\text{LaH}_{10}$  the instabilities occur in a donut shape centered on the  $L$  point. In both cases as well as in  $\text{CaH}_6$ , the instability involves wave vectors at or near the zone boundaries, with the short wavelengths being suggestive of the instabilities being related to  $\text{H}_2$  unit-type fluctuation and formation.

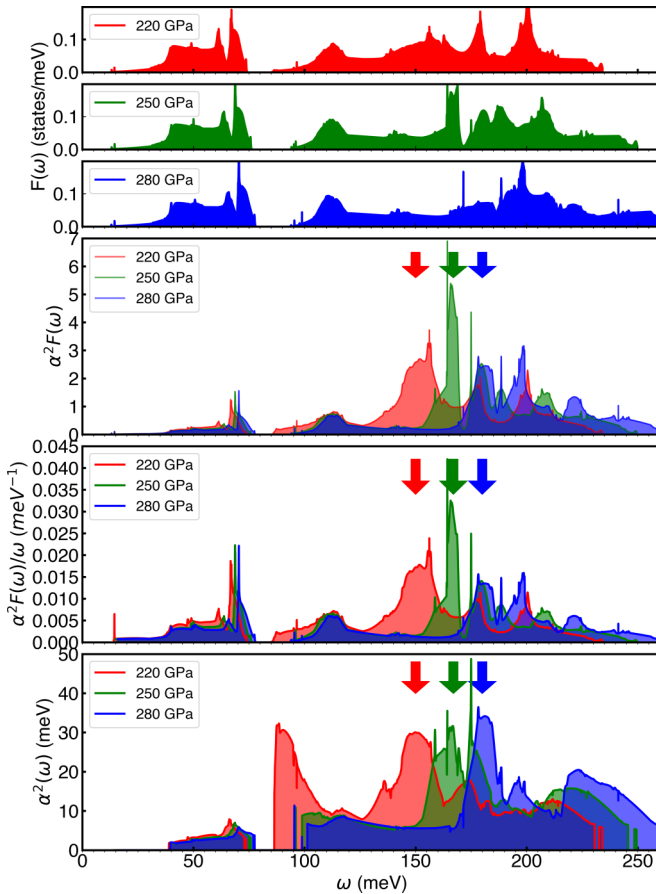


FIG. 3. Views of the evolution under pressure of phonon coupling strength and frequencies for  $\text{SH}_3$ . From the top:  $F(\omega)$  for the three pressures indicated, the Eliashberg function  $\alpha^2 F(\omega)$ , the ratio  $\alpha^2 F(\omega)/\omega$  that determines  $\lambda$  and frequency moments, and the coupling spectrum  $\alpha^2(\omega)$ . Note that in these zone-averaged functions there is no indication of the lattice instability that occurs just below 200 GPa.

### B. Highest $T_c$ class: Rare-earth decahydrides $\text{XH}_{10}$

A noteworthy feature is that, for  $\text{LaH}_{10}$  as in  $\text{SH}_3$ , which are the two materials so far observed to be superconducting close to room temperature, the Fermi level accidentally (if it is accidental) falls between the energies of a pair of closely spaced Van Hove singularities. The associated pieces of Fermi surface in  $\text{LaH}_{10}$  and resulting VHS peak in  $N(E)$  involve *solely* the H8 site (see Fig. 1). The additional physics [15] occurring in  $\text{SH}_3$  due to VHSs will also apply to  $\text{LaH}_{10}$  (but in a less prominent form), but that is not the topic of this paper. The variation of  $N(E)$  from 210 to 300 GPa is regular but minor, and the changes in the Fermi surface are not visible in surface plots.  $\text{YH}_{10}$  has a predicted  $T_c = 250\text{--}270$  K compared to  $\text{LaH}_{10}$  at 200–215 K. The values of  $\lambda$  at the two pressures studied are the same; the difference lies in the  $\sim 40\%$  higher value of  $\eta = N(0)I^2$  in  $\text{YH}_{10}$ , where a *much larger value of  $I^2$*  overcomes a somewhat lower value of  $N(0)$ . Based on current examples, increasing  $\lambda$  near the instability by phonon softening does increase  $T_c$  but also drives the instability, a familiar story from 1970s materials.

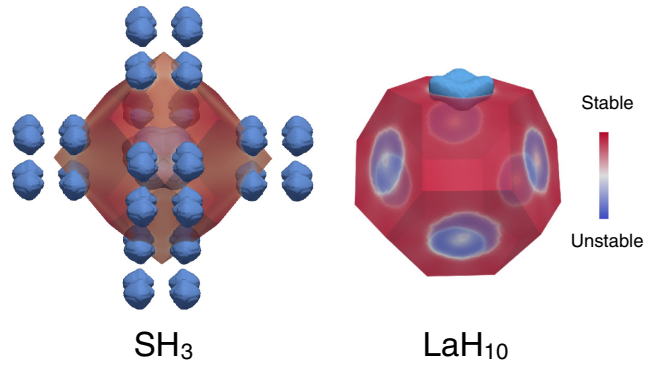


FIG. 4. Regions of unstable phonons. The indicated regions of the Brillouin zone indicate where phonons first become unstable, in harmonic approximation. For  $\text{SH}_3$  the instability regions are repeated outside the first zone for more clarity.

### C. Variations within a class: Alkaline-earth hexahydrides $\text{XH}_6$

Metal hexahydrides have been predicted to include high- $T_c$  superconductors at high pressure, but synthesis and study of their properties have not yet been reported. Given the regularities discussed above, it is eye-opening to note that both the lowest- and the highest- $T_c$  members in Fig. 2 are  $\text{CaH}_6$  and  $\text{MgH}_6$ , respectively, despite being isostructural, isovalent, and in neighboring rows in the periodic table. The difference, surprisingly, is not in higher frequencies in the smaller cell (the frequencies are similar) but in the matrix elements  $I_H^2$ . The origin of this difference is a topic of ongoing study for us.

A plot of the H-related parameters for  $\text{CaH}_6$  at 150–300 GPa in Fig. 5, normalized to their values at 300 GPa, illuminates relative increases and decreases with pressure. The main trends follow those of  $\text{SH}_3$ :  $T_c$  is highest at the lower pressure, with a quick upturn in  $\lambda$  and  $T_c$  just before the lattice becomes unstable. For this structure as for others, once the structure becomes stable,  $T_c(P)$  *decreases* with increasing pressure, by up to a factor of 2 in our range of study.

## VI. QUANTITIES DESERVING FOCUS

### A. $\eta_H$ versus $\kappa_H$

The hydrides studied here reach their maximum  $T_c$  just before instability, near a common value  $\lambda_H \approx 2.2$  (somewhat smaller in  $\text{SH}_3$ ), while  $T_c$  varies from 200 to 285 K. The distinction is that those with higher mean frequency just above the instability have the higher  $T_c$ . At first glance, the goal should be to retain strong coupling at the higher frequencies; for room temperature  $T_c$  Bergmann and Rainer’s analysis [41] suggests that for a 300 K superconductor, coupling at  $2\pi k_B T_c = 165$  meV and above is optimal; this is in the range of the mean frequencies of the highest- $T_c$  hydrides (see Tables I–III in the Appendix).

This choice of goal is somewhat simplistic, however, because (i) high mean frequencies reduce  $\lambda$  [see Eq. (1)] and (ii) the strongly coupled low-frequency modes are in the lower-frequency (not optimal frequency) range and are approaching instability precisely because they are the most strongly coupled (a chicken and egg relationship). This is

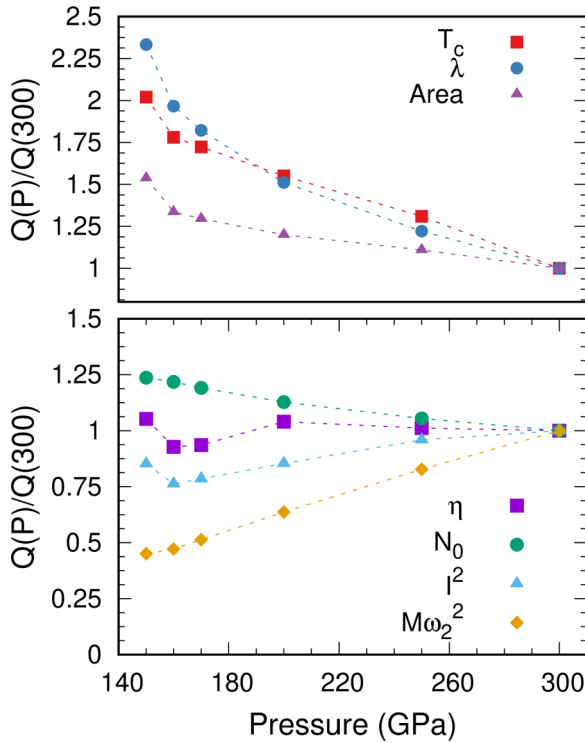


FIG. 5. Pressure dependence of various superconducting quantities of cubic  $\text{CaH}_6$ .  $A$  denotes the area under  $\alpha^2F$  (see the text). All quantities refer to the hydrogen contribution alone. As emphasized in the text,  $\lambda$  and  $T_c$  increase (rather strongly) at the low pressure end, before the instability. The bottom panel shows that the decrease of  $\omega_2^2$  is responsible, even though from frequency moments no impending instability can be inferred. For these data, norm-conserving pseudopotentials were used.

the limitation that has persisted for five decades: stronger coupling inches  $T_c$  upward but enforces lattice instability. The best strategy seems to be to (somehow) retain strong coupling as evenly as possible over all H vibrations, preferably utilizing all momenta. Such a scenario postpones a lattice instability until a large fraction of modes becomes soft.

This brings consideration to the McMillan-Hopfield constant  $\eta_H = N_H(0)I_H^2$ , which the analysis of Allen and Dynes indicates as the limiting behavior of  $T_c$  at large coupling. Figure 2(f) shows that  $\eta_H$  is much larger for the higher- $T_c$  materials (LaH<sub>10</sub> is an exception). The next challenge therefore is to engineer  $\eta_H$  because (i) so little is known about how to maximize the matrix elements  $I^2$  and (ii)  $N(0)$  can be sensitive to details of band structure that simply have to be calculated. Gaining an understanding of H scattering  $I_H^2$  is a current challenge but a realistic one and one that will be crucial in learning how to retain coupling over as many H branches as possible.

### B. Leavens-Carbotte analysis

An understanding of how to increase  $T_c$  requires one to internalize the actual factors that determine  $T_c$  in the current regime of coupling and  $T_c$ , which is not yet at all in the strong-coupling limit. In this respect, the somewhat involved Allen-Dynes expression is opaque—despite its appearance,

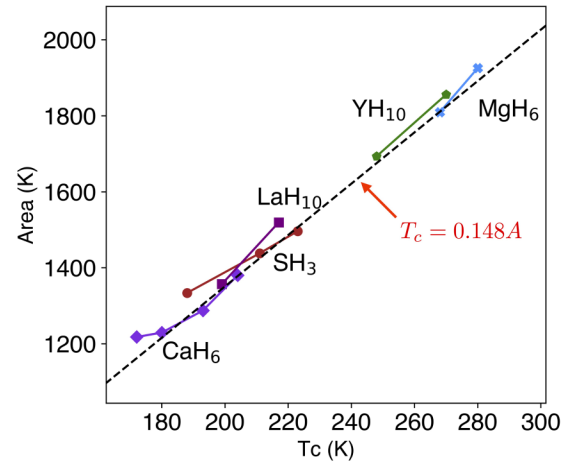


FIG. 6. Plot of area under  $\alpha^2F_H$  (the H contribution) versus  $T_c$  for binary hydrides using H-derived quantities. The slope of 0.148 denotes the Leavens-Carbotte line for strongly coupled superconductors existing in 1974.

it is not exponential except near  $T_c = 0$ , where it was never intended to be used. Leavens and Carbotte found for strong-coupling materials of the time (1974) [49] that the area  $A$  under  $\alpha^2F$ , which from the various definitions is  $A = \lambda\omega_1/2$ , was a faithful indicator of  $T_c$ :  $T_c \approx 0.148A$ .

Using our H-based (not total) values of  $A$  and  $T_c$ , their relationship is presented in Fig. 6, along with the Leavens and Carbotte slope of 0.148. The agreement for these five hydrides is stunningly close to their value; a least-squares fit to  $T_c = SA + T_0$  gives a practically equivalent slope of  $S = 0.150$  and a small intercept of  $T_0 = -6$  K, a *direct linear relationship* to within computational uncertainty. This relationship focuses the challenge: maximize the product  $\lambda\omega_1 \propto \eta_H/\langle\omega_H\rangle$ . Allen and Dynes proved that the strong-coupling (large- $\lambda$ ) limit of Eliashberg theory is  $T_c \propto \omega_2\sqrt{\lambda} = \eta/M$ . Note that the difference between  $\omega_1$  and  $\omega_2$  in these hydrides is nearly a constant ratio, so for consideration of these limits they may be considered to be interchangeable. Thus, the strong-coupling regime in hydrides has not been approached, and the Leavens-Carbotte quantity  $A$  provides the quantity to increase.

Our work provides another guide for reducing the pressure required for HTS hydrides. One objective is to find the element(s)  $X$  in  $\text{XH}_n$  that serves to disassociate the  $\text{H}_2$  unit into atomic H in the lattice at the lowest possible pressure—not a really new observation but also not one with any underlying understanding. Many examples indicate that a high- $T_c$  phase is then likely to emerge. Our view then is that the optimum set of material parameters, for higher  $T_c$  possibly at lower pressures, has yet to be achieved.

### ACKNOWLEDGMENTS

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TABLE I. Various computed properties related to the superconductivity of SH<sub>3</sub>, separated into contributions from the sulfur (S) and hydrogen (H) atoms separately, as well as the total. Other XH<sub>3</sub> compounds with the same structure have been predicted to be less promising as high-temperature superconductors.  $I^2$  and  $\eta$  are atomic quantities, not defined for generic compounds. Certain H quantities have been emphasized in bold. Note the small variation in  $\eta$  with pressure and that the frequency moments scale together well.

	$\mathcal{P}$ (GPa)	Atom	$\omega_{\log}$ (meV)	$\omega_1$ (meV)	$\omega_2$ (meV)	$N_{\uparrow}(0)$ (1/eV)	$I^2$ ( $\frac{eV^2}{\text{\AA}^2}$ )	$\eta$ ( $\frac{eV}{\text{\AA}^2}$ )	$M\omega_2^2$ ( $\frac{eV}{\text{\AA}^2}$ )	$A$ (meV)	$\lambda$	$T_c$ (K)
SH <sub>3</sub>	220	S	51	53	55	0.12	85	9.8	24.0	11	0.41	1
		H	151	155	158	0.13	<b>79</b>	10.1	6.1	128	1.66	222
		T	122	135	144	0.24			5.0	140	2.08	229
	250	S	52	55	57	0.14	67	9.4	25.5	10	0.37	0
		H	167	171	174	0.15	<b>71</b>	10.7	7.4	124	1.45	211
		T	132	147	157	0.29			6.0	134	1.82	218
	280	S	52	55	58	0.14	61	8.9	26.1	9	0.34	0
		H	178	182	186	0.15	<b>69</b>	10.7	8.4	115	1.27	189
		T	137	155	167	0.30			6.8	125	1.61	199

**APPENDIX: MATERIAL PARAMETERS FROM THE SEPARATION OF ATOMIC CONTRIBUTIONS**

Tables I–III provide the extensive numerical data calculated for the five hydrides in the three crystal structure classes that we have studied. The rows follow the separation of the various quantities into metal atom (S, Ca, Mg, La, Y), hydrogen (H), and total (T) compound values (the latter where appropriate). Procedures are described in the main text.

TABLE II. Contributions for CaH<sub>6</sub> and MgH<sub>6</sub> of the metal and H atoms separately (see the main text), as well as the total (T) value, to the parameters determining  $T_c$ . The  $I^2$  values for CaH<sub>6</sub> are not presented because the Ca density of states needed to derive them is too small and uncertain to obtain reliable values.

	$\mathcal{P}$ (GPa)	Atom	$\omega_{\log}$ (meV)	$\omega_1$ (meV)	$\omega_2$ (meV)	$N_{\uparrow}(0)$ (1/eV)	$I^2$ ( $\frac{eV^2}{\text{\AA}^2}$ )	$\eta$ ( $\frac{eV}{\text{\AA}^2}$ )	$M\omega_2^2$ ( $\frac{eV}{\text{\AA}^2}$ )	$A$ (meV)	$\lambda$	$T_c$ (K)
CaH <sub>6</sub>	150	Ca	31	32	33	0.01		4.0	10.7	6	0.37	0
		H	108	110	113	0.17	<b>39</b>	6.7	3.1	119	2.16	204
		T	90	99	105	0.17			2.7	125	2.53	200
	200	Ca	34	35	36	0.01		4.2	13.2	5	0.32	0
		H	134	136	139	0.17	<b>45</b>	7.7	4.7	111	1.64	193
		T	107	120	128	0.17			4.0	117	1.95	190
	250	Ca	37	38	39	0.01		4.7	15.4	5	0.30	0
		H	151	153	156	0.17	<b>49</b>	8.2	5.9	106	1.39	180
		T	117	133	142	0.17			4.9	112	1.69	180
300	Ca	39	40	42	0.01		5.8	17.1	6	0.34	0	
	H	165	168	170	0.13	<b>51</b>	8.8	7.0	105	1.25	172	
	T	122	141	152	0.18			5.6	111	1.59	175	
MgH <sub>6</sub>	300	Mg	48	49	50	0.04	128	5.6	15.1	9	0.37	0
		H	146	153	160	0.14	<b>97</b>	13.5	6.2	166	2.17	280
		T	124	138	149	0.18			5.4	175	2.54	279
	400	Mg	53	54	55	0.04	121	4.8	18.1	7	0.27	0
		H	174	181	188	0.13	<b>115</b>	14.8	8.6	156	1.73	268
		T	149	164	176	0.17			7.5	163	2.00	269



TABLE III. Various computed properties related to superconductivity for LaH<sub>10</sub> and YH<sub>10</sub> of the metal and H atoms separately (see the main text), as well as the total (T) value, for the parameters determining  $T_c$ .

	$\mathcal{P}$ (GPa)	Atom	$\omega_{\log}$ (meV)	$\omega_1$ (meV)	$\omega_2$ (meV)	$N_{\uparrow}(0)$ ( $\frac{1}{\text{eV}}$ )	$I^2$ ( $\frac{\text{eV}^2}{\text{\AA}^2}$ )	$\eta$ ( $\frac{\text{eV}}{\text{\AA}^2}$ )	$M\omega_2^2$ ( $\frac{\text{eV}}{\text{\AA}^2}$ )	$A$ (meV)	$\lambda$	$T_c$ (K)
LaH <sub>10</sub>	250	La	23	24	25	0.07	98	6.5	21.2	3	0.31	0
		H	112	121	130	0.38	<b>23</b>	8.9	4.1	131	2.15	217
		T	92	109	122	0.44			3.6	134	2.46	206
	300	La	24	25	26	0.07	77	5.1	24.0	2	0.21	0
		H	141	148	154	0.37	<b>24</b>	9.2	5.8	117	1.58	199
		T	115	133	145	0.43			5.1	120	1.80	189
YH <sub>10</sub>	300	Y	24	25	26	0.11	44	5.0	14.6	4	0.34	0
		H	145	154	163	0.25	<b>52</b>	13.4	6.4	160	2.08	270
		T	113	136	151	0.36			5.5	165	2.42	249
	400	Y	30	30	31	0.11	41	4.4	21.3	3	0.21	0
		H	174	183	191	0.23	<b>60</b>	14.2	8.8	146	1.60	248
		T	142	165	180	0.34			7.9	149	1.81	236

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*Correction:* The top row in the previously published Table III was not aligned correctly with the headings and has been fixed.