

Towards superconductivity in hydrides: computational studies of two hypothetical ternary compounds, $\text{Yb}^{\text{II}}\text{BeH}_4$ and $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$

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Abstract Two examples of novel, as yet unsynthesized ternary lanthanide hydrides - $\text{Yb}^{\text{II}}\text{BeH}_4$ and $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ - are investigated computationally. Their unprecedented electronic structure is discussed and the potential superconductivity of $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ explored. Methods of synthesis are postulated for both compounds.

Keywords DFT · Hydrides · Lanthanides · Superconductivity

Introduction

Within the classical BCS theory of superconductivity [1], one expects metallic hydride materials to be excellent candidates for high critical temperature (high- T_C) superconductors. This is due to: (i) the presence of light hydrogen atoms, which increases the pre-exponential factor

in the expression for T_C , and (ii) large values of the electron-phonon coupling constant (typical of many H-containing systems [2]), which magnifies the exponential factor. Despite these predictions, all presently known superconducting hydride materials exhibit pretty low values of T_C . The highest measured values do not exceed 20 K; typical examples are PdH_x with its $T_C=8$ K [3], $(\text{Pd}_{1-x}\text{Ag}_x)\text{H}_y$, $T_C=16$ K [4] or Th_4H_{15} , $T_C=8$ K [5]. One possible explanation for the so far disappointing performance of hydrides with respect to superconductivity is related to the anomalous inverse isotope effect seen for some hydrides; a simple model proposed in [6] suggests that genuinely high- T_C superconductivity could result only if sufficiently large electronic barriers (of the order of phonon frequencies) are encountered for electron transfer between metal centers.

High-frequency H-related phonons could noticeably increase the critical temperature, but only if the electronic density of states at the Fermi level has a significant contribution from H (1s) states. It was shown recently that such a situation may occur for selected main group hydrides (SiH_4 [7, 8] and GeH_4 [9]), but only at the ultra-high pressures (of the order of 1–2 Mbar) required for their metallization. Such pressures are routinely achievable in diamond anvil cells [10]. Alternatively, one might attempt to generate a conducting hydrogen sublattice by using selected outer- and inner-transition metals with holes in their d, or respectively, f, electronic manifold. The holes should be partially delocalized over hydrogen sub-network, thus possibly leading to metallic conductivity.

In this work we extend our preliminary theoretical study on four novel ternary lanthanide hydrides: CsLnH_3 and Cs_2LnH_4 ($\text{Ln} = \text{Yb}$ and Tm) [6]. Specifically, we have now investigated the as yet unsynthesized $\text{Yb}^{\text{II}}\text{BeH}_4$ and $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ (note: the oxidation states of Yb differ in the two compounds!). Our main aim is to predict thermody-

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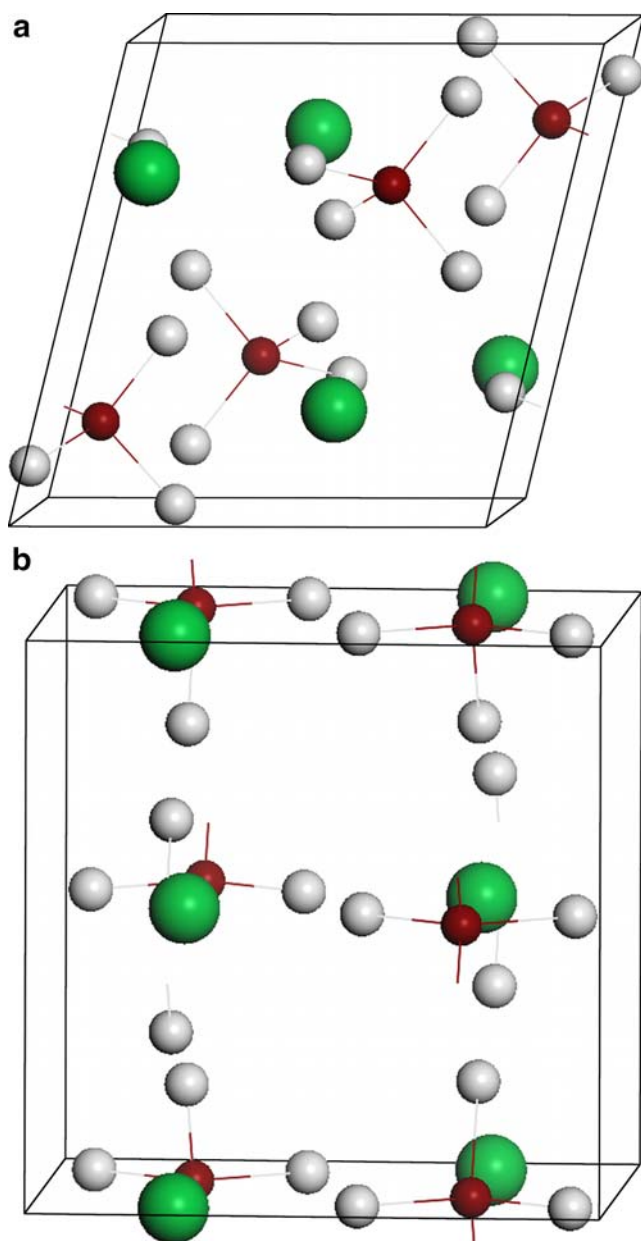


Fig. 1 Monazite-type ($P2_1/c$, left) and zircon-type ($I4_1/amd$, right) structures proposed for $\text{Yb}^{\text{II}}\text{BeH}_4$; green - Yb, dark red - Be, grey - H. In both structures the BeH_4^{2-} tetrahedrons can be identified

dynamic stability with respect to binary hydrides, and analyze the electronic structure of these species.

Methods of calculations

We used density functional theory (DFT) calculations within a GGA approximation, as implemented in VASP [11] (for YbBeH_4 , YbH_2 and BeH_2) and CASTEP [12] (for Cs_3YbH_6) codes. The Perdew-Burke-Ernzerhof (PBE) [13] functional was used for approximation of the exchange-correlation energy. The core electrons for constituent elements were described by ultrasoft, Vanderbilt-

type [14] pseudopotentials, while the valence set was expanded into planewaves ($\text{H } 1s^1$, $\text{Be } 1s^2 2s^2$, $\text{Cs } 5s^2 5p^6 6s^1$, $\text{Yb } 4f^{14} 5s^2 5p^6 6s^2$). Note, the f electrons were explicitly represented in our calculations, as required for reasonable description of the Yb^{III} (f^{13}) open-shell species.

Calculations were performed without ($\text{Yb}^{\text{II}}\text{BeH}_4$, $\text{Yb } f^{14}$) or with spin polarization ($\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$, $\text{Yb } f^{13}$) with the 450 eV cutoff of the kinetic energy of plane wave functions. The k -point grid for zone sampling was generated automatically via the Monkhorst-Pack scheme. The k -point sampling used in VASP calculations (YbBeH_4) was $5 \times 5 \times 5$, and $4 \times 4 \times 4$ in CASTEP calculations (Cs_3YbH_6). The SCF tolerance in our computations was equal to 1×10^{-5} eV/atom or 2×10^{-6} eV/atom in VASP and CASTEP calculations, respectively. For the time-consuming CASTEP optimizations the primitive cell of Cs_3YbH_6 was used; VASP computations (YbBeH_4) were performed for conventional cells. For the primitive cell of Cs_3YbH_6 (containing one f^{13} atom) the ferromagnetic calculation yielded energy much lower than the spin-unpolarized one, as previously seen for Tm^{II} (f^{13}) compounds and as anticipated for large magnetic moments of f -element compounds [6].

For each crystal structure considered we have relaxed the unit cell constants and the atomic positions using the BFGS algorithm. We have also computed the electronic band structure and the electronic density of states (DOS). In order to better analyze the chemical bonding, we have integrated the electron density for selected bands of Cs_3YbH_6 , a process made feasible by CASTEP.

Our calculations are for $T=0$ K; therefore, the entropy factor is neglected; we approximate the reaction enthalpy by the reaction energy, uncorrected for zero-point vibrations.

Results

YbBeH_4

In our previous study of CsLnH_3 and Cs_2LnH_4 ($\text{Ln} = \text{Yb}$ and Tm) we have pointed out the thermodynamic instability

Table 1 The unit cell constants, fractional atomic positions for atoms constituting an irreducible cell content, and volumes per formula unit calculated for YbBeH_4 in the two structure types considered

structure	YbBeH_4 zircon	YbBeH_4 monazite
a [Å]	6.683	6.166
b [Å]	6.683	6.402
c [Å]	5.750	5.857
V [Å ³ / YbBeH_4]	64.19	56.48
$(x,y,z)_{\text{Yb}}$	(0.000, 0.750, 0.125)	(0.284, 0.168, 0.096)
$(x,y,z)_{\text{Be}}$	(0.000, 0.250, 0.375)	(0.308, 0.171, 0.602)
$(x,y,z)_{\text{H1}}$	(0.000, 0.580, 0.783)	(0.232, 0.015, 0.431)
$(x,y,z)_{\text{H2}}$	–	(0.389, 0.337, 0.472)
$(x,y,z)_{\text{H3}}$	–	(0.489, 0.118, 0.793)
$(x,y,z)_{\text{H4}}$	–	(0.139, 0.236, 0.714)

Table 2 Calculated enthalpies of formation (ΔH) and volume changes per formula unit (ΔV) for the reaction of YbBeH_4 formation from binaries, for the zircon- and monazite-type structures

structure	YbBeH_4 zircon	YbBeH_4 monazite
ΔH [eV]	-0.10	-0.49
ΔV [\AA^3]	6.78	-0.93

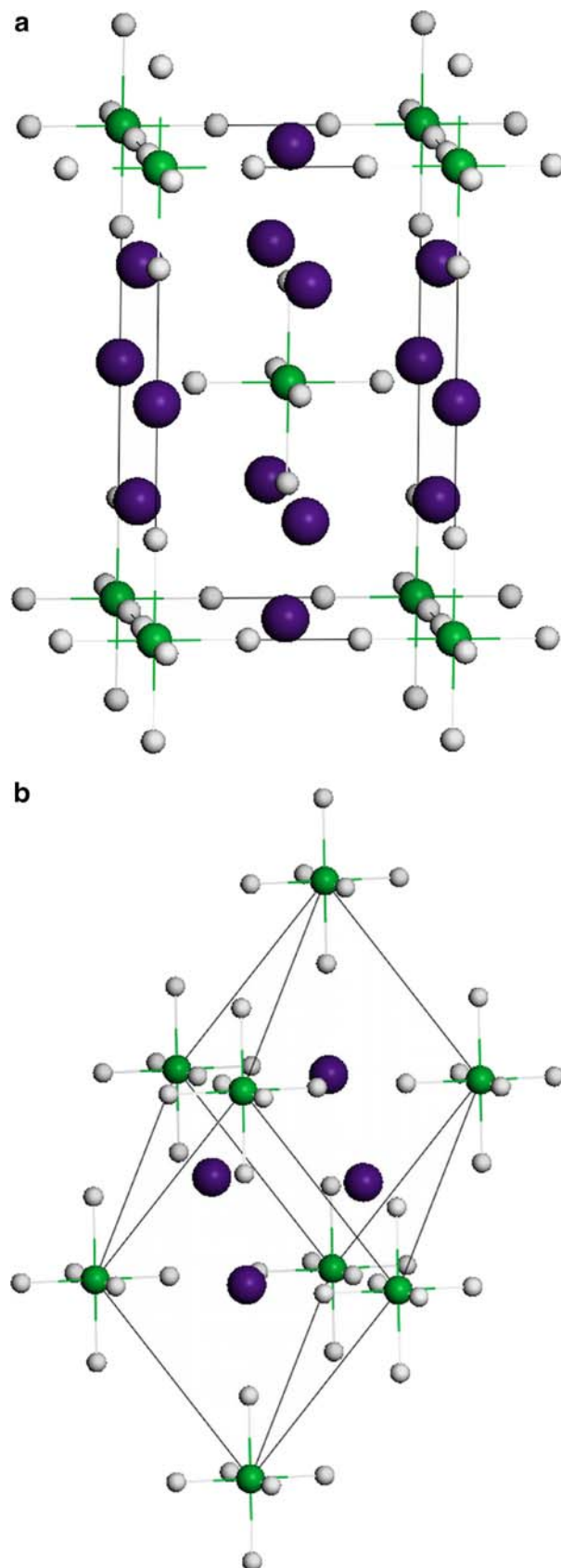
of these materials with respect to binary hydrides at ambient conditions [6]. We claimed that CsLnH_3 and Cs_2LnH_4 could be obtained only at elevated pressures of the order of 10–20 GPa. Lack of stability of these materials is related to the fact that they constitute products of direct chemical reaction between strong Lewis base (CsH) and a very poor Lewis acid ($\text{Yb}^{\text{II}}\text{H}_2$). One might obviously expect that if $\text{Yb}^{\text{II}}\text{H}_2$ is allowed to take its preferred role of a strong Lewis base with respect to very strong Lewis acids (BeH_2 , B_2H_6), the very stable ternary compounds (YbBeH_4 , $\text{Yb}(\text{BH}_4)_2$) would result. We have now tested this concept for YbBeH_4 .

The crystal structure of YbBeH_4 is unknown; as far as we know, synthesis of this compound has never been attempted. Therefore, in considering various possible structure types we follow the well-known hydride-fluoride structural analogy - it turns out that the structures of the corresponding hydrides and fluorides are often related, especially for the alkaline and alkaline earths metals [15]. Structures of hydrides and fluorides are also similar for compounds of lanthanide elements, except for small deviations from fully stoichiometric formulation, encountered by many transition element hydrides [16]. Therefore, we have assumed that YbBeH_4 would adopt the monazite structure ($P2_1/c$, Fig. 1), taken by an analogous ternary fluoride, YbBeF_4 [17]. In addition, we have considered the zircon-type structure ($I4_1/amd$, Fig. 1), as indicated by the structure map of ABX_4 compounds [17]; YbBeH_4 and YbBeF_4 fall in the vicinity of the zircon/monazite borderline.

The results of the unit cell optimization (VASP calculations) for $\text{Yb}^{\text{II}}\text{BeH}_4$ in zircon and monazite structure types, fractional atomic positions, and unit cell volumes per one formula unit, are presented in the Table 1. Monazite type turns out to be much more compact than the zircon one, the difference of volumes being about 7.7 \AA^3 per one YbBeH_4 unit.

In Table 2 we show the enthalpies of formation of monazite- and zircon- YbBeH_4 from binary hydrides (YbH_2 and BeH_2 [18]) and the volume changes associated with the formation reaction.

As pointed out in the Introduction, one expects that formation of YbBeH_4 from binaries should be thermodynamically favored due to the strong ‘acid-base neutralization’ character of this reaction. Indeed, the calculated formation enthalpy of YbBeH_4 is negative for both

**Fig. 2** View of the conventional (left) and primitive (right) unit cells of the Cs_3YF_6 structure type ($I4/mmm$) used here for Cs_3YbH_6 ; violet - Cs, green - Yb, grey - H

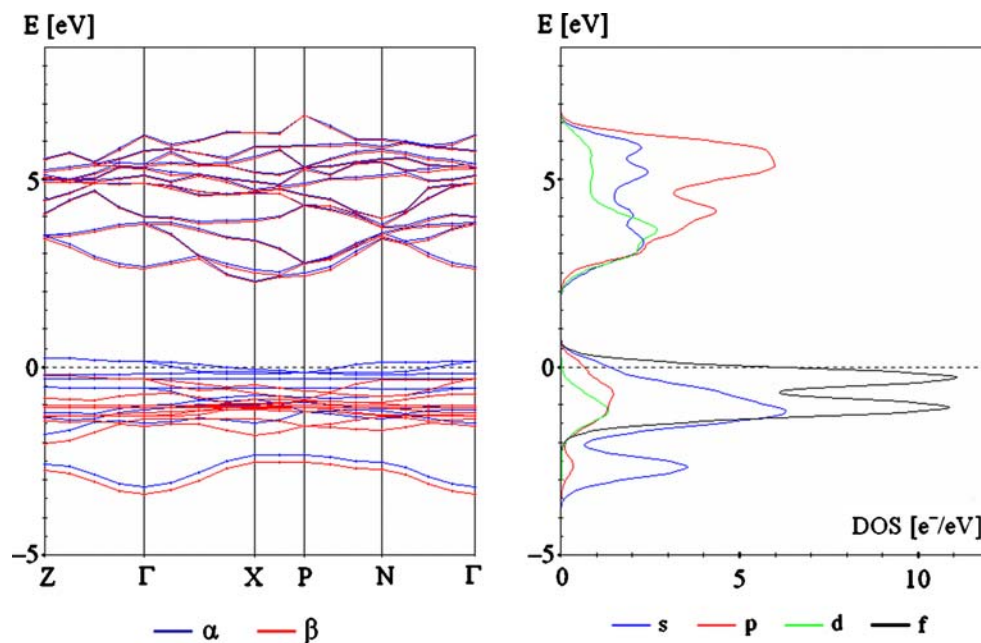
structure types, indicating preference for monazite-type (-0.49 eV) over the zircon-type (-0.10 eV). This feature was also seen in experiment for the fluoride analogue, YbBeF_4 [16]. The monazite polymorph of YbBeH_4 should also be preferred over a zircon one if the formation reaction is conducted under elevated pressure, due to the negative volume change for the reaction leading to monazite-type, and in strong contrast to the zircon-type (the volume change is positive).

The large negative formation enthalpy of monazite- YbBeH_4 (~ -0.5 eV) suggests that this species might form easily from binary substrates in a solid-solid reaction, either by prolonged modest heating of YbH_2 and BeH_2 together in a closed autoclave, or by a mechanochemical synthesis (high-energy ball-milling). The reaction should be performed below the thermal decomposition temperature of BeH_2 (250 °C) if no H_2 overpressure is used. Alternatively, one might attempt to hydrogenate the fine mixture of Be and Yb metals.

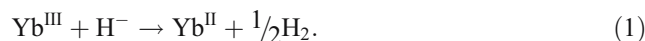
Cs_3YbH_6

Hypothetical Cs_3YbH_6 is an example of a ternary hydride containing Yb^{III} . Although many compounds of Yb^{III} have been prepared in various ligand environments [19], hydrides containing this cation are scarce and poorly documented in the literature. Genuine YbH_3 is unknown, the limiting composition $\text{YbH}_{2.67}$ corresponding to mixed-valence $\text{Yb}^{\text{II}}(\text{Yb}^{\text{III}}\text{H}_4)_2$ [20]. A (dangerous) synthesis of this compound under extremely large hydrogen pressures (up to 320 MPa) has been claimed, but the published crystal structure seems to us surprising [21]. Still, we think, synthesis of $\text{YbH}_{2.67}$ seems plausible.

Fig. 3 Band structure and electronic DOS as computed for Cs_3YbH_6 . Notice an unusually large mixing of the f and s states within the lower set of bands



Inherent instability of Yb^{III} in a hydride environment can be traced back to facile reduction of this species to Yb^{II} with its stable f^{14} electronic configuration. The standard redox potential of the $\text{Yb}^{\text{III}}/\text{Yb}^{\text{II}}$ pair is as positive as -1.05 V, which greatly facilitates the reaction:



Therefore, the equilibrium (plateau) H_2 pressure for the stoichiometric YbH_3 must be very large at room temperature, and synthesis of this binary compound will meet difficulties (if use of diamond anvil cells is ruled out) [22]. Nevertheless, the chemical path towards ternary hydrides of Yb^{III} still remains open. As known from many examples, strong Lewis bases significantly stabilize high oxidation states of metals [23], and this simple rule holds nicely for a multitude of hydride materials as well [22]. Therefore, one might expect that $\text{Ba}(\text{Yb}^{\text{III}}\text{H}_4)_2$ (by analogy to $\text{Yb}^{\text{II}}(\text{Yb}^{\text{III}}\text{H}_4)_2$) and to the known $\text{Ba}(\text{TmF}_4)_2$, $\text{CsYb}^{\text{III}}\text{H}_4$, or even $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ might form under slightly elevated H_2 pressure and modest temperature conditions.

With this working hypothesis in mind, we have investigated theoretically the crystal and electronic structure of Cs_3YbH_6 . As for YbBeH_4 before, a reasonable model of the crystal structure must first be proposed for Cs_3YbH_6 . Taking into consideration the pronounced structural analogies between hydrides and fluorides, closeness of the ionic radii of Y^{III} and Yb^{III} and similar chemical properties of these lanthanide elements, the well-known Cs_3YF_6 structure type (I4/mmm, Fig. 2) [24] was adopted for subsequent unit cell optimization. To significantly reduce the computational burden, all calculations for Cs_3YbH_6 were performed using a primitive cell, Fig. 2.

Our calculations predict tetragonal unit cell constants of $a = b = 6.820 \text{ \AA}$, and $c = 10.817 \text{ \AA}$. The $\text{Yb}^{\text{III}}\text{H}_6^{3-}$ anion is predicted to show a moderate Jahn-Teller effect (elongation of an octahedron with 4 short and 2 long Yb-H bonds), with computed Yb-H distances of 2.310 \AA (H at 0.0, 0.0, 0.214) and 2.132 \AA (H at 0.313, 0.0, 0.0). These values correspond to the weighted average Yb-H separation of 2.191 \AA , and a Jahn-Teller distortion ratio of 1.083. The Jahn-Teller effect is usually much smaller than that for the inner-shell lanthanides (a typical Jahn-Teller distortion ratio is <1.01 [25]); here, the larger value testifies to the noticeable covalence of the $\text{Yb}^{\text{III}}\text{-H}^-$ bonds. We will return to this unusual feature later.

The valence and conduction band region in the electronic structure of Cs_3YbH_6 is shown in Fig. 3. Three main regions may be distinguished: (i) the occupied broad ‘hydride band’ (1s of H) between around -3.5 and -2.0 eV; (ii) the set of flat bands (similar to those computed for CsYbH_3 [26]) between around -2.0 and $+0.5$ eV, corresponding mainly to the f orbital set of a lanthanide (the uppermost f bands are partially occupied i.e. they cross the Fermi level), and (iii) a set of broad unoccupied states between around $+2.5$ and $+6.5$ eV, consisting of various s, p and d states of Yb and Cs. In our spin-polarized calculation all alpha bands are firmly split from the beta ones, sometimes as much as 0.5 eV, as noticed also for the magnetic Tm^{II} cation (yet another f^{13} system) [6].

There is a fundamental difference between electronic structure of $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ and those of previously studied Yb^{II} (and Tm^{II}) hydrides [6], as indicated by simple analysis of the number of bands in each region and by division of DOS into s, p, d and f contributions. For $\text{CsYb}^{\text{II}}\text{H}_3$, the ‘hydride band’ is entirely separated from the f manifold in the energy scale, and there is a negligibly small contribution from the 1s states of H to the states at, or close to, the Fermi level [6]. However, for $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$, some part of the hydride band penetrates - and firmly mixes into - the f set, and a significant s partial DOS appears for the states crossing the Fermi level.

This feature testifies that f electrons of Yb^{III} are engaged in a genuine σ bonding to H (they can no longer be considered core electrons), which is pretty unusual among compounds of trivalent lanthanides [27, 28]. The enhanced covalence of the $\text{Yb}^{\text{III}}\text{-H}^-$ bonding (as compared to the rather ionic $\text{Yb}^{\text{II}}\text{-H}^-$ bonding) is also seen from significant dispersion of each ‘hydride band’. This cannot be due to direct H...H interaction, as the shortest H...H distance is as large as 2.556 \AA ; it must be due to direct involvement of the 4f orbitals of the *bridging* Yb^{III} centers.

We are convinced that the substantial f/s mixing obtained in our calculations for $\text{Cs}_3\text{Yb}^{\text{III}}\text{H}_6$ is not an artifact but a true feature of Yb^{III} hydrides; it may also be anticipated from the ease of thermal rupture of $\text{Yb}^{\text{III}}\text{-H}^-$ bonding

(Eq. 1), which pushes experimentalists to use very large H_2 pressures and relatively small temperatures to synthesize similar materials.

The electronic density integrated in one of the bands crossing the Fermi level is visualized in Fig. 4. Analogous information for more selected bands (and for spin density) is given in [Supplementary Material](#).

As seen in Fig. 4, the electronic density in a selected band crossing the Fermi level contains significant contribution from both the H 1s and the Yb 4f states. This is still another way how the unusual covalence of the $\text{Yb}^{\text{III}}\text{-H}^-$ bonding can be illustrated. It is worth mentioning that the spin density also has a noticeable contribution on four H atoms, which are at short separation from the paramagnetic Yb^{III} center (see [Supplementary Material](#)).

Since the pronounced f/s mixing clearly results in a partial depopulation of the hydride states (i.e. formation of holes in the H-centered bands, or of a sublattice of ‘metallic hydrogen’), one might pose an interesting question: could Cs_3YbH_6 with its high-frequency H-based phonons, with or

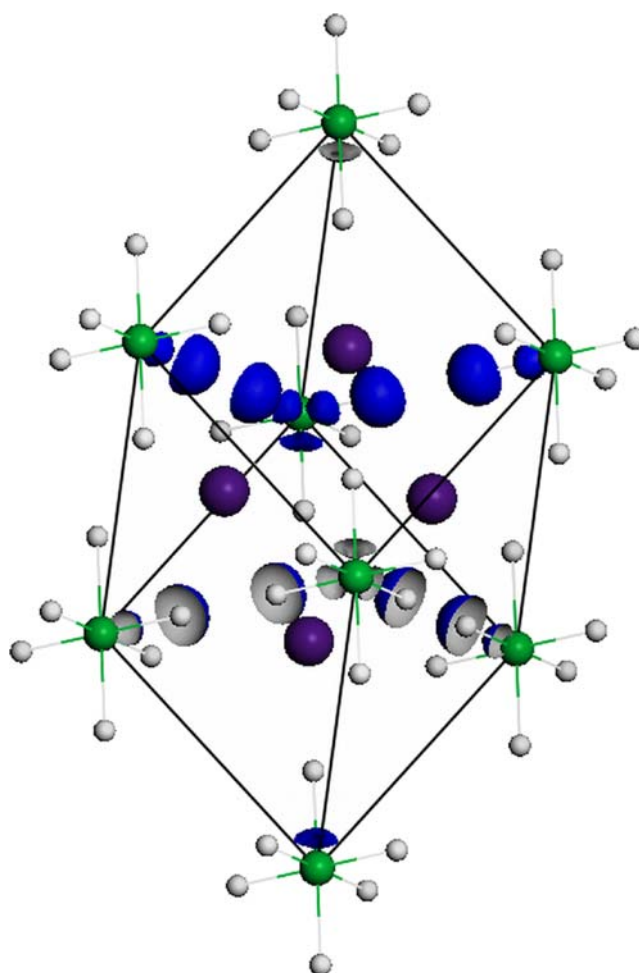


Fig. 4 The electronic density (in blue) in one of the a bands crossing the Fermi level (Cs_3YbH_6). Note significant contribution on four (out of six) H atoms with the shortest separation to Yb

without chemical doping [29], and with or without applying external pressure, be turned into a high- T_C superconductor?

Regretfully, it is extremely difficult to answer this question precisely, using current computational methods based on one-electron approximation, and given the richness of electronic and magnetic phenomena [30] known for the compounds of lanthanide metals [31]. In turn, it would be very interesting to attempt synthesis of Cs_3YbH_6 and verify its properties experimentally.

Summary

We predict the existence of two novel ternary hydrides: $YbBeH_4$ and Cs_3YbH_6 . $YbBeH_4$ could be synthesized under 1 atm of H_2 via high energy milling or thermal annealing, and it is likely to adopt a monazite-type structure. Cs_3YbH_6 is a completely different story; very large H_2 pressures will be needed to synthesize this material. There is an unprecedented mixing of the valence 4f states of Yb and 1s states of H in this compound, similar to one observed for the 5f electrons in chemical compounds of actinides. A f^{13} electron count of Yb^{III} in the vicinity of the f shell closure (resembling the d^9 count for parent high- T_C oxocuprates) and the significant involvement of H 1s states at the Fermi level are likely to promote superconductivity in this interesting material. This exciting possibility calls for experimental testing.

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18. Experimental crystallographic data comes from: (a) Messer CE, Gianoukos PC (1968) *J Less Common Met* 15:377–383 (cubic YbH_2) and (b) Smith GS, Johnson QC, Smith DK, Cox DE, Snyder RL, Zhou RS, Zalkin A (1988) *Solid State Commun* 67:491–494 (orthorhombic BeH_2). We have relaxed YbH_2 and BeH_2 , using crystallographic data to build initial structures in our optimizations. It is important to realize that cubic β - YbH_2 transforms to orthorhombic α - YbH_2 below 125 °C, yet “the difference in free energies between the two forms is extremely small” [18a]. Therefore, we have chosen less computationally demanding β - YbH_2 for calculations
19. For example, the following halides of Yb^{III} have been synthesized: $LiYbF_4$, $NaYbF_4$, Li_3YbCl_6 , Cs_4YbCl_7 , KYb_2F_7 , KYb_3F_{10} , $CsYb_3F_{10}$, $CsYb_4F_{13}$, $Ba_4Yb_3F_{17}$, $SrYb_3F_{11}$, Ca_2YbF_7 , and others
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