Electronic structure, phase stability and chemical bonding in Th$_2$Al and Th$_2$AlH$_4$

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Abstract

We present the results of theoretical investigation on the electronic structure, bonding nature and ground state properties of Th$_2$Al and Th$_2$AlH$_4$ using generalized-gradient-corrected first-principles full-potential density-functional calculations. Th$_2$AlH$_4$ has been reported to violate the ”2 Å rule” of H-H separation in hydrides. From our total energy as well as force-minimization calculations, we found a shortest H-H separation of 1.95 Å in accordance with recent high resolution powder neutron diffraction experiments. When the Th$_2$Al matrix is hydrogenated, the volume expansion is highly anisotropic, which is quite opposite to other hydrides having the same crystal structure. The bonding nature of these materials are analyzed from the density of states, crystal-orbital Hamiltonian population and valence-charge-density analyses. Our calculation predicts different nature of bonding for the H atoms along $a$ and $c$. The strongest bonding in Th$_2$AlH$_4$ is between Th and H along $c$ which form dumb-bell shaped H-Th-H subunits. Due to this strong covalent interaction there is very small amount of electrons present between H atoms along $c$ which makes repulsive interaction between the H atoms smaller and this is the precise reason why the 2 Å rule is violated. The large difference in the inter-atomic distances between the interstitial region where one can accommodate H in the $ac$ and $ab$ planes along with the strong covalent interaction between Th and H are the main reasons for highly anisotropic volume expansion on hydrogenation of Th$_2$Al.

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I. INTRODUCTION

Hydrides of intermetallics have been extensively studied because of their applications in rechargeable batteries. Unfortunately, most metals that absorb large amounts of hydrogen are either heavy or expensive. Consequently, there is a constant search for hydrides that may be suitable for practical applications. First of all, it is very important to understand how crystal structural evolution takes place in the course of hydrogenation. Numerous studies have been done to explain observed stabilities, stoichiometries, and preferred H sites in hydrides of metallic and intermetallic compounds. Structural studies of hydrides have provided empirical rules that can be used to predict the stability of the H sublattice in a given metal configuration. A survey of stable hydrides show that the H–H distance does not go below 2.1 Å (the 2 Å rule) with a minimum radius of 0.4 Å for the inter-site to be used for the accommodation of H. These rules have been used to predict new hydrides whose existence is verified experimentally.

The review of Yvon and Fischer states that Th$_2$AlH$_4$ and K$_2$ReH$_9$ are violate the 2 Å rule, the shortest H–H separation being 1.79, and 1.87, respectively. K$_2$ReH$_9$ is classified among complex transition metal hydrides, which comprise highly covalent solids with nonmetallic properties. Th$_2$AlH$_4$, on the other hand, has metallic character.

Th$_2$Al$_7$ together with Zr$_2$Fe, Zr$_2$Co and Zr$_2$Ni crystallize in the CuAl$_2$-type structure, whereas their hydrides form rather different crystal structures. Zr$_2$Fe and Zr$_2$Co form the isostructural deuterides Zr$_2$MD$_5$ (M = Fe,Co) with a change in symmetry from $I4/mcm$ to $P4/ncc$ on deuteration. Th$_2$AlH$_4$ and Zr$_2$NiH$_{1.74}$ are formed without any change in the symmetry from their parent structures. Th$_2$AlH$_4$ belongs to the exclusive class which does not obey the 2 Å rule. The lattice expansion along $a$ and $c$ has proved to be highly anisotropic on hydrogenation of Th$_2$Al. In order to shed light on this effect we need theoretical understanding about bonding nature in this compound. Further, the understanding of the lattice expansion and distortion during hydrogenation will be important for the evaluation of stability of the hydride. So, we have made detailed study of Th$_2$Al and Th$_2$AlH$_4$ by first-principle calculations.

Two different powder neutron diffraction (PND) of Th$_2$AlH$_4$ give different H-H separations, viz. the older value is 1.79 Å and the more recent value is 1.97 Å. So one aim of this study has been to solve this discrepancy. In principle, the stability of hydrides can be evaluated directly from a theoretical study of the total energy. However, owing to the complexity of the structure of transition metal hydrides, no reliable theoretical heat of formation has hitherto been reported. Nakamura et al. were the first to calculate heat of formation. However, these authors obtained positive and unrealistically large heat of formation even for stable La-Ni based hydrides except for (La$_2$Ni$_{10}$H$_{14}$). This unfavorable result clearly indicates that local relaxation of the metal atoms surrounding the hydrogens must be included in the calculations in order to predict the structural stability parameters. Hence our calculations take into account local relaxation by optimizing the atom positions globally.

We present the electronic structure of Th$_2$Al and Th$_2$AlH$_4$, obtained by the full-potential linearized-augmented plane wave (FPLAPW) method. A central feature of the paper is the evaluation of the electronic structure and bonding characteristics on introduction of H into the Th$_2$Al matrix. In addition to regular band-structure data, we also provide crystal
orbital Hamiltonian population (COHP) results to illustrate the chemical bonding in more detail.

This paper is organized as follows. Details about the involved structure and computational method are described in Sec. II. Sec. III gives the results of the calculations and comparisons with the experimental findings. Conclusions are briefly summarized in Sec. IV.

II. STRUCTURAL DETAILS

Th$_2$Al and Th$_2$AlH$_4$ crystallize in space group $I4/mcm$ with the lattice parameters $a = 7.618$, $c = 5.862$ Å for Th$_2$Al and $a = 7.626$, $c = 6.515$ Å for Th$_2$AlH$_4$. The crystal structure of Th$_2$AlH$_4$ is illustrated in Fig. 1. The crystal structure of Th$_2$Al contains four crystallographically different interstitial sites, which are the suitable sites for hydrogen accommodation, 16$l$ and 4$b$ each coordinated to four Th, 32$m$ coordinate to three Th and one Al 16$k$ coordinate to two Th and two Al. Each 16$l$ based intersite tetrahedra share a common face with another 16$l$-based tetrahedron, whereas the 4$b$-based tetrahedra share each of its four faces with 16$l$-based tetrahedra. Some of the tetrahedral intersites are closely separated owing to the face sharing of the coordination polyhedra. According to the experimental findings, the 16$l$ sites are fully occupied in Th$_2$AlD$_4$, and also the structure is completely ordered.

A. Computational details

In our calculations we use the full-potential linearized augmented plane wave (FP-LAPW) method in a scalar relativistic version without spin-orbit coupling as embodied in the WIEN97 code. In brief, this is an implementation of density-functional theory (DFT) with different possible approximations for the exchange and correlation potential, including the generalized-gradient approximation (GGA). The Kohn-Sham equations are solved using a basis of linearized augmented plane waves. For the exchange and correlation potential, we used the Perdew and Wang implementation of GGA. For the potential and charge density representations, inside the muffin-tin spheres the wave function are expanded in spherical harmonics with $l_{max} = 10$, and non spherical components of the density and potential are included up to $l_{max} = 6$. In the interstitial region they are represented by Fourier series and thus they are completely general so that such a scheme is termed full-potential calculation. The present calculations we used muffin-tin radii of 2.5, 2.1 and 0.9 Bohr for Th, Al and H respectively.

The basis set includes 7s, 7p, 6d and 5f valence and 6s and 6p semi-core states for Th, 3s, 3p valence and 2p semi-core states for Al and 1s states for H. These basis functions were supplemented with local orbitals for additional flexibility to the representation of the semi-core states and for generalization of the linearization errors. We have included the local orbitals for Th 6s, 6p and Al 2p semi-core states. In all our calculations we have used tetrahedron method on a grid of 102 k points in the irreducible part of the hexagonal Brillouin zone (IBZ), which corresponds to 1000 k points in the whole Brillouin zone. The calculations are done at several cell volumes (around the equilibrium volume) for both Th$_2$Al and Th$_2$AlH$_4$ and corresponding total energies are evaluated self-consistently by iteration to an
accuracy of $10^{-6}$ Ry./cell. Similar densities of $k$ points were used for the force minimization and $c/a$ optimization calculations.

In order to measure the bond strengths we have computed the COHP which is adopted in the TBLMTO-47 package. COHP is the density of states weighted by the corresponding Hamiltonian matrix elements, which if negative indicates a bonding character and positive indicates an anti-bonding character. The simplest way to investigate the bonding between two interacting atoms in the solid would be to look at the complete COHP between them, taking all valence orbitals into account. However, it may sometimes be useful to focus on pair contributions of some specific orbitals.

III. RESULT AND DISCUSSION

The H–H separation is one of the most important factors in identifying the potential candidate for hydrogen storage, because if the H–H separation is small one can accommodate more H within a small region. From this point of view, Th$_2$AlH$_4$ may be considered as a potential candidate for storing H. To the best of our knowledge no theoretical or experimental attempts have been made to study cohesive properties like heat of formation ($\Delta H$), cohesive energy ($E_{coh}$), bulk modulus ($B_0$) and its pressure derivative ($B'_0$) for this compound. Hence, this is the first theoretical attempt to study the ground state properties and bonding in this compound.

A. Structural optimization from total energy studies

In order to analyze the effect of hydrogenation on the crystal structure of Th$_2$Al and to verify the discrepancy between the experimentally observed H–H separation, we have optimized the structural parameters for Th$_2$Al and Th$_2$AlH$_4$. For this purpose, first we have relaxed the atomic positions globally using the force-minimization technique, by keeping experimental $c/a$ and cell volume ($V_0$) fixed to experimental values. Then the theoretical equilibrium volume is determined by fixing optimized atomic positions and experimental $c/a$, and varying the cell volume by $\pm 10 \%$ of $V_0$. Finally the optimized $c/a$ ratio is obtained by a $\pm 2 \%$ variation in $c/a$ ratio (in steps of 0.005), while keeping the theoretical equilibrium volume fixed. It is important to note that experimentally observed lattice parameters are almost same, while the atomic position of H alone differs between the two experimental results (according to Bergsma et al. H coordinates are 0.368, 0.868, 0.137 and Sørby et al. give 0.3707, 0.8707, 0.1512). The total energy vs. cell volume and $c/a$ ratio curves for Th$_2$Al and Th$_2$AlH$_4$ are shown in Figs. 2 and 3 respectively. From these illustrations it is clear that the equilibrium structural parameters obtained from our theoretical calculations are in very good agreement with those obtained recently by PND measurements.

The optimized atomic positions along with the corresponding experimental values are given in Table I. Table II gives calculated lattice parameters and interatomic distances, along with corresponding experimental values for both Th$_2$Al and Th$_2$AlH$_4$. The theoretically estimated equilibrium volume is underestimated by 0.27% for Th$_2$Al and 1.8% for Th$_2$AlH$_4$. The underestimation of bond length in the present study is partly due to the limitation of local density approximation used in the calculations and also neglect of the zero-point motion.
and thermal expansions. The difference between the experimental values may be due to the poor resolution of the earlier (1961) PND data.

**B. Cohesive properties**

The method of calculation for cohesive properties for intermetallic compounds are well described in Refs. [23–27] The cohesive energy is a measure of the force that binds atoms together in the solid state. The cohesive energy of a system is defined as the sum of the total energy of constituent atoms at infinite separation minus the total energy of the particular system. This is a fundamental property which has long been the subject of theoretical approaches. The chemical bonding in intermetallic compounds is a mixture of covalent, ionic and metallic bonding and therefore the cohesive energy cannot be determined reliably from simple models. Thus, first principle calculations based on DFT have become a useful tool to determine the cohesive energy of solids. For the study of phase equilibrium the cohesive energy is more descriptive than the total energy, since the latter includes a large contribution from electronic states that do not play a role in bonding. From our cohesive energy calculations we get $E_{coh} = 0.15, 0.185$ eV/atom for Th$_2$Al and Th$_2$AlH$_4$ respectively, indicating that hydrogenation enhances the bond strength in Th$_2$Al.

The formation energy ($\Delta H$) is introduced in order to facilitate a comparison of system stability. $\Delta H$ is defined as the total energy difference between the compound and weighted sum of the corresponding total energy of the constituents. For the $\Delta H$ calculations, we used the total energy value of 2.320 Ry for the hydrogen molecule which was calculated with the von Barth-Hedin exchange-correlation potential. $\Delta H$ provides information about the stability of Th$_2$Al towards hydrogenation. The calculated $\Delta H$ values for La-Ni based hydrides were almost double the experimental $\Delta H$. As the LMTO-ASA method was used in this study, this discrepancy is expected because the internal relaxation of the atoms was not taken into account and the interstitial potential is not well represented in LMTO-ASA method. Therefore, $\Delta H$ calculated by using the full-potential method should be more reliable. Our calculated values for $E_{coh}$ and $\Delta H$ are given in Table III. Since ($\Delta H$) is more negative and $E_{coh}$ is higher for Th$_2$AlH$_4$ than for Th$_2$Al, we can conclude that Th$_2$AlH$_4$ is more stable than Th$_2$Al. However, no experimental $\Delta H$ values for Th$_2$Al and Th$_2$AlH$_4$, are available, but we note that our calculated $\Delta H$ is close to the experimentally observed values of other Th-based hydrides, like ThNi$_5$H$_4$, ThCo$_5$H$_4$ and ThFe$_5$H$_4$ all having the $\Delta H$ value of $-36.63$ kJ/(mol-H).

The bulk modulus of Th$_2$Al and Th$_2$AlH$_4$ was obtained by self-consistent total energy calculations for 8 different volumes within the range of $V/V_0$ from 0.75 to 1.10 (see Fig. 2). From the derivative of total energy with respect to the volume, the calculated bulk modulus for Th$_2$Al is 93.42 GPa and for Th$_2$AlH$_4$ is 111.36 GPa. The corresponding pressure derivative of the bulk modulus ($B'_0$) are 3.43 and 3.51, respectively. The enhancement in $B'_0$ value in the hydrogenated phase indicates that hydrogen plays an important role in bonding behavior of Th$_2$AlH$_4$. In particular, the hydrogenation enhances the bond strength, and hence the change in volume with hydrostatic pressure decreases with hydrogenation. This conclusion is consistent with the observation made from our calculated heat of formation and cohesive energy for Th$_2$Al and Th$_2$AlH$_4$. 

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C. Anisotropic behavior

For compounds which maintain the basic structural framework, the occupancy of hydrogen in interstitial sites is determined by its chemical environment (different chemical affinity for the elements in the coordination sphere also results in different occupancy). Although the H atom is small and becomes even smaller by chemical bonding to the host, it may deform and stress the host metal considerably depending upon the chemical environment. Lattice expansion usually of the order of 5 to 30%, often anisotropic, results from hydride formation. The maximum volume expansion observed for CeRu$_2$ to CeRu$_2$D$_5$ (37%) is due to a hydrogen induced electron transition as shown by XPS measurements A lattice contraction upon hydrogenation has so far only been observed for ThNi$_2$ to ThNi$_2$D$_2$ (2.2%). For most hydrides formed from intermetallic compounds the crystal structure usually changes with a loss of symmetry. In general the symmetry decreases as a function of hydrogen content and increases as a function of temperature. However, on hydrogenation of Th$_2$Al the symmetry remains unchanged.

The volume expansion during hydrogenation of Th$_2$Al is 12.47% ($\Delta V$/H atom is 10.32Å$^3$). This volume expansion is strongly anisotropic and proceeds predominantly perpendicular to the basal plane of the tetragonal unit cell; $\Delta a/a = 0.026\%$, $\Delta c/c = 12.41\%$. This indicates a relatively flexible atomic arrangement in the [001] direction. In spite of the isostructurality between Th$_2$Al, Zr$_2$Fe (hydrated: Zr$_2$FeH$_5$) and Zr$_2$Co (hydrated: Zr$_2$CoH$_{4.82}$) the latter two exhibit a quite opposite anisotropic behavior in that the the unit cell expands exclusively along the basal plane. The $c/a$ ratio plays an important role for the structural properties of intermetallic compounds including metal hydrides. For example, in the case of Zr$_2$Fe, Zr$_2$Co, and Th$_2$Al $c/a$ is 0.878, 0.867, 0.812 and 0.7695 respectively, and for the corresponding hydrides Zr$_2$FeH$_5$, Zr$_2$CoH$_{4.82}$, Zr$_2$NiH$_{4.74}$ and Th$_2$AlH$_4$ $c/a$ is 0.810, 0.815, 0.833 and 0.8543 respectively (see Fig. 4). The increase in $c/a$ for Zr$_2$CoH$_{4.82}$ and Zr$_2$FeH$_5$ compared with the corresponding unhydrated parents is smaller than that for other compounds. On hydrogenation, the increase in $c/a$ ratio for Th$_2$Al is considerably larger than for Zr$_2$Ni, which may be the reason why the former retains the symmetry on hydrogenation. Our calculations describe well the anisotropic changes in the crystal structure on hydrogenation of Th$_2$Al (see Table II). The $c/a$ ratio increases almost linearly (Fig. 4) on going from Zr$_2$Fe to Th$_2$Al whereas the corresponding hydrides show the opposite behavior. Hence, it appears that the systematic variation in $c/a$ plays a major role in deciding the crystal structure for the CuAl$_2$-type hydrides. When $c/a < 0.825$ the symmetry is changed from I4/mcm to P4/ncc on hydrogenation, whereas when $c/a > 0.825$ the crystal symmetry is apparently not affected.

D. Electronic structure

In order to understand the changes in the electronic bands on hydrogenation of Th$_2$Al we show the energy band structure for Th$_2$Al and Th$_2$AlH$_4$ in Fig. 5a and b respectively. The illustration clearly indicates that inclusion of H in the Th$_2$Al matrix has a noticeable impact on the band structure, mainly in the valence band. The two lowest lying broad bands in Fig. 5a originate from Al 3s electrons. As the unit cell contains two formula units, eight electrons are additionally introduced when Th$_2$AlH$_4$ is formed from Th$_2$Al. These
electrons form four additional bands (Fig. 5b), a large deformation of the band structure is introduced by the of hydrogen in the Th$_2$Al lattice. These bands become localized, the lowest lying energy band is moved from $-7.34$ to $-9.20$ eV, and, the character of the latter band is changed from Al 3s to H 1s character. The Al 3s bands are located in a wide energy range from $-2.8$ to $-7.34$ eV in Th$_2$Al and are in a narrow energy range from $-2.5$ to $-4.2$ eV in the hydride. The drastic change in the Al bands on hydrogenation of Th$_2$Al is due to the electron transfer from H to Al and this is discussed further in Sec. III E. The H s bands are found in the energy range from $-2$ eV to the bottom of the valence band. Their contribution at $E_F$ is negligibly small indicating the formation of localized bands. The bands at $E_F$ is dominated by the Al 3p and Th 6d electrons in both Th$_2$Al and Th$_2$AlH$_4$. Owing to the creation of the pseudogap feature near $E_F$, the contribution of the Al 3p electrons to the bands at $E_F$ level are significantly reduced by the hydrogenation of Th$_2$Al.

E. Nature of Chemical Bonding

1. Density of state

In order to obtain a deeper insight into the changes in chemical bonding behavior on hydrogenation of Th$_2$Al we give the angular-momentum and site-decomposed DOS for Th$_2$Al and Th$_2$AlH$_4$ in Fig. 6. DOS features for Th$_2$Al and Th$_2$AlH$_4$ show close similarity. Both exhibit metallic character since there is finite DOS at $E_F$. From the DOS histogram we see that $E_F$ is systematically shifted towards higher energy in Th$_2$AlH$_4$. This is due to the increase in the number of valence electrons when Th$_2$Al is hydrogenated. DOS for both Th$_2$Al and Th$_2$AlH$_4$ lie mainly in four energy regions (a) the lowest region around $-20$ eV stems mainly from localized or tightly bound Th 6p states, (b) the region from $-9.25$ to $-2.5$ eV originates from bonding of H 1s, Al 3p and Th 6d (Th-6d and Al-3p states in Th$_2$Al), (c) the region from $-2.5$ to 0 eV comes from bonding states of Al 3p and Th 6d and (d) the energy region just above $E_F$ (0 to 3.5 eV) are dominated by unoccupied Th 4f states.

The semi-core Th 6p states are well localized and naturally their effect on bonding is very small. On comparing the Th 6p DOS of Th$_2$Al and Th$_2$AlH$_4$, it is seen that the width is significantly reduced in Th$_2$AlH$_4$ owing to the lattice expansion and the inclusion of additional energy levels below $E_F$. In the valence band region, the band width and DOS are larger for Th$_2$AlH$_4$ than for Th$_2$Al. Hydrogenation enhances interaction between neighboring atoms and thereby increases the overlap of orbitals and in turn results in the enlarged valence band width in Th$_2$AlH$_4$. In particular, the strong hybridization between Th 6d and H 1s states increases the valence band width from 7.1 eV in Th$_2$Al to 8.4 eV in Th$_2$AlH$_4$. Th 6d, Al 3p and H 1s states are energetically degenerate in the valence band region indicating a possibility of covalent Th-H, Th-Al and Al-H bonds. However, the spatial separation Th-Al (3.22 Å) and Al-H (3.02 Å) is larger than Th-H (2.26 Å). Therefore, covalent bonds between the former part is small whereas there is a significant covalent contribution between Th and H. In conformity with this the COHP and charge density analyses show directional bonding between Th and H (see Sec. III E 2 and III E 3). The accommodation of H in the interstitial position between Th and Al creates new bonding states between Th and H. This also enhances Th-Al distance around 2.2% compared with that in Th$_2$Al. The consequence of this enhancement is that the Al DOS at the valence band region becomes
narrow and the splitting between the Al 3s and 3p states is almost doubled (see Fig. 6). The finite DOS at $E_F$ which gives the metallic character of Th$_2$Al and Th$_2$AlH$_4$ comes from Th$d$ states in addition to some states of Al $p$ character.

Another interesting feature of the total DOS of Th$_2$AlH$_4$ is presence of a deep valley around $E_F$ which is termed as a pseudogap. Pseudogap features are formed not only in crystalline solids but occur also in amorphous phases and quasicrystals. Two mechanisms have been proposed for occurrence of pseudo gap in binary alloys, one attributed to ionic features and the other to the effect of hybridization. Although the electronegativity differences between Th, Al and H are noticeable, they are not large enough to explain the pseudogap in Th$_2$AlH$_4$. Hence hybridization must be the cause for creation of the pseudogap in Th$_2$AlH$_4$. There is a correlation between the occurrence of pseudogaps and structural stability, that materials which possess pseudogaps in the vicinity of $E_F$ usually have higher stability. This may be the reason for the higher value of $\Delta H$ in Th$_2$AlH$_4$ than in Th$_2$Al (Table III).

2. Charge density

The analysis of the bonding between the constituents will give better understanding about the anisotropic changes in the structural parameters on hydrogenation of Th$_2$Al. Fig. 7 shows the calculated valence charge density (obtained directly from the self-consistent calculation) within $ab$ and $ac$ planes for Th$_2$AlH$_4$. Th, Al and H atoms are confined to layers along $c$, Th and Al being situated in alternating metal layers with hydrogen in between, hence establishing a sequence of Th-H-Al-H-Th-H-Al-H-Th layers (see Fig. 1). The H atoms are arranged in a chain like manner within the $ab$ plane as also evident from Fig. 7b. It is interesting to note that the nature of H-H bonding is quite different along $a$ and $c$. Although the H-H distance is 2.34 Å within the basal plane and 1.95 Å perpendicular to the basal plane, the bonding between the H atoms is not totally dominated by the latter interactions. In fact the COHP analysis (sec. III E 3) shows that the covalent H-H interaction within the $ab$ plane is larger than within $ac$ plane. The electron distribution between Al and H suggests ionic bonding between them, in line with their electronegativity difference of 0.7. In conformity with this the integrated charge inside the Al sphere is around 0.59 (0.8 according to the TBLMTO method) electrons larger in Th$_2$AlH$_4$ than in Th$_2$Al.

The bonding between Th and H is predominantly covalent as evidenced by the finite charge between these atoms. The H-s electrons are tightly bound to the Th-$d$ states, and Th-H arrangement forms a H-Th-H dumb-bell pattern. Now we will try to obtain a possible explanation for the short H-H distance within $ac$ plane of Th$_2$AlH$_4$ from the charge density analysis. The strong covalent interaction between Th and H in the $ac$ plane (see Fig. 7b) and the dumb-belled pattern tend to draw the electrons of H towards Th leaving only a small amount of electrons between the H along $c$ to repel each other. The main reason for this short H-H distance is then reduced repulsion rather than bonding interaction between them.
3. COHP

COHP is an extremely useful tool to analyze covalent bonding interaction between atoms, the simplest approach being to investigate complete COHP between the atoms concerned, taking all valence orbitals into account. COHP between Th-H, Th-Al, Al-H and H-H in \( \text{Th}_2\text{AlH}_4 \) are given in Fig. 9.

Owing to the very different interatomic distances between the H atoms in the \( ab \) and \( ac \) planes, special attention is paid to COHP in these planes. Both bonding and antibonding states are present almost equally in the VB region indicating that covalent interaction between the H atoms is not participating significantly to the stability of \( \text{Th}_2\text{AlH}_4 \). On the other hand, the bonding states are present in the whole VB region in COHP of Th-Al and Th-H indicating that covalent interaction between these pairs is contributing to structural stability. The presence of the large bonding states in the VB region of COHP for Th-H is the main reason for large value of heat of formation for \( \text{Th}_2\text{AlH}_4 \) compared with \( \text{Th}_2\text{Al} \). In order to quantify the covalent interaction between constituents of \( \text{Th}_2\text{AlH}_4 \) we have integrated the COHP curves up to \( E_F \) for Th-Al, Th-H and Al-H giving \(-0.778\), \(-1.244\) and \(-0.072\), respectively. Owing to the presence of both bonding and antibonding states below \( E_F \) in COHP the integrated value for H-H becomes negligibly small \((−0.086\) and \(-0.011\) within the \( ac \) and \( ab \) plane, respectively, but as the integrated value of bonding states alone is \(-0.571\) and \(-0.136\) respectively, the bonding H-H interaction is quite different in the two planes). Hence, one can conclude that the bond strength between the constituents of \( \text{Th}_2\text{AlH}_4 \) decrease in the order Th-H > Th-Al > Al-H > H-H.

The experimental and theoretical studies show highly anisotropic changes in the lattice expansion on hydrogenation of \( \text{Th}_2\text{Al} \). According to the crystal structure of \( \text{Th}_2\text{Al} \) the interatomic distance between the interstitial regions where one can accommodate H in the \( ab \) plane is 2.4 Å. Hence, there is a large flexible space for accommodation of the H atoms in this plane without the need to expand the lattice. In contrast, the interatomic distance between the interstitial regions in the \( ac \) plane is only 1.65 Å. So, large expansion of the lattice along \( c \) is necessary to accommodate H within the \( ac \) plane. As a result, even with a short H-H separation of 1.95 Å, a volume expansion of 12.41% is needed when \( \text{Th}_2\text{AlH}_4 \) is formed from \( \text{Th}_2\text{Al} \). The experimental observation of 0.105% lattice expansion along \( a \) and 12.15% along \( c \) is found to be in excellent agreement with theoretically obtained value of 0.03 and 12.41%, respectively.

IV. CONCLUSION

This study reports a detailed investigation on the electronic structure, bonding nature and ground state properties of \( \text{Th}_2\text{Al} \) and \( \text{Th}_2\text{AlH}_4 \) using first-principle method. The following important conclusions are obtained.

1) \( \text{Th}_2\text{Al} \) and \( \text{Th}_2\text{AlH}_4 \) are formed in the \( \text{CuAl}_2 \)-type crystal structure, the optimized atomic positions and lattice parameters are in very good agreement with recent experimental results.
2) Structural optimization gave a shortest H-H separation of 1.95 Å, which is close to the recent experimental value of 1.97 Å.
3) We observed a highly anisotropic volume expansion of 12.47% of the Th$_2$Al matrix on hydrogenation to Th$_2$AlH$_4$, of which 99.76% volume expansion occurs perpendicular to the basal plane and negligible change along the basal plane.

4) The large difference in interatomic distance between the interstitial regions within the $ab$ and $ac$ planes and the strong covalent interaction between Th and H along $c$ keeps the H atoms close together in the $c$ direction. This is the main reason for highly anisotropic volume expansion on hydrogenation in Th$_2$Al.

5) Charge density and COHP analysis revealed that the Th-H bonds are stronger than the H-H bonds and other localized bonds in this structure. The formation of strongly bonded ThH$_2$ subunits in Th$_2$AlH$_4$ makes repulsive interaction between the H atoms smaller along $c$ and this is the precise reason for the violation of 2 Årule.

6) There is a correlation between $c/a$ and the structural stability of hydrated CuAl$_2$-type phases. For phases with $c/a < 0.825$ the symmetry changes from $I_4/mcm$ to $P_4/nnc$ on hydrogenation, whereas for $c/a > 0.825$ the crystal symmetry is not affected on hydrogenation.

7) Density of states and bandstructure studies show that Th$_2$Al and Th$_2$AlH$_4$ are having non vanishing N(E$_F$), resulting in metallic character. The cohesive energy analysis show that, Th$_2$AlH$_4$ is more stable than Th$_2$Al.

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### TABLE I. Atomic position of Th$_2$Al and Th$_2$AlH$_4$

|       | Th$_2$ Al       | Th$_2$AlH$_4$ |       |
|-------|----------------|---------------|-------|
|       | x   | y   | z   | x   | y   | z   |
| Th    |     |     |     |     |     |     |
| Theory| 0.1583 | 0.6583 | 0.0000 | 0.1632 | 0.6632 | 0.0000 |
| Exp. 17 | 0.1588 | 0.6588 | 0.0000 | – | – | – |
| Exp. 9 | – | – | – | 0.1656 | 0.6656 | 0.0000 |
| Exp. 5 | – | – | – | 0.162 | 0.662 | 0.0000 |
| Al    |     |     |     |     |     |     |
| Theory| 0.0 | 0.0 | 0.25 | 0.0 | 0.0 | 0.25 |
| Exp. 17 | 0.0 | 0.0 | 0.25 | – | – | – |
| Exp. 9 | – | – | – | 0.0 | 0.0 | 0.25 |
| Exp. 5 | – | – | – | 0.0 | 0.0 | 0.25 |
| H     |     |     |     |     |     |     |
| Theory| – | – | – | 0.3705 | 0.8705 | 0.1512 |
| Exp. 9 | – | – | – | 0.3707 | 0.8707 | 0.1512 |
| Exp. 5 | – | – | – | 0.368 | 0.868 | 0.137 |

### TABLE II. Lattice parameters and inter atomic distances of Th$_2$Al and Th$_2$AlH$_4$(all values are in Å).

|       | Th$_2$ Al       | Th$_2$AlH$_4$ |       |
|-------|----------------|---------------|-------|
|       | Theory | Exp. 17 | Theory | Exp. 17 | Exp. 5 |
| a     | 7.602 | 7.618 | 7.604 | 7.626 | 7.629 |
| c     | c = 5.723 | 5.862 | 6.433 | 6.515 | 6.517 |
| c/a   | 0.753 | 0.769 | 0.846 | 0.854 | 0.854 |
| Th-H  | – | – | 2.273 | 2.305 | 2.387 |
| Th-Al | 3.199 | 3.219 | 3.269 | 3.278 | 3.291 |
| Th-Th | 3.403 | 3.421 | 3.509 | 3.571 | 3.495 |
| Al-H  | – | – | 3.051 | 3.061 | 3.072 |
| Al-Al | 2.861 | 2.931 | 3.216 | 3.257 | 3.258 |
| H-H (ac-plane) | – | – | 1.945 | 1.971 | 1.790 |
| H-H (ab-plane) | – | – | 2.344 | 2.305 | 2.495 |

### TABLE III. Ground state properties of Th$_2$Al and Th$_2$AlH$_4$

| Compound |                | Th$_2$Al | Th$_2$AlH$_4$ |
|----------|----------------|----------|---------------|
| – ΔH (in kJ mol$^{-1}$) | 18.35 | 29.50 |
| $E_{coh}$(eV/atom) | 0.15 | 0.185 |
| $N(E_F)$(states/Ry-cell) | 58.42 | 41.13 |
| $B_0$(GPa) | 93.42 | 111.36 |
| $B'_0$ | 3.41 | 3.48 |
FIGURES

FIG. 1. The crystal structure of Th$_2$AlH$_4$. Five Th in face sharing tetrahedral configuration surrounding two hydrogen. Legends to the different kinds of atoms are given on the illustration.

FIG. 2. Total energy (a) vs. c/a and (b) vs. unit cell volume for Th$_2$Al where $\Delta E = E + 106632$.

FIG. 3. The total energy (a) vs. c/a and (b) vs. unit cell volume for Th$_2$AlH$_4$ where $\Delta E = E + 106636$.

FIG. 4. c/a for CuAl$_2$-type phases and their corresponding hydrides.

FIG. 5. Electronic band structure of (a) Th$_2$Al and (b) Th$_2$AlH$_4$. The Fermi level is set to zero.

FIG. 6. Total, site and orbital projected density of states for (a) Th$_2$Al and (b) Th$_2$AlH$_4$.

FIG. 7. Valence electron charge density plot for Th$_2$AlH$_4$ in the $ab$ plane with 40 contours drawn between 0 and 0.25 electrons/a.u.$^3$.

FIG. 8. Valence electron charge density plot between the Th and H atoms for Th$_2$AH$_4$ in the $ac$ plane with 40 contours drawn between 0 and 0.25 electrons/a.u.$^3$.

FIG. 9. COHP of Th$_2$AlH$_4$, depicting the contributions from Th-Al, Th-H, Al-H and H-H interactions. The COHP for H atoms in the $ab$ plane and $ac$ plane are given in solid line and dotted lines respectively.
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Figure (a) shows the variation of $\Delta E$ (in Ry/f.u.) with $c/a$. Figure (b) illustrates the change in cell volume (f.u.$^3$) for different values of $c/a$. The graphs exhibit a minimum at a specific $c/a$ ratio, indicating the optimal structural condition for the system.
Cell volume (f.u.)

-0.375
-0.325
-0.275
-0.225
-0.175
0.82 0.84 0.86

\(\Delta E\text{(Ry/f.u.)}\)

(a)

-0.3745
-0.3755
-0.3765
0.82 0.84 0.86

(b)

-0.175
-0.225
-0.275
-0.325
-0.375

Cell volume (f.u.)

475 525 575 625 675 725
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This figure "fig8.jpg" is available in "jpg" format from:

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