Prediction of thermodynamic stability and electronic structure of novel ternary lanthanide hydrides†

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We theoretically examine four hypothetical ternary lanthanide hydrides, $CsLn^{II}H_3$ and $Cs_2Ln^{II}H_4$, where Ln^{II} = Yb, Tm. We optimize their crystal unit cells in the $BaTiO_3$ and K_2NiF_4 structures, respectively, and compute their electronic band structures. Our calculations indicate that the novel hydrides should be unstable with respect to decomposition into binaries (CsH and $Ln^{II}H_2$); ternaries would form only under elevated pressure (>7–22 GPa). We predict that significant perturbation of the electronic and magnetic properties of $CsYb^{II}H_3$ and $Cs_2Yb^{II}H_4$ will take place *via* a progressive exchange of f^{14} Yb^{II} for f^{13} Tm^{II}, while promoting magnetic ordering and valence fluctuations. Analysis of the phonon dispersion for these hydrides suggests that metallic forms of doped $CsLn^{II}H_3$ and $Cs_2Ln^{II}H_4$ would exhibit substantially high Debye temperatures of $\sim$1800 K. This is likely to prompt moderate-T_C superconductivity in these as yet unknown materials.

Introduction

Among lanthanide metals, the divalent state is favored predominantly for Yb and Eu, due to the stability of—respectively—filled (f^{14}) and half-filled (f^7) f shell. Significantly lesser stability is noticed for the elements preceding Yb and Eu in the periodic table, namely Tm and Sm, respectively.[1] This is attested to by the standard redox potentials for the M^{III}/M^{II} redox pairs (E^0 = −1.05 V for Yb, while −2.30 V for Tm; −0.35 V for Eu, while −1.55 V for Sm).[2] As a consequence, the nearly stoichiometric trihydrides of trivalent Tm and Sm are known, while genuine YbH_3 and EuH_3 have never been synthesized. For Yb only the mixed-valence $Yb^{II}(Yb^{III}H_4)_2$ has been obtained so far,[3] while for Eu, $EuH_{1.95}$ is a limiting composition, in agreement with the ranking of the E^0 values and other thermodynamic arguments.[4]

Yb^{II} and Eu^{II}, the most prominent representatives of stable divalent lanthanide cations, are often compared to closed shell Ca^{II} and Sr^{II}, respectively, in terms of ionic radius.[5] A nice series of isomorphic compounds of Yb^{II} and Ca^{II}, and those of Eu^{II} and Sr^{II}, are known; examples include $YbBeF_4$ and $CaBeF_4$, $EuLiF_3$ and $SrLiF_3$, and—among the hydrides—$Yb_4Mg_3H_{14}$[6] and $Yb_4Mg_4Co_3H_{19}$[7] (and their Ca analogues), $Eu_6Mg_7H_{26}$[8] and inverse perovskite $EuLiH_3$ (and their Sr analogues). In all these compounds, binary components of divalent Yb and Eu (*i.e.*, EuF_2, YbH_2 *etc.*) formally serve as

Lewis bases, while donating their ligands to the stronger and smaller Lewis acids (Mg^{II}, Be^{II}).

Tm^{II} (ionic radius, R, of 1.17 Å in the octahedral environment), an electron-deficient analogue of Yb^{II}, is virtually isomorphic with Yb^{II} (R = 1.16 Å)[9] and with Ca^{II} (R = 1.14 Å). However, because of the enormous reducing properties of Tm^{II},[10] its compounds are scarce, and very difficult to preserve in the presence of traces of O_2 or humidity.

Prompted by the existence of $M^I CaX_3$ and $M^I_2 CaX_4$, where M^I = Cs, Rb and X = H or F,[11] of ternary lanthanide salts such as the perovskites $CsYbF_3$,[12] $CsYbI_3$ and $RbTmI_3$,[13] and driven by the fluoride-hydride analogy,[14] we examine theoretically and attempt to predict the possible existence and selected properties of $CsLn^{II}H_3$ and $Cs_2Ln^{II}H_4$ where Ln^{II} = Yb, Tm. In these hypothetical compounds, and in contrast to all known ternary hydrides containing divalent lanthanide cations, LnH_2 would formally serve as a Lewis acid while accepting hydride anion from the very strong base (CsH). Here, our interest in ternary hydrides of divalent lanthanides has origin in (i) anticipated involvement of f orbitals in bonding, *i.e.* a mixing of Ln^{II} (4f) and H (1s) orbitals (moderate 'covalence'), (ii) large values of electronic density of 4f states in the vicinity of the Fermi level, and (iii) concomitant consequences of hole- and electron-doping for electronic and magnetic properties of the stoichiometric compounds of Ln^{II}, and possible promotion of superconductivity.

Methods of calculations

Our computations were based on density functional theory and used a generalized gradient approximation (GGA) with ultrasoft Vanderbilt-type pseudopotentials, as implemented in the CASTEP[15] code. For each structure, we relaxed the unit cell constants and atomic positions (whenever possible), and also determined the stress tensor. The electronic density of states, band structure and electronic density within a desired energy window were subsequently calculated for the optimized

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unit cell. The k-point grids for zone sampling were generated automatically *via* the Monkhorst–Pack scheme. The k-point sampling used by CASTEP was $4 \times 4 \times 4$ (structures of $CsLnH_3$), and $4 \times 4 \times 2$ (Cs_2LnH_4). We used a 450 eV cutoff for the kinetic energy of the plane waves and an SCF tolerance of 2×10^{-6} eV per atom. In our calculations we used plane waves originating from an expansion of four valence and sub-valence orbitals for Cs ($5s^2$, $5p^6$, $6s^2$, $6p^6$), two orbitals for each H (1s, 2s) and six orbitals for Yb and Tm ($5s^2$, $5p^6$, $4f^{14}$, $6s^2$, $6p^2$, $5d^{10}$). This gives a total of 31 bands for $CsYbH_3$ (Z = 1); 18 of these are occupied, 13 are unoccupied. No other atomic functions (in particular no polarization functions on H, 2p) are embedded in the CASTEP package for these atoms.

For compounds of Tm^{II} (an open-shell f^{13} configuration with large magnetic moment) we have always done spin-polarized calculations (SP). Calculations without spin polarization ('metallic' or 'antiferromagnetic' polymorph) always yielded a larger energy per unit cell (by about 0.5 eV per Tm atom) than for those with polarized spins ('ferromagnetic' polymorph). At the same time, calculations without spin polarization typically result in minor changes in the unit cell vectors (for example, compare results for Cs_2TmH_4: SP $a = b = 4.601$ Å, $c = 15.696$ Å, no SP $a = b = 4.616$ Å, $c = 15.613$ Å).

We have also performed supplementary VASP[16] calculations for several Yb- and Tm-containing compounds (see the electronic supplementary information (ESI)†). Here we could use dense k-point sampling of $11 \times 11 \times 11$ ($CsLnH_3$), and $11 \times 11 \times 6$ (Cs_2LnH_4). We tested two types of pseudo-potentials: those which explicitly involve f electrons on Ln atoms (PBA set) and those which do not; it turned out that optimizations with VASP (pseudopotentials without f electrons) and CASTEP (pseudopotentials with f electrons) yielded only minor differences in unit cell vectors for $CsYbH_3$ and Cs_2YbH_4.

For phonon dispersion and phonon DOS calculations we have used the PHONON[17] code as implemented in the MEDEA package. PHONON uses VASP-preoptimized unit cells in order to determine vibrations of the crystal lattice. To speed up the time-demanding frequency calculations we used norm-conserving pseudopotentials which do not explicitly involve f electrons on Ln atoms.

Results and discussion

Crystal structures

Due to the Ca^{II}–Ln^{II} (Ln = Yb, Tm) isomorphism mentioned above, one may expect that $CsLn^{II}H_3$ and $Cs_2Ln^{II}H_4$ will adopt, respectively, the $Cs^{I}CaH_3$ (perovskite) and $Cs^{I}_2CaH_4$ (K_2NiF_4) structures. In Table 1 we present the results of unit cell optimization for four novel ternary lanthanide hydrides, and compare them with the experimental and computational data for analogous calcium salts.[11]

Our GGA-PBA calculations predict a cubic unit cell constant of 4.609 Å for $CsYbH_3$ and 4.609 Å as well for $CsTmH_3$; the deviation from the experimental value for $CsCaD_3$ (4.617 Å) is very small (<0.01 Å) and slightly negative; in fact small positive deviations (*ca.* +0.03 to 0.04 Å) are expected based on comparison of the crystal radii (see the previous section). The difference between calculated and experimental cubic unit cell constants for $CsCaD_3$ is as small as 0.002 Å.

Our result is entirely within the limitations of the computational method utilized (we note slightly positive deviations for smaller energy cutoffs). The calculated unit cell constant of 4.609 Å for $CsYbH_3$ also matches well the experimental value of 4.61 Å for $CsYbF_3$; indeed, the close hydride–fluoride analogy has been pointed out to apply for similar compounds.[14] For $CsTmH_3$, the environment of Tm^{II} is predicted to be that of an ideal octahedron; the Jahn–Teller (JT) distortion apparently does not influence the coordination shell of the f^{13} cation, similar to the crystal structure of $CsTmCl_3$.[18] This feature points to the relatively ionic character of Tm–H bonding.

For Cs_2YbH_4, slight deviations from regular octahedral coordination of Yb^{II} are predicted, with four equivalent longer equatorial Ln–H distances of 2.305 Å and two shorter apical distances of 2.301 Å. This effect is of course slightly larger for ferromagnetic (f^{13}) Cs_2TmH_4 (equatorial 2.300 Å, apical 2.286 Å). An inverse JT effect is computed to be small for the inner transition metal f^{13} configuration of Tm^{II} (the ratio of apical to equatorial Tm–H distances is 0.994), in agreement with experimental data for similar compounds of Tm^{II} (the analogous ratio being 0.986 for $KTmI_3$,[19] and 1.006 for Cs_2TmCl_4[20]).

The fractional z atomic coordinate for an apical $H_{(0,0,z)}$ atom (which quantitatively determines the distortion of the $\{LnH_6\}$ octahedron), has been predicted to be 0.146 for Cs_2TmH_4, *via* 0.148 for Cs_2YbH_4, up to 0.149 for Cs_2CaH_4, always close to the experimental value of 0.149 for Cs_2CaD_4.

The predicted unit cell vectors are very similar for hydrides of Yb^{II} and for isostructural compounds of Tm^{II} (identical for $CsLnH_3$, and within 1% deviation for Cs_2LnH_4). This should facilitate formation of solid solutions for analogous compounds of these Ln metals, *i.e.*, ease of electronic doping.

Thermodynamic stability

In Table 2 we present the calculated enthalpies of formation[21] (at T = 0) of the ternary caesium lanthanide hydrides studied, with respect to formation from CsH and LnH_2 (CsH and LnH_2 have been optimized based on the experimental crystallographic data[22]).

Ternary Tm and Yb hydrides are predicted to be thermo-dynamically unstable with respect to decomposition to binary

Table 1 The optimized unit cell vectors for $CsMH_3$ and Cs_2MH_4 where M = Yb, Tm, Ca, and the corresponding experimental values for Ca salts (CASTEP results). Fractional z atomic coordinate for an apical $H_{(0,0,z)}$ atom is given in bracket

Compound	$CsYbH_3$	$CsTmH_3$	$CsCaH_3$	$CsCaD_3$ exp.	Cs_2YbH_4	Cs_2TmH_4	Cs_2CaH_4	Cs_2CaD_4 exp.
$a = b$/Å	4.609	4.609	4.619	4.617	4.609	4.601	4.615	4.597
c/Å	4.609	4.609	4.619	4.617	15.531 (0.148)	15.696 (0.146)	15.558 (0.149)	15.528 (0.149)

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Table 2 The calculated enthalpies of formation (ΔH), volume changes (ΔV) and estimated formation pressures, p, for the formation reaction from binaries for $CsMH_3$ and Cs_2MH_4 where M = Yb, Tm

Compound	$CsYbH_3$	$CsTmH_3$	Cs_2YbH_4	Cs_2TmH_4
ΔH/eV per molecule	0.27	0.55	0.19	0.47
ΔV/Å^3 per molecule	−6.02	−5.30	−5.66	−3.85
p/GPa	7.3	16.7	5.3	19.7

hydrides, and it is not expected that vibrational zero-point correction and entropy effects—typically small for solid reagents—will easily reverse this trend. Diamagnetic forms of Tm^{II} compounds are computed to have higher electronic energy than their magnetically ordered (ferromagnetic) polymorphs, in agreement with the strong magnetism of unpaired f electrons. In the following sections we will discuss exclusively ferromagnetic compounds of Tm^{II}.

The enthalpy of the reactions of synthesis of ternary hydrides is positive for all ternaries studied, while the associated volume change is computed to be negative (Table 2). This suggests that hydrides might form from binaries at elevated pressure. A rough estimate of the formation pressure can be obtained from the "common tangent" method, as a ratio of reaction enthalpy to the volume change. The estimated formation pressures—listed in Table 2—range from 5 to 20 GPa.[23]

Our conclusion is that ternary hydrides of Tm^{II} and Yb^{II} could be synthesized at increased pressures, and at relatively low temperatures up to 200 °C (to avoid decomposition of fragile CsH) and with rather small H_2 overpressure (to avoid formation of compounds of trivalent lanthanides, especially for compounds of divalent Tm, strong reducing agents). Some of these ternary phases might be quenchable upon decompression to 1 atm.

Electronic structure

Let us now analyze the electronic structure of $CsLnH_3$ and Cs_2LnH_4.

The band structure of Cs/Yb(Tm) hydrides (see ESI†) consists of: (i) very narrow filled subvalence bands originating from $5s^2$ (at about −52 eV) and $5p^6$ (at about −24 eV) states of Yb(Tm), and from $5s^2$ (at about −23 eV) and $5p^6$ (at about −10 eV) states of Cs, (ii) a filled 'hydride band' at −6 to −2.5 eV, (iii) a very narrow 4f valence band and (iv) a very broad set of bands constituting the conducting band. In the analysis to come we will omit the sub-valence bands, *i.e.* set (i).

The CASTEP software does not allow direct atomic identification of a given segment of the density of states, only decomposition by angular momentum type—s, p, d, or f. Nevertheless an atomic assignment can be made, both by the energy range in which the density is found, and also by computing the disposition in space of the states in a given energy interval.

The 'hydride band' (ii) is visibly split from the valence band (iii) for all ternary hydrides studied (by some 3 eV) and it is composed predominantly of H (1s) states (Fig. 1), with a little contribution from lanthanide s, p and d states; in turn, the valence 4f band contains very little contribution from H (1s) states, which might point to an ionic formulation of the hydrides studied, to be written formally as $Cs^I Ln^{II}(H^-)_3$ and

$(Cs^I)_2 Ln^{II}(H^-)_4$. The 'hydride band' is usually split in several separate bands, some of which show significant dispersion (up to 3 eV). This cannot be due to direct H···H interactions, as the hydrides are far apart (usually at >3.2 Å). The band width in the hydride band is due to interactions between H ions and lanthanide and alkali centers; the title hydrides are not as ionic as one might think.

The set of bands (iii) originating from 4f states either gives rise to a single and large peak in the DOS (as for diamagnetic f^{14} Yb^{II}) or is split equally into two bands separated by some 2 eV (as for ferromagnetic f^{13} Tm^{II}). This description of f electrons in these phases is unsatisfactory; unfortunately it is common to all first-principles calculations within the independent electron approximation.[24,25]

The broad conduction band, or rather, the set of interpenetrating bands (with a collective width of up to 9.5 eV for $CsLn^{II}H_3$ and of only 3 eV for $Cs_2Ln^{II}H_4$) is built of s, p and d states, predominantly coming from Yb, but in some part also from the alkali metal. For Yb hydrides, the bottom of the (formally empty) conduction band is remarkably close (0.25–0.5 eV) to the uppermost part of the (formally filled) valence band. For Tm compounds, however, the broad conduction band penetrates through (and for CsTmH3 even 0.5 eV below) the narrow 4f band, thus closing the direct band gap.

The electronic density at the Fermi level consists mainly of rather localized 4f electrons (Fig. 2) with no contribution from H 1s states.

Phonon density of states

Prompted by our continuing search for novel superconducting materials (with particular emphasis on fluorides and hydrides),[26] and by an unprecedented dynamic scale of all H-containing solids, we have investigated the phonon dispersion and phonon density of states for $CsYb^{II}H_3$ (Fig. 3).

The unit cell of $CsYbH_3$ contains 5 atoms, so there are 15 degrees of freedom: 12 vibrational and 3 translational ones. Three phonon bands are seen in the highest frequency range of the spectrum (30.9–37.7 THz, 128–156 meV, 1030–1260 cm^{-1}).[27] They are degenerate at the zone center (recollect, the cell is cubic), and correspond to the Yb–H stretching modes. Six other modes are seen in the moderate-frequency range (11.0–21.9 THz, 46–90 meV, 370–730 cm^{-1}). These are the Ln–H–Ln bending modes, which also show significant amplitude of H motions. The last set of three phonons is centered at low frequency (3.07 THz, 13 meV, 120 cm^{-1}). These are deformational modes of the lattice, with predominant contribution from heavy elements (Yb, Cs). The remaining three lowest-frequency motions correspond to translations of the entire lattice; their calculated wavenumbers (at the zone center, Γ) are close to zero within narrow error margin, as expected. The dispersion of Ln–H stretching modes is significant ($\sim$7 THz, 29 meV, 230 cm^{-1}); that of Ln–H bending modes is even larger ($\sim$10.8 THz, 45 meV, 360 cm^{-1}).

The phonon density of states is composed of a single narrow and intense peak originating from the lowest-frequency phonons; a low dispersion, broad band coming from moderate-frequency phonons; and a double peak of moderate intensity marking the highest energy range of the spectrum.[28]
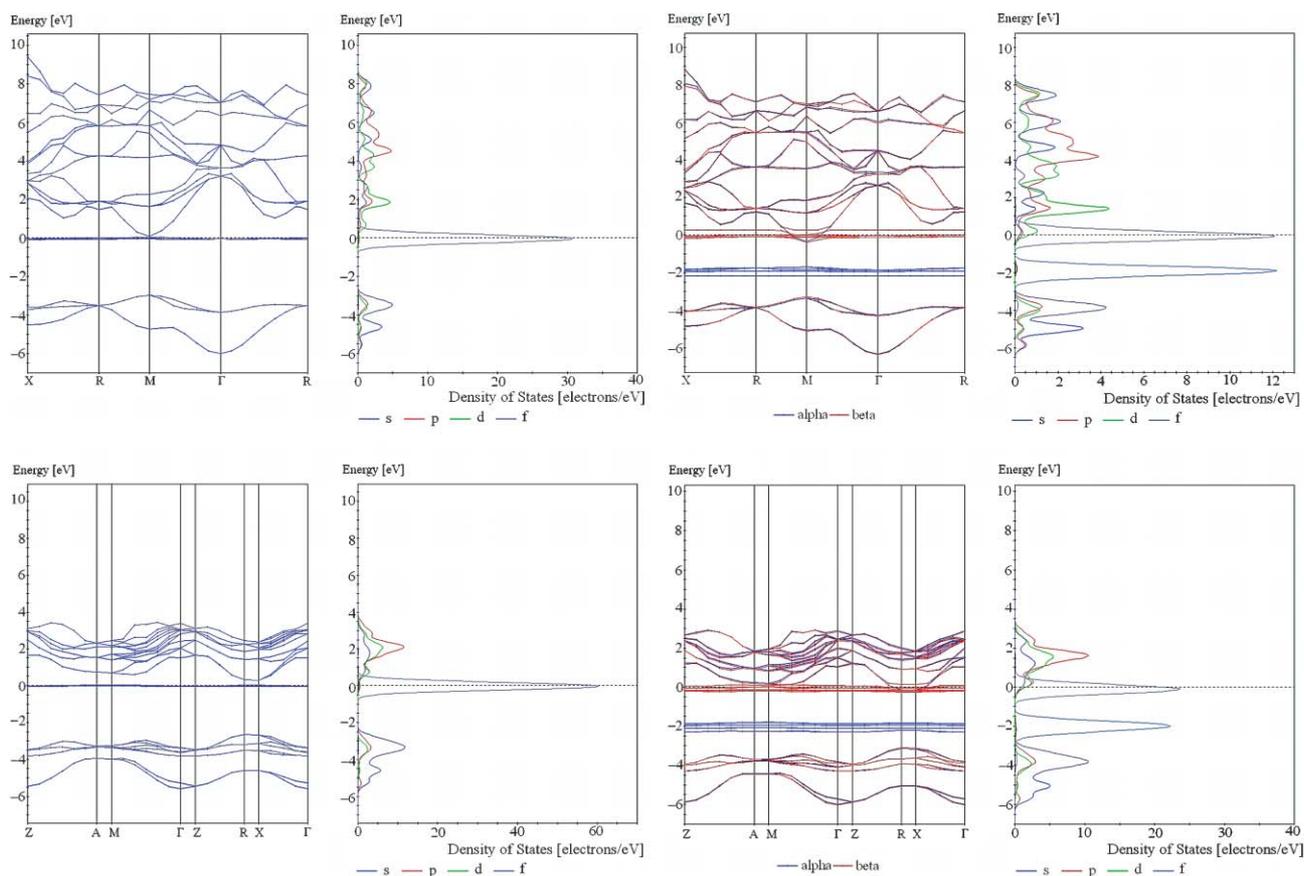
Fig. 1 Band structure and DOS for $CsYbH_3$ (upper left), $CsTmH_3$ (upper right), Cs_2YbH_4 (lower left) and Cs_2TmH_4 (lower right). Focus is on hydride, f and conduction bands.

In the first section we have considered the 'static' crystal structure of lanthanide hydrides, and we have pointed to minor structural distortions predicted for the $Cs_2Ln^{II}H_4$ compounds. We think that dynamic inversion of the Jahn–Teller effect (a set of local two short and four long Ln–H bonds transforms into two long and four short bonds) is undoubtedly within vibrational amplitude of H atoms, at least within the Born–Oppenheimer approximation. Interestingly, such fluctuating transformation of a JT species should decrease the anisotropy of electron density around the lanthanide cation, in particular for compounds of Tm^{II}.

Superconductivity in hydrides and valence fluctuations. Why is T_C for hydrides so low?

As one knows for many other systems, moderate and high-temperature superconductivity arises in the vicinity of the metal-to-insulator transition.[29] For mixed-valence systems, motions of ligands bridging two metal centers seem to be of crucial importance for phonon-driven superconductivity. Superconductivity has been detected for several hydride materials (for example Th_4H_{15}), yet despite the presence of a light H atom, the values of the transition temperature (T_C) are remarkably small (not exceeding 20 K). In addition, the isotope effect on the value of T_C is opposite to the predictions of the classical BCS theory[30] for Pd hydride, the best studied hydride superconductor.[31]

In a simplistic chemical picture, $PdH_{x \approx 1.0}$ is formally a mixed valence system, $Pd^0Pd^{II}H^{-1}_2$.[32] A molecular mixed-valence systems can be either localized, delocalized (*i.e.*, intermediate valence), or an intermediate case between the two.[33] These three classes of molecular mixed-valence systems may naturally be compared to, respectively, insulating, metallic and superconducting mixed-valence solids.[34] In this picture, the electronic wavefunction of a system (be it a solid or a molecule) is most affected by motions of nuclei when the vibrational zero-point energy (ZPE) of metal–ligand–metal stretching (or of the highest-energy optical phonon in solids) is close to the energy barrier for the electron transfer (E_B) between the metal centers (Fig. 4).

When the ZPE is too small, the system is localized (insulating, Fig. 4A). When the ZPE is too large, the system is delocalized ('simple' metal) and two distinct oxidation states cannot be recognized in the molecular (crystal) structure (Fig. 4C). We suggest that when the ZPE is close to E_B, strong electron–phonon coupling dramatically influences the shape of the wavefunction and superconductivity may arise (Fig. 4B).

For PdH, electron transfer between Pd centers is greatly affected by motions of the hydride ligand.[32] Hydrogen is *the* lightest ligand available to chemistry; here the ZPE can reach as much as 0.25 eV (for molecular H_2). In cases when the ZPE for the proton isotope is larger than E_B, and since the (classical) amplitude of vibrations—and also the vibrational
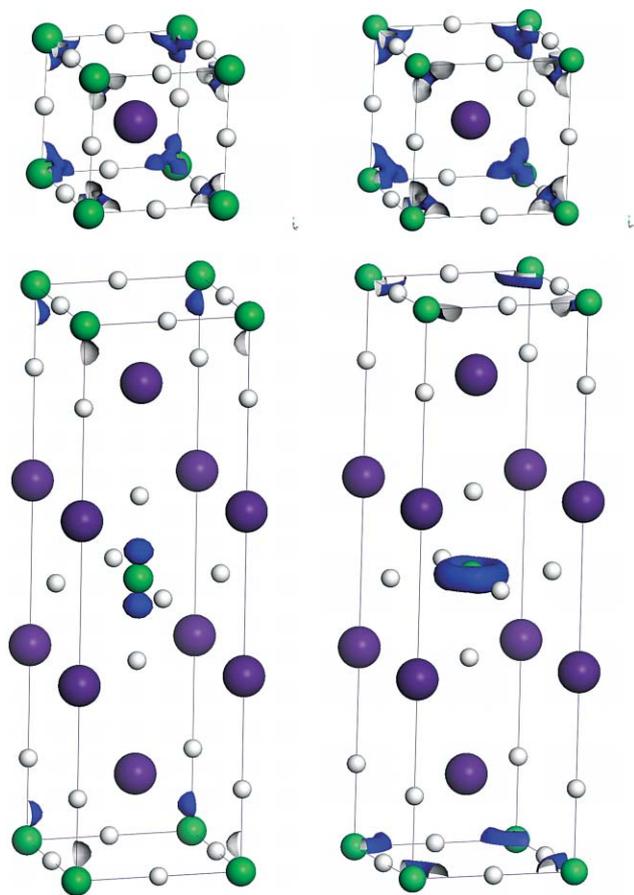
Fig. 2 Electronic density (in blue) at the Fermi level ($E_F \pm 0.03$ eV) for $CsYbH_3$ (upper left), $CsTmH_3$ (upper right), Cs_2YbH_4 (lower left) and Cs_2TmH_4 (lower right). Density isovalue 0.012 e Å^{-3}.

zero point energy—decreases as the atomic mass increases for three isotopes of H, inverse isotope effect might indeed occur (Fig. 4D).

The case of PdH (small T_C because of large energy of hydrogen motions (!), and concomitant easy mixing of d orbitals on Pd centers linked by H) brings to mind an idea
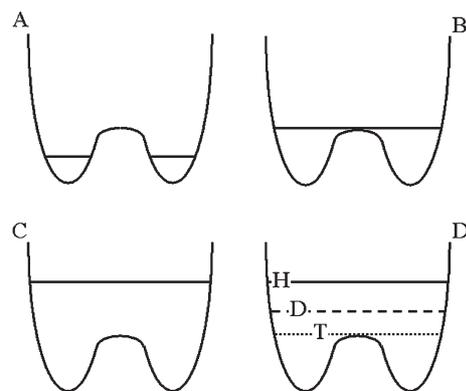
Fig. 4 The double-well PES for a mixed-valence compound for three different zero-point vibrational energy situations: (A) a separated (localized) mixed valence compound; (B) a fluctuating valence species; (C) an intermediate (delocalized) valence compound. Solid state analogues are likely to be (A) insulators, (B) superconductors, (C) 'normal' metals. Case (D) illustrates the postulated explanation for the inverse isotope effect observed experimentally for palladium hydride (PdH, PdD, PdT).

for increasing the E_B value by (i) involving in the electronic transport such orbitals, which are deeper lying (in energy) and more contracted than the 4d set of Pd (in this contribution we want to use 4f electrons), or by (ii) increasing the separation of the metal centers.[35] It might allow a reversal of the atypical isotope effect, and also larger T_C values by hydride super-conductors. $CsTmH_3$ and Cs_2TmH_4, which have a nearly filled yet significantly contracted f-shell, seem promising in terms of possible heavy-fermion superconductivity via appropriate chemical doping to these compounds; if E_B proves to be too large, external pressure might be applied to bring these systems back towards the metal–insulator transition.

Cs_2TmH_4 (f^{13} Tm^{II}) is a quite formal analogue of other important systems with a nearly filled electron shell, namely Ln_2CuO_4 and Nd_2CuO_4 (d^9 Cu^{II}). The latter two are parent (undoped) compounds of, respectively, hole-doped ($La_{2-x}Ba_xCuO_4$) and electron-doped ($Nd_{2-x}Ce_xCuO_4$) oxocuprate superconductors. Simultaneously, $CsTmH_3$
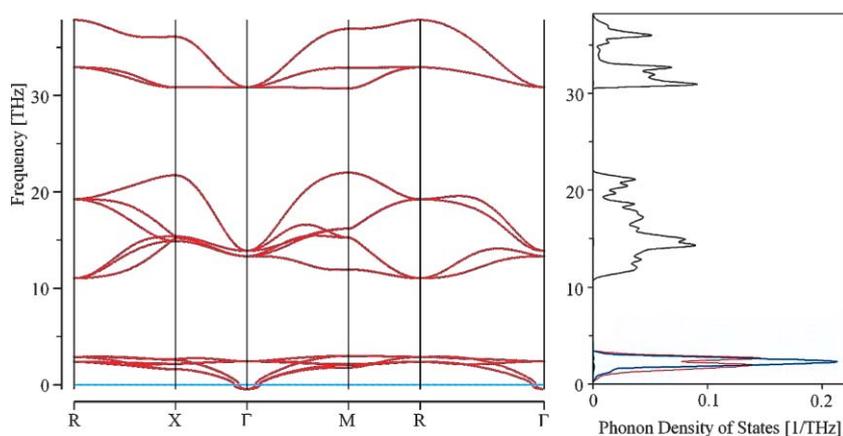
Fig. 3 Phonon band structure (left) and phonon DOS (right) for $CsYbH_3$; PHONON/VASP calculation. H's contribution to phonon DOS is in black, Yb's one in red, Cs's one in blue.

perovskite (f^{13} Tm^{II}) may be treated as a distant sibling of $BaBiO_3$, with a distorted perovskite structure (s^1 Bi^{IV}). The latter becomes $Ba_{1-x}K_xBiO_3$, a regular perovskite superconductor, upon hole-doping.[36]

Thus, in terms of a formal electron count on the transition metal, $Cs_2Tm^{II}_{1-x}Yb^{II}_xH_4$ would be equivalent to $Nd^{III}_{2-x}Ce^{IV}_xCu^{II/I}O_4$, while $Cs_{1-x}\square_xTm^{II/III}H_3$ (where $\square$ stands for a vacancy)[37] would be analogous to $Ba_{1-x}K_xBi^{IV/V}O_3$.[38]

We expect that tuning the transition between the f^{13} and f^{14} electron count[39] within the LnH_2 sublattice may bring $Cs_2Tm^{II}_{1-x}Yb^{II}_xH_4$ and $CsTm^{II}_{1-x}Yb^{II}_xH_3$ towards the anticipated metal/insulator borderline. At this stage, it is impossible to evaluate correctly from first principles whether these quaternary lanthanide hydrides will exhibit genuine heavy-fermion superconductivity, or plain 'valence fluctuations' (commonly observed for compounds of Yb, Tm, Eu, Sm, and also Ce and Tb).[40,41] The consequences for the electronic and magnetic properties of novel hydride phases of the interplay of strong magnetism of 4f electrons and of the varying electron count (at the edge of the f shell closure), should be probed experimentally.

The estimated Debye temperature of $CsYbH_3$ is substantial, ~ 1800 K, while DOS below the Fermi level rises very steep, due to narrowness of the 4f electron band. The BCS theory predicts that these features alone are likely to prompt low-T_C superconductivity in as yet unknown hole-doped hydrides of Yb^{II}, despite rather small involvement of H states into the DOS at the Fermi level of these compounds. Ultra-high pressure experiments constitute another prospective path of research. External pressure is an independent experimental variable which might enforce larger mixing of hydride 1s states into the quasi-valence 4f electrons and thus provoke larger involvement of the former in the electronic transport in these compounds. In this way a moderate-T_C superconductivity could be achieved while making use of strong electron–phonon coupling of the states at the Fermi level with the high-frequency H-based phonons.

Conclusions

We predict the existence and some properties of four novel stoichiometric ternary hydrides of Tm and Yb. Our calculations indicate that—under easily achievable pressure of ~ 20 GPa—$CsLnH_3$, Ln = Yb, Tm, could be stable in the perovskite structure, while Cs_2LnH_4 might adopt the K_2NiF_4 one. These two structures are also shared by many 3D and 2D superconductors, and by some metallic hydrides.[42] The electronic structure of these novel hydrides reveals a very narrow f band, very close to—or even interpenetrated by—the broad (s, p, d) conduction band. In addition, the phonon spectrum benefits from the high-frequency (up to 156 meV, 1800 K) modes involving motion of H atoms.[43] The crystal structures adopted by hydrides in question, the isostructurality of Yb^{II} and Tm^{II}, and the electron count in the vicinity of shell closure (f^{13}–f^{14}) create the potential for tuning of electronic and magnetic properties of novel phases in the vicinity of the metal-to-insulator transition. An alluring possibility of valence fluctuations, or even heavy fermion superconductivity, arises.

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J. Mater. Chem., 2006, **16**, 1154–1160 | 1159

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Both properties point rather to a $Pd^{\delta+}/H^{\delta-}$ polarization in a palladium hydride, but the Pd–H bonding should of course be quite covalent.

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36 The hydride ligand is unique among all inorganic ligands, as it has no p orbitals and therefore π bonding is not available. This is important in terms of hole-doping, and progressive depopulation of the $1s^2$ band, as compared to analogous situations in oxides. Introducing holes into the hydride anion band by necessity means substantial weakening and even rupture of the element–hydrogen bond, in contrast to anions carrying p orbitals. This feature of H^- also helps to explain the low-T_C value of Th_4H_{15}. Th_4H_{15} is formally a nonstoichiometric e$^-$-doped $(ThH_4)_4$ (f^0); an extra f^1 electron thus needs to sit in a band originating from Th–H nonbonding states, built predominantly from Th 5f orbitals. Thus, conducting electron density is delocalized predominantly on Th network, with no contribution of H; the metallic form of Th_4H_{15} (a 'low-D metal' in Zaanen–Sawatzky–Allen diagram) cannot fully benefit from high-frequency H-based phonons. In contrast, the f^{13}/f^{14} doping for our systems introduces changes in a (weakly antibonding) σ^* Ln–H states; the vibronic effects should thus be larger than for the f^0/f^1 perturbation.

37 Here, two important differences between hole-doping to Cu^{II} and to Tm^{II} come to mind. Hole-doping (which proved very successful in introducing superconductivity in oxocuprates), might be realized for Tm^{II} compounds by their partial oxidation to trivalent Tm. Note, however, that, first, f^{12} Tm^{III} is a strongly magnetic ion for most ligand fields (magnetic moment of ~ 7.5 μB), in contrast to classical low-spin d^8 Cu^{III} for oxocuprate superconductors, and, second, the magnetic moment of f^{13} Tm^{II} itself (~ 4.5 μB) is much greater than that of d^9 Cu^{II} (~ 1.8 μB). This means that magnetic ordering will be much easier for doped compounds of Tm than for those of Cu. Instead of introducing vacancies, other variations can also be used, *e.g.*, Ln$^{II}H_2$ layer could be sandwiched between Ba^{II}O sheets, and then doped by substitution at Ba^{II} site with either K^I (hole-doping) or with Ac^{III} (electron-doping).

38 The electron doped $BaPb_{1-x}Bi_xO_3$ superconductor does not have an isostructural lanthanide analogue. Hypothetical $\square_1Yb^{III}_{1-x}Tm^{III}_xH_3$ might be formally treated as such; unfortunately, parent stoichiometric YbH_3 has not been synthesized. Also $La_{2-x}Ba_xCuO_4$ does not have any counterpart among the hydrides of Tm and Yb.

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