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A Valence Balanced Rule for Discovery of 18-electron Half-Heuslers with Defects

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Abstract

Using first-principles DFT we systematically investigate the thermodynamic stability and off-stoichiometry in 108 nominal 19-electron half-Heusler (hH) compounds. We demonstrate unambiguously that considering a cation deficiency towards the off-stoichiometric *valence balanced*, VEC=18 composition is *necessary* for explaining the stability of all previously reported nominal VEC=19 compounds. This is understandable in terms of an energy benefit from valence balance considering the valence of each atom using Zintl chemistry that offsets the energy penalty of forming defects in nearly all cases. Thus, we propose a *valence balanced rule* to understand the ground state stability of half-Heuslers irrespective of stoichiometry and nominal electron count (8, 18 or 19). Using this generalized rule we (a) predict 16 previously unreported nominal 19-electron XYZ half-Heuslers and (b) rationalize the reports of giant off-stoichiometries in compounds such as $\text{Ti}_{(1-x)}\text{NiSb}$ which has been known for over 50 years. Of the 16 new compounds predicted here, $\text{Ti}_{(1-x)}\text{PtSb}$ was synthesized and the half-Heusler phase confirmed through X-ray studies. The flexibility in stoichiometry of the half-Heusler systems to attain a stable valence balanced composition by accommodating large defect concentrations opens up multiple dimensions for discovery of multi-component *defective* half-Heuslers based on intrinsic and extrinsic defects which compensate for the *nominally* non-18-electron count of the structure.

Broader Context

Half-Heusler (hH) compounds are emerging as state-of-the-art thermoelectric materials. Stable defect-free hH compounds with the stoichiometric composition XYZ typically exhibit a valence electron count (VEC) of 18. Compounds reported with other electron counts are often thought of as outliers to this '18-electron rule'. However, emerging interest in VEC=19 hHs for their exciting thermoelectric and magnetic properties demands a better understanding of their stability to reliably distinguish the stable compounds from the unstable ones. Understanding of compositional phase stability in these compounds will help tuning carrier concentrations of these compounds to optimize

their thermoelectric performance. We show that hH systems can accommodate large concentration of vacancies to attain a stable valence balanced composition. This valence balanced rule opens up multiple dimensions for discovery of multi-component *defective* half-Heuslers based on intrinsic and extrinsic defects which compensate for the *nominally* non-18-electron count of the structure.

1. Introduction

Valence electron counting (VEC) in half-Heusler (hH) compounds with the general formula XYZ is widely used for a straightforward understanding of their electrical and magnetic properties¹. While 18-valence electron compounds are typically semiconducting, non-18-electron systems should exhibit a metallic behaviour. The band-gap in typical VEC=18 hH compounds are tunable over a large range of 0-4 eV through changes in chemical composition, thereby making them suitable for a wide range of applications¹. VEC=18 hHs have been studied for topological band-structure properties⁵, transparent conductor applications⁶ and potential for solar cell applications¹. The lack of inversion symmetry in these semiconducting materials has also generated interest for its applicability as piezoelectrics⁷. In recent years, VEC=18 half-Heuslers have been explored as potential thermoelectric materials⁸⁻²¹ due to their high thermoelectric performance associated with their semiconducting nature. By moving slightly off the 18-electron count one can tune the carrier concentration and hence optimize the compound's thermoelectric properties^{22,12}. Half-Heusler are also relatively less toxic than the well known lead-based thermoelectric materials and exhibit robust mechanical stability^{23,43} making them suitable for implementation in thermoelectric modules on a large scale.

Reports of hHs predominantly consist of compounds with VEC = 18 (e.g. TiNiSn, TiCoSb etc). On the other hand, reports of non-18-electron hHs (VEC = 17 (e.g. ScPtSn, TiCoSn), VEC = 19 (e.g. TiNiSb, VCoSb)) are more rare (see Figure 1)²⁴. The larger number of VEC=18 compounds is attributed to the strong bonding interaction associated with the filled bonding and unfilled anti-bonding states that occurs when the Zintl valences are balanced¹². The electron count of 18 corresponds to when Y is a late transition metal (such as Ni or Co) as considered here. Y can also be a p -block element in the same structure (for instance, LiSiAl⁴¹ and LiGeAl⁴⁶ etc), in which case the stable, valence-balanced VEC is 8.⁴¹ Hence the semiconducting electronic structure is often presumed to drive the thermodynamic stability of typical hH compounds.

VEC=18 half-Heuslers have already been investigated extensively with 43 compounds synthesized previously (from ICSD and Ref. [25]). In addition, if the compounds predicted stable from the reliable first-principles based 0 K methodology are also considered the number of VEC=18 hHs adds to a total of 61.²⁵ The number of experimental reports of non-18-electron hHs in ICSD however, are typically an order of magnitude smaller in number (see Figure 1) and are often thought to be stable despite the weak bonding interactions associated with their partially occupied bonding or anti-bonding states¹. Due to their smaller number these compounds are mostly considered as outliers to this '18-electron rule' for stability of hHs.

The electrical properties of the few known VEC=19 hHs have long been discussed in the light of their metallic electronic structure. However, contrary to expectations, these compounds are also emerging as potential thermoelectric materials which typically require heavily doped semiconductors²⁶⁻²⁹. Initial reports studying

thermoelectric performance in NbCoSb and VCoSb report a $zT \sim 0.5$ at 700°C ^{26,27}. In addition to the promising thermoelectric performance these systems also allow for large isoelectronic substitutions to reduce thermal conductivity through an alloy scattering mechanism²⁸. The good thermoelectric properties of these materials suggest that we should consider them as heavily doped n-type semiconductors instead of simply classifying them as metals. This heavy n-type doping alongside the large band gap feature in its electronic structure makes them suitable for high-temperature thermoelectric applications. In addition to its exciting thermoelectric properties, VCoSb has also been widely studied for its magnetic properties. VCoSb has been predicted as a half-metallic ferromagnet and is still studied for spintronic applications³². Recently, the hH phase with nominal composition of NbCoSb was shown to contain large amounts of cation vacancies (Nb_{0.84}CoSb) bringing its VEC closer to its ground state 18-electron composition³⁵. These Nb_(1-x)CoSb exhibit a $zT \sim 0.9$ at 1100 K,⁴² which is comparable to state of the art VEC=18 half-Heusler thermoelectrics such as (Ti,Zr,Hf)NiSn compounds^{8,18}.

Owing to their interesting thermoelectric and magnetic properties, it is important to explore the phase space of VEC=19 hHs further. However, hHs occur in a very large number of chemically reasonable combination of elements and checking for the thermodynamic stability of each compound experimentally is laborious. However, laboratory discovery can be significantly expedited by first narrowing down the likely compositions using first-principles density functional theory predictions which often reliably predict the stable, experimentally-synthesized phase.²⁵ Unlike the VEC=18 systems however, high throughput prediction^{33,34} of VEC=19 hHs using the defect-free structure underpredicts the number of stable compounds (see Figure 1) with respect to the few known compounds. Hence the stability of VEC=19 half-Heuslers are not well-understood to reliably distinguish stable compounds from the unstable ones.

Here, using first-principles DFT, we rigorously demonstrate that the ground state stability of the previously reported VEC=19 hHs *cannot* be understood unless vacancies on the sub-lattice of the electropositive atom are considered. In other words, these compounds are not, in fact, VEC=19, but the vacancies effectively reduce the electron count. We find that a vacancy concentration which reduces the VEC to ~ 18 is energetically preferred across a wide range of “nominally VEC=19” compounds. However, the 18-electron rule by itself is not enough to determine the compound stoichiometry: We find the off-stoichiometry in these structures is uniquely determined by their valence balanced configuration (net valence (NV) = 0) from a set of infinitely many possible 18-electron compositions. This robust valence balanced rule for stability of hHs - developed by assigning valence to each atom under a Zintl-framework - holds true irrespective of the large vacancy concentration in the half-Heusler structure. Thus, the compositional stability of hHs with different nominal VEC (18 (stoichiometric), 19 (off-stoichiometric)) can be better understood from counting valence on individual atoms rather than counting electrons in the system. The fundamental *valence balanced* rule is used to predict 16 new stable *nominally* 19-electron compounds of the 108 ternary systems investigated here. The predicted half-Heusler phase for Ti_(1-x)PtSb was synthesized experimentally and confirmed through X-ray studies. The reliable predictive power of the valence balanced rule can be extended to include other defects in non-18-electron half-Heuslers to discover a huge phase space of multi-component stable Heuslers.

2. Results and Discussion

2.1 Methodology to predict Thermodynamic stability

The thermodynamic stability of a phase is determined by constructing the so-called convex hull of formation energies of *all* phases in the respective composition space.³³ By definition, every phase that lies *on* the convex hull is thermodynamically stable, i.e., it has a formation energy lower than any other phase or linear combination of phases at its composition. By extension, all other phases that do not lie on the convex hull are metastable or unstable, i.e., there exists a phase or mixture of phases lower in energy at that composition. The construction of the convex hull and determination of thermodynamic stability of a phase is illustrated using a model binary system in Section S1 of the ESI. For the phase stability analysis in this work, we consider all known and hypothetical phases in each composition space from the Open Quantum Materials Database (OQMD).^{33,34}

Further, the convex hull construction can be used to estimate the *extent* of thermodynamic stability (or instability) of a given phase. For this, we construct an additional convex hull in the composition space *after excluding the phase of interest* and determine the lowest-energy mixture of phases at that composition. The difference between the formation energy of the phase and the lowest-energy mixture of phases from the second convex hull construction quantifies the extent to which the phase is stable (or unstable). In other words, the extent of stability ($E_{Instability}$, also referred to as “distance to convex hull”) of a phase is calculated using:

$$E_{Instability} = E_{form} - \sum_{i=1}^3 c_i \Delta\mu_i$$

where c_i is the composition and μ_i is the chemical potential of the constituent element i , determined by the 2- or 3-phase equilibria from the second convex hull construction excluding the phase of interest (see Section S1 of the ESI for an illustration). Thus, a negative $E_{Instability}$ for a phase implies its overall thermodynamic stability while a positive $E_{Instability}$ indicates that other lower-energy mixture of phases exist at that composition. We study 108 compounds from VEC=19 family belonging to the IV-X-V, IV-XI-IV, V-IX-V, V-X-IV sub-groups.

2.2 A Valence Balanced Rule for half-Heuslers using Zintl Chemistry

The half-Heusler XYZ structure (space group F-43m) consists of three atomic sites located at the Wyckoff positions $X=4a$ (0, 0, 0), $Y=4c$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and $Z=4b$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Typically X-site atoms are early transition metal elements, Y-site atoms are late transition metal elements and the Z-site is occupied by p-block elements.¹ The electronegativities of the X-site atom lies in the range 1.2-1.7, whereas that of the Y and Z-site atoms are quite similar and lie in much higher ranges 1.8-2.4 and 1.7-2.2 respectively.¹ Hence X-site atoms form an electropositive sub-lattice of the structure.

The electronegativity difference and strong coupling between the d -states from the nearest neighbour X- and Y-site atoms gives rise to a band-gap in typical VEC=18 hHs.^{12,25} While hHs are typically thought of as intermetallic compounds, the semiconducting properties of VEC=18 systems allows for an understanding analogous to that of ionic compounds using a Zintl chemistry framework.¹² As the states in the

conduction band are primarily constituted by the electropositive X -site atom, it is thought of as the cationic sub-lattice which donates its valence electrons and becomes s^0d^0 .¹² The more electronegative Y - and Z -site atoms on the other hand, form an sp^3 covalently-bonded tetrahedrally-coordinated anionic substructure due to their similar electronegativities.

The electron count of 18 in hHs corresponds to empty and filled valence shells ($X s^0d^0 + Y d^{l0}s^0p^0 + Z s^2p^6$) of the cation and anions respectively – where the filled d^{l0} states of the Z atom are not considered valence electrons and ignored for the counting.¹² Hence the historic ‘18-electron rule’ is simply a special condition of the valence balanced configuration (e.g. $NV = 4 (\text{Ti}^{+4} s^0d^0) + 0 (\text{Ni}^0 d^{l0}) - 4 (\text{Sn}^{-4} s^2p^6) = 0$) in structures with XYZ composition (see Figure 1) where the electron count refers to one filled s^2p^6 -bonding configuration (attributed to anion Z) and one filled d^{l0} -bonding configuration (attributed to late transition metal Y). This special condition equals to 8 electrons for the same structure if the compound has Y atom which is a p-block element (for example:- LiSiAl , Mg_2Si etc). In the case of both 8 and 18 electron compounds valence balancing ensures a completely filled bonding states and completely empty anti-bonding states. Deviating from this closed shell configuration leads to a weakening of bonding interactions, thereby destabilizing the material.¹ Thus we conclude that having a valence balanced configuration, irrespective of its electron count (8 or 18), is a *necessary* condition for stabilizing the ground state of stoichiometric half-Heusler structure.

As can be expected from their structural similarities with hHs, well known Zintl compounds are also commonly known to stabilize with valence balancing. For instance, binary skutterudite compounds such as CoSb_3 consist of a covalently bonded polyanionic unit $(\text{Sb}_4)^{4-}$ and a cationic sub-lattice Co^{3+} in the d^6 configuration.⁴⁹ The structure of CoSb_3 can be understood as $NV = 3 (4 \text{Co}^{+3} d^6) - 4 (3 \text{Sb}_4^{-3} s^2p^6) = 0$ valence balanced compound.⁴⁹ Similarly, more complex Zintl compounds such as $\text{Ca}_{14}\text{AlSb}_{11}$ is found in a semiconducting valence balanced ($NV = 2 (14 \text{Ca}^{2+}) - 7 (\text{Sb}_3^{7-}) - 3 (4 \text{Sb}^{3-}) = 0$) configuration.⁵⁰ It is important to note that while the electron count per formula unit between these compounds differ from each another, the valence balanced $NV=0$ feature is common. This powerful valence balanced rule has been used in design of complex mult-component Zintls for thermoelectric and magnetic applications.^{49,50,51}

2.3 Extending the Valence Balanced rule to accommodate defects

One can also understand the compositional stability of the ground state 18-electron $\text{Nb}_{0.8}\text{CoSb}$ half-Heusler using its valence balanced configuration.³⁵ While the 18-electron electron count in this system can be achieved at infinitely many compositions by creating vacancies at the Y - and/ or Z -site of the stoichiometric structure, its stable X -site deficient composition can be uniquely identified by its valence balanced configuration ($NV = 4 (0.8 \text{Nb}^{+5} s^0d^0) - 1 (\text{Co}^{-1} d^{l0}) - 3 (\text{Sb}^{-3} s^2p^6) = 0$). For example, when compared to the stoichiometric structure ($NV = 5 (\text{Nb}^{+5} s^0d^0) - 1 (\text{Co}^{-1} d^{l0}) - 3 (\text{Sb}^{-3} s^2p^6) = 1$), the Y -site deficient 18-electron composition $\text{NbCo}_{8/9}\text{Sb}$ ($NV = 5 (\text{Nb}^{+5} s^0d^0) - 1 (8/9 \text{Co}^{-1} d^{l0}) - 3 (\text{Sb}^{-3} s^2p^6) = 1.12$) deviates away from the valence balanced configuration. Similarly, the Z -site deficient 18-electron composition $\text{NbCoSb}_{0.8}$ also deviates away from the valence balanced configuration ($NV = 5 (\text{Nb}^{+5} s^0d^0) - 1 (\text{Co}^{-1} d^{l0}) - 3 (0.8 \text{Sb}^{-3} s^2p^6) = 1.6$). While the 18-electron count imposes a constraint only on the (i) combination of atoms chosen and (ii) type of defect in stoichiometric $\text{VEC}=19$ NbCoSb ,

the valence balanced configuration ($NV=0$) imposes additional constraints on the site of the defect to uniquely determine its composition. While this *valence balanced rule* can be applied consistently across all stoichiometric hHs with $VEC=8$ and 18 , it can be generalized even further to include defects in hHs if all nominally 19-electron compounds show a similar trend in compositional stability. In the following sections we establish the generality of this *valence balanced rule* by (a) explaining all previous reports of stable nominal $VEC=19$ half-Heuslers and (b) using it to reliably predict nominal $VEC=19$ TiPtSb, which was not possible under the framework of the previously known 18-electron rule for stoichiometric 1-1-1 half-Heuslers.

2.4 Confirming the valence balanced rule from previously reported $VEC=19$ half-Heuslers

Out of the 108 nominally $VEC=19$ hH compounds considered here, the stoichiometric hH structure is predicted to be unstable *in all cases* (see Figure 2). The extent of instability ($E_{Instability}$) of these nominal $VEC=19$ hHs varied largely across families, ranging from 30 meV/atom for ZrNiSb to ~ 558 meV/atom for HfAgGe. The seven $VEC = 19$ half-Heuslers reported in ICSD (namely VCoSb, TiNiSb, NbCoSb, NbRhSb, NbIrSb, TaCoSb and ZrNiBi, see circles in Figure 3) also constitute a subset of these hH structures predicted to be unstable. Even among these compounds, the instabilities are rather large (ranging up to ~ 195 meV/atom for TaCoSb) and cannot be simply attributed to DFT error or the entropy associated with the temperatures at which the materials were synthesized. This is in contrast to the case of typical stoichiometric $VEC=18$ hHs such as TiNiSn where Open Quantum Materials Database (OQMD)^{33,34} correctly predicts the thermodynamic phase stability of 40 of the 43 previously known compounds. For each of the previously reported nominal $VEC=19$ hHs however, the off-stoichiometric valence balanced ($NV = 0$, $VEC=18$) structures (example $Ti_{0.75}NiSb$, $Ta_{0.8}CoSb$) is predicted stable (see Figure 3), thereby resolving the multiple discrepancies between DFT and experimental^{26,39,36,48} reports via the valence balanced rule. In contrast to a methodology which considers only defect-free structures, the valence balanced rule can be used to reliably distinguish stable nominal $VEC=19$ compounds from the unstable ones (see Supplementary Figure 2). This reliability in predictive power is crucial for the accelerated discovery of new compounds. The prediction and confirmation of previously unreported $VEC=19$ half-Heuslers is discussed in the sections below.

In addition to the large instabilities, we find that the stoichiometric compositions lie in multi-phase regions suggesting a driving force for phase separation at the $VEC=19$ composition. Based on this result one would expect to observe impurity phases in previously reported compounds. Indeed, studies reporting synthesis of the nominally $VEC=19$ hHs (NbCoSb²⁶, NbIrSb³⁹, VCoSb³⁶, TiNiSb⁴⁸) often contain reports of impurity phases. For instance, NbCoSb is often synthesized with Nb₅Sb₄ or Nb₃Sb impurities²⁹. Half-Heusler NbIrSb samples were prepared with persistent impurity phases despite several efforts (grinding, higher reaction temperature) to make the material single phase³⁹. In contrast to this, initial report of the stoichiometric $VEC=18$ hH NbIrSn was obtained as pure-phase samples through very straightforward synthesis procedure involving a low reaction temperature. Large amounts of ferromagnetic impurity phases have been reported for VCoSb, rendering its magnetic susceptibility data inconclusive³⁶. The amount and type of impurity phases however, were often not analyzed and in a few cases small amounts impurity phases might also have been missed²⁷.

Our-prediction of a cation deficient off-stoichiometry in these compounds also agrees well with experiments. The single phase region of nominal VEC=19 hH $\text{Nb}_{1-x}\text{CoSb}$ was found to lie in the off-stoichiometric range $x = 0.16-0.2$.⁴² Electron probe microanalysis (EPMA) studies of multi-phase samples indicate up to 20% cation vacancies in half-Heusler TiNiSb annealed at 873 K⁴⁰. We suggest here that the impurity phases in stoichiometric hH composition of nominal VEC=19 hHs occur due to the formation (18+ δ)-electron based hH phase.

2.5 Previously unknown compounds predicted stable using the valence balanced rule

Out of the 108 compounds studied here we find a total of 23 nominal VEC=19 hHs stable in their valence balanced (NV = 0, VEC=18) cation poor structures (see Figure 3), 16 of which are previously unreported. We reiterate here that the stoichiometric VEC=19 hH structures predict all the 108 compounds unstable, including the 7 previously reported compounds. On the other hand, in the case of stoichiometric VEC=18 XYZ compounds simply considering defect free structures constituted an extremely efficient prediction methodology.²⁵ The valence balanced rule is central to our structure prediction methodology for nominal VEC=19 half-Heuslers.

We predict previously unreported hH phases in 10 Sb-based, 2 As-based and 4 Sn-based ternary systems (see Figure 3). We also find 4 cases which are too close to call as their $E_{\text{Instability}}$ falls within the range [-10 meV/atom, 10 meV/atom] and could be attributed to a DFT error. HHs with nominal VEC =19 have only been reported for Sb and Bi-based compounds. We propose Sn and As-based compounds as new additions to the nominal VEC=19 hH family. These compounds are significantly stable (< -20 meV/atom) and comparable to the already reported example of hH $\text{Zr}_{0.75}\text{NiBi}$ ($E_{\text{instability}} = -11$ meV/atom). Some compounds such as $\text{Nb}_{0.8}\text{NiSn}$ (see Figure 3) contain only relatively inexpensive and abundant elements and could be explored as inexpensive alternatives for thermoelectric applications.

The nominal VEC=19 compounds are a large family consisting of ~300 combination of elemental groups for the X, Y and Z-site atoms¹ (namely the sub-groups III-XI-V, III-X-IV, IV-IX-III, IV-X-V, IV-XI-IV, V-IX-V, V-X-IV, V-XI-III, VI-VIII-V, VI-IX-IV, VI-X-III). The fact that stability of these compounds is almost never limited by the large defect concentrations (see Figure 2) suggests that the robust valence balanced rule can be used in their further discovery with reasonable confidence. Similar to the previously unreported Sn- and -As-based compounds predicted here one might expect to find more nominal VEC=19 compounds from the large phase space of possible ternary systems, opening up a new dimension for potential materials research and discovery. While other nominal VEC=19 compounds can be explored, the current prediction of 23 compounds is already more than one-third of the 61 predicted exhaustively for nominal VEC =18 hHs. Just like stoichiometric VEC =18 hHs, the pseudo 18-electron nature of new nominal VEC=19 compounds could be suitable for thermoelectric applications.

2.6 Stability of nominally VEC=19 half-Heuslers driven by semiconducting electronic structure

Most of the cation deficient, valence balanced (NV = 0, VEC=18) structures studied here are found to be semiconducting ($E_g > 0$). Generally, the compounds with

larger band-gaps ($E_g > 0.55$ eV) are stabilized to a greater extent relative to the small band-gap ($E_g < 0.55$ eV) cases (see Figure 2). The stabilizing effect of the band-gap may be associated with the electronic energy gained after losing 1 electron/formula-unit from the ‘conduction band’ of the stoichiometric VEC=19 hH as the structure becomes cation deficient. This gain in electronic energy may overcome the $E_{Instability}$ at the VEC=19 composition, giving rise to thermodynamic stability in the 23 compounds predicted here. It seems that, for a particular value of $E_{Instability}$ at the VEC = 19 composition a correspondingly large band-gap in the off-stoichiometric structure is required to stabilize the nominal VEC=19 hH phase (see dotted line in Figure 4). Most compounds predicted stable however, exhibit both (i) a small $E_{Instability}$ for the defect-free structure and (ii) a large stabilizing band-gap (see solid line in Figure 4). It is interesting to note that all the compounds predicted stable lie in the larger band-gap range with $E_g > 0.55$ eV (see Figure 2).

For off-stoichiometries of the magnitude discussed here (20-25% vacancies), one would expect an energy penalty for formation of vacancies to be quite significant. This energy penalty should compete with stabilizing effect of E_g , possibly even overcoming it in a few cases. Contrary to this expectation, we find that off-stoichiometric hH structures are nearly always (107 out of 108 cases) more stable with respect to the defect-free structure (see Figure 2) even for systems with small E_g (~ 0 eV) (see Figure 4). This suggests that the structure readily accommodates the large vacancy concentrations to attain the valence balanced configuration. The spontaneous formation of large concentration of vacancies might seem counterintuitive. However, complete vacancies on the cationic X -site leads to the stable zinc blende structure with the same sp -bonding as in the hH. This suggest hHs have some chemical similarities to intercalation compounds where the X cation add flexibly to tune the electron count towards the thermodynamically stable valence balanced composition.

2.7 Experimental verification of valence balanced rule

To verify our predictions of new 19-electron compounds we synthesized the predicted, but previously unknown nominal VEC=19 compound TiPtSb using levitation melting and spark plasma sintering (SPS), which are among commonly used methods for making hHs.⁴⁷ The samples were subsequently annealed at 1073 K. We chose to study TiPtSb on the basis of its high predicted stability at the off-stoichiometric composition $Ti_{0.75}PtSb$ (-100 meV/atom) whereas stoichiometric TiPtSb is quite unstable (110 meV/atom). We synthesized compositions $Ti_{0.75}PtSb$ and $Ti_{0.85}PtSb$. The powder XRD pattern of $Ti_{0.75}PtSb$ indicates that the main phase of the samples are the hH phase (see Figure 5) and some impurity peaks of the $PtSb_2$ phase. The impurity peaks almost vanish for the $Ti_{0.85}PtSb$ sample, indicating it is nearly phase pure. The location of the XRD peaks vary only slightly with Ti composition indicating narrow phase width.

The pure phase hH $Ti_{0.75+x}PtSb$ deviates from the predicted $Ti_{0.75}PtSb$ towards a X -rich composition. This is due to the strong temperature dependence of compositional phase stability in nominally 19-electron hHs. For instance, the high temperature ($\sim 900^\circ$ C) conditions in which $Nb_{0.8+x}CoSb$ is synthesized, the half-Heusler phase deviates significantly towards the XYZ composition ($x = 0-0.04$).^{35,42} Similarly, the phase boundary in $Ti_{(0.75+x)}NiSb$ was found at $x = 0.05$ at the 873 K, which also deviates from the valence balanced $x=0$ composition.⁴⁰ The $Ti_{0.75+x}PtSb$ samples prepared for the

present work were annealed at 1073 K. At these high temperatures similar deviation from ground state ($T=0$ K) valence balanced $\text{Ti}_{0.75}\text{PtSb}$ composition are expected to be Ti-rich $\text{Ti}_{0.75+x}\text{PtSb}$ with ($x > 0$).

The discovery of a cation-deficient half-Heusler $\text{Ti}_{0.75+x}\text{PtSb}$ in the nominally 19-electron system provides a strong experimental validation of our prediction strategy based on the valence balanced rule. Hence, we suggest this rule can reliably predict the small fraction of stable compounds from all possible combinations of nominal $\text{VEC}=19$ hHs, thereby expediting the discovery of these compounds.

2.8 Extending the valence balanced rule to include other point defects

The flexibility in stoichiometry from cation vacancies in the hH structure to achieve the valence balanced ground state composition points towards the powerful role other defects can play in discovery of hH compounds.

- (a) **Interstitial Defects:** The full-Heusler site $Y_2=4d$ ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$) constitutes the largest interstitial site in the hH structure which can easily accommodate extrinsic defects to compensate for the non-valence balanced configuration of the defect-free structure. The full Heusler site in nominally 17-electron TiFeSb was shown to be partially occupied by Fe in its ground state $\text{TiFe}_{1.5}\text{Sb}$ Slater-Pauling phase⁴⁴ that may also satisfy the valence balanced rule. Recently, it was shown that an additional Li atom on the Y_2 -site acts as an intercalant atom, adding electrons without significantly altering the electronic structure near the band gap in nominally $\text{VEC}=17$ hHs.⁴⁵ The predicted number of such stable quaternary Li-based valence balanced Heuslers (99) alone is over a factor 1.5 times those predicted for stable defect-free 18-electron hHs (61, see Figure 1). Similar combinations of quaternary valence balanced compounds ($\text{VEC}=16$ half-Heusler and +2 cation such as Ca, $\text{VEC}=19$ half-Heusler and -1 anion such as F) can be explored for other ternary systems which a nominally non-18-electron count.
- (b) **Substitutional Defects:** The non-valence-balanced configuration of nominally $\text{VEC}=19$ hHs can also be compensated by substituting atoms with a different valence. In contrast to the case of compensation through vacancies in the ternary nominal $\text{VEC}=19$ hH, the substitution can occur at any of the three sites without violating the valence balanced necessary condition. These substitutions can occur with different types of atoms opening up the phase space for materials discovery even further.

Thus the valence balanced rule can be extended to include extrinsic defects as well. This opens up a huge phase space for discovery 18-electron valence balanced Heuslers as it adds additional components to the system.

3. Conclusion

In conclusion, we demonstrate that the stability of half-Heuslers at multiple nominal electron counts 8, 18 and 19 are best understood using a *valence balanced rule*. We establish that while the nominal electron counts for these half-Heusler systems might be different, their ground state structures always have a common net valence (NV) of 0

when described within a Zintl framework. This rule allows the nominally 19-electron hHs to flexibly tune its stoichiometry by accommodating large concentrations of cation vacancies to attain the ground state valence balanced configuration. This understanding of compositional stability in the emerging thermoelectric nominal VEC=19 hHs, previously not available from the '18-electron rule' for stoichiometric hHs, was used to predict 16 new compounds. The newly predicted off-stoichiometric hH phase $\text{Ti}_{(0.75+x)}\text{PtSb}$ was synthesized and confirmed using x-ray studies. The valence balanced rule adds multiple dimensions to the phase space for discovery of possible hHs by including different intrinsic and extrinsic defects in the structure to attain a valence balanced configuration.

4. Materials and Methods

The lowest energy X-site deficient structures for half-Heuslers were determined by first enumerating structures using ENUM for 14 different systems (namely HfNiSb, HfPdSb, HfPtSb, NbCoSb, NbRhSb, TaCoSb, TaRhSb, TiNiSb, TiPdSb, TiPtSb, VCoSb, ZrNiSb, ZrPdSb and ZrPtSb). The lowest energy structures were found in the teragonal I-4 space group structure for systems based on Group-V cations (for example $\text{Ta}_{0.8}\text{CoSb}$) and teragonal I-4m space group structure for systems based on Group-IV cations (for example $\text{Ti}_{0.75}\text{NiSb}$). These structures were used for all the 108 compounds in the present study. These structures differ in symmetry from the defect-free VEC =19 structure (space group F-43m). But as these ordered structures are derivatives of the corresponding stoichiometric VEC=18 structure and transition into a high temperature disordered phase with the same symmetry, these are simply referred to as off-stoichiometric structures of the defect-free VEC=19 structure.

The off-stoichiometric 18-electron composition of the orthorhombic (space group Pnma) structure was also considered. For 54 cases where the X-site atom belonged to the group-IV, the off-stoichiometric structure was derived by simply removing the X-site atom from a 12 atom unit cell. For the cases where the X-site atoms belonged to the group-V, the possible energetically distinct 56-atom off-stoichiometric structures ($\text{X}_{0.8}\text{YZ}$) generated using ENUM were $> 10^3$. As these structures are metallic, the lowest energy structures selected based on electrostatic interactions could not be trusted. To avoid these computationally expensive calculations, we chose 17 off-stoichiometric structures at random at $\text{V}_{0.8}\text{CoAs}$. These structures were 37-78 meV/atom higher than the off-stoichiometric structure.

The density functional theory (DFT) calculations³¹ in this study were performed using Vienna ab initio simulation package (VASP)^{43,44}. We have used Perdew–Burke–Ernzerhof (PBE) formulation of the exchange correlation energy functional derived under a gradient-generalized approximation (GGA).^{44,45} Plane-wave basis sets truncated at a constant energy cutoff of 390 eV were used, as were Γ -centered k-point meshes with a density of $\square 8000$ k-points per reciprocal atom (KPPRA). All structures (perfect crystal and defective hH structures) were relaxed with respect to cell vectors and their internal degrees of freedom until forces on all atoms were less than 0.1 eV/nm before calculating their formation enthalpies (E_{form}). The Open Quantum Materials Database (OQMD)^{33,34} was used for the convex hull construction to check for thermodynamic stability against all other known phases in the respective composition space.

The $\text{Ti}_{0.85}\text{PtSb}$ and $\text{Ti}_{0.75}\text{PtSb}$ sample was prepared by levitation melting and spark

plasma sintering (SPS).⁴⁷ The ingots (~5 g) were prepared by levitation melting of stoichiometric amounts of Ti (rod, 99.99%), Pt (piece, 99.95%) and 1% excess Sb (block, 99.999%) under an argon atmosphere. Mechanical milling was carried out in a ball milling system (Mixer Mill MM200, Retsch) with an oscillation frequency of 24 Hz for 1 hour. The fine powders were then sintered by SPS (LABOX-650F, SINTER LAND INC.) at 1173 K under 65 MPa in a vacuum for 10 min. The samples were subsequently annealed for 10 days at 1073 K.

Conflict of interest:

The authors declare that they have no conflict of interest.

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