Gordon J. Miller*, Ranuri S. Dissanayaka Mudiyansele and Weiwei Xie

Theoretical investigations of hydrogen absorption in the A15 intermetallics Ti_3Sb and Ti_3Ir

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Abstract: Ti_3Sb and Ti_3Ir adopt the A15 (Cr_3Si type) structure and are reported to incorporate hydrogen atoms to an extent, respectively, of $\text{Ti}_3\text{SbH}_{\sim 3}$ and $\text{Ti}_3\text{IrH}_{3.8}$. First-principles electronic structure calculations were performed to identify factors contributing to the difference in maximum hydrogen composition for these two intermetallic compounds. Relative energies and changes in energy densities of states and crystal orbital Hamilton populations upon H insertion in the intermetallic compounds were examined. In both compounds, hydrogen atoms are attracted to $[\text{Ti}_4]$ tetrahedral interstitial sites over any others. The natures of metal-hydrogen and metalloid-hydrogen bonding and the effects of hydrogen insertion on metal-metal and metal-metalloid bonding have an influence on the maximum hydrogen contents for Ti_3Sb and Ti_3Ir .

Keywords: A15 compounds; electronic structure; hydrides; intermetallic compounds.

Dedicated to: Professor Richard Dronskowski of the RWTH Aachen on the occasion of his 60th birthday.

1 Introduction

The absorption of hydrogen in metals and intermetallics has interested chemists, physicists, materials scientists, and material engineers over many decades for fundamental and applied scientific reasons. For example, hydrogen uptake in intermetallic compounds may cause a change of crystal structure [1, 2], which can lead to embrittlement or to significant changes in the physical properties [3, 4]. In superconducting compounds, for

example, hydrogen absorption lowers and eliminates the superconducting transition temperature [5, 6]. With regards to applied sciences, metal and intermetallic hydrides can store hydrogen for use in a “hydrogen economy”, but useful weight percent hydrogen and reversibility of hydrogen uptake and release are persistent challenges [7, 8].

An important class of intermetallic compounds is the set of cubic A15 compounds, which have the nominal composition A_3B , and show some of the highest superconducting transition temperatures for intermetallics [9–12]. Many of them absorb considerable amounts of hydrogen without changing structure and exhibit a linear expansion of the lattice parameter as the hydrogen concentration increases. Of these compounds, only a few have been examined by neutron diffraction to locate the hydrogen or deuterium atoms, such as Nb_3SnH_n [13], Ti_3SbD_n [14] and Ti_3IrD_n [15]. More numerous are the studies of hydrogen composition to determine the maximum hydrogen content, which varies from $\text{Nb}_3\text{SnH}_{1.0}$ to $\text{Nb}_3\text{PtH}_{5.1}$ [16]. For the related pair Ti_3SbH_n and Ti_3IrH_n , the maximum values of n are, respectively, ~ 3 [17] and 3.8 [18] with Ti_3IrH_n reported to have a two-phase region for n between 0.9 and 2.3. Furthermore, superconductivity is eliminated generally before the maximum hydrogen composition is reached, e.g., in Ti_3SbH_n no superconductivity is observed for $n \geq 1$ [19].

This communication attempts to elucidate factors in the electronic structures of Ti_3SbH_n and Ti_3IrH_n ($n \geq 0$) that contribute to their maximum hydrogen compositions and site preferences.

2 Structural features and physical characteristics of Ti_3Sb and Ti_3Ir

The structure of A15 intermetallics A_3B involves a bcc network of late or post transition elements B that are icosahedrally surrounded by an early transition metal atoms A. The superconductivity observed for many of these compounds is generally attributed to three mutually perpendicular, nonintersecting, and yet moderately interacting chains of the early transition metals [20]. In the cubic unit cell, space group $\text{Pm}\bar{3}\text{n}$, B atoms occupy $2a$ sites (0, 0, 0) with T_h point symmetry, and A atoms occupy $6c$

*Corresponding author: Gordon J. Miller, Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA, E-mail: gmiller@iastate.edu

Ranuri S. Dissanayaka Mudiyansele and Weiwei Xie, Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA

sites ($1/4, 0, 1/2$) with D_{2d} point symmetry. A purely geometrical analysis of the structure leads to the increasing sequence of internuclear separations (a_0 = cubic lattice parameter): A – A ($2\times; 0.5a_0$), A – B ($12\times; 0.559a_0$), A – A ($8\times; 0.612a_0$), B – B ($8\times; 0.866a_0$).

When hydrogen atoms enter intermetallic structures, they often occupy tetrahedral interstices and occasionally fill octahedral or trigonal planar voids [21]. In the A15 structure, there are 46 tetrahedral voids and 32 $[A_3]$ trigonal planar positions per unit cell. As shown in Figure 1, the tetrahedral sites occur in three inequivalent sets: $6c$ sites ($1/4, 1/2, 0$) surrounded by 4 A atoms $[A_4]$; $16i$ sites (x, x, x ; $x \sim 0.19$) surrounded by 3 A atoms and 1 B atom $[A_3B]$; and $24k$ sites ($x, y, 0$; $x \sim 0.33, y \sim 0.13$), also coordinated by $[A_3B]$ units. With respect to polyhedral volumes, these tetrahedra increase in size from $24k$ to $6d$ to $16i$. The two types of A_3 trigonal planar sites are $24k$ ($x', y', 0$; $x' = 0.42, y' = 0.17$) and $8e$ ($1/4, 1/4, 1/4$), which are really both trigonal bipyramidal sites. The $8e$ trigonal planar sites have two B atoms on opposite axial positions, whereas the $24k$ trigonal planar sites have one A and one B atom on opposite axial positions.

There are some differences between Ti_3Sb and Ti_3Ir that can affect their hydrogen absorption capacities and the corresponding effects on physical properties. To the best of our knowledge, neither binary phase diagram has been completely characterized. The current Ti–Sb phase diagram is based on sparse microstructural data, but Ti_3Sb may be an interstitially stabilized phase [22, 23]. However, samples for the study of $Ti_3SbD_{2.6}$ were prepared from “ Ti_3Sb ” using high-purity elements, so it may indeed exist [14]. On the other hand, more is known about the Ti–Ir phase diagram [24]. Ti_3Ir melts peritectically and is the lower limit of the homogeneity range Ti_3Ir – $Ti_{2.92}Ir_{1.08}$ (25–27 atomic percent Ir).

Concerning their structural and physical characteristics, the lattice parameter a_0 (Ti_3Ir) is less than $a_0(Ti_3Sb)$, an outcome that can be attributed to the lanthanide contraction which affects the sizes of the sixth period transition metals relative to their fifth period analogues. Compounds of the type Ti_3SbH_n are reported as single phases for most of $n \leq 3$ [17], while superconductivity becomes unobserved for $n > 1$ [19]. A neutron diffraction study on $Ti_3SbD_{2.6}$ indicates deuterium atoms to be exclusively at the $6d$ tetrahedral sites [14]. On the other hand, Ti_3IrH_n is reported to show a two-phase region in the range of hydrogen composition $0.9 < n < 2.3$, with the maximum n value approaching ~ 3.8 [18]. Again, neutron powder diffraction experiments have demonstrated that the $6d$ site is preferentially occupied for $n < 1$, while a fraction of tetrahedral $24k$ sites are occupied for $n = 3.6$ [15]. Both Ti_3SbH_n and Ti_3IrH_n show a linear expansion of the lattice parameter with increasing hydrogen content [18, 19]. From hydrogen absorption isotherms of Ti_3IrH_n in the temperature range 820–1070 K, the partial enthalpies of solution have been determined to range between -20 kJ mol^{-1} ($n = 3.8$) to -32 kJ mol^{-1} ($n \sim 2.8$) [18].

Given the larger unit cell volume for Ti_3Sb over Ti_3Ir , it is at first surprising that *more* hydrogen atoms can be incorporated into Ti_3Ir than into Ti_3Sb . This observation precludes H···H repulsions as the crucial factor determining the maximum hydrogen concentration levels in each compound. Furthermore, the minimum H···H distance between $6d$ sites is $0.5a_0$, which exceeds the value of $2.1 \text{ \AA}$ (the accepted minimum distance between hydrogen atoms in intermetallic compounds [1]) in each system. Surrounding each $6d$ interstitial site, there are 24 neighboring $24k$ tetrahedral sites, 4 of which occupy $[A_3B]$ tetrahedra that share faces with the $[A_4]$ tetrahedron of the $6d$ site and violate the $2.1 \text{ \AA}$ criterion. Therefore, if $24k$ sites are filled with H atoms, then these neighboring $6d$ sites

Figure 1: Tetrahedral sites showing the H atoms surrounded by (a) $[A_4]$ in $6d$ sites, (b) $[A_3B]$ in $16i$ sites, and (c) $[A_3B]$ in $24k$ sites.

must be vacant, or vice versa. Given these geometrical restrictions and the characteristics observed for Ti_3SbH_n and Ti_3IrH_n , there must be significant influences from the electronic structures of these compounds that contribute to their chemistry with hydrogen.

3 Theoretical methods

3.1 WIEN2K

The electronic band structure and the density of states of Ti_3Sb , Ti_3Ir , and their hydrides were calculated with LDA type (local density approximation) pseudopotentials using the WIEN2K program, which utilizes the full-potential linearized augmented plane wave method (FP-LAPW) [25, 26]. The optimized lattice parameters from WIEN2K for Ti_3Sb and Ti_3Ir were used in the electronic structure calculations and spin-orbit coupling effects were applied to all atoms. The reciprocal space integrations were completed over an $(8 \times 8 \times 8)$ Monkhorst-Pack k -point mesh. The convergence of total energies for the self-consistent calculations was taken as 0.1 meV per atom. The total energies for different distributions of Ti and Sb/Ir among the $2a$ and $6c$ sites were also examined. For that, supercells were created to achieve different extents of switching Ti and Ir/Sb atoms within the optimized rigid structure in both Ti_3Sb and Ti_3Ir (see Supplementary Figure S1).

3.2 Tight-Binding Linear Muffin-Tin Orbital Approach

The electronic structures of Ti_3Sb , Ti_3SbH_n , Ti_3Ir , and Ti_3IrH_n were calculated using the self-consistent, scalar relativistic linearized muffin-tin orbital (TB-LMTO) program of Andersen et al. [27–29] within the atomic sphere and frozen core approximations. The combined correction terms were included, and the exchange-correlation potential of density-functional theory was calculated within the local density approximation using the method of Barth and Hedin [30]. The Wigner-Seitz (WS) radius for each atom in the intermetallics was determined by calculating the Hartree potential for the compound using neutral atom charge densities, and then scaling until the volume of the unit cell equaled the sum of the volumes of all WS spheres in the unit cell. Integrations over reciprocal space were carried out by the tetrahedron method and utilized over 300 k -points in the irreducible wedge of the first Brillouin zone. The basis sets consisted of valence s , p , and d orbitals of Ti, Sb, Ir. $4f$ orbitals of Ir were included using a

downfolding procedure [31]. Crystal orbital Hamilton population (COHP) curves and their integrated values were determined using a procedure developed for density-functional theory-based calculations by Dronskowski and Blöchl [32].

4 Total energy analysis

Total energy optimizations for Ti_3Sb and Ti_3Ir yielded calculated lattice parameters that are, respectively, 2.2 and 2.7% smaller than the experimental lattice parameters. Using these energy optimized lattice parameters, three different structural models arising from mixing the Ti and Sb or Ir atoms among the $2a$ and $6c$ sites in A15-type Ti_3Sb and Ti_3Ir were constructed and their total energies calculated using the WIEN2K program. Supplementary Figure S1 illustrates these models and Supplementary Tables S1 and S2 summarize the atomic positions and the calculated total energies for each model. For Ti/Sb mixing in Ti_3Sb , all models reveal a significant energetic penalty of 628–697 meV per formula unit (7290–8090 K). Mixing Ti and Ir in Ti_3Ir is also energetically prohibitive by 167–401 meV per formula unit (1940–4650 K), but not to the extent observed for Ti_3Sb . As a result of these outcomes, we have examined hydrogen absorption using the completely ordered A15 structures of Ti_3Sb and Ti_3Ir .

To assess the energetics of inserting H atoms into various sites, Table 1 lists total energies per formula unit and per H atom of Ti_3XH_n ($X = \text{Sb, Ir}$) relative to those of Ti_3X . In both cases, filling the $6d$ [Ti_4] tetrahedra is preferred over occupying $16i$ and $24k$ [Ti_3X] tetrahedra. As H atoms sequentially fill the $6d$ [Ti_4] tetrahedra in both Ti_3Sb and Ti_3Ir , the relative total energy per H atom remains stabilizing but steadily becomes less negative, an outcome which is indicative of intermediate range H...H repulsions within the structures as H content increases. Occupying other tetrahedra, such as the $16i$ [Ti_3Sb] sites, is much less favorable. Also, these results suggest that the maximum H content for Ti_3Sb is Ti_3SbH_3 , but is $\text{Ti}_3\text{IrH}_{3.5}$ for Ti_3Ir .

5 Electronic structures of Ti_3SbH_n and Ti_3IrH_n

To analyze the maximum hydrogen content in Ti_3Sb and Ti_3Ir , the electronic density of states (DOS) curves and crystal orbital Hamilton population (COHP) curves for various pairwise interactions were calculated using the TB-LMTO method for Ti_3X ($X = \text{Sb, Ir}$), Ti_3XH_3 (H filling all

Table 1: The total energies of hydrogen addition into different tetrahedra in Ti_3SbH_n and Ti_3IrH_n relative to the energies, respectively, of Ti_3Sb and Ti_3Ir (calculated total energies are listed in Supplementary Table S3).

Compound	H site	Relative total energy per formula unit (eV)	Relative Total Energy per H atom (eV)
Ti_3Sb		0	0
Ti_3SbH	$6d$	-33.60	-16.80
	$24k$	-31.74	-15.87
	$16i$	-32.00	-16.00
Ti_3SbH_2	$6d$	-66.28	-16.57
Ti_3SbH_3	$6d$	-98.57	-16.43
$\text{Ti}_3\text{SbH}_{3.5}$	$6d + 24k$	-113.40	-16.20
Ti_3SbH_4	$16i$	-117.82	-14.73
Ti_3Ir		0	0
Ti_3IrH	$6d$	-32.77	-16.39
	$24k$	-32.16	-16.08
	$16i$	-32.33	-16.17
Ti_3IrH_2	$6d$	-64.49	-16.12
Ti_3IrH_3	$6d$	-96.28	-16.05
$\text{Ti}_3\text{IrH}_{3.5}$	$6d + 24k$	-112.66	-16.09
Ti_3IrH_4	$16i$	-121.88	-15.24

$6d$ sites), and $\text{Ti}_3\text{XH}_{3.5}$ (H occupying 5 $6d$ + 2 $24k$ sites). The DOS curves for Ti_3X (X = Sb, Ir) and Ti_3XH_3 (H filling all $6d$ sites) were also calculated including spin-orbit coupling using the WIEN2K program, which gave qualitatively similar results to TB-LMTO calculations.

5.1 Ti_3Sb and Ti_3Ir

Sb and Ir share a subtle similarity in their atomic electronic configurations: both elements can accept three electrons to achieve a closed shell or subshell configuration. Upon filling its valence $5p$ orbitals, “Sb³⁺” adopts a noble gas configuration, whereas “Ir³⁺” gives $[\text{Lu}](6s)^2(5d)^{10}$. However, their valence atomic orbital energies relative to those of Ti are significantly different, which leads to distinct energy DOS curves for Ti_3Sb and Ti_3Ir as shown in Figure 2 (Supplementary Figure S2 shows the band structures and DOS curves for both intermetallic compounds). The valence $5p$ orbitals of Sb contribute largely to a band that is 3–6 eV below the calculated Fermi level and is separated from the conduction band, which is mostly Ti $3d$ and $4s$ and in line with the relative electronegativities of Ti and Sb. A band arising mostly from Sb valence $5s$ orbitals falls 10–11.6 eV below the Fermi level, and is not included in Figure 2a. On the other hand, the conduction band of Ti_3Ir extends continuously to ~7.6 eV below its Fermi level, but the relative electronegativities of Ti and Ir reveal themselves in the projected states: Ir $5d$ and $6s$ orbitals dominate the lower portions whereas Ti $3d$ and $4s$ wavefunctions dominate the higher portions. For both Ti_3Sb and Ti_3Ir , the Fermi levels fall on peaks in the DOS curves, an outcome that can rationalize these compounds to be BCS-type superconductors.

Figure 2: DOS and COHP curves calculated by TB-LMTO for (a) Ti_3Sb and (b) Ti_3Ir . Energies are given relative to the corresponding Fermi levels. Shadings of the DOS curves indicate contributions of each elemental component: Ti, gray; Sb, green; and Ir, blue. In the COHP curves, in addition to the calculated Fermi level (0 eV), the energies corresponding to (a) maximum Ti–Ti COHP; and (b) maximum Ti–Ir COHP are indicated.

Examination of the COHP curves for both compounds offers some valuable insights. A pseudogap in the DOS curve for Ti_3Sb near 20 valence electrons per formula unit corresponds to a region of Ti–Sb and Ti–Ti nonbonding states. Maximum Ti–Sb and Ti–Ti orbital interactions occur, respectively, below and above the Fermi level for Ti_3Sb at 17 valence electrons per formula unit. As a result, a qualitative prediction for the optimal compositions for A15-type A_3B compounds involving a main group element B yields $\sim 17\text{--}21$ valence electrons per formula unit. A survey of the Inorganic Crystal Structure Database [33] shows that this range does account for the vast majority of reported cases. COHP analysis of Ti_3Ir suggests that Ti–Ir and Ti–Ti pairwise orbital interactions are not optimized so that more valence electron-rich B-metals would be tolerated. Indeed, Ti_3Ir , Ti_3Pt , Ti_3Au , and Ti_3Hg have been reported [33].

Early theoretical assessments of hydrogen uptake in metals and simple intermetallics applied a rigid-band model to the electronic DOS of the parent compound and simply shifted the positions of Fermi levels upwards by including one valence electron for each H atom to the metal/intermetallic DOS curves. According to this approximation, we see that a maximum H content might be “ Ti_3SbH_3 ” and “ $\text{Ti}_3\text{IrH}_{1.5}$ ” by achieving the next highest pseudogap in their respective DOS curves. This approach works satisfactorily for the antimonide, but fails to account for the H addition chemistry of Ti_3Ir .

5.2 Ti_3SbH_n and Ti_3IrH_n ($6d$; $n \leq 3$)

When H atoms are introduced into intermetallic compounds in general, there are two criteria that significantly influence the sites found most attractive for hydrogen: orbital overlap and relative orbital energies. According to the *overlap criterion*, because the valence 1s orbital of H has no nodal surfaces, H atoms effectively interact with metal-metal bonding orbitals in the intermetallic compounds. For Ti_3Sb and Ti_3Ir , these orbitals contribute to bands dominated by Sb or Ir atomic orbitals, as well as the lower portions of the conduction band, which is Ti–Ti bonding (see Figure 2). The *energy criterion* indicates that partially filled bands lying close in energy to the energy of the H 1s atomic orbital energy will give the greatest stabilizing interaction. In Ti_3Sb and Ti_3Ir , these bands also occur at the bottom of the conduction band, which is mostly Ti 3d with some 4s character. Since each H atom has one valence electron, the metals in the intermetallic are formally oxidized as metal-hydrogen bonding bands form and hydrogen behaves more as “hydride” than a “proton”. In

this picture, hydrogen does not completely eliminate metal-metal bonding in an intermetallic compound, but simply redistributes electron density to give strong metal-hydrogen and somewhat weaker metal-metal bonding interactions than in the parent intermetallic compound. These effects are seen when analyzing the percent contributions to the total integrated COHP values for Ti_3Sb and Ti_3SbH_3 as well as for Ti_3Ir and Ti_3IrH_3 , listed in Table 2. The additional electron provided by each hydrogen atom and the orbital energy shifts ultimately affect the position of the Fermi level, which often remains constant or increases.

Results of fitting neutron diffraction patterns of Ti_3SbD_n and Ti_3IrD_n for low H content and total energy calculations indicate that the preferred sites of H atom insertion are the $[\text{Ti}_4]$ tetrahedral $6d$ sites. Figure 3 illustrates the DOS and certain COHP curves calculated for Ti_3SbH_3 and Ti_3IrH_3 in which the $6d$ sites are fully occupied (Supplementary Figure S3 shows the DOS curves for both intermetallic hydrides). For Ti_3SbH_3 , the Fermi level falls in a pseudogap of the DOS. According to the corresponding COHP curves, both Ti–Sb and Ti–Ti orbital interactions are very nearly optimized. In comparison with the DOS curve for Ti_3Sb , we see that Ti–Ti bonding states in Ti_3Sb have been disrupted by H atom insertion and states rich in H fall 7–9 eV below the Fermi level in Ti_3SbH_3 . Therefore, filling the $6d$ sites with H atoms provides sufficient valence electrons to optimize metal-metal and metal-metalloid bonding.

Supplementary Figures S4 and S5, two sets of DOS curves illustrate how filling alternative sites or partially filling the $6d$ sites with H atoms influence the electronic structure. In summary, adding H atoms to $24k$ or $16i$ sites broadens the energy ranges of occupied states that are assigned mostly to Sb valence orbitals, but placing H atoms into $6d$ sites essentially introduces a H 1s band 6–8 eV below the Fermi level and between valence states arising from Sb 5s and 5p orbitals. As a result, the

Table 2: Percent contributions to the integrated COHP values for different pairwise interactions in Ti_3SbH_n and Ti_3IrH_n .

Interaction	Ti_3Sb	Ti_3SbH_3 (filled $6d$)	$\text{Ti}_3\text{SbH}_{3.5}$ (5 $6d$ + 2 $24k$)
Ti–Sb	32.7%	25.2%	22.5%
Ti–Ti	67.3%	35.0%	37.5%
Ti–H		39.8%	37.5%
Sb–H			2.5%
Interaction	Ti_3Ir	Ti_3IrH_3 (filled $6d$)	$\text{Ti}_3\text{IrH}_{3.5}$ (5 $6d$ + 2 $24k$)
Ti–Ir	43.4%	34.4%	31.2%
Ti–Ti	56.6%	25.9%	31.7%
Ti–H		39.7%	33.4%
Ir–H			3.7%

Figure 3: DOS and COHP curves calculated by TB-LMTO for (a) Ti_3SbH_3 and (b) Ti_3IrH_3 for H atoms occupying the $6d$ sites. In the COHP curves for (b) Ti_3IrH_3 , the energy at which the Ti–Ir COHP is maximized is indicated.

structures with H atoms in $24k$ or $16i$ sites are less stable than those derived with H atoms occupying the $6d$ sites. Furthermore, the DOS curves obtained by sequentially adding H atoms to the $6d$ sites indicates that a large DOS value at the Fermi level remains until the H content rises above ~ 1 per Ti_3Sb , i.e., Ti_3SbH . These changes in the DOS arise from how the valence $1s$ orbital of H and its 1 valence electron perturb the DOS and affect the Fermi level. This result on the DOS curves is also consistent with how the superconducting transition in Ti_3SbH_n is affected by H addition. Without further investigation, we surmise that the hydrogen interstitials create stronger vibrational modes in the structure and the density of states at the Fermi level drops, which together lead to a drop in T_c .

The picture for Ti_3IrH_3 is somewhat different from than for Ti_3SbH_3 . The Fermi level for Ti_3IrH_3 falls in a minimum of the DOS curve, but it is not a pseudogap. Furthermore, at the calculated Fermi level, neither Ti–Ir nor Ti–Ti orbital interactions are optimized; some bonding states remain unfilled. As a result, Ti_3IrH_3 with all $6d$ sites occupied by H atoms could accept more H atoms to optimize these interatomic orbital interactions. However, this would necessitate occupying sites that are close to Ir atoms and to form Ir–H bonds. Experiments and total energies indicate that occupation of $24k$ sites is preferred over occupation of $16i$ sites. However, $24k$ site tetrahedra share their faces with $6d$ tetrahedra (see Figure 4). As a result, as $24k$ sites become occupied, the neighboring $6d$ site must be vacated.

Figure 4: Structural environment for the H $6d$ site (black sphere) in A15 structures. Ti (blue); Sb/Ir (green) and $24k$ sites (red and gray) are shown. The four red atoms at $24k$ sites occupy $[\text{Ti}_3\text{X}]$ tetrahedra that share faces with the $[\text{Ti}_4]$ tetrahedra surrounding each $6d$ site.

5.3 Ti_3SbH_n and Ti_3IrH_n ($6d + 24k$; $n \geq 3$)

Figure 5 examines the electronic structures of two similar models for $\text{Ti}_3\text{SbH}_{3.5}$ and $\text{Ti}_3\text{IrH}_{3.5}$, in which one $6d$ site per cubic cell is vacated and two surrounding $24k$ sites are occupied. Therefore, each Sb or Ir atom is engaged in one bond with a H atom and there are 7 H atoms per cell or 3.5 H atoms per Ti_3X ($\text{X} = \text{Sb}, \text{Ir}$) unit. For hypothetical “ $\text{Ti}_3\text{SbH}_{3.5}$ ”, the Fermi level lies just above a minimum in the DOS curve and falls on the cusp of filling Ti–Sb antibonding states. Most noteworthy are the occupied Sb–H antibonding states falling 2–6 eV below the Fermi level. Analysis of the integrated COHP values (Table 2) indicates that interactions involving Sb atoms, i.e., Ti–Sb and Sb–H, decrease slightly compared to those in Ti_3SbH_3 . As a result, occupying any $24k$ sites with H in Ti_3SbH_n is energetically

Figure 5: DOS and COHP curves calculated by TB-LMTO for (a) $\text{Ti}_3\text{SbH}_{3.5}$ and (b) $\text{Ti}_3\text{IrH}_{3.5}$ for H atoms occupying the $6d + 24k$ sites.

unfavorable and limits the upper limit of the H content to $n = 3$.

For $\text{Ti}_3\text{IrH}_{3.5}$, the calculated Fermi level falls just above a pseudogap (deep minimum) in the DOS curve. According to the COHP curves, weakly antibonding Ti–Ir states are occupied, but only Ir–H bonding and nonbonding states are filled. Interactions with Ir, unlike those with Sb in Ti_3SbH_n , are not decreased. Therefore, Ti_3IrH_n can adopt a hydrogen content with n exceeding 3.

6 Summary

Through analysis of total energies as well as DOS and COHP curves for various Ti_3SbH_n and Ti_3IrH_n structures, the maximum H atom content can be qualitatively rationalized. In both cases, the structures adopt valence electron counts that nearly optimize heteroatomic Ti–Sb or Ti–Ir bonding as well as avoid Sb–H or Ir–H antibonding interactions. Furthermore, the nature of how H atoms affect intermetallic electronic structures shows that Ti–Ti bonding is partly exchanged for Ti–H bonding, an effect that influences their superconducting behavior.

7 Supporting information

Tables of supercell atomic coordinates and relative total energies of various structural models (Supplementary Tables S1–S3) as well as figures of supercell models (S1), DOS curves and band structures for Ti_3Sb and Ti_3Ir (S2), DOS

curves for Ti_3SbH_3 and Ti_3IrH_3 (S3) from WIEN2K, and DOS curves from TB-LMTO for $\text{Ti}_3\text{SbH}_{0.5}$ (different H sites; S4) and Ti_3SbH_n ($0 \leq n \leq 3$; S5) are given as supplementary material available online (<https://doi.org/10.1515/znb-2021-0137>).

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