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Structural, Chemical, Electrical, and Thermal Properties of *n*-Type NbFeSb

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Abstract

We report on the structural, chemical, electrical, and thermal properties of *n*-type polycrystalline NbFeSb synthesized by induction melting of the elements. Although several studies on *p*-type conduction of this half-Heusler composition have recently been reported, including reports of relatively high thermoelectric properties, very little has been reported on the transport properties of *n*-type compositions. We combine transport property investigations together with short- and long-range structural data obtained by Mössbauer spectroscopy of iron-57 and antimony-121 and by neutron total scattering, as well as first-principles calculations. In our investigation, we show that *n*-type conduction can occur from antiphase boundaries in this material. This work is intended to provide a greater understanding of the fundamental properties of NbFeSb as this material continues to be of interest for potential thermoelectric applications.

Graphical Abstract

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ASSOCIATED CONTENT

Supporting Information

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Thermal properties of NbFeSb, and temperature dependent κ_L for NbFeSb (PDF)

INTRODUCTION

Half-Heusler compounds have been of interest for thermoelectric applications for over two decades.¹ They form in cubic crystal structures, space group $F\bar{4}3m$ (no. 216), with compositions XYZ, where X and Y represent transition metals or lanthanides and Z typically represents Sn or Sb. The half-Heusler crystal may be considered as a Heusler phase XY_2Z with a vacancy at one of the Y atom sites. The structural arrangement also allows for numerous compositional variations, as well as the possibility of tuning the transport properties with composition. Doping of these materials has resulted in excellent thermoelectric properties, with ZT values of 1.5 reported for *p*-type NbFeSb.^{1–7} Half-Heusler compounds are also mechanically robust. This is another important, and often overlooked, materials property for high-temperature thermoelectric applications.^{8–10}

The dimensionless thermoelectric figure of merit, $ZT = S^2\sigma T/\kappa$, defines the effectiveness of a material for thermoelectric applications, where S is the Seebeck coefficient, ρ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature.¹¹ Materials that are of interest for thermoelectric power generation applications typically possess low κ values.^{11–15} Thus, high ZT values are possible if the power factor, $S^2\sigma$, can be optimized, thereby providing the best electronic properties that can be obtained for a given bulk composition.¹¹ This is also the case for half-Heusler compounds, as has been demonstrated over the past two decades.^{1,7,16}

First-principles theoretical calculations of the electronic structure and thermoelectric properties of *p*-type NbFeSb indicate that higher ZT values can be obtained at elevated temperatures if lower κ values are realized at the optimum doping levels.¹⁷ As stated above, doping studies of the half-Heusler composition NbFeSb have revealed rather high ZT values at elevated temperatures for *p*-type compositions,^{2–5} while, most recently, Tavassoli et al.¹⁸ showed modest ZT values while demonstrating that small changes in composition may result in large effects on the transport properties. Earlier studies indicate that NbFeSb also exhibits *n*-type conduction,^{19,20} but this type of doping is far less studied in these materials. In this report, we present structural, chemical, electrical, and thermal properties, as well as first-principles theoretical calculations, on *n*-type NbFeSb. Our aim is to develop a better

understanding of the fundamental properties of this material in light of the varying properties reported and the interest in this material for thermoelectric applications. The particular interest here derives from the lack of an extensive study of *n*-type NbFeSb, relative to *p*-type NbFeSb. Structural refinements based on neutron diffraction data as well as Mössbauer spectroscopy were performed and complemented by theoretical analyses of the electrical properties of this material.

EXPERIMENTAL AND COMPUTATIONAL METHODS

NbFeSb was prepared from high purity elements (all from Alfa Aesar) that were weighed in the nominal composition NbFeSb.²¹ The elements were then placed in a silica ampoule and sealed inside a quartz tube under vacuum. Induction melting of the elements utilizing a 3-coil water cooled setup was performed 4 times in order to promote homogeneity, resulting in the complete melting of the product with melt flow observed visually. The specimen was then ground into fine powder (325 mesh) and placed into a graphite die for densification using spark plasma sintering (SPS) at 1123 K and 80 MPa for 10 min under vacuum, giving a density of 7.62 g/cm³. To ensure homogeneity, the specimen was placed in an evacuated quartz tube and annealed in a furnace at 1073 K for 72 h after SPS densification.

X-ray diffraction (XRD) data of the powdered specimen were collected with CuK α radiation and a graphite receiving monochromator in a Bragg–Bretano geometry using a Bruker D8 Focus Diffractometer. Neutron diffraction data were acquired at the NOMAD beamline of the Spallation Neutron Source,²² Oak Ridge, TN, USA, at 300 K on ~300 mg of powdered specimen in a 2 mm diameter quartz glass capillary. The neutron total scattering structure function was produced from the diffraction data by normalizing the specimen scattering intensity to the intensity from a vanadium rod after subtracting the background of an empty 2 mm quartz capillary. The pair distribution function (PDF), $G(r)$, was obtained through the Fourier transform of the total scattering function with momentum transfer between 0.1 and 31.4 Å⁻¹. The peak position in the PDF is indicative of interatomic distances. Mössbauer spectra of NbFeSb were acquired using the ¹²¹Sb and ⁵⁷Fe Mössbauer resonance, employing a Wissel constant acceleration drive calibrated with α -iron at 295 K. Thirty milligrams of powdered NbFeSb mixed with boron nitride was used. The sources were 15 mCi of cobalt-57 in a rhodium matrix and 0.3 mCi of Ca¹²¹SnO₃, and the detectors were NaI@Tl with 1 mm thickness (Rietverc) and 1 in. thickness (Ortec). An additional spectrum with high statistics (error bar: 0.0082%) was recorded at room temperature using a yttrium aluminum (YAP:Ce) detector in an MS-96 spectrometer (Palacky University Olomouc). The isomer shifts are reported relative to α -Fe and CaSnO₃, for ⁵⁷Fe and ¹²¹Sb, respectively. The specimen was placed in a Janis SHI-850 closed cycle cryostat, and spectra were acquired at temperatures between 7 and 295 K.

The compositional stability was investigated using a TA Instruments Q600 that performed Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The densified pellet was cut using a wire saw into a 2 × 2 × 5 mm³ parallelepiped for simultaneous low-temperature (12–300 K) four-probe gradient sweep resistivity, ρ , and Seebeck coefficient, S , as well as steady state thermal conductivity, κ , measurements on a custom built radiation-shielded vacuum probe.^{23,24} The electrical contacts to the specimen

were made using direct soldering to nickel plated surfaces, and thermal contacts were made using Stycast epoxy. The maximum experimental uncertainties are 7%, 6%, and 8% for ρ , S , and κ , respectively. A $2 \times 2 \times 10 \text{ mm}^3$ parallelepiped was cut for high-temperature (300–700 K) four-probe ρ and S measurements under -0.05 MPa static He in a ULVAC ZEM-3 system with experimental uncertainty between 5% and 8%. A 1 mm thick disk was also cut for high-temperature laser flash diffusivity measurements under flowing Ar on a NETZSCH LFA475 system with an experimental uncertainty of 5%. The κ values for high temperature were calculated using $\kappa = D \cdot d \cdot C_p$, where D is the measured density, d is the measured thermal diffusivity, and C_p is the specific heat. A commercial Quantum Design Physical Property Measurement System measured temperature dependent isobaric heat capacity, C_p , for 24 mg of NbFeSb from 2 to 393 K, with an uncertainty (2σ) of the measurement between 1.0% and 1.5% for the entire temperature range.

Calculations of antiphase boundary energies and the resulting Seebeck coefficients were performed using first-principles ab initio density functional theory (DFT) using the Vienna Ab initio Simulation Package (VASP) within the generalized gradient approximation.^{25–28} Five valence electrons for Sb ($5s^2 5p^3$), 13 for Nb ($4s^2 4p^6 4d^4 5s^1$), and 8 for Fe ($4s^1 3d^7$) were used in the PAW pseudo potentials. A well-converged k -point grid of $12 \times 24 \times 24$ was used for the Brillouin-zone integration for the $2 \times 1 \times 1$ cell, and for the larger supercell sizes, the k -grid was scaled accordingly. The transport properties were obtained by solving the Boltzmann transport equation within the constant relaxation time approximation (CRTA)^{29,30} as implemented in the BoltzTraP code.³¹

Calculations of S of the stoichiometric ordered cell (without antiphase boundaries) were performed using the all-electron density functional theory code WIEN2K³² within the generalized gradient approximation of Perdew, Burke, and Ernzerhof.²⁸ Sphere radii of 2.36, 2.42, and 2.42 bohr were used for Nb, Fe, and Sb, respectively, and for Seebeck coefficient calculations, a minimum of 10 000 k -points in the full Brillouin zone were used. No internal coordinate optimization was performed as all internal coordinates are symmetry-dictated.

RESULTS AND DISCUSSION

Powder XRD data illustrated in Figure 1 shows phase-pure NbFeSb with the crystal planes indexed for each respective peak. The neutron scattering data and analysis of the PDF provide information on the long-range order, possible short-range order, and crystallinity of the material. The PDF data, shown in Figure 2, were modeled with the PDFgui software and utilized to refine the structural model for NbFeSb (ICSD CIF 83928).³³ As noted above, the half-Heusler structure has no free positional parameters and the atoms are located at $4a$ (0,0,0), $4c$ (0.25,0.25,0.25), and $4b$ (0.5,0.5,0.5) for Nb, Fe, and Sb, respectively. The refinement yields atomic displacement parameters $\langle u^2 \rangle$ of 0.0032(2), 0.0049(2), and 0.0066(2) $\text{\AA}^2$ for Nb, Fe, and Sb, respectively, and a lattice parameter $a = 5.9505(1) \text{ \AA}$ at 300 K. The scattering vector dependent dampening and broadening factors were 0.026(1) and 0.027(1), respectively. The fits were carried out in a large range of distance r , between 1.5 and 40 $\text{\AA}$, and an R_w adjustment quality factor of 7.44% was obtained. The possible presence of Fe on the empty $4d$ site of the half-Heusler structure, at (0.75,0.75,0.75), was assessed in the final refinement with the constraint that the total occupancy for both Fe sites

is 1. We note that a small decrease in R_w to 7.39% was observed, with 0.9(3)% occupation of Fe on the empty $4d$ site, and the other parameters were unchanged. We further note that the sites are *a priori* equivalent and that a small concentration of antiphase boundaries between a domain with one or the other $4d$ site being occupied would effectively yield a small occupation of the empty site. No signs of short-range order were observed in the PDF data. We assessed the possibility of Fe antisite occupation of the Nb site;³⁴ however, our refinement of the structural data excluded the presence of Fe on the Nb site given the sensitivity of neutron scattering for such defects due to the good contrast between Fe and Nb. This suggests that defect formation in stoichiometric NbFeSb may be strongly dependent on the synthesis conditions.

At first glance, the ^{57}Fe Mössbauer spectra at 7 and 295 K (Figure 3) consist of a single sharp absorption line; however, a more detailed analysis reveals that 2.3(3)% of the spectral area requires further investigation. We discuss the majority component first. The 7 K spectrum (see inset to Figure 3) reveals no evidence for magnetic hyperfine splitting. The spectra are remarkably simple, featuring a single absorption line. The isomer shifts are 0.092(1) and 0.21(1) mm/s at 295 and 7 K, respectively. The absence of the quadrupole interaction is in accordance with the location of Fe on a site with cubic point symmetry in the half-Heusler phase.

There are remarkably few reports of iron-57 Mössbauer spectroscopy in half-Heusler alloys. In the structurally close compound VFeSb, a single line Mössbauer spectrum is observed with an isomer shift of ~ 0.05 mm/s (the value is not reported).^{35,36} In contrast, in $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$, the Mössbauer spectrum reveals a small quadrupolar interaction ($E_Q = 0.17$ mm/s) and an isomer shift of 0.13 mm/s, with a small additional component that corresponds to 6% Fe occupancy of the Sb site. In the $\text{TiFe}_{1.33}\text{Sb}$ phase,³⁷ two components are observed for Fe, with isomer shifts of 0.108 and 0.279 mm/s, for a doublet (90% area) and singlet line (10% area), respectively. A detailed analysis reveals that the singlet line corresponds to Fe atoms on the $4c$ site *without* any of the neighboring vacancies occupied by any Fe, whereas the doublet acquires its quadrupole splitting from an Fe occupying a $4d$ vacancy site and disturbing the symmetric charge distribution. The authors also remark that the distribution of the 1.33 Fe on the $4d$ sites is not perfectly random.³⁷ Our observation of a single line spectrum in NbFeSb indicates that the majority of Fe occupies a $4d$ site without occupation of surrounding vacancy sites.

The ^{121}Sb Mössbauer spectra at 10 K (not shown) and 90 K (Figure 3) are simple single line spectra with a line width of 3.0(1) mm/s and an isomer shift of $-6.27(3)$ mm/s with no evidence for quadrupole interactions, which is also compatible with the location of Sb on a site with cubic point symmetry. Since the natural line width for ^{121}Sb spectroscopy is rather broad (2.1 mm/s), the spectra are much less sensitive to small variations in the local environment. The spectrum that we observe here is rather typical for paramagnetic Sb-based half-Heusler alloys. In the paramagnetic Sc based half-Heusler compounds ScNiSb, ScPdSb, and ScPtSb, very similar spectra are observed with a line width of 3 mm/s and isomer shifts of -6.77 , -7.0 , and -6.9 mm/s, respectively.³⁸ In TiCoSb, a single line spectrum with an isomer shift of -5.77 mm/s is observed, whereas, in the magnetic MnNiSb and MnCoSb phases, more complex spectra are observed, with isomer shifts of -7.5 and -10.4 mm/s.³⁹

Note that the isomer shift varies substantially upon substitution of the transition metals, and that MnNiSb and MnCoSb do not fulfill the 18 valence electron rule for half-Heusler phases.⁴⁰ However, NbFeSb does fulfill this rule, with the number of valence electrons being 8 for Fe and 5 for Nb and Sb. This is in accordance with the number of valence electrons in our VASP calculations, noting that the Nb 4*s* and 4*p* electrons are generally located well below the Fermi level, E_F .

Upon closer inspection, the fit of the ^{57}Fe Mössbauer spectrum reveals small residuals that warrant additional attention. First, two small lines are observed at -0.8 and 3 mm/s. Measurements at high velocity rule out that these line are part of a magnetic subspectrum. Second, residuals near $+0.4$ mm/s indicate the presence of a doublet. In order to achieve fits without unexplained signal, two additional components were added. The first, labeled D1 in Figure 3, is a small component with an isomer shift of $1.13(2)$ mm/s, a quadrupole splitting of $3.85(4)$ mm/s, which amounts to $0.8(1)\%$ of the spectral area. The second, labeled D2 in Figure 3, is a doublet with an isomer shift of $0.44(2)$ mm/s, close to the majority phase, and a quadrupole splitting of $0.33(3)$ mm/s, which amounts to $1.7(2)\%$ of the spectral area. We attribute the first doublet (D1) to an unidentified tiny Fe(II) impurity and the second doublet (D2) to Fe on either 4*c* or 4*d*, which have an Fe next-nearest neighbor that may originate in local Fe excess or antiphase boundaries. The quadrupole splitting for the D2 doublet is similar to that for the doublet in $\text{TiFe}_{1.33}\text{Sb}$;³⁶ however, the isomer shift is rather different which could reflect different local electronic density near an antiphase boundary. Note that, with an occupation of 0.9% suggested from the neutron PDF data, the binomial probability of having Fe with one or more of the four vacancies occupied is $\sim 3.5\%$.

Temperature dependent S and ρ measurements are shown in Figure 4. Temperature dependent κ and specific heat measurements (Figure S1) as well as analyses are described in the Supporting Information. The excellent agreement between the high- and low-temperature data indicates the homogeneity of the polycrystalline specimen. The ρ values (Figure 4a), are plotted so that the solid line fit to the highest temperature data is of the form $\rho = \rho_0 \exp(E_g/2k_B T)$, where E_g is the band gap and k_B is the Boltzmann constant. The ρ values exhibit typical semiconductor behavior, decrease with increasing temperature, and the slope of our linear fit gives $E_g = 0.4$ eV, in agreement with previous reports.^{41,42} The measured S values (Figure 4b), are negative throughout the entire temperature range¹⁹ and tend to zero at low temperature. The S values peak to -67 $\mu\text{V/K}$ at 420 K before decreasing to -40 $\mu\text{V/K}$ at 700 K.

It is noteworthy that, despite our observation of exponentially activated resistivity, with an inferred 0.4 eV gap close to the 0.5 eV theoretical value, the S values near room temperature are only in the -50 $\mu\text{V/K}$ range. Activated resistivity behavior is ordinarily associated with very small carrier concentrations and therefore large magnitudes of S , typically in the hundreds of $\mu\text{V/K}$ at ambient temperatures. The uniqueness of this juxtaposition is in our view indirect evidence for an unconventional doping scenario. Supported by our theoretical analysis, we submit that the doping in fact arises from antiphase boundaries.

Charge doping in a semiconductor is often taken to originate from the presence of dopants, elements not present in the original compound that effectively add or subtract charge from

the dispersive component of the electronic structure, thereby yielding *n*- or *p*-type doping, respectively. Another means of charge doping is through defects such as antisite defects, or vacancies, which can yield either *n*- or *p*-type doping. Such defects are well-known to be a primary source of charge doping in the prototypical high-performance thermoelectric material Bi₂Te₃, for example, and have also recently been invoked in the isostructural and isoelectronic material Bi₂Te₂Se.⁴³ We here propose an alternative possibility for the *n*-type conductivity in NbFeSb. Our experimental and theoretical analyses suggest that this effective doping may originate, in part, from antiphase boundaries.

In order to assess this possibility, we have constructed cells of dimensions (in units of the original fcc unit cell) $2 \times 1 \times 1$, $4 \times 1 \times 1$, $6 \times 1 \times 1$, $8 \times 1 \times 1$, $12 \times 1 \times 1$, $16 \times 1 \times 1$, and $24 \times 1 \times 1$ and computed the electronic structure. In each of these cells, the antiphase boundary (APB), a plane of mirror symmetry not present in the original cell, has been placed in the center of the cell. While strictly speaking, the APB should not cross an atomic plane, we are here concerned with the Fe sublattice, which is properly located away from the APB. This is described in Figure 5a,b for a $4 \times 1 \times 1$ NbFeSb supercell, where the APB is indicated by a green plane. We have extended the cell dimensions to rather long distances in order to isolate the APB energy from the confounding effects of the replication of periodic images of this APB. The formation energy of various APB within a supercell can be calculated as

$$E = \frac{E_{\text{tot}}^{\text{APB}} - E_{\text{tot}}^{\text{bulk}}}{2 * A}$$

where $E_{\text{tot}}^{\text{APB}}$ is the total energy of a supercell that contains an APB, $E_{\text{tot}}^{\text{bulk}}$ is the total energy of an equivalent supercell representing an ideal bulk crystal without APB, and A is the APB cross-sectional area which is in this case ($b \times c$). The factor of 2 in the denominator arises due to the existence of 2 phase boundaries in the structure because of periodic boundary conditions.

The calculated APB formation energies as a function of APB spacing are shown in Figure 5c. The formation energy is nearly independent of this spacing, changing by only a few percent from the $2 \times 1 \times 1$ cell to the $24 \times 1 \times 1$ cell, which has this spacing more than 70 Å. This suggests that our calculations accurately capture the APB energy for large spacing. The final value of some 76 meV/Å² is comparable to previously calculated⁴⁴ values for GaAs, though higher (as expected) than for metallic systems such as Fe–Al and Ni–Al alloys.^{45,46} Hence, such boundaries could be present in our NbFeSb system. The exact proportion, however, is unclear and will clearly depend on the synthetic conditions.

We next evaluate the effect of the APB on electronic structure. The calculated densities of states for bulk NbFeSb and NbFeSb with an APB are compared in Figure 5d. For bulk NbFeSb, our calculations show a band gap of 0.5 eV, in good agreement with the value of 0.4 eV estimated from the resistivity. In this plot, the APB introduced in the Fermi level moves into the highly dispersive conduction band (green and blue curves) indicative of effective *n*-type behavior, despite the lack of “dopants” *per se*. We note also that the $24 \times 1 \times$

1 DOS curve is closer to the bulk behavior than the $8 \times 1 \times 1$, as one would expect, given the lower APB effective concentration of the larger cell.

The calculated room-temperature average values of S for NbFeSb with 1 APB (in addition to the boundary replica) per $8 \times 1 \times 1$, $12 \times 1 \times 1$, and $16 \times 1 \times 1$ unit cell, respectively, are shown in Figure 6a as a function of dopant concentration, i.e., dopants added *in addition* to the APB. As expected, for an increasing concentration of APBs (2 per $8 \times 1 \times 1$ cell as opposed to 2 per $16 \times 1 \times 1$ cell), thermopower for small n -type charge doping ($n < 10^{20} \text{ cm}^{-3}$) is reduced significantly, consistent with the effective n -type behavior inferred from the DOS. For comparison, 300 K n -type average S for bulk NbFeSb (without APB) is also shown in Figure 6a. As can be seen at room temperature and at low additional carrier concentrations, the bulk magnitude of S is about $150 \mu\text{V/K}$, more than 2 times higher than the systems where an APB is present. The experimentally measured room-temperature S value, shown in Figure 4b, is $\sim -50 \mu\text{V/K}$, a value that compares reasonably well with the calculated S with the APB.

In fact, one can make a stronger and more experimentally relevant statement about the S dependence on APB concentration. The $16 \times 1 \times 1$ supercell modeled contains 64 Fe atoms, as the fcc half-Heusler structure contains 4 formula units per full cell. In this modeled structure, as depicted in Figure 5a,b, there are two next-nearest-neighbor Fe “pairs” which are symmetric around the APB, corresponding to a occupation probability of 3.1%. This accords with the $\sim 0.9\%$ Fe antisite occupation probability independently inferred from the Mössbauer and neutron data. That this modeled cell exhibits an average room-temperature thermopower of $-70 \mu\text{V/K}$, reasonably close to the $-45 \mu\text{V/K}$ from experiment, is in our view solid evidence for the soundness of the APB hypothesis. This is particularly true in light of the simplicity of our computational approach. In the actual experiment, one may reasonably expect randomly oriented antisite defects, with greatly variable distances between APBs. Therefore, to arrive at good agreement with the S values (both in *sign* and magnitude), as well as the antisite occupation probability found independently from experiment, speaks to the plausibility of the argument.

In addition, these results find a favorable explanation in terms of the 18-electron rule.⁴⁷ The apparent semiconducting nature of the base NbFeSb compound is relatively easily explained in terms of the 8 valence electrons of Fe, and the 5 each of Nb and Sb. The structure of NbFeSb has eight-fold nearest-neighbor coordination of Fe – 4 Nb and 4 Sb, each at a distance of $2.48 \text{ \AA}$; however, an Fe adjacent to the APB has an additional Fe next-nearest neighbor at $2.98 \text{ \AA}$ that is sufficiently close to substantially perturb the electronic structure. In order to illustrate this point, we plot the calculated density of states for a $4 \times 1 \times 1$ cell in Figure 5e, with an APB in the center as depicted in Figure 5a. In this cell, there are two types of Fe atoms, those adjacent to the APB (“APB Fe”) with Fe next-nearest neighbor located across the APB) and those located away from it (“non-APB Fe”) with only the usual bulk-like environment.

We plot the Fe atom-specific DOS, as well as the total DOS, in Figure 5e. We observe that the APB Fe atom DOS forms an impurity band, with finite DOS at E_F and a peak in this DOS near E_F . The n -type behavior observed experimentally and theoretically (for the APB

hypothesis) is readily explained in terms of this additional charge donated by Fe. In contrast, the non-APB Fe atom DOS is essentially gapped at E_F , with negligible DOS for a range of approximately 0.5 eV around E_F , the band gap as found theoretically for *bulk* NbFeSb. Hence, the impact of the APB is clearly to *locally* disrupt the 18- electron valence electron count and charge dope the system, leading to the *n*-type behavior.

In order to define the optimal *intentional* doping ranges for this thermoelectric material, we have computed S of a stoichiometric, ordered bulk NbFeSb (without APB), which we present in Figure 6b. This charge doping arises not from phase boundaries but from the more conventional factors. We focus on the *n*-type behavior. As expected, the magnitude of S increases with temperature, with the exception of the low-doping 1000 K regime where bipolar conduction becomes active. Thermoelectric performance will therefore likely be maximum for higher temperatures, as expected. We estimate the optimal doping range based on the criterion that ZT is usually maximum for S magnitudes, $|S|$, such that $200 < |S| < 300$ $\mu\text{V/K}$. At 1000 K, this *n*-type doping range is approximately $6 \times 10^{19} \text{ cm}^{-3}$ to $2 \times 10^{20} \text{ cm}^{-3}$, with correspondingly lower optimal dopings at lower temperature. Optimal *p*-type dopings are much larger, consistent with the generally larger masses of valence bands in this material.

The two methods of effective “doping” considered here, that resulting from APBs and more conventional charge *n*-type doping as might originate from Mo substitution for Nb, are distinct scenarios. Future research efforts on NbFeSb may reveal *both* types of doping. It is clearly more difficult experimentally to intentionally introduce a specified quantity of phase boundaries than a specified charge doping level. High thermoelectric performance necessarily depends upon achieving specified doping levels so that future experimental efforts will likely need to employ a more conventional doping route. Nevertheless, the theoretical results presented here suggest that phase boundaries generate the observed *n*-type behavior, and the thermoelectric properties, in NbFeSb. In particular, the good agreement between measured and calculated S values, along with the general agreement with experimental Fe antisite occupation probabilities in the APB scenario, and explanation of the 18-electron count disruption of the APB, supports the hypothesis that APBs are responsible for the *n*-type behavior observed.

CONCLUSION

To better understand the less-studied *n*-type behavior of NbFeSb, we have synthesized *n*-type NbFeSb and investigated Mössbauer spectroscopy of iron-57 and antimony-121, neutron total scattering, transport properties from 12 to 700 K, as well as first-principles electronic structure calculations. Although *p*-type conduction is more commonly expected, as shown in Figure 5, our first-principles calculations find that antiphase boundaries can in fact lead to *n*-type behavior in NbFeSb. This is consistent with our experimental results, in particular the finding of a disorder-related doublet in the ^{57}Fe Mössbauer results, as well as the improved neutron diffraction data associated with partial occupancy of Fe in an antiphase boundary site. Our calculations also find that such boundaries would exhibit a moderate energy of 76 meV/ $\text{\AA}^2$, which is comparable to published values for GaAs, and suggest the thermodynamic feasibility of such phase boundaries for NbFeSb. In terms of

thermoelectric applications, where both *n*- and *p*-type transport is required, we have also described the optimal charge doping regimes for this material. The findings in this work contribute substantially to the fundamental understanding of this half-Heusler alloy, and continues the effort to investigate new half-Heusler compositions of interest for thermoelectric applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Powder XRD data for NbFeSb.

Figure 2.
Neutron scattering pair distribution function for NbFeSb.

Figure 3.

Iron-57 (top) and antimony-121 (bottom) Mössbauer spectra of NbFeSb measured at 295 and 90 K, respectively. Top: Difference plot of the 295 K ^{57}Fe spectrum with the singlet contribution subtracted, where D1 and D2 denote two minor doublet contributions, see text. Inset: ^{57}Fe spectrum at 7 K.

Figure 4. Temperature dependent transport data for NbFeSb. (a) ρ , where the solid line is a fit to the form $\rho = \rho_0 \exp(E_g/2k_B T)$, and (b) S .

Figure 5.

(a) Example of APB in the Fe sublattice in a $4 \times 1 \times 1$ NbFeSb supercell. The APB here has a plane of mirror symmetry not present in the original unit cell. An equivalent cell without APB is also shown for comparison in (b). Note that these figures are rotated slightly with respect to the out-of-plane direction to better depict the locations of the Fe atoms. (c) APB formation energy (E_{APB}^f) as a function of distance (d_{APB}) between APBs. The increasing distance corresponds to increasing supercell size (from $2 \times 1 \times 1$ to $24 \times 1 \times 1$). (d) The calculated densities of states of bulk NbFeSb and cells with the indicated APBs. (e) The calculated density of states of a $4 \times 1 \times 1$ APB cell, with the Fe-atomic specific DOS indicated. The Fe APB and non-APB sites are shown in (a).

Figure 6.

(a) Calculated 300 K n -type average S as a function of carrier concentration for various NbFeSb supercells with APB for bulk NbFeSb. (b) Calculated p - and n -type average S as a function of carrier concentration for bulk NbFeSb at various temperatures.