

# General trend for pressurized superconducting hydrogen-dense materials

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The long-standing prediction that hydrogen can assume a metallic state under high pressure, combined with arguments put forward more recently that this state might even be superconducting up to high temperatures, continues to spur tremendous research activities toward the experimental realization of metallic hydrogen. These efforts have however so far been impeded by the enormous challenges associated with the exceedingly large required pressure. Hydrogen-dense materials, of the  $MH_4$  form (where  $M$  can be, e.g., Si, Ge, or Sn) or of the  $MH_3$  form (with  $M$  being, e.g., Al, Sc, Y, or La), allow for the rather exciting opportunity to carry out a proxy study of metallic hydrogen and associated high-temperature superconductivity at pressures within the reach of current techniques. At least one experimental report indicates that a superconducting state might have been observed already in  $SiH_4$ , and several theoretical studies have predicted superconductivity in pressurized hydrogen-rich materials; however, no systematic dependence on the applied pressure has yet been identified so far. In the present work, we have used first-principles methods in an attempt to predict the superconducting critical temperature ( $T_c$ ) as a function of pressure ( $P$ ) for three metal-hydride systems of the  $MH_3$  form, namely  $ScH_3$ ,  $YH_3$ , and  $LaH_3$ . By comparing the obtained results, we are able to point out a general trend in the  $T_c$ -dependence on  $P$ . These gained insights presented here are likely to stimulate further theoretical studies of metallic phases of hydrogen-dense materials and should lead to new experimental investigations of their superconducting properties.

ab initio calculations | high pressure | lattice dynamics | metal-hydride | superconductivity

Hydrogen, while isoelectronic to the alkali metals, is in fact insulating under ambient conditions, which is a consequence of the comparatively high binding energy of its electron. Enormous pressure would be required to reach a hypothetical metallic phase of hydrogen (1), which remains so far elusive to the available experimental techniques. Most intriguingly, it was proposed about a decade ago that metallic hydrogen could also be superconducting up to room temperature (2), inspiring numerous studies in the direction toward realizing this goal. Hydrogen-dense materials have been recognized as a potential route to investigate such phenomena, because in these metal alloys, the combination of chemical precompression (3) from the metal host and of experimentally applied pressures could facilitate hydrogen densities in a range where metallization can occur. For example, metallization in silane ( $SiH_4$ ) has been experimentally observed (4, 5) and was analyzed from a theoretical perspective by us (6).

The emergence of high-temperature superconducting phases in several pressurized hydrogen-dense materials has been predicted (7–12), but, until now, no systematic study had been carried out on how the critical temperature ( $T_c$ ) of superconductivity evolves under the applied pressure. Here, we demonstrate on the examples of  $ScH_3$ ,  $YH_3$ , and  $LaH_3$ , that the respective pressure dependencies of  $T_c$  exhibit remarkably similar behavior, hinting at a general rule for the  $MH_3$  class of hydrogen-dense materials.

Many metal-hydride alloys investigated for metallization and superconductivity possess either the stoichiometry  $MH_3$  or  $MH_4$ . The mechanism by which they are expected to conduct is markedly different: In the  $MH_3$ -type systems,  $M$  and  $H$  form a 3-D network, and both participate in the conduction process, whereas in the  $MH_4$ -type systems,  $M$  and  $H$  separate into individual layers, and conduction occurs only through the  $H$ -layers. The three isoelectronic trihydride systems that we have concentrated on in the present work, crystallize in the fcc structure when sufficiently pressurized, with the metal located at the fcc lattice sites, and two distinct groups of hydrogen atoms positioned at the octahedral ( $H_O$ ) and tetrahedral interstitial sites ( $H_T$ ), respectively. The  $M - H_T$  bonds form a  $MH_2$ -network that acts as a cage structure, encapsulating the  $H_O$ .

## Results and Discussion

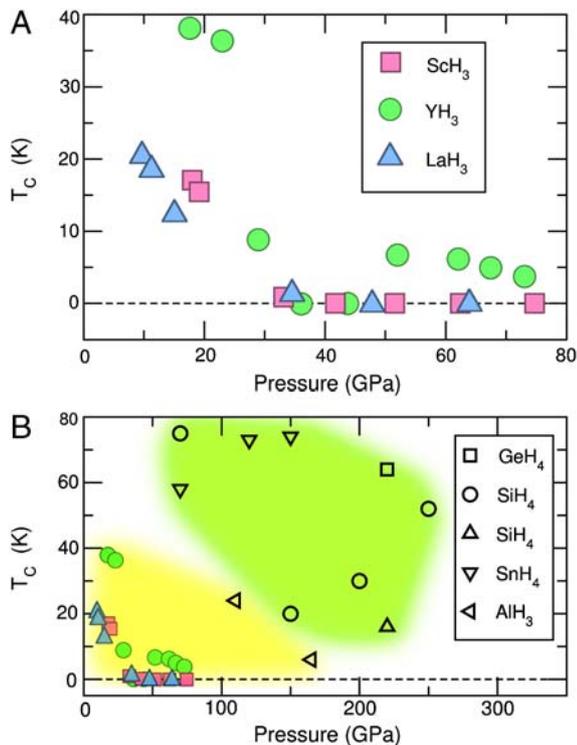
The main result of our study is presented in Fig. 1A, where we provide a summary of our calculated  $T_c$  values for  $ScH_3$ ,  $YH_3$ , and  $LaH_3$  as a function of pressure. It is important to note that several other theoretical works have predicted isolated  $T_c$  values for several tetrahydrides (7–9) and for one trihydride ( $AlH_3$ ) (11), the latter having only recently been found to possess a metallic phase (13–15). Typically, these studies predicted  $T_c$  only at very few pressure values, making it difficult to discern a particular trend. For the sake of facilitating a more direct comparison, these data are put side by side in Fig. 1B with our own data. It becomes noticeable that for the  $MH_3$ -type systems investigated by us, the pressure at which superconductivity sets in (10–20 GPa) is nearly an order of magnitude lower than that for the  $MH_4$  compounds. Around 10 GPa, fcc- $LaH_3$  is dynamically stabilized and possesses its highest  $T_c$  of 20 K. Slightly below 20 GPa, fcc- $ScH_3$  and fcc- $YH_3$  are stabilized and mark their highest  $T_c$ , 18 K and 40 K, respectively. This phonon-mediated superconductivity is seen to become reduced under increasing pressure, and eventually, all three  $MH_3$  systems become normal metallic (i.e., not superconducting) around 35 GPa. In our calculations, we checked the dynamical stability of the three metal hydrides up to much higher pressure and for  $ScH_3$  and  $YH_3$  we did not observe any dynamical instability up to 80 GPa, but it is worth noting that  $LaH_3$  is dynamically destabilized above 65 GPa, which implies that another high pressure phase of  $LaH_3$  could exist in that pressure regime. We will return to a more detailed discussion of these results below. First however, let us look at some other calculated properties of the three  $MH_3$  systems.

Fig. 2 shows the phonon dispersion curves that we obtained from our lattice dynamics calculations for  $ScH_3$ ,  $YH_3$ , and  $LaH_3$ . For all three materials, the dispersion relation was calculated at

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The authors declare no conflict of interest.

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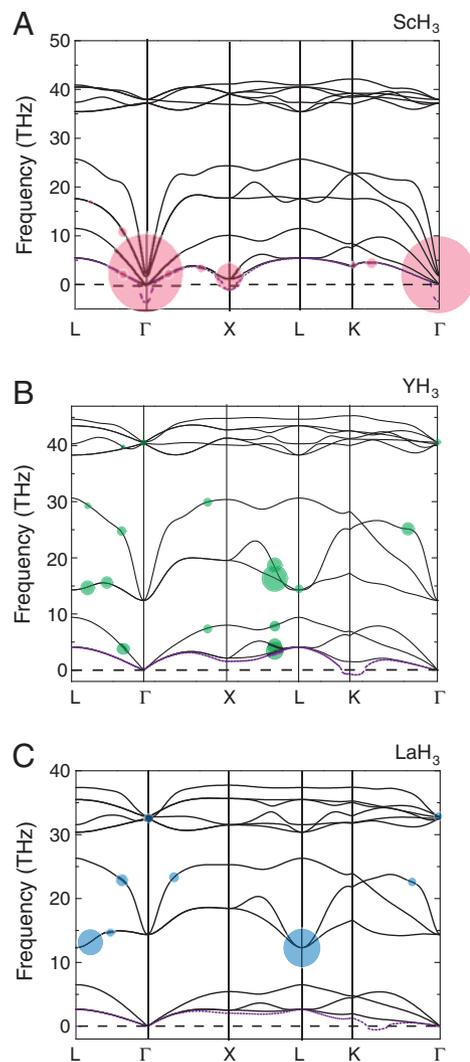
**Fig. 1.** Calculated critical temperature of superconductivity ( $T_c$ ) as a function of pressure. (A) Our predictions for  $\text{ScH}_3$ ,  $\text{YH}_3$  (12), and  $\text{LaH}_3$ . (B) The data for  $\text{GeH}_4$  (8),  $\text{SiH}_4$  (9, 10),  $\text{SnH}_4$  (7), and  $\text{AlH}_3$  (11) (Hollow Symbols), as predicted by various groups, compared with our data for the three trihydride systems (Filled Symbols). The approximate grouping of the  $\text{MH}_3$  and  $\text{MH}_3$   $T_c - P$  data pairs is respectively highlighted by the yellow and green colored areas.

a respective pressure that lies just slightly above the stability threshold for the corresponding metal hydride. This ensures that the phonon dispersions are captured near the onset of dynamical stability. For the case of  $\text{ScH}_3$ , dynamical stability sets in for pressures  $>18$  GPa. As it can be seen from the violet dashed line (drawn only for the acoustic mode below the transition pressure in the destabilized dispersion regime) in the corresponding plot of the phonon dispersion for  $\text{ScH}_3$  in Fig. 2A, the instability is driven by the softening at both the  $\Gamma$ -point and the  $X$ -point. In contrast to that, one can note from Fig. 2B and C that for  $\text{YH}_3$  and  $\text{LaH}_3$ , the instability due to softening occurs at or near the  $K$ -point. It becomes apparent that the phonon dispersion curves for  $\text{YH}_3$  and  $\text{LaH}_3$  are highly similar to each other, whereas they differ substantially from  $\text{ScH}_3$ . One of the main disparities lies in the much stronger dispersion at the  $\Gamma$ -point in  $\text{ScH}_3$  than in  $\text{YH}_3$  and  $\text{LaH}_3$ , which can be seen to even reach down to the acoustic phonon bands.

Whereas there exists no comprehensive experimental study for the low-temperature phase diagram of these trihydrides, the calculated phonon softening near the  $K$ -point in  $\text{YH}_3$  and  $\text{LaH}_3$  indicates equivalent structural transformations in both. For  $\text{ScH}_3$ , the situation regarding the evolution of structural changes with pressure is less clear, and it could very well be that another crystal structure may be stabilized in the pressure range below 18 GPa.

The filled circles in Fig. 2 mark the electron-phonon coupling with the radius proportional to their respective normalized strength. We see that only in the case of  $\text{ScH}_3$ , the electron-phonon coupling is very strong around the  $\Gamma$ -point, whereas for  $\text{YH}_3$  and  $\text{LaH}_3$ , the strongest coupling occurs around the  $L$ -point.

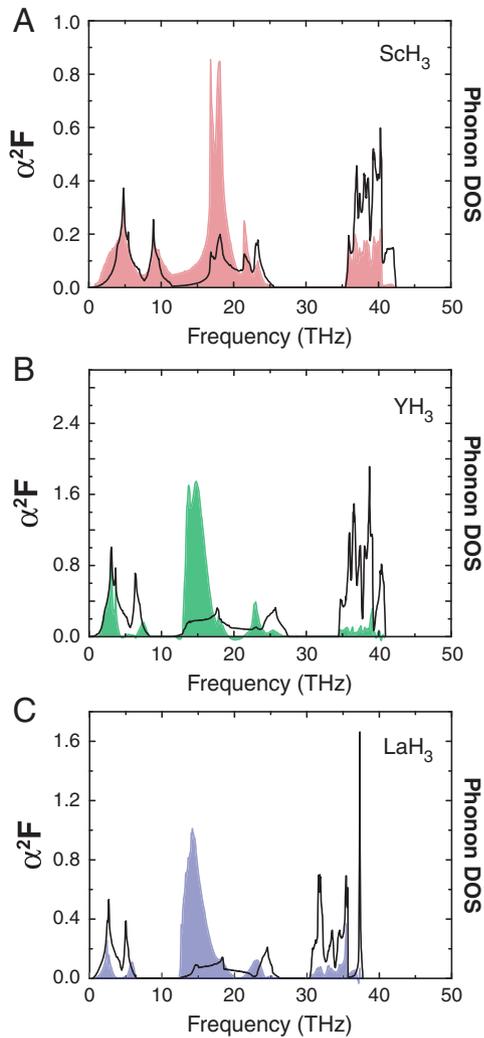
As it could already be seen above from the phonon dispersion relations (Fig. 2), the behavior of  $\text{ScH}_3$  is markedly different from  $\text{YH}_3$  and  $\text{LaH}_3$ . A similar conclusion can also be reached from



**Fig. 2.** Phonon dispersion curves at the lowest possible stabilizing pressure plotted along high symmetry lines for (A)  $\text{ScH}_3$  at 18 GPa, (B)  $\text{YH}_3$  at 18 GPa, and (C)  $\text{LaH}_3$  at 11 GPa. In all three panels, the black solid lines show the stabilized phonon dispersion relation, whereas the dashed violet line illustrates the destabilized phonon dispersion relation (shown only for the acoustic mode) at a slightly lower pressure in the dynamically unstable regime. The colored filled circles highlight points of strong electron-phonon coupling, with the radius proportional to the respective coupling strengths.

Fig. 3, where we plot the calculated spectral functions for all three systems. We note that the acoustic band and optical band are merged together in the case of  $\text{ScH}_3$  (Fig. 3A). Thus, Sc-Sc vibrations and Sc-H vibrations are seen to contribute equally to the spectral function. This is in contrast to the situation for  $\text{YH}_3$  (Fig. 3B) and  $\text{LaH}_3$  (Fig. 3C) that once again appear rather similar to each other. For a higher pressure level, the spectral function is seen to go to zero for  $\text{ScH}_3$  and  $\text{LaH}_3$ , whereas it reappears with a finite value only for  $\text{YH}_3$ . This helps to explain the evolution of  $T_c$  with pressure as shown in Fig. 1.

Let us now return to the discussion of the  $T_c$  vs.  $P$  data of Fig. 1A. Our data for the trihydrides clearly show that  $T_c$  is always highest in the vicinity of a structural transformation. This is a strong indication that the superconducting mechanism is driven by electron-phonon coupling. As we recently discussed just for the case of  $\text{YH}_3$  (12), at the lowest possible stabilizing pressure, the electron-phonon coupling is strong for Y and Y- $\text{H}_0$  vibrations, which couple with a high density of electronic states near the Fermi level belonging to the atomic-like  $\text{H}_0$ . With rising



**Fig. 3.** The spectral function  $\alpha^2F$  is shown as colored shaded areas together with the phonon density of states (Black Curves) as a function of frequency for (A) ScH<sub>3</sub> at 18 GPa, (B) YH<sub>3</sub> at 18 GPa, and (C) LaH<sub>3</sub> at 11 GPa.

pressure, the coupling diminishes and the superconducting state eventually ceases to exist. Combined with the new results that we obtained for ScH<sub>3</sub> and LaH<sub>3</sub>, these data suggest the rather intriguing conclusion that this general trend does in fact hold true for all MH<sub>3</sub> systems studied by us.

We note that for higher pressures (>50 GPa), the superconducting phase reemerges in YH<sub>3</sub>, but not so in ScH<sub>3</sub> and LaH<sub>3</sub>. This second superconductivity region can be mostly attributed to Y-H<sub>0</sub> vibrations coupling with the electronic states near the Fermi level (12). Because Sc, Y, and La are isoelectronic, the only essential difference between the three trihydrides is the mass of the metal. It thus appears that the mass of Y happens to fall into just the right range to generate vibrational energies of the Y-H<sub>0</sub> mode that can give rise to this second superconducting regime. Sc and La, on the other hand, seem to have masses either too low or too high that lead to nonmatching vibrational energies, thus preventing the possibility of a reemerging second superconducting regime at higher pressure.

### Conclusions

In summary, based on our first-principles calculations, we were able to identify a general trend of pressure-induced superconductivity for the metal trihydrides ScH<sub>3</sub>, YH<sub>3</sub>, and LaH<sub>3</sub>, and drew

comparison with other hydrogen-dense materials, including those of the MH<sub>4</sub> form. We found that the three transition metal hydrides studied by us possess the highest  $T_c$  at the vicinity of a structural transformation to the cubic (fcc) phase and that  $T_c$  always drops as the pressure increases, until they turn into a normal metallic state (i.e., not superconducting). A secondary superconductivity regime is seen to arise only for YH<sub>3</sub>.

As with any other theoretical prediction, we also naturally hope that our work will not merely lead to further computational studies of related metallic hydrogen-dense materials, but actually inspire experimental measurements to test our data. Certainly, the pressure range of 10–80 GPa, for which we have predicted here superconducting states in ScH<sub>3</sub>, YH<sub>3</sub>, and LaH<sub>3</sub>, is easily accessible with contemporary diamond anvil cell techniques. Rather, the challenge might actually lie in preparing metal-hydride samples of the proper stoichiometry. Even slight deviations of the perfect 1 : 3 ratio of metal to hydrogen could prevent the superconducting state from emerging. Nevertheless, we hope that experimentalists will embrace this challenge to test our predictions, because we strongly believe that there is tremendous merit for the understanding of the underlying physics in metallic hydrogen-rich systems if such measurements could indeed be carried out.

### Methods

**Density Functional Theory and Lattice Dynamics Calculations.** Electronic structure calculations are based on the generalized gradient approximation (16) with the Perdew–Burke–Ernzerhof parametrization (17) for the exchange–correlation functional to density functional theory (18, 19). Phonon dispersion and electron–phonon calculations were performed with density functional perturbation theory (20) using the program Quantum ESPRESSO with a kinetic energy cutoff of 60 Ryd and a  $24 \times 24 \times 24$  Monkhorst–Pack mesh (21) for Brillouin zone integration. Electron–phonon coupling matrix elements were computed in the first Brillouin zone on a  $8 \times 8 \times 8$   $q$ -mesh.

**$T_c$  Calculations.** We calculated the critical temperature for superconductivity ( $T_c$ ) using the Allen–Dynes equation (22)

$$T_c = \frac{\omega_{\log} f_1 f_2}{1.2} \exp\left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right). \quad [1]$$

In terms of the normalized weighting function that arises in Eliashberg theory,

$$g(\omega) \equiv \frac{2}{\lambda \omega} \alpha^2 F(\omega). \quad [2]$$

The parameter  $\lambda$  is a dimensionless measure of the strength of  $\alpha^2 F$

$$\lambda \equiv 2 \int_0^\infty d\omega \alpha^2 F(\omega) / \omega \quad [3]$$

and the logarithmic average frequency  $\omega_{\log}$

$$\omega_{\log} = \exp\left(\int_0^\infty d\omega g(\omega) \ln \omega\right). \quad [4]$$

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