Electronic structure of Zr–Ni–Sn systems: role of clustering and nanostructures in half-Heusler and Heusler limits

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Abstract
Half-Heusler and Heusler compounds have been of great interest for several decades for thermoelectric, magnetic, half-metallic and many other interesting properties. Among these systems, Zr–Ni–Sn compounds are interesting thermoelectrics which can go from semiconducting half-Heusler (HH) limit, ZrNiSn, to metallic Heusler (FH) limit, ZrNi2Sn. Recently Makongo et al (2011 J. Am. Chem. Soc. 133 18843) found that dramatic improvement in the thermoelectric power factor of HH can be achieved by putting excess Ni into the system. This was attributed to an energy filtering mechanism due to the presence of FH nanostructures in the HH matrix. Using density functional theory we have investigated clustering and nanostructure formation in ZrNi1+xSn (0 ⩽ x ⩽ 1) systems near the HH (x = 0) and FH (x = 1) ends and have found that excess Ni atoms in HH tend to stay close to each other and form nanoclusters. On the other hand, there is competing interaction between Ni-vacancies occupying different sites in FH which prevents them from forming vacancy nanoclusters. Effects of nano-inclusions on the electronic structure near HH and FH ends are discussed.

Keywords: nanocluster, thermoelectric, Heusler, electronic structure, defect, energetics

1. Introduction

Half-Heusler and Heusler compounds have been of great interest for several decades for thermoelectric, magnetic, half-metallic and many other interesting properties. Development in the study of this family of compounds can be found in several review articles [1–9], among which Graf et al [6] gave a comprehensive overview of the field. Interesting examples of such compounds are M–Ni–Sn, M=Zr,Ti, and Hf, which are promising thermoelectric materials [10–26]. They can go from semiconducting half-Heusler (HH) [15] limit, i.e. ZrNiSn with cubic MgAgAs structure, to metallic Heusler limit (some times referred to as full-Heusler, FH), ZrNi2Sn [15] with cubic MCu2Al-type structure. Because of their excellent thermoelectric properties, MNiSn and their solid solutions have attracted considerable experimental and theoretical interests over last several years [16, 18, 19, 24–43].

Recently Makongo et al [33, 34] (MK) have observed that large enhancements of both thermopower (S) and electrical conductivity (σ) and hence the powerfactor PF=S^2σ of half-Heusler (HH) phase of (Zr,Hf)NiSn can be achieved at high temperatures through insertion of nanometer-scale FH coherent inclusions within the HH matrix, caused by adding a small concentration of extra Ni atoms. They refer these systems as HH(1–x)/FH(x) nanocomposites, which can be alternatively characterized as ZrNi1+xSn, where 0 < x <1. In their work, Bi-doped HH(0.94)/FH(0.06) was found to have a PF of 3.3 mW mK−2 compared to 1.6 mW mK−2 of Bi-Doped HH around 700 K. Chai and Kimura [37] (CK) also saw a large density of nanosized FH precipitates on the electronic structure near HH and FH ends are discussed.
in slightly Ni-rich TiNiSn and found an increase in the power factor at high temperatures (∼3.5 mW mK⁻² at 700 K compared to ∼2.5 mW mK⁻² at the same temperature for the parent compound TiNiSn [29]). Both MK and CK suggested that an energy filtering mechanism proposed by Faleev and Léonard [44] was operating in these systems due to the presence of metallic nano-structured inclusions in a semi-conducting host. There is, however, no direct experimental evidence of such energy filtering caused by the FH nano-particles; more careful studies of electronic structure are needed to examine this idea. The main idea behind the energy filtering mechanism proposed by Faleev and Léonard [44] is the energy dependent scattering of the carriers by the metallic inclusion which filters out the low energy carriers from energy transport. Another possible way of incorporating energy filtering mechanism, particularly at high T, is to filter out either electrons or holes from energy transport, thereby, suppressing electron-hole cancellation [45].

Romaka et al [25] have carried out a thorough investigation of structural phase transitions in half-Heusler–Heusler stannides (Zr,Hf)Ni₁₋ₓSn over the entire range of x=0 → 1, and have shown how different physical properties change as one goes from HH to FH limit. Similar studies in Ti–Co–Sn system was carried out by Stadnyk et al [46] who found that in TiCo₁₋ₓSn, electrical conductivity changed from metallic to semi-conducting as they varied x from 0 to 1. Romaka et al [25] found that in ZrNi₁₋ₓSn, macroscopic phase separation of HH and FH phases took place in the region 0.3 ≤ x ≤ 0.7. Their x-ray diffraction (XRD) measurements matched very well to the cubic MgAgAs structure for x ≤ 0.3 and to the cubic MCu₂Al-type structure for x ≥ 0.7. In the intermediate range 0.3 < x < 0.7, a two-phase coexistence was seen. The presence or absence of nanostructures of one phase in the matrix of the other phase in the concentration ranges (x ≤ 0.3 or x ≥ 0.7) could not be established from their XRD measurements. One has to note that nanostructures of FH of 2–8 nm were observed in TEM measurements by Makongo et al [33] for x ~ 0.06. One of the interesting observations by Romaka et al was the increase in the density of states at the Fermi energy (inferred from susceptibility measurement in the range 0 < x < 0.1, suggesting that new states appear at the Fermi energy with increasing x.

One can visualize the structure of these HH and FH compounds as follows (figure 1). One starts from a NaCl-type lattice of, say, ZrSn consisting of two interpenetrating FCC sub-lattices. Inside the cubic unit cell of length a, there are 8 small cubes of length a/2. In ZrNiSn, the centers of 4 out of these 8 cubes are occupied by Ni atoms (h-site) so that each Zr or Sn is tetrahedrally bonded to 4 Ni atoms. In ZrNi₂Sn, all the 8 small cube centers are occupied by Ni atoms (f- and h-sites). Thus one can tune from HH to FH or vice versa by varying the amount of Ni. The lack of mutual solubility of the HH and FH phases with similar crystal structures is quite remarkable in view of the fact that either adding Ni atoms to HH or removing Ni atoms from FH do not change the basic structure of the ZrSn matrix. There are several fundamental questions that arise in the study of these mixed HH–FH systems. For example, in ZrNi₁₋ₓSn, what is the nature of the phase diagram in the T versus x plot? What are the short and long range structural features and how they change with x? What are the electronic and lattice properties of the mixed system? There are some recent attempts to address these questions. For example, Romaka et al [25] have looked at the electronic structure issue using local density approximation (LDA)-single site coherent phase approximation (CPA) [47], and Kirievsky et al [41] have studied the thermodynamics of Ni-rich TiNiSn compound, i.e. the phase separation and energetics of anti-site defects using the supercell model. However, there are some limitations in these studies. For example, CPA used by Romaka et al [25] cannot address the question of clustering and nanostructures and the cubic supercell used by Kirievsky et al [41] in their electronic structure calculations is small (1 × 1 × 1 cubic unit cell). We will discuss some of their results and compare with ours in the appropriate limit.

In this work we address two of these basic questions. First, do the additional Ni atoms (or Ni vacancies) go randomly or arrange to form some sort of local ZrNi₂Sn (or ZrNiSn) nano-clusters? Second, what is the effect of these nano-clusters, if they form, on the electronic structure? In order to address these questions we have carried out electronic structure calculations using ab-initio density functional theory (DFT) and the supercell model [48] to describe the nanostructures. Our preliminary results were reported at ‘International Symposium on Clusters and Nanostructures—Richmond, VA, 2011’.

This paper is organized as follows. In section 2, we discuss briefly details of electronic structure calculations and the model to describe the nanostructures. In section 3, we discuss the energetics of ZrNi₁₋ₓSn and their electronic structures,
focusing on the nature of the gap states as one adds Ni atoms to ZrNiSn or the modification in the density of states near the Fermi energy as one adds Ni-vacancies to ZrNi2Sn. Finally, in section 4, we present a summary of our main findings and discuss possible further work in this area.

2. Methods of electronic structure calculation and modeling nanostructures

It is well known that LDA/GGA calculations usually underestimate the band gaps in semiconductors [48–50]. However, the problem is opposite in the case of HH, MNiSn (M=Ti, Zr, Hf) [15, 17, 51] where local density approximation (LDA) and generalized gradient approximation (GGA) calculations give band gaps about two times larger than that found from resistivity measurements [11] \((E_g = 0.12, 0.18 \text{ and } 0.22 \text{ for } M=\text{Ti}, \text{Zr} \text{ and Hf respectively})\). The smaller band gap values have been ascribed to defects [15, 21]. We have tested the case of ZrNiSn with different improved approximations, namely modified-Becke-Johnson (mBJ) [52] and hybrid functional (which includes non-local exchange partially) proposed by Heyd–Scuseria–Enzerhof (HSE06) [53–55] methods. We have found that the band gap increased slightly from \(-0.48 \text{ ev in GGA to} \sim 0.51 \text{ eV with mBJ and to} \sim 0.58 \text{ eV with HSE06, indicating that GGA is sufficient to treat exchange-correlation in this system. In the FH limit, the systems are metallic and hence nonlocal effects are not expected to be important. Therefore, in this work total energy and electronic structure calculations were done using GGA. For the exchange-correlation potential we used the model suggested by Perdew, Burke, and Ernzerhof (PBE) [56]. We employed projector-augmented wave (PAW) method [57, 58] as implemented in the VASP code [59–61], with a plane-wave energy cutoff of 400 eV and an energy convergence criterion (between two successive self-consistent cycles) of \(10^{-4} \text{ eV/unit cell.}\) The charge densities and total energies were calculated self-consistently with an \(8 \times 8 \times 8 \text{ Monkhorst–Pack} [62] \text{ k-grid.}\) The electronic density of states (DOS) was obtained using a denser \(k\)-mesh of \(12 \times 12 \times 12.\)

In the present work, the lattice parameters of HH and FH are found to be 6.151 Å and 6.321 Å respectively, in good agreement with the experiments [15]. The defective structures were obtained from these host structures and ionic positions were then allowed to relax. To study how the electronic structure differs from the HH and FH limits as one adds and removes Ni atom(s) respectively, we have done calculations for ZrNi2+\(x\)Sn using supercell method [48]. For convenience, we define \(\delta\) as the defect concentration, where \(\delta = x\) is the concentration of Ni atoms added to HH and \(\delta = 1 - x\) is the concentration of Ni-vacancies in FH. The values of \(\delta\) (or \(x\)) depends on the size of the supercell used in a calculation and the number of defects added. The supercell method has also been used by Kirievsky et al [41] for TiNi2+\(x\)Sn, with a cubic \(1 \times 1 \times 1 \text{ cell (maximum 8 Ni atoms per unit cell) which gives large concentrations of defects (}\delta \geq 0.25.\) Since, they focused primarily on the thermodynamics of the HH–FH mixture and the quasi-binary-system phase diagram, total energy calculation using a small supercell is reasonable. However, because we are interested in nanostructure formation for small concentrations of extra Ni atoms or vacancies, we use a larger unit cell, mostly \(2 \times 2 \times 2 \text{ (containing 32 Zr, 32 Sn and up to 64 Ni atoms per supercell) with } \delta = m/32 = 0.03125 m = 1, 2, 3, 4.\) For a few cases we have also used a \(3 \times 3 \times 3 \text{ supercell.}\) We study the dilute limit of the defect by (i) starting from the HH structure and adding more Ni atoms and (ii) starting from the FH structure and removing some Ni atoms to create Ni-vacancies. We use the notation HH+nNi (FH-nNi) to denote a super cell of HH with \(n\) additional Ni (FH with \(n\) deficient Ni). Near the HH end, to understand how the FH nano-phase forms, all possible configurations of excess Ni-pairs were considered to find the lowest-energy (the most favorable) configuration. Once the preferred pair-configuration was found, the third Ni was added and we looked for the lowest energy configuration. An analogous procedure was applied for the FH end with Ni vacancies.

In studying properties of defects in a material, it is useful to calculate their formation energies. There are extensive theoretical studies dedicated to this problem. Here we follow the work of Zhang et al [63] and apply to HH–FH system where formation energy of a defect is given by

\[
\Delta E_f (X_n) = \Delta E_f (X_0) = E(X_0) - E(0) + nE_{Ni},
\]

where

\[
\Delta E_f (X_n) = E(X_n) - E(0) + nE_{Ni},
\]

In these equations, \(E(X_n)\) and \(E (0)\) are the ground state energies of the \(2 \times 2 \times 2\) supercell with and without defect \(X_n, n\) is the number of Ni added (\(n < 0\)) or removed (\(n > 0\)) from the host-system (HH or FH), \(E_{Ni}\) is the ground state energy per atom of Ni solid, and \(\mu_{Ni}\) is the chemical potential of Ni. \(\mu_{Ni}\) is usually considered as a parameter which varies from Ni-rich to Ni-poor environment. The limits of \(\mu_{Ni}\) can be defined from thermodynamic equilibrium conditions which was carefully discussed by Zhang et al [63]. In the present calculations, we will take \(\mu_{Ni} = 0\) and focus on \(\Delta E_f (X_n)\.

In an earlier calculation of defect formation energies by Kirievsky et al [41] a \(1 \times 1 \times 1 \text{ supercell was used,}\) and the formation energies of the quasi-binary system,\(\text{(TiNi}_2\text{Sn)}_{1-x}\text{(TiSn)}_x,\) were calculated with respect to ground state energy of two end-systems. Furthermore, the physical meaning of their formation energies is unclear since TiSn is not a physical system. Thus, a direct comparison of numbers between their results and ours is not meaningful.

3. Results and discussions

3.1. Formation energy and energetics of clustering

3.1.1. HH with excess Ni. Table 1 gives the values of \(\Delta E_f (X_n)\) needed to add or remove \(n\) Ni atoms to the HH matrix or FH matrix respectively. All the formation energies are positive, i.e. it costs energies to form HH–FH alloys at \(T = 0 \text{ K starting from each end.}\) If we start from the HH end, it costs 0.423 eV to insert 1 Ni atom into one of the 32 available Ni sites. On the other hand, removing a Ni atom from FH (equivalent to...
creating a vacancy at this end) is 0.417 eV. When more than one defect is created at either end, there is evidence of strong interaction between the defects. We will discuss this physics separately for the two ends, focusing more at the HH end due to its thermoelectric significance.

With the first excess Ni (Ni₁) fixed, when the second Ni (Ni₂) is added to the HH matrix, there are several possible empty cube sites it can occupy. In figure 2 (left column) we plot the ground state energy of HH+2Ni as a function of the distance between the Ni-pair (Ni₁ and Ni₂). It is clear that two Ni are attracted, since the energy is lowest at the smallest distance (4.22 Å). The preferred configuration of Ni-pair is shown in figure (right column). The ground state energy increases as the distance increases and then tends to saturate at large distances (∼ 10 Å). The small decrease in the energy when the distance goes from 9 → 10 Å is due to the effect of the periodic supercell. Even with a 2 × 2 × 2 unit cell, the size is only 12.3 Å × 12.3 Å × 12.3 Å, and there is an artificial periodicity of the defects. At large distances, the interaction of the excess Ni with their images in the neighboring unit cells counteract the intra-unitcell interaction. For a larger supercell, one should expect the energy to saturate at larger distances. The energy difference between the lowest- and the highest-energy configurations is ∼0.1 eV. From table 1 we can estimate the binding energy of two Ni atoms as ∼0.088 eV (2 × 0.423 eV = 0.0758 eV), close to 0.1 eV.

When the third Ni (Ni₃) is added to HH with two excess Ni, the problem is more complicated. As one can see from table 2, the ground state energy depends on both the distance from Ni₃ to Ni₁ (r) and the Ni₁-Ni₂-Ni₃ angle (θ). However, if one plots the ground state energies as a function of the sum of the distance of Ni₃ from Ni₁ and Ni₂ (as shown in figure 3 (left column)), one gets a much simpler picture in which energy increases with increasing distance and saturates at large distance (similar to the case of Ni-pair discussed above). The difference between the highest- and lowest-energy configurations is about 0.14 eV. The lowest energy of HH+3Ni is found where Ni₃ is closest to both Ni₁ and Ni₂ so that the three Ni atoms occupy three corners of a tetrahedron, forming an equilateral triangle, as shown in figure 3 (right column). Three excess Ni atoms tend to come close to each other and form a nano-cluster (a tetrahedron) in the HH matrix.

Now let us look at the case of four excess Ni (note that a 2 × 2 × 2 unit cell is 0.417 eV). Similar to the case of HH+2Ni, the energy cost for removing 1 Ni out of 4 excess Ni atoms (to form a tetrahedron), forming a rhombus (R), a deformed rhombus (DR) which is in between T and R. (see figure 4). It is believed that for (Ni₄) clusters in free space, the T is the lowest energy structure. If the T structure in ZrNiSn matrix has the lowest energy then it would form an embryonic FH cell. However, we find that neither T nor R have the lowest energy, rather the intermediate DR structure has the lowest energy (figure 4). In this structure all of the Ni–Ni bonds except one have equal (short) lengths with one long bond. Note that in the T structure all Ni–Ni bonds are same (short bonds).

For the 2 × 2 × 2 supercell, the energy difference between T and DR structures E(T)−E(DR) = 0.015 eV and the difference between R and DR, E(R)−E(DR) = 0.022 eV. One may suspect that 4 excess Ni atoms in 2 × 2 × 2 supercell are too many and the effect of the periodic boundary condition is strong. In order to circumvent this situation we increase the supercell size to 3 × 3 × 3 (allowing more local relaxation and reducing the effect of periodic boundary condition), we find that the energy difference between T, R and DR decrease, especially between R and DR, indicating that planar structures relax more than the compact tetrahedral structures.

The above results show that excess Ni in HH tend to stay close to each other, forming clusters. However, upto four excess Ni atoms, the formation of nanostructure of FH is not favorable in both 2 × 2 × 2 and 3 × 3 × 3 supercells. These clusters (n = 1 – 4), however, may form nuclei for larger clusters which include the FH structure as observed in experiments. It will be interesting to study the evolution of the cluster of excess Ni atoms in HH for clustering size larger than four.

3.1.2. FH with deficient Ni. At the FH end, one should note that there are two different Ni-sites (figure 1): ‘h’-site (h) at (1/4,1/4,1/4) and its equivalents, which are occupied by Ni in HH, and ‘f’-site (f) at (3/4,3/4,3/4) and its equivalents, which are empty in HH. When removing Ni, the Ni-vacancy can be located at either of these two types of sites.

When one Ni is removed, due to symmetry, f- and h-sites are equivalent. The energy cost for removing 1 Ni out of a 2 × 2 × 2 unit cell is ∼0.417 eV. Similar to the case of HH+nNi, the energy cost to remove the second Ni (to add the second vacancy) is smaller (by 0.045 eV) than that needed to remove the first Ni (table 1). We chose the first vacancy (V1) to be at a f site and the second one can be at either h or f site. We denote the pair of vacancies by the name of the sites

**Table 1.** Formation energies (eV) of HH–FH systems (for the lowest energy configurations).

| HH+1Ni | HH+2Ni | HH+3Ni | HH+4Ni | FH-1Ni | FH-2Ni |
|--------|--------|--------|--------|--------|--------|
| ΔE f(X) | 0.425  | 0.758  | 1.083  | 1.440  | 0.417  | 0.759  |

Figure 2. Left column presents energetics of two extra Ni in HH: energy versus distance. Right column presents the preferable configuration of the excess Ni (orange sphere) (only the Ni matrix (blue spheres) is shown).
which they occupy, i.e. f–f and f–h. Note that f–f and h–h are equivalent. In figure 5(a), we plot the energy of the supercell with a pair of vacancies as a function of the distance between them, considering f–f and f–h separately. In figures 5(b)–(d) we show three possible di-vacancy configurations. Figure 5(a) shows that f–f and f–h are energetically different. For the f–h case, the interaction between two vacancies is repulsive, i.e. the total energy is the lowest for the largest distance. The relation between energy and distance is almost linear. The difference between the lowest and the highest energies is about ∼0.22 eV. For the f–f case, in contrast, the interaction between the two vacancies is, in general, attractive, the smaller is the distance, the lower is the energy. There is, however, a competing effect between repulsion and attraction at small distance, which makes the energy higher at the smallest distance, 4.47 Å (f–f1), than at the larger one, 6.32 Å (f–f2) (−805.00 eV for f–f1 compared to −805.055 eV for f–f2, as shown in figure 5(a)). The energies saturate at large f–f distance, however the actual value of the saturation energy is affected by the periodicity of the supercell. The structure of f–f2 (figure 5(c)) has 2 Ni-vacancies distributed evenly at every other site along the cubic axis (say x), forming a quasi one dimensional chain.

The structure consisting of quasi 1-dimensional chains of vacancies discussed above is similar to the configuration (i) of Kirievsky et al [41], except that they put one vacancy in a 1 × 1 × 1 simple cubic super cell; thus the vacancies form a 3-dimensional cubic lattice. In their work, Kirievsky et al [41] calculated electronic structures of 11 configurations with different numbers of Ni occupying eight cubic sites available for Ni atoms in a TiSn matrix and studied their energetics using a quasi binary model (TiNi$_2$Sn)$_x$(TiSn)$_{1-x}$. They defined the formation energy as

\[ \Delta U = E_{\text{tot}}^{\text{mixture}} - (c \cdot E_{\text{tot}}^{\text{TiNi}_2\text{Sn}} + (1 - c) \cdot E_{\text{tot}}^{\text{TiSn}}), \]  

where $E_{\text{tot}}$ is the total energy per cubic cell of corresponding systems. They found that the configuration (i), $c = 0.875$, had negative free-energy of formation whereas most of the other configurations (except $c = 0.5$ which corresponds to Half-Heusler phase TiNiSn) have positive free-energy of formation. As mentioned earlier, one should note that the definition of formation energy used by Kirievsky et al [41] is different from the definition used in the present work. Furthermore, they have used a 1 × 1 × 1 supercell where the periodic cell constraints are more important than ours. Thus, it is not possible to directly compare the values of formation energies between these two works.

### Table 2

| $r$ (Å) | 4.349 | 6.151 | 7.533 | 8.699 | 10.654 |
| --- | --- | --- | --- | --- | --- |
| $\theta$ (°) | 60 | 90 | 120 | 180 | 90 |
| E (eV) | −654.14 | −654.10 | −654.08 | −654.06 | −654.03 |

Figure 3. Left column presents energetics of HH+3Ni as a function of the sum of the distances of Ni$_3$ from Ni$_1$ and Ni$_2$ whose positions are predetermined by studying the energetics of a pair of excess Ni (figure 2). Right column shows the preferred configuration of the Ni$_3$ (only the Ni matrix (blue sphere) is shown). The excess Ni are orange spheres, forming an equilateral triangle.

Figure 4. Total energies of selected configuration of (Ni)$_4$ clusters in HH matrix (with respect to the energy of the most stable configuration) calculated for 2 × 2 × 2 and 3 × 3 × 3 supercell.

\[ E_{\text{tot}} \]

3 However, it is reasonable to use a 1 × 1 × 1 supercell here because Kirievsky et al [41] used DFT energies to get effective parameters for their finite $T$ calculations.
before we discuss the electronic structure of HH–FH mixture, let us first review the electronic structures of the two end compounds ZrNiSn and ZrNi2Sn. Electronic structures of ZrNiSn and ZrNi2Sn are well understood and were extensively studied both theoretically [15, 51] and experimentally [11, 12, 51]. ZrNiSn is a semiconductor with a band gap of ~0.5 eV [15, 51, 74] between Γ and X points in the FCC Brillouin Zone (BZ) (not shown). The band gap is formed mainly from the hybridization of Zr- and Sn-p orbitals with a mixing of some Ni-d orbitals. The band gap formation was carefully discussed by Öğüt and Rabe [51] and Larson et al [74]. The top three valence bands are degenerate at the Γ point but split as one goes away from it. One of these three bands has light effective mass while the other two have heavier mass. On the other hand, the lowest conduction band is non-degenerate with anisotropic effective mass. All Ni-d and Sn-s bands are fully occupied, the latter is located at about 15 eV below the valence band maximum. ZrNi2Sn, on the other hand, is a paramagnetic metal with finite density of states at the Fermi level. In this system, the d-levels of Ni strongly hybridize with the Sn-p and Zr-d levels. The states below the Fermi energy (0 eV) in the energy range (~3 to 0 eV) are dominated by the Ni-d orbitals with significant mixing with Zr-d orbitals near the Fermi energy. In fact, such a mixing gives rise to peaks in the DOS at ~0.5 eV, caused by Van-Hove singularity, which plays an important role in the high-Tc superconductivity of the related compound ZrNi2Ga [75].

Figure 6 gives the band structures of ZrNiSn (figure 6(a)) and ZrNi2Sn (figure 6(b)) in the Brillouin zones (BZ) of 2 × 2 × 2 simple-cubic supercell, and the corresponding density of states (DOS) per supercell (figure 6(c)). Going from a fcc primitive unit cell to 2 × 2 × 2 simple-cubic supercell, due to band folding, the band structure of ZrNiSn shows a direct (instead of indirect as in FCC (not shown) band gap of ~0.5 at the Γ point, in good agreement with earlier works [15, 51, 74]. Figure 6(c) shows comparison between the DOS of the two compounds, near the Fermi level (E_F = 0 eV). The inset shows the DOS in the vicinity of Fermi level. Our calculation finds DOS(E_F) = 2.1 states/eV per formula unit, corresponding to electronic specific heat coefficient γ = 5 mJ mol^{-1} K^{-2} which is about two times smaller the experimental value [76]. This discrepancy between theoretical and experimental estimations of γ is well-known for Heusler compounds and may be ascribed to the renormalization by electron–phonon or electron–magnon (for magnetic systems) interactions [76].

When one Ni (Ni1) is introduced into the HH matrix (or removed from FH), there is a change in the electronic structure and a redistribution of the charge density with respect to the host system (HH or FH). To analyze this charge redistribution, we calculate the charge density difference (charge-difference) Δρ = ρ_{HH}(r) - ρ_{FH}(r), where ρ_{HH}(r) and ρ_{FH}(r) are the total charge densities of the defective system and the corresponding host system. Figure 7 shows the charge difference
where Γ₀ is the Fermi level, and X₂ is the valence band maximum. With these channels defined, one can realize that the charge density of states of HH with 1, 2, 3 and 4 additional Ni.

A subtle difference between FH⁻¹Ni and HH⁺¹Ni is that the Ni©V₁ direction but along the Ni-Sn direction, as shown in figure 7(b). The red lobe around Ni₁ is closer to V₁ than the red lobe, opposite to those around the other Ni atoms with linear link Ni-Sn(Zr)-V₁, whose red lobes are closer to V₁. This difference in charge rearrangement is most likely the reason for the difference in energetics of FH+nNi from HH+nNi and is a reflection of different local bondings in FH and HH systems.

In figure 8, we give the band structures and DOS of HH+nNi systems for different values of n for the lowest energy structures. As one can see in figures 8(a)–(c), band structure of the host matrix is mainly unchanged when adding Ni to HH, except that defects split the degeneracy of host HH bands due to impurity-induced symmetry-lowering and introduce defect states into the gap. There is still some local residual symmetry which preserves the degeneracy of the valence band maximum at the Γ point. The splitting of the HH conduction bands reduce the band gap (between HH valence band maximum and conduction bands minimum) from ~0.5 ev to ~0.4 ev. There are two defect states per additional Ni (Ni-eg states) located just below the HH conduction band edge.

When one excess Ni is added to the HH matrix, it brings 10 more electrons which occupy 5 Ni₁-d bands, 3t₂g and 2 e_g. All the Ni₁-d bands are below the Fermi level, the t₂g bands are located around ~ -1.5 ev, whereas the e_g bands are located right below the HH conduction bands, giving rise to the in-gap states. The charge density associated with the in-gap defect states is given in figure 9, clearly showing the Ni-e_g character.

Figure 7. Charge difference between (a) HH+1Ni and (b) FH-1Ni and their parent compounds (HH and FH), the blue color indicates charge depletion and the red color indicates charge accumulation. The figure shows the contour plot in the (-1 1 0) plane. Charge difference is defined as ρ₀(r)−ρ(r), where ρ₀(r), and ρ(r) are charge densities of defective and pure systems, respectively. Host-Ni atoms are blue spheres, excess Ni is the red sphere, Zr are brown spheres, Sn are gray spheres.

Figure 8. Evolution of electronic structure of HH with excess Ni: band structures (a) HH+1Ni, (b) HH+2Ni, and (c) HH+3Ni, and (d) density of states of HH with 1, 2, 3 and 4 additional Ni.
The defect bands have a bandwidth of \(\sim 0.14\) eV. The dispersion is small in \(x, y,\) or \(z\) directions, but larger in other directions, such as \(\Gamma-M (110),\) \(\Gamma-R (111),\) which are directions of \(\text{Ni}_1-Zr(\text{Sn})\) bonds. In order to understand the nature of these defect states, we have studied \(3 \times 3 \times 3\) supercell with one excess Ni (\(\delta = 0.009\)). This increases the distance between the defect and its supercell images from \(\sim 12\) Å to \(\sim 18\) Å. We find that the dispersion of the defect bands decreases dramatically (to almost flat bands). This result implies that the coupling between the defects is weak at extremely dilute concentration but is important for moderate and high concentrations.

When more Ni are added to the HH matrix, more impurity bands are introduced into the gap region, and eventually they fill up the gap, converting the semiconducting HH into a metallic FH. Comparing the DOS of HH+\(n\)Ni (figure 8(d)), one can clearly see the evolution of the electronic structure. With one extra Ni, DOS starts to show a peak below the conduction bands. As the number of excess Ni increases the peak gets higher and shifts downwards in energy. These localized defect states are occupied and do not contribute directly to charge transport but can act as donor-states injecting carriers into the conduction band. Also they can suppress \(p\)-type behavior by destroying the holes in the valence band. The presence of such localized states in HH–FH alloys for a small concentration of excess Ni (beyond HH limit) can dramatically affect their transport properties.

The effect of Ni-vacancy in FH is less subtle than that of Ni excess in HH. Figure 10 gives the electronic structure of FH+\(n\)Ni. The dominant effect of Ni-vacancy on the band structure of FH is the band splitting. One can see some extra bands appearing around \(\sim 1\) eV. These extra bands give rise to a small peak in the DOS at \(\sim 1\) eV (figure 10(d) inset). These effects, however, introduce small changes in the DOS (figure 10(d)), particularly near the Fermi level and do not change the metallic properties of FH, at least for small concentrations of Ni-vacancy.

4. Summary and conclusion

To summarize our work, we have discussed the energetics and electronic structures of the HH–FH mixture, \(\text{ZrNi}_1+\text{Sn},\) using 2 \(\times\) 2 \(\times\) 2 supercells. The focus is on the small concentration (\(\leq 0.125\)) limit of defects (excess Ni in HH and Ni-vacancy in FH). We have also done some limited calculations using 3 \(\times\) 3 \(\times\) 3 supercells.

Our calculations predict an attractive interaction between excess Ni atoms in the HH matrix, i.e. the excess Ni atoms tend to come close to each other and form nano-clusters within the HH matrix. The lowest energy nanoclusters are: dimers (2 Ni), trimers (3 Ni) with equilateral triangle structure, and tetramers (4 Ni) with a distorted rhombus (DR) structure. Tetramers with tetrahedral structure which form an embryonic FH unit cell have slightly higher energy than the DR structure. In order to mimic the nanometer size FH inclusions in a HH matrix (seen by Makongo et al [3]) one needs to go to larger clusters of Ni atoms, which requires much larger supercell or other non \textit{ab-initio} theoretical methods. Vacancies in the FH matrix, on the other hand, are found to possibly occupy either of two crystallographic sites, h(1/4,1/4,1/4) or f(3/4,3/4,3/4), and their energetics are distinctively different from that of excess Ni in the HH matrix. If two Ni-vacancies in FH occupy the equivalent sites (either type h or f), the interaction between them is attractive at a distance larger or equal 6.32 Å and repulsive at smaller distance. If two Ni-vacancies in FH occupy the sites of different types (one at h-site and another at f-site), then the interaction is repulsive, the two vacancies tend to stay away from each other.

Analysis of the change in the charge density shows that excess Ni (or Ni-vacancy) in HH (FH) causes large charge rearrangement in the host matrix. The charge rearrangement occurs mostly on the Ni-sites and is larger at Ni sites which are connected to the excess Ni (Ni-vacancy) indirectly through one channel mediated by either a Zr or a Sn atom. The charge rearrangement is modest at the Ni-sites which are connected to the defect site through two channels mediated by atoms of the same type. FH with one Ni-vacancy has an interesting charge rearrangement at the Ni-sites connected to the vacancy through two channels, one mediated by Zr and the other by Sn. This charge rearrangement is in different directions compared to HH, i.e. the Ni-vacancy interacts with the HH matrix through two channels, one mediated by Zr and the other by Sn.

Figure 9. The isosurface of the charge density associated with the in-gap defect states in HH+1Ni. Host Ni are blue spheres, excess Ni is the red sphere, Zr are brown spheres, Sn are gray spheres.

Figure 10. Evolution of electronic structure of FH with deficient Ni: band structures (a) FH, (b) FH-1Ni, and (c) FH-2Ni, and density of states of those systems. The inset shows the DOS, indicated by the arrow, around \(-1\) eV in small range [−1.2, −0.9] eV.
to that at other Ni-sites and is most likely responsible for the difference in energetics between FH-nNi and HH+nNi.

While the effect of Ni-vacancies in FH on the electronic structure is modest, the excess Ni in HH changes the HH’s electronic structure dramatically. The excess Ni in HH introduces new impurity states in the gap of the HH band structure, giving rise to finite density of states below the conduction bands. Due to the in-gap impurity states, HH with excess Ni can behave like a n-type semiconductor.

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