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# Nanoscale structural heterogeneity in Ni-rich half-Heusler TiNiSn

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The structural implications of excess Ni in the TiNiSn half-Heusler compound are examined through a combination of synchrotron x-ray and neutron scattering studies, in conjunction with first principles density functional theory calculations on supercells. Despite the phase diagram suggesting that TiNiSn is a line compound with no solid solution, for small *x* in TiNi<sub>1+x</sub>Sn there is indeed an appearance—from careful analysis of the scattering—of some solubility, with the excess Ni occupying the interstitial tetrahedral site in the half-Heusler structure. The analysis performed here would point to the excess Ni not being statistically distributed, but rather occurring as coherent nanoclusters. First principles calculations of energetics, carried out using supercells, support a scenario of Ni interstitials clustering, rather than a statistical distribution. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4900497]

## INTRODUCTION

Among the various materials studied for use in thermoelectric devices, semiconductors of the half-Heusler crystal structure have attracted significant attention for power generation in moderate temperature applications.<sup>1,2</sup> In particular, materials of the formula XNiSn (where X = Ti, Zr, or Hf) tend to show very desirable electrical properties, exhibiting particularly large Seebeck coefficients (*S*) given their high electrical conductivities ( $\sigma$ ).<sup>3,4</sup> This makes half-Heusler compounds promising, considering that a good value for the thermoelectric figure of merit  $ZT = (S^2 \sigma/\kappa)T$ , where  $\kappa$  is thermal conductivity, relies on both terms being large. However, the  $\kappa$  of these materials is often large as well, frequently 3 to 5 times that of state-of-the-art materials.<sup>1</sup> Thus, reducing  $\kappa$ through phonon scattering greatly benefits the ZT of these materials.

In the past two decades, various approaches to reducing  $\kappa$  have been considered, mainly isovalent substitution for mass contrast<sup>5,6</sup> and grain size reduction.<sup>7,8</sup> More recently, there has been significant focus on the inclusion of a full-Heusler (fH) phase into the half-Heusler (hH) matrix, which can be used to improve ZT.<sup>9–14</sup> This is an attractive method, as the microstructure develops naturally by thermodynamic phase separation in Ni-rich compositions of  $XNi_{1+x}Sn$ . Interestingly, the presence of the full-Heusler phase induces a reduction in  $\kappa$ , from  $6 \text{ W m}^{-1} \text{ K}^{-1}$  to  $4 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature in TiNi<sub>1+x</sub>Sn, for instance, has  $\kappa$  close to 20 W m<sup>-1</sup> K<sup>-1</sup>.<sup>11</sup> It is also suggested that in nanoparticle form this second phase can additionally lead to "hot-carrier" filtering process, which enhances the Seebeck coefficient.<sup>14</sup>

The question of disorder<sup>15,16</sup> and Ni occupancy<sup>17-20</sup> in the pseudobinary between XNiSn and XNi2Sn has been of general interest. The XYZ half-Heusler crystal structure, space group  $F\bar{4}3m$ , can be thought of as an XZ rocksalt sublattice with half of the tetrahedral sites (in terms of coordination with Z) being occupied by Y, forming a YZ zincblende sublattice; in the full-Heusler  $XY_2Z$ , space group  $Fm\bar{3}m$ , all 8 of these sites within each unit cell are filled. Experimentally, Rietveld refinements of TiNi1+xSn powder x-ray and neutron diffraction data for the half-Heusler phase are typically best fit by models that allow for some Ni occupancy in the vacant 4d Wyckoff site  $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$  of  $F\overline{4}3m$ , on the order of 5% to 10%.<sup>13</sup> There also tends to be a linear increase in the half-Heusler lattice parameter,  $a_{\rm hH}$ , with increasing x, indicating a degree of Ni solubility in the structure.<sup>11,18</sup> That said, equilibrium ternary phase diagrams report TiNiSn as a line compound, i.e., with no excess Ni.<sup>21,22</sup> This assertion has been argued from density functional theory (DFT) calculations as well, invoking an orbital ordering argument,<sup>22</sup> and statistical thermodynamics approach based on formation energies.<sup>19</sup>

Together these studies raise the question of whether the excess Ni being refined on vacant sites (herein referred to as Ni "interstitials") using the Rietveld method is randomly distributed, or represent local nanoclusters of a full-Heusler constrained to the half-Heusler lattice parameter. Recently, Do *et al.* have explored this clustering in the ZrNi<sub>1+x</sub>Sn system by DFT,<sup>23</sup> finding excess Ni atoms to be attracted to one another, forming local clusters. In this study, we detail observations from powder neutron and synchrotron x-ray diffraction (XRD) data experiments with insight into the Ni interstitial occupancy in TiNi<sub>1+x</sub>Sn. Additionally, we report DFT calculations to evaluate the defect energies of high Ni interstitial concentration, up to  $\approx 16\%$ , and the effect of interstitial proximity to one another, relating these to the diffraction studies.

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FIG. 1. (a) Nominal TiNi<sub>1+x</sub>Sn compositions and forms of radiation for which scattering data were collected. Neutron diffraction data and Rietveld refinement fits for (b) TiNiSn and (c) TiNi<sub>1,15</sub>Sn samples, with contributions from the half- and full-Heusler phases displayed beneath. (d) Three different defect models for refinements of "half-Heusler" diffraction peaks.

#### **EXPERIMENTAL METHODS**

Samples of TiNi<sub>1+x</sub>Sn were prepared for the diffraction experiments via levitation induction melting followed by annealing, as described in a previous report.<sup>11</sup> Powder synchrotron XRD (SXRD) data were collected at the 11-BM beamline of the Advanced Photon Source (APS) at Argonne National Laboratory, with a wavelength  $\lambda$  of 0.440645 Å to reduce Sn absorption. Constant-wavelength, room temperature neutron diffraction data were collected at the National Institute of Standards and Technology Center for Neutron Research (NCNR) (see Figure 1). A Cu(311) monochromator and 60' collimator with no filter were used,  $\lambda = 1.5409$  Å. The patterns were analyzed using the TOPAS Academic program suite implementation of the Rietveld method.<sup>24</sup>

To find the energy of different Ni interstitial arrangements, the total energy and electronic states of various defect structures were calculated using DFT as implemented in the Vienna *ab initio* Simulation Package (VASP)<sup>25,26</sup> with projector-augmented wave (PAW) pseudopotentials.<sup>27</sup> The exchange-correlation was described by Perdew-Burke-Ernzerhof within the generalized gradient approximation (GGA-PBE).<sup>28</sup> A cutoff energy of 550 eV was used, with a  $\Gamma$ -centered **k**-mesh of  $4 \times 4 \times 4$  and a tetrahedron smearing method.

Defect energies were calculated employing  $2 \times 2 \times 2$ , 96 + *n* atom supercells with *n*, the number of interstitials, being between 0 and 5. Site disorder was not included in our analysis, as we expect it to be infrequent due to the large formation energies associated with these defects,<sup>18,20</sup> making direct calculation difficult. Five interstitials correspond to a 15.625% site occupancy of the interstitial site, or equivalently Ti<sub>32</sub>Ni<sub>37</sub>Sn<sub>32</sub>. Calculations allowed for volume relaxation, with ions held fixed on their initial special positions and the cell constrained to remain cubic.

#### **RESULTS AND DISCUSSION**

#### Interstitials contribution to powder diffraction

With the high resolution of synchrotron x-ray diffraction data, we are able to observe an asymmetry in the diffraction

peaks of the half-Heusler, as exemplified in Figure 2(a) for the x = 0.15 material, similar to that noted in the previous literature.<sup>9,29</sup> The SXRD for the stoichiometric, x = 0, sample itself *cannot* be fit to a single phase, showing a distinct shoulder on each peak, potentially due to antisite defects and phase separation. We do not discuss this in detail in this report. However, the peak shape for our materials with excess Ni is not well captured by a defect-free TiNiSn model either, due to the asymmetry. Difference Fourier maps of such refinements show the presence of residual electron density on the 4d vacant sites of the half-Heusler structure (see Figure 2(b)). As such, a typical approach is to allow some Ni occupancy on this site when modeling the data, shown as model 1 in Figure 1(d). In our materials, however, we observe that even this model fails to accurately capture the higher-Q region of the peaks. This supports the notion that



FIG. 2. (a) Synchrotron XRD data of the (220) half-Heusler phase peak of the x=0.15, TiNi<sub>1.15</sub>Sn material, fit with a defect-free TiNiSn model. (b) Accompanying Fourier difference map, the observed intensity minus calculated fit of the data, in the (001) plane. Residual electron density is observed in the vacant 4*d* sites, denoted by white arrows.

these peak anisotropies arise from nanoscale inhomogeneity in the distribution of Ni interstitials rather than a statistical distribution; if the latter were the case, a single phase would be sufficient to model the diffraction, which is not the case for the present data. We find that it is therefore necessary to use a model which incorporates multiple structural domains to describe the diffraction peaks.

While a number of models were attempted, including antisite defects, interstitials, and vacancies, we only consider models 2 and 3 (see Fig. 1(d)) in detail here, as these other point defects have been found in the previous literature to be much more energetically costly, and therefore less likely to occur, than interstitial Ni defects.<sup>18,20</sup> Models 2 and 3, however, both consider a "pure" TiNiSn structure with a secondary structural nanoscale inhomogeneity: one with a compressed TiNi<sub>2</sub>Sn with lattice parameter  $a'_{\rm fH} \approx a_{\rm hH}$  as the subsidiary hH phase, analogous to coherent fH nanoprecipitates (model 2), and another with a second half-Heusler structure, "hH-*i*," that *does* allow for Ni occupancy at the  $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$  site (model 3). Representative fits of these models are displayed in Figure 3(a).

Though the coherent-fH model (model 2) does improve the fit criteria over a single hH-*i* model (half-Heusler TiNiSn with Ni interstitials, it does not fit the data as well as hH + hH-*i*), as measured qualitatively and by the  $\chi^2$  values (Fig. 3(b)). Unlike the two other models, thermal parameters, particularly the Sn site, tend to refine to unphysical, nonpositive values using model 2. Additionally, the model refines the crystallite dimensions of these fH structures to be several microns, which is inconsistent with transmission electron microscopy observations.<sup>9,17</sup> Such a large crystallite of TiNi<sub>2</sub>Sn would also not be expected to remain coherent with the TiNiSn matrix.

Of all models, it was found that model 3, two half-Heusler structures, one of which allows for Ni interstitials, was the best descriptor of the diffractograms, without the unphysical parameters exhibited by model 2. This model, hH + hH-*i*, is analogous to local clusters of interstitial Ni atoms distributed throughout the material, but in which they are neither extended nor ordered enough to diffract as fH TiNi<sub>2</sub>Sn. This is somewhat of an intermediate arrangement between models 1 and 2, i.e., completely random interstitial distribution and coherent, well-ordered fH precipitates.

It was found that model 3 also leads to the smallest lattice parameter for the hH structure, shown by the solid bars in Figure 4(a), and estimates small crystallite sizes for this phase, typically of a few hundred nanometers. This is reasonable given that only small contiguous regions of the material are expected to be completely devoid of the interstitial defects that cause an expansion of the lattice. If the data are fit with a model that considers 12 phases with the relation

$$a_i = Cx_i + a_{i=0},\tag{1}$$

where  $i = \{0, 1, ..., 11\}$ , *C* is a scaling parameter, and  $x_i$  is the Ni interstitial occupancy (with  $x_0 = 0$  and  $x_{i+1} - x_i$  a constant), this idea of small pure-hH crystallites is observed similarly: As shown in the contour plot in Figure 4(b), the minimum  $a_{hH} \approx 5.925$  Å persists to a small degree even in the very Ni-rich materials, though these latter samples are dominated by material with large incorporation of interstitials (the two lattice parameters that model 3 finds, in Fig. 4(a)).

When utilizing these models to explore total Ni atom fraction, including that in the TiNi<sub>2</sub>Sn phase, we found almost no variation between the three models, but significant deviation between synchrotron XRD and neutron diffraction (Fig. 3(c)). For the synchrotron data, the refined Ni concentration only matches that of the nominal composition in half of the samples; for TiNi<sub>1.10</sub>Sn, TiNi<sub>1.15</sub>Sn, and TiNi<sub>1.25</sub>Sn, the effective concentration is significantly higher. The neutron data, however, estimate compositions much closer to nominal, with the interstitial occupancies of the hH-*i* phase



FIG. 3. (a) Rietveld fits of (220) half-Heusler peak for diffraction data of TiNiSn and TiNi<sub>1.15</sub>Sn samples, using three different models. Contributions from each structure displayed beneath. (b) Goodness of fit,  $\chi^2$ , and (c) refined Ni atomic fraction by these models. ND: neutron diffraction.



FIG. 4. (a) Refined lattice parameters,  $a_{hH}$ , of the half-Heusler phase (solid) and second phase (shaded)—i.e., coherent TiNi<sub>2</sub>Sn or TiNiSn with interstitials—by the three models. Dashed line is fit to average  $a_{hH}$  of model 3. Error bars, which represent one standard deviation, are smaller than the line width for SXRD. (b) Contour plot of  $a_{hH}$ , fitting with a 12 phase structural model.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to ] IP: 129 6 121 240 On: Thu, 18 Jun 2015 14:35:32 converging to values more similar to those reported in the literature:<sup>13</sup> Neutron refinements put interstitial occupancy at approximately 5%, whereas the synchrotron converged to values as high as 30% for the intermediate compositions.

Because the occupancies are more highly correlated with the lattice parameter and phase scale in synchrotron than neutron diffraction data, the occupancy values from XRD here are more aptly viewed as qualitative measures of chemical inhomogeneity in TiNi<sub>1+x</sub>Sn than direct probes of Ni concentration. The synchrotron thermal parameters for the interstitial site are also extremely large in all models—  $B_{iso} \approx 13 \text{ Å}^2$ , whereas  $B_{iso} \approx 1 \text{ Å}^2$  for the Sn site—suggesting that these parameters are acting as much to fit peak shape and broadness as merely total electron density.

#### **Energetics of Ni interstitials**

With the diffraction data in mind, we looked to examine what the energetic tendencies of Ni interstitials might be between random distribution (cf. model 1) and local clustering (model 3). For each number of interstitials n, the positions were varied so that the defect energies were determined when clustered—where all interstitials occupy sites adjacent to one another—when completely separated in a pseudorandom fashion, and each arrangement in between (see Figure 5).



FIG. 5. (a) TiNiSn half-Heusler unit cell and the  $2 \times 2 \times 2$  supercell base used for DFT calculations. (b) Representative supercells of calculations with 4 Ni interstitials, which corresponds to TiNi<sub>1.125</sub>Sn. Interstitials are represented here as black spheres. The defect structures calculated include all n = 4 interstitials clustered together, n - 1 = 3 with 1 separated, and so on until each possible n - i was represented.

A "fatband" analysis of the electronic structure—with bands weighted by contribution from the Ni interstitial, Figure 6—for n = 1 highlights the addition of defect states into the TiNiSn band gap. This shifts the Fermi level such that the compound should exhibit electron conductivity, as opposed to *p*-type conduction calculated for the undoped TiNiSn,<sup>15</sup> and the band gap is reduced from 0.45 eV to 0.12 eV. These findings correspond very well with both experimental observations of bulk TiNiSn<sup>4</sup> and previous theoretical reports.<sup>20</sup>

The differences in defect energies for further Ni excess are shown in Figure 7(a). Do *et al.* demonstrated in the Zr–Ni–Sn system that the distance between Ni interstitials can have a large effect on the ground state energy.<sup>23</sup> We have therefore ensured that "separated" interstitials are as distant apart as is allowed by the supercell and periodic boundary conditions. To reassure ourselves that the influence of periodicity on the calculated interactions is minor, we also calculated the energies of a limited number of  $3 \times 3 \times 3$ defect supercells and found that the observed trends are the same.

Clustering is found to be consistently lower in energy than a random distribution of interstitial Ni. At n = 4, clustering corresponds to a single full-Heusler TiNi<sub>2</sub>Sn unit cell embedded in pristine half-Heusler, but even with only 3 interstitials there is an energetic drive to cluster rather than separate, on the order of 50 meV/interstitial. The energy gains for clustering in the Zr–Ni–Sn system reported by Do *et al.* are approximately twice that we find for Ti–Ni–Sn.<sup>23</sup> Aside from the change of Zr to Ti on the *X* site, they allowed ionic positions to relax in their study, whereas we did not, which likely accounts for the difference in magnitude. However, we observe very similar behavior.

Despite the energetic differences between various interstitial arrangements, the lattice parameter is indistinguishable



FIG. 6. Band structure diagram (left) and density of states, DOS, (right) of the single-interstitial supercell,  $x \approx 0.03$ . In band diagram, line thickness corresponds to contribution from the Ni interstitial atom,  $P\bar{4}3m$  symmetry. Dark shaded area in DOS represents states arising from the interstitial Ni.

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FIG. 7. (a) Defect energies in the 96 + *n* atom supercell. Energies are plotted against the average of the total energy of two pseudorandom arrangements. (b) Percent difference in the calculated effective lattice parameters of supercells from that of TiNiSn, a = 5.9448 Å.

between the different interstitial configurations, as detailed in Figure 7(b). This suggests that the electronic stabilization that occurs is more integral to the clustering behavior than a simple stress relaxation. That is, even with coherency strains of the nanoclusters—the calculated forces on the interstitial Ni atoms are higher when clustered—it is more energetically favorable than separated interstitials.

### CONCLUSIONS

Rather than a statistical distribution of Ni atoms on the vacant tetrahedral site, analysis of synchrotron x-ray and neutron powder diffraction data supported by density functional theory calculations has shown that the Ni-lean phase of these  $TiNi_{1+x}Sn$  materials is best thought of as a half-Heusler matrix with nanoclusters of Ni interstitial atoms pocketed throughout the material. In order to model this local chemical heterogeneity in the hH matrix and its effect on the diffraction peaks for Rietveld refinement, it is best to use multiple structures, a pure half-Heusler in conjunction with a phase which allows for vacant site occupation by Ni atoms.

By XRD, this occupancy parameter acts almost as a probe of Ni inhomogeneity itself, while neutrons are a better probe of actual interstitial occupancy. We understand that structure and chemistry both contribute to the thermoelectric properties of  $XNi_{1+x}Sn$  materials, and in our materials the refined Ni atom fraction deviation from expected, from SXRD, correlates well with measured *ZT* values.<sup>11</sup> As this points to a strong structural influence, experimental studies of the local structure and Ni environment of  $TiNi_{1+x}Sn$  materials, as well as the kinetics, would be very beneficial in further understanding interstitials in this system. This knowledge will be important for informing preparation techniques and for the improvement of  $TiNi_{1+x}Sn$  thermoelectric efficiency.

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