Searching for hexagonal analogues of the half-metallic half-Heusler XYZ compounds

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Abstract

The XYZ half-Heusler crystal structure can conveniently be described as a tetrahedral zinc blende YZ structure which is stuffed by a slightly ionic X species. This description is well suited to understanding the electronic structure of semiconducting 8-electron compounds such as LiAlSi (formulated Li\textsuperscript{+}[AlSi]\textsuperscript{−}) or semiconducting 18-electron compounds such as TiCoSb (formulated Ti\textsuperscript{4+}[CoSb]\textsuperscript{4−}). The basis for this is that [AlSi]\textsuperscript{−} (with the same electron count as Si\textsubscript{2}) and [CoSb]\textsuperscript{4−} (the same electron count as GaSb) are both, structurally and electronically, zinc blende semiconductors. The electronic structure of half-metallic ferromagnets in this structure type can then be described as semiconductors with stuffing magnetic ions which have a local moment: for example, 22-electron MnNiSb can be written Mn\textsuperscript{3+}[NiSb]\textsuperscript{3−}. The tendency in the 18-electron compound for a semiconducting gap—believed to arise from strong covalency—is carried over in MnNiSb to a tendency for a gap in one-spin direction. Here we similarly propose the systematic examination of 18-electron hexagonal compounds for semiconducting gaps; these would be the ‘stuffed wurtzite’ analogues of the ‘stuffed zinc blende’ half-Heusler compounds. These semiconductors could then serve as the basis for possibly new families of half-metallic compounds, attained through appropriate replacement of non-magnetic ions by magnetic ones. These semiconductors and semimetals with tunable charge carrier concentrations could also be interesting in the context of magnetoresistive and thermoelectric materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Half-metallic ferromagnets [1, 2], in contrast to more usual ferromagnets, are completely spin polarized, possessing a gap in one-spin direction at the Fermi energy $E_F$. Recent interest in the idea that solid state devices can function through manipulation of the spin of electrons [3, 4] has given rise to a wealth of research in the area of half-metals, which play an important role in spin-injection [5, 6]. An important fundamental question is what makes some ferromagnets half-metals, whilst others are not. This question has been addressed across large classes of materials such as the system Fe\textsubscript{1−x}Co\textsubscript{x}S\textsubscript{2} [7, 8], in proposed epitaxial transition metal compounds with the zinc blende structure [9], in some chromium chalcogenide spinels [10, 11] and in the half-Heusler [1, 12, 13–15] and Heusler [16–18] compounds, CrO\textsubscript{2} [19, 20] and some members of the colossal magnetoresistive manganites [21]. With the exception of the perovskite manganites, in all these different classes of half-metallic compounds, an interesting common theme that emerges is the...
existence of a band semiconductor that is quite proximal in terms of composition and electron count.

As an example, in $\text{Fe}_{x-1}\text{Co}_x\text{S}_2$ perhaps the first series of compounds that were reported with integer moments on the magnetic substituents [22], the starting point is semiconducting $\text{FeS}_2$ whose empty $e_g$ band is populated through Co substitution. Similarly, the basis for zinc blende half-metalics [9, 23] is the replacement of cations in a semiconductor with magnetic ions: Half-metallic zinc blende $\text{CrAs}$ can be considered the magnetic analogue of $\text{GaAs}$, or perhaps even more appropriately, as the magnetic analogue of zinc blende $\text{ScAs}$, with the semiconducting gap being retained in the magnetic compound albeit in one-spin direction. Similar analogies can be drawn for systems such as rutile $\text{CrO}_2$ [19, 20].

One of the best studied systems of half-metalics are the half-Heusler compounds $\text{XYZ}$ exemplified by $\text{MnNiSb}$ [1]. Whangbo and coworkers pointed [13] out that the 18-electron half-Heusler compounds must be non-magnetic and semiconducting, with earlier hints along these lines from deGroot [24]. Recently, Galanakis [12] has placed these half-Heusler compounds on a systematic footing, suggesting that in the half-metallic compositions, the magnetic moment obtained from the saturation magnetization $M$, per formula unit, should vary as $M = Z_t - 18$, where $Z_t$ is the total number of valence electrons. Some of us [14] have examined the role that covalency plays and have proposed that the half-Heusler compounds are both structurally and electronically best treated as an $X$ ion stuffing a zinc blende $YZ$ structure. When the $X$ ion is non-magnetic and $Z_t = 18$, the compound is a band semiconductor. If $X$ is magnetic and $Z_t \neq 18$, such as in $\text{MnNiSb}$ with $Z_t = 22$, the compound is a half-metallic ferromagnet, with, in the case of $\text{MnNiSb}$, a magnetic moment of $4\mu_B$ per formula unit.

In this contribution, we ask the following question: if $\text{XYZ}$ stuffed zinc blende compounds with $Z_t = 18$ are semiconducting, can similar 18-electron semiconductors be found amongst 18-electron $\text{XYZ}$ stuffed wurtzites, given that wurtzite and zinc blende are simply stacking variants of one another with very similar topologies and hence bonding patterns. We suggest the answer is yes, and examine different closely related hexagonal $\text{XYZ}$ compounds: $\text{ScCuSn}$, $\text{LaCuSn}$ and $\text{YCuSn}$. We use this to propose related magnetic compounds that would potentially comprise a novel class of half-metallic $\text{XYZ}$ compounds with hexagonal crystal structure.

Hexagonal $\text{XYZ}$ compounds with cerium, europium, ytterbium and uranium as the $X$ atom have been investigated in the last 20 years in light of their unusual properties. Examples include valence fluctuations in $\text{EuPtP}$ [25], the Verwey type transition in $\text{EuNiP}$ [26], intermediate-valent $\text{YbCuAl}$ [27], the 10 K ferromagnet $\text{CeAuGe}$ [28], the Kondo system $\text{CePtSn}$ [29] and the heavy fermion material $\text{CePtSi}$ [30]. $\text{CeRhAs}$ is a Kondo semiconductor in the stuffed wurtzite structure, which undergoes an electronic transition at high temperature and pressure into a metallic phase simultaneously with a structural transition into the $\text{TiNiSi}$ structure [31]. The rare-earth–$\text{Pd–Sb}$ system is particularly interesting since $\text{CePdSb}$ is a 17 K Kondo ferromagnet with a resistance minimum, while many members of this series prepared with other magnetic rare-earths are antiferromagnetic [32]. The tunability of electronic structure and the charge carrier density in this structure type make the compounds of this structure type interesting for magnetoresistance effects [33, 34], and it is likely that they would be a fertile class of thermoelectric compounds as well.

2. Computational methods

Density functional theory-based electronic structure calculations reported here were performed using the linear muffin tin orbital method [35] within the local spin density approximation. The crystal structure inputs for the calculations were obtained from experimental data in the literature, except when hypothetical structures are considered. Crystal orbital Hamiltonian populations (COHP) [36] and the electron localization function (ELF) [37, 38] were used to obtain insights into bonding in the title compounds, respectively, in terms of the strengths of individual bonds, as well as in real space.

3. Results and discussion

3.1. Crystal structures of the hexagonal compounds $\text{XCuSn}$

A huge variety of the equiatomic intermetallic compounds $\text{XYZ}$ ($X = \text{rare-earth}, \ Y = \text{late transition metal element}, \ Z = \text{main group element}$) crystallize in structure types related to the $\text{AlB}_2$ family. The ordered superstructures crystallize in the $\text{LiGaGe}$, $\text{NdP}_3\text{Sb}$ and $\text{ZrBeSi}$ type structures. The late transition metals and the main group elements form $Y_2Z_2$ hexagons, which are connected in a two-dimensional honeycomb network. Disorder between the transition metals and the main group elements leads to the pseudobinary structure types like $\text{AlB}_2$, $\text{Ni}_3\text{In}$ or $\text{CaN}_2$. The layers can be planar as in graphite (found in the $\text{ZrBeSi}$ and $\text{AlB}_2$ types), weakly puckered (NdP$_3$Sb type) or strongly puckered with short interatomic distances between the layers leading to a wurtzite-related structure with a three-dimensional network (LiGaGe-type). Compared with the compounds with the stuffed zinc blende structure, namely the $\text{C}_6$ half-Heusler compounds, the LiGaGe structure type which is the focus of this contribution has a free lattice parameter, the $c/a$ ratio, which should be 1.633 for the ideal hexagonal wurtzite structure. Beside the variable $c/a$ ratio, the free $z$ parameter of the $2b$ positions (see table 1) allows different degrees of puckering of the hexagons leading to structures that can vary almost continuously from three dimensional to quasi-two dimensional, with anticipated changes in electronic properties. Due to this reduction in symmetry in comparison with the half-Heusler compounds, a large variety of different structure types are possible as described above. The different superstructures are related via group–subgroup relations as recently reviewed [40]. The bonding features in such materials have been discussed in several overview [41–46]. Of the compounds discussed here, $\text{ScCuSn}$ and $\text{YCuSn}$ are examples for the puckered LiGaGe-type structure, whereas $\text{LaCuSn}$ is an example of a planar $[Y\ Z]^+$ (here CuSn$^{1+}$) network [39]. $\text{CeCuSn}$ is dimorphic with different degrees of puckering in the low- and high-temperature modifications [47].

Figure 1 compares the crystal structure of a typical cubic half-Heusler compound, (a) $F\bar{4}3m \text{TiNiSn}$, with the crystal
structures of two variants of the hexagonal XYZ compounds discussed here: P6₃/mmc ScCuSn [39], crystallizing in the LiGaGe-type structure and the planar P6₃/mmc LaCuSn [39]. TiNiSn is displayed with bonds connecting the zinc blende network of Ni and Sn. The Ti atoms stuff the (6 + 4)-coordinate TiNiSn unit, (c) LaCuSn in the ZrBeSi structure type. The structure is displayed with the [1 1 1] direction pointing up in the plane of the page, in order to emphasize the ABC stacking each of the three (a) TiNiSn, (b) ScCuSn, and (c) LaCuSn in the wurtzite ScCuSn structure. The inset shows the DOS of the three compounds in a region close to $E_F$. (Colour online.)

Table 1. Crystal structures of the compounds whose electronic structures are described in this contribution. X (Sc, Y, La) at $(0,0,0)$, Cu at $(\frac{1}{2}, \frac{1}{2}, z$(Cu)$)$ and Sn at $(\frac{1}{4}, \frac{1}{4}, z$(Sn)$)$. The first three experimental crystal structures are taken from [39].

| Compound     | Space group | $a$ (Å) | $c$ (Å) | $c/a$ | Z(Cu) | Z(Sn) |
|--------------|-------------|---------|---------|-------|-------|-------|
| LaCuSn       | P6₃/mmc     | 4.583   | 8.173   | 1.783 | 0.75  | 0.25  |
| YCuSn        | P6₃/mmc     | 4.513   | 7.274   | 1.612 | 0.8148| 0.2318|
| ScCuSn       | P6₃/mmc     | 4.388   | 6.830   | 1.557 | 0.8254| 0.22914|

Hypothetical structures

| Compound     | Space group | $a$ (Å) | $c$ (Å) | $c/a$ | Z(Cu) | Z(Sn) |
|--------------|-------------|---------|---------|-------|-------|-------|
| LaCuSn [LiGaGe] | P6₃/mmc   | 4.583   | 8.173   | 1.783 | 0.78  | 0.22  |
| LaCuSn [wurtzite] | P6₃/mmc    | 5.005   | 8.173   | 1.633 | 0.8125| 0.1875|

3.2. Electronic structures of the hexagonal compounds XCuSn

We have examined the XCuSn compounds using LMTO calculations. The experimental lattice constants and experimental $z$ parameters were employed in the input crystal structures to investigate the influence of puckering of the honeycomb Y$_3$Z$_3$ networks on the electronic structure. Additionally, calculations were performed for LaCuSn in two hypothetical structures described in table 1: the LiGaGe structure with experimental lattice parameters and hypothetical $z$ parameters which result in puckered Cu$_3$Sn$_3$ honeycombs, and an ideal wurtzite structure with the experimental $c$ parameter, and $a$ and $z$ chosen so that the ideal wurtzite structure is obtained ($c/a = 1.633$). In this ideal structure, all CuSn$_4$ and SnCu$_4$ tetrahedra are regular.

In the three panels of figure 2, we compare the densities of states (DOS) near the Fermi energy $E_F$ for LaCuSn, YCuSn and ScCuSn calculated for the experimental structures. We see trends in the electronic structure as the CuSn networks in these structures are increasingly puckered. All compounds have a noticeable pseudo band gap at $E_F$, with a more pronounced gap in the more puckered Y and Sc compounds. Projections of the densities of state on the different orbitals (not displayed) reveal that the valence band has mainly Sn p character. The Sn s states are separated by a gap from the valence band at around $-8$ eV. The bottom of the valence band is built from Sn p states. Cu d states lead to spikes in the electronic structure around $-3.5$ eV (ScCuSn) or $-3$ eV (LaCuSn). The Cu d bands are very flat.
with an overall dispersion of 0.5 eV. In the three-dimensional compound ScCuSn all Sn p states contribute to the states below and above the copper states. In the two-dimensional LaCuSn, the bottom of the valence states around \(-4\) eV has a pronounced Sn p\(_{x}\) character, whereas the top of the valence band is built mainly from Sn p\(_{y}\) and p\(_{z}\) states. Sc or rare-earth d states form the conduction band with a band width around 5 eV and have a small contribution to the Sn p states below \(E_F\). From the density of states we can conclude that a description of the compound as \(X^{3+}\) ion stuffing a wurtzite or ‘decorated graphite’ \([\text{CuSn}]^{3-}\) substructure is appropriate. The total DOS of these hexagonal compounds look very similar to those of the half-Heusler compounds [14], with some differences in the projected densities due to the different electronegativities of the constituent elements.

The similarities and differences in the electronic structure of the three compounds are further emphasized through an analysis of the Cu–Sn COHPs of the three stannides displayed in figure 3. Cu–Sn is the main bonding interaction in these compounds and bonding and antibonding states are separated by the Fermi energy. The dashed line in this figure is an integration of the COHP up to the \(E_F\), yielding a number that is indicative of the strength of the bonding. The extents of the bonding and the antibonding states of the Cu–Sn COHPs are slightly larger in the puckered compounds compared with the planar LaCuSn. Integrating the COHPs, we find that the strongest bonding interaction is in the planar LaCuSn. The planar Cu–Sn layers seem to lead to a stronger Cu–Sn interaction than the puckered Cu–Sn layers. However, the total bonding interaction seems to be stronger in the puckered compounds. Cu–Sn interactions are non-bonding around and above \(E_F\) and therefore do not contribute to the states around \(E_F\). In YCuSn and ScCuSn, the other pairwise interactions are significantly smaller: the \(X–Cu\) interaction is only 10\%, and the \(X–Sn\) interaction is around 20\% of the Cu–Sn interaction. The \(X–Cu\) interaction is bonding below \(E_F\) and small and slightly bonding above \(E_F\). We can conclude that the bonding interactions in the hexagonal compounds ScCuSn and YCuSn are similar to what are found in the half-Heusler compounds [14]. A much stronger La–Cu interaction is found in the planar compound LaCuSn (not shown). The La–Cu interaction leads to a strong bonding interaction leading to the high density of states peak slightly above \(E_F\). The La–Sn states build the top of the valence band and are responsible for reducing the magnitude of the pseudogap in this compound. It is clear from this discussion that YCuSn and ScCuSn are electronically well described as stuffed wurtzite compounds, with pseudogaps at \(E_F\) between the bonding and antibonding states.

3.3. The influence of puckering on the band structure and the electron localization function

The fact that the puckering of the Cu–Sn layer seems to be responsible for the metallic or semimetallic behaviour of hexagonal 18-electron compounds has motivated us to look more closely at the influence of puckering on the band structure and the gap of these compounds. Here we discuss the band structure of LaCuSn in the experimental structure and in the hypothetical LiGaGe-type and the wurtzite-type structures. Figure 4 displays the band structure of (a) LaCuSn with the experimental ZrBeSi-type structure, (b) hypothetical LaCuSn with the LiGaGe-type and (c) LaCuSn with the ideal wurtzite-type structure. These structures are described in table 1. LaCuSn in its experimental structure is clearly a metal in the \(\Gamma–K–M–\Gamma\) direction and shows a gap of nearly 0.3 eV along the direction at the surface of the Brillouin zone \(A–L–H–A\). In the LiGaGe structure the compound would be a semimetal due to the dipping of the conduction band at the M point and the valence band at the \(\Gamma\) point. In the hypothetical wurtzite structure LaCuSn becomes semiconducting. A closer view of the bands and their eigenvectors around \(E_F\) shows that the metallicity is due to an overlap between the conduction band with mainly La d\(_{3z^2-r^2}\) and d\(_{3z^2-r^2}\) and Sn p\(_x\) and p\(_y\) valence bands. Symmetry induces a metal to semiconductor transition by going from the ZrBeSi-type structure to the LiGaGe-type structure. For the experimental structure the La band dips below the Fermi energy at the M point with mainly La d\(_{3z^2-r^2}\) and d\(_{3z^2-r^2}\) and Sn p\(_x\) and p\(_y\) bands cross \(E_F\) around \(\Gamma\). It is surprising that the overall band dispersion in the planar layers is much higher compared with the puckered layers. However a detailed look at the eigenvectors leads to a simple explanation. In the case of the planar Cu–Sn layers the bands with Sn p\(_x\) and p\(_y\) contribution have a larger dispersion compared with the puckered layers. The strength of this interaction depends on the bonding distance and the effective overlap of the orbitals; both are stronger in the case of the planar layers. The strong sigma type bonding interaction between Sn and Cu pushes the valence band above the Fermi level at the \(\Gamma\) point. The conduction band which is derived from La d\(_{3z^2-r^2}\) displays a dispersion of nearly 2 eV and dips below \(E_F\) along the \(\Gamma\) to the M direction.

The same band of the puckered structures, the La d\(_{3z^2-r^2}\) band, has a much smaller dispersion of 0.5 eV and touches the Fermi energy slightly at the M point. The most important point is that the degeneracy at the M point between the La d\(_{3z^2-r^2}\) and the Sn p\(_x\) band is lifted by reducing the symmetry from
Figure 4. Band structures of experimental and hypothetical LaCuSn structures.

Figure 5. Electron localization functions (ELFs) of the valence electrons of LaCuSn in (a) the experimental crystal structure and in (b) the hypothetical wurtzite structure. The ELF isosurface is displayed for a value of 0.75. (Colour online.)

the $P6_3/mmc$ to $P6_3mc$, which renders the opening of the gap possible in the LiGaGe-type and wurtzite-type structure. In a manner similar to the half-Heusler compounds, the hexagonal compounds display an indirect gap, here between the $\Gamma$ and the M point.

By puckering the structure in going from the graphite type structure via LiGaGe to the ideal wurtzite-type structure the overlap between the conduction and the valence band becomes smaller and the symmetry is reduced. The compounds with LiGaGe structure can show semiconducting or semimetallic behaviour, which is experimentally and theoretically found for CePdSb [48] and CeRhAs [31]. Introducing $f$-elements like Gd leads to half metallic ferromagnets for example in GdPdSb [49].

Real space visualization of the electronic structure employed the electron localization function (ELF) for LaCuSn in figure 5(a) for the experimental ZrBeSi-type and in figure 5(b) for the hypothetical wurtzite structure. The value of localization runs from 0 (no localization, deep blue) to 1 (high localization, white). The isosurface of 0.75 is displayed here.

The coloured map in the background is the ELF shown on a (1 1 0) plane to visualize the bonding interaction along the Cu–Sn network. For the ZrBeSi type structure, figure 5(b), the Sn p electrons perpendicular to planar Cu–Sn layer are strongly localized. These p states interact strongly with La d$_{3z^2-r^2}$ states with the layer, and are responsible for closure of the gap and the metallicity of the compound. In figure 5(b), we find clear evidence for highly covalent and three-dimensional bonding between between Cu (cyan) and Sn (blue) in the wurtzite substructure of the wurtzite-type LaCuSn. As observed in the half-Heusler compounds, the localization is closer to the more electronegative Sn atom [14].

The valence charge densities displayed in figures 6(a) and (b) are again very similar to the valence charge densities of the half-Heusler compounds [14]. Because of the filled d shells on Cu it forms nearly large spherical blobs around that atom, visualized for a charge density of 0.025e Å$^{-3}$. We find that these blobs of charge are pulled out into four strongly localized (as seen from the colouring) lobes arranged tetrahedrally and facing Sn in (b), whilst in the LiGaGe structure, the bonding
interaction in the third dimension is removed, leading to three lobes arranged trigonally in the plane and facing the Sn in the plane.

4. Conclusion

We have carried out a systematic examination of XYZ compounds with hexagonal structures: LaCuSn, YCuSn and ScCuSn, and demonstrated that 18-electron compounds can become semiconductors depending on the degree of puckering of the [CuSn]$_3^-$ substructure. We demonstrate that the most instructive way of considering these systems is to think of them as being built up of a wurtzite [YZ] framework that is stuffed with the electropositive X. An effective strategy for new half-metals, in analogy with half-Heusler half-metals, would be to stuff these wurtzite-derived structures with magnetic ions.

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