Interplay of chemical pressure and hydrogen insertion effects in CeRhSn from first principles

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Abstract

Investigations within the local spin density functional theory (LSDF) of the intermetallic hydride system CeRhSnH$_x$ were carried out for discrete model compositions in the range 0.33 $\leq x_H \leq$ 1.33. The aim of this study is to assess the change of the cerium valence state in the neighborhood of the experimental hydride composition, CeRhSnH$_{0.8}$. In agreement with experiment, the analyses of the electronic and magnetic structures and of the chemical bonding properties point to trivalent cerium for 1 $\leq x_H \leq$ 1.33. In contrast, for lower hydrogen amounts the hydride system stays in an intermediate-valent state for cerium, like in CeRhSn. The influence of the insertion of hydrogen is addressed from both the volume expansion and chemical bonding effects. The latter are found to have the main influence on the change of Ce valence character. Spin polarized calculations point to a finite magnetic moment carried by the Ce 4f states; its magnitude increases with $x_H$ in the range 1 $\leq x_H \leq$ 1.33.

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I. INTRODUCTION

Equiatomic ternary alloys CeTX (1:1:1), where T is a transition-metal of first, second and third period and X is a p-element, form a rich family of intermetallic systems, due to the presence of X belonging to the 3A, 4A and 5A main groups. These 1:1:1 intermetallics have attracted considerable interest in the past two decades, due to a large variety of the magnetic and electrical properties. For instance, CeRhSn is an intermediate-valent system, CePdSn has a trivalent cerium while CeRuSn comprises both trivalent and intermediate-valent cerium. Furthermore, several 1:1:1 systems have the ability to absorb hydrogen. The hydrogenation of these compounds induces interesting physical properties relevant to the modification of the valence of cerium with respect to the initial 1:1:1 alloy system. Two effects can occur: (i) the expansion of the lattice by hydrogen intake, which should lead to an enhancement of the localization of the 4f states due to the reduced f-f overlap; this effect occurs in the intermediate-valent CeNiIn, which on hydration transforms into a long-range magnetically ordered ferromagnet with trivalent Ce, (ii) the chemical interaction between the valence states of Ce, T, and X with H, which induces a decrease of the magnetic polarization and, eventually, a loss of magnetization such as in CeCoSiH and CeCoGeH.

Despite the numerous studies on 1:1:1 systems and corresponding hydrides, only little is known about the hydrogenation effects within the family of Sn based intermetallic systems. Recent experimental studies report the formation of a hydride CeRhSnHₓ, within which a trivalent ground state of Ce was evidenced, but no detailed H positions were reported. Using the framework of the density functional theory (DFT), we examine in this work the electronic and magnetic properties of the experimental hydride composition within a range of discrete hydrogen amounts, for which full geometry optimizations were carried out. This allowed to assess the threshold for the change of Ce valence character upon hydrogenation found to be mainly induced by chemical interactions between the lattice constituents and H.

II. CRYSTAL STRUCTURES

Like intermetallic CeRhSn, the corresponding hydride systems CeRhSnHₓ crystallize in the ZrNiAl-type structure (space group P62m). In this structure, Rh atoms are in 1a and
Theoretical Framework of Computations

A. Computational methodology

Two computational methods were used in the framework of density functional theory (DFT).\textsuperscript{12,13,14} A pseudo potential approach within the Vienna ab initio simulation package (VASP) code\textsuperscript{15} was firstly used to optimize starting structures for different hydride compositions using projector augmented wave (PAW)\textsuperscript{16,17} potentials built within LDA\textsuperscript{18} scheme. The calculations were converged at an energy cut-off of 301.01 eV for the plane-wave basis set with respect to the $k$-point integration with a starting mesh of $4^*4^*4$ up to $8^*8^*8$ for best convergence and relaxation to zero strains. The Brillouin-zone integrals were approximated using a special $k$-point sampling. Further, this method allows for a first insight into the charge density of the hydride system.

The all-electron calculations are based on density-functional theory and the local-density approximation (LDA) as parametrized according to Vosko, Wilk, and Nusair.\textsuperscript{19} They were performed using the scalar-relativistic implementation of the augmented spherical wave (ASW) method (see Refs.\textsuperscript{20,21} and references therein). In the ASW method, the wave
B. Assessment of chemical bonding properties

To extract more information about the nature of the interactions between the atomic constituents from electronic structure calculations, the crystal orbital overlap population (COOP)\textsuperscript{27} or the crystal orbital Hamiltonian population (COHP)\textsuperscript{28} may be employed. While both the COOP and COHP approaches provide a qualitative description of the bonding, nonbonding, and antibonding interactions between two atoms, the COOP description in some cases exaggerates the magnitude of antibonding states. A slight refinement was recently proposed in form of the so-called covalent bond energy ECOV criterion, which combines the COHP and COOP to calculate quantities independent of the particular choice of the potential zero.\textsuperscript{29} In the present work, the ECOV criterion was used for the chemical bonding analysis. In the plots, negative, positive and zero magnitudes of the unitless ECOV are indicative of bonding, antibonding, and nonbonding interactions respectively.

IV. GEOMETRY OPTIMIZED DISCRETE COMPOSITIONS OF HYDRIDES

In as far as no structural determination for the particular Ce, Sn and H positions were available, trends in cell volumes and ground state crystal structures for the different amounts of H were necessary in the first place. The equilibrium structures were obtained starting from CeRhSn\textsuperscript{5} structural setup for u\textsubscript{Ce} and u\textsubscript{Sn} internal parameters for Ce and Sn positions. As for H, our starting guesses were based on the experimental study performed by Yartys
et al.\textsuperscript{6} on CeNiInD\textsubscript{x} structures. An initial input for the lattice $a$ constant for the different compositions was done on the basis of the experimental increase of $a$ between the 1:1:1 alloy and the experimental hydride composition, \emph{i.e.}, $\Delta a / a = 1.5\%$. The hexagonal $c / a$ ratio of 0.547 of CeRhSnH\textsubscript{0.8} taken from the experimental data\textsuperscript{8} was preserved throughout the calculations, thus allowing for an isotropic volume evolution of the different structures upon the intake of discrete amounts of hydrogen. After that, computations were carried out for the hydride systems with different amounts of H. From the results, the hexagonal symmetry was preserved for the optimized geometries of all systems. The new values for $u_{\text{Ce}}$, $u_{\text{Sn}}$ and $u_{\text{H}}$ internal parameters are given in table I. As it can be expected, $u_{\text{Ce}}$, $u_{\text{Sn}}$ are close to starting values. As for $u_{\text{H}}$ all results are in agreement with starting ones except for CeRhSnH\textsubscript{0.33} where the small value of 0.028 is obtained. This value is close to zero, which allows assuming that H within CeRhSnH\textsubscript{0.33} is relaxed into the general 2-fold position $2c$ at $(\frac{1}{3}, \frac{2}{3}, 0)$. According to the total energies values extracted from the VASP calculations, which are shown in table II, stabilization is proportional to the amount of the absorbed hydrogen. Further, the values of $\Delta E$, which is the relative energy of the hydride system with respect to CeRhSn, confirm this tendency. However, to investigate the origin of this stability, the energetic amount $\frac{n}{2} E_{\text{H}_2}$ was substracted from $E$. Here $n$ is an interger ranging from 0 to 4, and $E_{\text{H}_2}$ is the energy of H\textsubscript{2} (-0.489 Ryd) considered as the sum of the energy of two widely separate hydrogen atoms and the dissociation energy of H\textsubscript{2} (0.329 Ryd/mol H\textsubscript{2}) as given by experiment.\textsuperscript{20} As presentend in table II these values point to the chemical bonding of H with other atomic constituents as responsible of this stability. Furthermore, we notice that $(E - \frac{n}{2} E_{\text{H}_2})$ value for CeRhSnH\textsubscript{0.66} is smaller than that of CeRhSn, pointing to a difficulty to obtain such a hydride experimentally.

One can also analyze the electron charge density around the chemical species which allows determining the amount of localization of electrons. Fig. 2 shows the isosurface as well as the volume slice of the charge density both divided by the unit cell volume within the saturated hydride system. This illustration points to the strong bonding between Rh2 and H along the $c$-axis.
V. ALL-ELECTRON ASW COMPUTATIONS

The crystal parameters provided by the VASP geometry optimizations (table I) were used for the input of all-electron calculations. For CeRhSnH\textsubscript{x} compositions lower than that of the saturated hydride system CeRhSnH\textsubscript{1.33}, the positions of the lacking hydrogen atoms within the \textit{4h} interstices were considered as interstitial sites (IS) where augmented spherical waves were placed. The resulting breaking of initial crystal symmetry was accounted for from the differentiation of the crystal constituents in the calculations. In a first step the calculations were carried out assuming non-magnetic configurations (non spin polarized NSP), meaning that spin degeneracy was enforced for all species. However, note that such a configuration is different from that of a paramagnet, which could be simulated for instance by a super-cell entering random spin orientations over the different magnetic sites. Subsequent spin polarized calculations (spin-only) lead to an implicit long-range ferromagnetic ordering. In order to provide a model for an antiferromagnetic (AF) ground state of the hydride system and since neutron diffraction data were not available, we have constructed a double unit cell along the \textit{c}-axis. This provides one possible model of a long-range AF spin structure which should be validated as a ground state configuration from the relative energies of the band theoretical calculations. On the other hand, other sets of computations were performed for hydrogen-free models within ASW, starting from the previous four hydride systems with an additional model at the same volume of the experimental hydride. This procedure evaluates the manner in which the volume expansion affects the magnetic behavior of cerium.

A. Spin degenerate calculations

1. Density of states

The characteristic features of the site-projected DOS (PDOS) for the saturated hydride system CeRhSnH\textsubscript{1.33} plotted in Fig. 3(b) enable the discussion of the bonding in the CeRhSnH\textsubscript{x} models. Here and in all following figures, energies are referred to the Fermi level \textit{E\textsubscript{F}}. In the PDOS three energy regions can be distinguished. The first one, from -12 to -5 \textit{eV}, comprises 5\textit{s} (Sn) and 1\textit{s} (H) states. Then from -6 \textit{eV} up to \textit{E\textsubscript{F}} shows 5\textit{p} (Sn) states which hybridize with 4\textit{d} (Rh) states and itinerant Ce states. Finally, rather localized Ce 4\textit{f} states are found at and above \textit{E\textsubscript{F}}. The resulting high density of states at \textit{E\textsubscript{F}} is indicative
for an instability of the system in a degenerate spin configuration as is discussed next. In comparison with previous results obtained for CeRhSn (Fig. 3(a)) Fig. 3(b) shows that on hydrogenation new states are formed around -12 to -8 eV. Hence the valence band (VB) is shifted to lower energies and $E_F$ is pushed slightly upwards due to the additional electrons, resulting in a larger width of the VB with respect to CeRhSn.

2. Analysis of the DOS within Stoner theory

In as far as $4f$ (Ce) states were treated as band states by our calculations, the Stoner theory of band ferromagnetism$^{14}$ can be applied to address the spin polarization. The total energy of the spin system results from the exchange and kinetic energies counted from a non-magnetic state. Formulating the problem at zero temperature, one can express the total energy as

$$E = \frac{1}{2} I n(E_F) [1 - n(E_F)].$$

Here $I$ is the Stoner exchange integral, which is an atomic quantity that can be derived from spin polarized calculations.$^{32}$ $n(E_F)$ is the PDOS value for a given species at the Fermi level in the non-magnetic state. The product $In(E_F)$ from the expression above provides a criterion for the stability of the spin system. The change from a non-magnetic configuration towards spin polarization is favorable when $In(E_F) \geq 1$. The system then stabilizes through a gain of energy due to exchange. From Ref. $^{33}$, $I(Ce-4f) \sim 0.02 \text{ Ryd}$ and the computed $n(E_F)$ values of Ce ($4f$) for all the model systems are given in table [II]. The calculated values for $In(E_F)$ of 0.53, 0.41, 1.05, and 2.30 for CeRhSnH$_{0.33}$, CeRhSnH$_{0.66}$, CeRhSnH, and CeRhSnH$_{1.33}$, respectively, point to a magnetic instability of for the latter two hydride systems. This prediction for the behavior of the valence of Ce will be checked within the spin-polarized calculations for further confirmation, whereby finite magnetic moment are expected to be carried by $4f$ (Ce) states of CeRhSnH and CeRhSnH$_{1.33}$. Also, table [II] gives the values of Stoner product for hydrogen-free models. Among the computed hydrogen-free models, CeRhSnH and CeRhSnH$_{1.33}$ are the only ones, which are susceptible to a magnetic disorder, but their clearly weaker $In(E_F)$ values of 0.93 and 0.96, with respect to their pure hydride models analogues, emphasizes the contribution of hydrogen chemical bonding to the arising of the trivalent character of cerium over the volume expansion. Lastly, an additional hydrogen-free model at the same volume of the experimental hydride$^8$ was computed. The calculated value of its Stoner product is equal to 0.76, which points to a non favorable trend for magnetic instability. This is a further
confirmation of the dominant role of hydrogen chemical bonding.

3. Chemical bonding

Chemical bonding properties can be readily addressed on the basis of the spin-degenerate calculations. This is due to the fact that the spin-polarized bands, to a large degree, result from the spin-degenerate bands by a rigid spin splitting. The hydride models CeRhSnH$_x$ have the same bonding trends of CeRhSn obtained from the calculations of Matar et al. (Fig. 4(a)) using the ECOV criterion. A visual inspection of Fig. 4(b) shows that the dominant interactions within the VB result from the Ce-Rh2 and Rh1-Sn bonds. This is concomitant with the interatomic distances given in table II. Whereas the smaller the distance is the stronger is the interaction, Ce-Rh2 as well as Rh1-Sn have the shortest separations with respect to other Ce-T and T-Sn distances. However, compared to each other, the separation of Ce-Rh2 has the larger value with respect to that of Rh1-Sn suggesting a stronger Rh1-Sn bond. Nevertheless, Ce-Rh2 remains the most stabilizing contribution, which is due to the Rh2 interaction with hydrogen. In fact, Fig. 2 shows the continuous isosurface shape of charge density for the two hydrogens surrounding Rh2. This is confirmed by the interatomic distances given in table II for all CeRhSnH$_x$ models, where the Rh2-H separation is clearly the shortest.

B. Spin polarized configurations

From the NSP calculations and their analysis within the Stoner mean field theory of band ferromagnetism, it has been established that the hydride system is unstable in such a configuration for H content close to the experiment, i.e. with $x_H = 1$ up to 1.333. Consequently, spin polarized calculations were carried out, assuming implicitly a hypothetic ferromagnetic order. This is done by initially allowing for two different spin occupations, then the charges and the magnetic moments are self-consistently converged. The relative energies differences ($\Delta E$), with respect to the spin-degenerate energy of CeRhSn, for spin-degenerate and spin-polarized calculations given in table II slightly favor the ferromagnetic state. The experimental finding suggested a trivalent character of Ce within CeRhSnH$_{0.8}$. Theoretical non-magnetic computations of the discrete intake of hydrogen within the hydride
systems CeRhSnH\textsubscript{x} also reported a magnetic instability threshold at the hydride composition of three hydrogen. Spin-degenerate calculations confirmed these tendencies by identifying finite spin-only magnetic moments of 0.173 and 0.377 $\mu_B$ carried by 4\textit{f} (Ce) states for both CeRhSnH and CeRhSnH\textsubscript{1.33} respectively. These results are illustrated at Fig. 5 showing the site and spin projected density of states of CeRhSnH\textsubscript{1.33}. The exchange splitting is observed for cerium. The main bonding characteristics follow the discussion above of the non-magnetic PDOS.

Lastly, in order to check for the nature of the magnetic ground state, AF calculations were carried out using a supercell built from two simple cells along the \textit{c}-axis. These two structures were used to distinguish between the up- and down-spin atoms. At self-consistency, the energy difference ($\Delta E = E_{\text{Ferro}} - E_{\text{AF}} = -10^{-2} \text{Ryd}$) extracted from the spin-polarized calculation for both ferro- and antiferromagnetic state favors the ferromagnetic ordering, thus pointing to a ferromagnetic ground state. Further experimental investigations are underway.

VI. CONCLUSION

In this work we have undertaken a theoretical investigation of the effects of the insertion of hydrogen into CeRhSn on the valence state character of cerium. Hydride models CeRhSnH\textsubscript{x}, are computed herein to estimate both volume and hydrogen chemical bonding interplay within the change of the valence character for Ce. The properties of these models were addressed both by spin-degenerate and spin-polarized LSDF based calculations. Analyses of the electronic structures and of the chemical bonding reveal different types of chemical bonds due to the nature of the hydrogen tetrahedral interstices and their environment with mainly Rh2 atoms. Furthermore, a local magnetic moment is expected only for the cerium site with trivalent character whose arising threshold is for 1 H per formula unit. Compared to the experimental finding of 2.4 hydrogen atoms, this result is rather satisfying. Spin-polarized calculations lead to a finite moment showing up only at the trivalent Ce site.
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|                   | CeRhSn | CeRhSnH<sub>0.33</sub> | CeRhSnH<sub>0.66</sub> | CeRhSnH | CeRhSnH<sub>1.33</sub> |
|-------------------|--------|------------------------|------------------------|---------|------------------------|
| a (Å)             | 7.448  | 7.465                  | 7.532                  | 7.598   | 7.664                  |
| c (Å)             | 4.080  | 4.136                  | 4.136                  | 4.136   | 4.136                  |
| Volume (Å<sup>3</sup>) | 196    | 197                    | 202                    | 208     | 213                    |
| E (Ryd)           | -4.35  | -4.62                  | -4.83                  | -5.12   | -5.36                  |
| E − \( \frac{n}{2} E_{H_2} \) (Ryd) | -4.35  | -4.37                  | -4.34                  | -4.39   | -4.38                  |
| \( \Delta E \) (Ryd) | 0      | -0.489                 | -0.489                 | -0.771  | -1.016                 |
| \( u_{Ce} \)     | -      | 0.412                  | 0.412                  | 0.404   | 0.395                  |
| \( u_{Sn} \)     | -      | 0.743                  | 0.744                  | 0.744   | 0.743                  |
| \( u_{H} \)      | -      | 0.028                  | 0.130                  | 0.131   | 0.139                  |

TABLE I: CeRhSn and CeRhSnH<sub>x</sub> model systems: \( u_{Ce} \), \( u_{Sn} \) and \( u_{H} \) are particular positions for Ce, Sn and H refined from geometry optimization calculations using VASP code.
|                   | CeRhSnH₂ | CeRhSnH₀.₃₃ | CeRhSnH₀.₆₆ | CeRhSnH | CeRhSnH₁.₃₃ |
|-------------------|----------|--------------|--------------|----------|--------------|
| ∆E                | 0        | -0.607       | -1.736       | -2.684   | -3.794       |
|                   | 0        | -0.608       | -1.796       | -2.685   | -3.797       |
| In(Eₘ)            | 0.69     | 0.53         | 0.41         | 1.05     | 2.30         |
|                   | 0.69     | 0.81         | 0.69         | 0.93     | 0.96         |
| dₐCe−Rh₁          | 3.084    | 3.095        | 3.121        | 3.148    | 3.174        |
| dₐCe−Rh₂          | 3.031    | 3.036        | 3.063        | 3.089    | 3.116        |
| dₐCe−Sn           | 3.227    | 3.232        | 3.264        | 3.290    | 3.317        |
|                   | 3.375    | 3.386        | 3.412        | 3.444    | 3.475        |
| dₐRh₁−Rh₂         | 4.756    | 4.772        | 4.814        | 4.856    | 4.898        |
| dₐRh₁−Sn          | 2.761    | 2.767        | 2.793        | 2.814    | 2.841        |
| dₐRh₂−Sn          | 2.846    | 2.851        | 2.878        | 2.904    | 2.925        |
| dₐCe−H            | -        | 2.306        | 2.328        | 2.343    | 2.365        |
| dₐRh₁−H           | -        | 4.338        | 4.380        | 4.417    | 4.454        |
| dₐRh₂−H           | -        | 1.534        | 1.545        | 1.561    | 1.571        |
|                   | -        | 4.576        | 4.613        | 4.655    | 4.697        |
| dₐSn−H            | -        | 3.237        | 3.264        | 3.296    | 3.322        |

TABLE II: CeRhSn and CeRhSnHₓ model systems: interatomic distances are given in Å. Given in units of Ryd, ∆E represents the energy of the hydride with respect to the scalar-relativistic energy of CeRhSn (E₀=-118836.5904 Ryd) both resulting from spin-degenerate calculations. The values in italic font for ∆E correspond to the energy of the hydride for the spin-polarized computations relative to E₀. As for In(Eₘ), the italic font results are related to hydrogen-free hydride models.
FIG. 1: The hexagonal crystal structure of CeRhSnH$_{1.33}$ (space group $P\overline{6}2m$). Hydrogen atoms are drawn as small black spheres. The tetrahedral site in which H are inserted is drawn in dotted lines.

FIG. 2: Charge density plot for CeRhSnH$_{1.33}$: the isosurface and volume slice are sketched on the left and right hand sides respectively, both are drawn with c hexagonal axis along the paper sheet. (Plots with VMD software$^{34}$).
FIG. 3: Non-magnetic site projected DOS for: CeRhSn (a) and CeRhSnH_{1.33}, for the sake of clear presentation hydrogen PDOS are multiplied by 10 (b).

FIG. 4: Chemical bonding with ECOV criterion for: NM-CeRhSn (a), and NM – CeRhSnH_{1.33} (b).
FIG. 5: Site and spin projected DOS of CeRhSnH$_{1.33}$ in the ferromagnetic state.