

Influence of point defects on thermal conductivity in $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$ alloysZhuoyang Ti,^{1,2,3} Jesús Carrete⁴, Jingyu Li⁵, Yongsheng Zhang,^{6,*} and Georg K. H. Madsen^{2,†}¹Key Laboratory of Materials Physics, *Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China*²*Institute of Materials Chemistry, TU Wien, A-1060 Vienna, Austria*³*Science Island Branch of Graduate School, University of Science and Technology of China, Hefei 230026, China*⁴*Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, E-50009 Zaragoza, Spain*⁵*Spallation Neutron Source Science Center, Dongguan 523803, China*⁶*Laboratory of High-Pressure Physics and Materials Science (HPPMS), Advanced Research Institute of Multidisciplinary Sciences, Qufu Normal University, Qufu, Shandong 273165, China*

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Point defects and impurities are highly effective mechanisms for manipulating thermal conductivity, primarily because they significantly enhance phonon scattering. However, accurately computing thermal conductivities in defect-laden systems using density functional theory is computationally expensive, leading to a scarcity of theoretical simulations. Here we tackle the case of the widely studied double half-Heusler compound $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$, using first principles and Green's function methods to calculate the phonon-defect scattering rates. Existing predictions for the lattice thermal conductivity of pristine $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ are significantly higher than measurements in actual samples. In contrast, we achieve excellent agreement with experimental points for Fe-rich systems with 1.16% Fe_{Ni} substitutions and Ni-rich systems with 0.87% Ni_{int} interstitial defects. We provide detailed results for three types of defects and assess their contributions to the behavior of specific compositions. The data suggests that Hall concentrations can significantly overestimate defect concentrations. These results highlight the predictive capabilities of *ab initio* phonon transport modeling and its importance in understanding and quantifying defects in semiconductors.

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I. INTRODUCTION

Thermoelectric (TE) materials enable the direct conversion of thermal gradients into electrical energy, offering innovative solutions for energy harvesting and efficient temperature management [1]. The efficiency of TE materials is quantified by the dimensionless figure of merit, $zT = S^2\sigma T/(\kappa_{\text{lat}} + \kappa_{\text{ele}})$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_{lat} is the lattice thermal conductivity, and κ_{ele} is the electronic thermal conductivity. S , σ , and κ_{ele} are all strongly dependent on carrier concentration, which makes substantial improvements of zT a significant challenge. In contrast, the lattice thermal conductivity, κ_{lat} depends on phonon transport and can, to a certain extent, be modified independently. Reducing it is essential for achieving a significant enhancement in thermoelectric performance [2–4]. Defects and impurities are a powerful avenue to simultaneously reducing κ_{lat} by means of increased phonon

scattering [3,5–9], and influencing the charge carrier mobility and concentration [2].

Double half-Heusler (DHH) compounds, derived from the half-Heusler (HH) family through balanced aliovalent substitution, have attracted significant attention due to their intriguing properties. Research on DHH compounds has focused on investigating their optical [10] and electronic structures [11] and their thermoelectric properties [12–14]. One would expect the enhanced structural complexity of DHH would lead to a notable reduction in thermal conductivity, which would underscore their potential for thermoelectric device applications. The reduction has been realized for $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$, a semiconductor formed by substituting Fe and Ni for Co in TiCoSb [15]. Compared to its ternary counterpart TiCoSb , it exhibits an approximate 50% reduction in κ_{lat} [12,13,16]. There is, however, a significant discrepancy between theoretical predictions ($\kappa_{\text{lat}}=13.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K) and experimental measurements ($\kappa_{\text{lat}}=7.8 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K) of the thermal conductivity of nominally stoichiometric $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ [12,14]. The discrepancy underscores the complexity of thermal transport mechanisms in DHH compounds and is puzzling considering the typically good agreement between experimental results and predictions made using density functional theory (DFT) combined with the linearized Boltzmann transport equation (BTE) [17–19]. One possible explanation of this disparity could lie in the idealized character of theoretical models versus the defect-laden nature of synthesized samples.

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Rather remarkably, DHHs have been shown to be tunable for both p -type or n -type thermoelectric performance. Due to the different valence electron counts of Fe and Ni, adjusting the Fe-Ni ratio in $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ can effectively control the concentration of electrons or holes, thereby influencing its conductive properties. This was demonstrated in Ref. [13] where variations such as $\text{TiFe}_{0.4}\text{Ni}_{0.6}\text{Sb}$ and $\text{TiFe}_{0.6}\text{Ni}_{0.4}\text{Sb}$ show either an n -type or p -type conductivity. Modulating the Fe/Ni ratio was also found to further lower the thermal conductivity to $\kappa_{\text{lat}} \approx 4 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [13]. Interestingly, the electronic transport behavior (Seebeck coefficients and electric conductivities) and the measured Hall concentration ($1/|R_H| = 4.9 \times 10^{21} \text{ cm}^{-3}$ for the Fe-rich sample and $1/|R_H| = 6.0 \times 10^{21} \text{ cm}^{-3}$ for the Ni-rich sample) of these samples are characteristic of heavily doped semiconductors. Together with the observed reduction in lattice thermal conductivity, this would indicate a substantial phonon-defect scattering. Although the influence of defect types and concentration on the thermal conductivity has been studied in doped ternary HH systems [20,21], very little is known about phonon scattering by defects in DHH systems. Understanding and manipulating these point defects is crucial in optimizing the TE efficiency of DHH compounds. Therefore, a first-principles understanding of how dopants affect κ_{lat} in DHHs is essential, as it can unlock deeper insights and innovations in thermal management.

In this paper we employ the *ab-initio* Green's function method to study the thermal conductivity of intrinsically doped $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ as a function of temperature and defect concentration. We compare our calculated thermal conductivities with experimental results and investigate the connection between the different defect types and the depression in thermal conductivity caused by their elastic point-defect phonon scattering. We demonstrate that Ni_{Fe} substitutions and Fe_{int} interstitials cause the strongest scattering. Furthermore, we attribute the discrepancy between the predicted and experimental lattice thermal conductivity to additional scattering by point defects. To assess the feasibility of each defect type, we compare the required defect concentration with the experimentally measured carrier concentration. In the Fe- and Ni-rich regimes, defect concentrations of approximately $\chi_{\text{Fe}_{\text{Ni}}} = 6.7 \times 10^{20} \text{ cm}^{-3}$ and $\chi_{\text{Ni}_{\text{int}}} = 5 \times 10^{20} \text{ cm}^{-3}$, respectively, result in reasonable agreement with both the corresponding experimental carrier concentrations and thermal conductivities. To shed further light on the mechanisms underpinning the contrasting behavior of different defect types with respect to phonons, we analyze the scattering introduced by each defect in the host structure.

II. METHODOLOGY

A. Lattice thermal conductivity

Under the relaxation-time approximation, the μ, ν Cartesian component of the lattice thermal conductivity tensor (κ) is given by [22]

$$\kappa_{\mu\nu} = \frac{1}{k_B T^2 \Omega} \sum_j \int d^3 \mathbf{q} n_{0,j\mathbf{q}} (n_{0,j\mathbf{q}} + 1) (\hbar \omega_{j\mathbf{q}})^2 v_{j\mathbf{q}}^\mu v_{j\mathbf{q}}^\nu \tau_{j\mathbf{q}}, \quad (1)$$

where T is the temperature, Ω is the unit cell volume, and the phonon-mode-dependent (j : branch index; $\mathbf{q}$: wave vector) quantities ω , v , n_0 , and τ correspond to the phonon frequencies, group velocities, equilibrium occupancy, and relaxation time, respectively. The total phonon scattering rate $\tau_{j\mathbf{q}}^{-1}$ can be expressed as the sum of the contributions from different scattering mechanisms using Matthiessen's rule

$$\frac{1}{\tau_{j\mathbf{q}}} = \frac{1}{\tau_{j\mathbf{q}}^{\text{anh}}} + \frac{1}{\tau_{j\mathbf{q}}^{\text{iso}}} + \frac{1}{\tau_{j\mathbf{q}}^{\text{def}}}, \quad (2)$$

where $\frac{1}{\tau_{j\mathbf{q}}^{\text{anh}}}$ encapsulates the influence of three-phonon processes, arises from the intrinsic anharmonicity of the crystal, and can be determined by obtaining the third-order interatomic force constants (IFCs) of the unperturbed crystal [23], $\frac{1}{\tau_{j\mathbf{q}}^{\text{iso}}}$ is introduced by isotopic mass disorder and estimated using Tamura's formula [24,25], and $\frac{1}{\tau_{j\mathbf{q}}^{\text{def}}}$ describes the elastic scattering caused by defects and is calculated following the *ab initio* Green's function approach [26] starting with an atomistic description of each defect.

The phonon-defect scattering rate for the incident phonon mode $j\mathbf{q}$ can be obtained by employing the optical theorem from perturbation theory,

$$\frac{1}{\tau_{j\mathbf{q}}^{\text{def}}} = -\chi_{\text{def}} \Omega \frac{1}{\omega_{j\mathbf{q}}} \text{Im}\{\langle j\mathbf{q} | \mathbf{T} | j\mathbf{q} \rangle\} \quad (3)$$

where χ_{def} is the number of defects per unit cell.

Equation (3) provides a direct connection between the macroscopic thermal conductivity and the microscopic $\mathbf{T}$ -matrix. Evaluated at frequency $\omega_{j\mathbf{q}}$, $\mathbf{T}$ serves as a link between the phonon wave functions of the pristine and perturbed systems, and can be represented in terms of the retarded Green's function of the unperturbed host lattice, $\mathbf{g}^+$, and the perturbation matrix, $\mathbf{V}$, as

$$\mathbf{T} = (\mathbf{I} - \mathbf{V}\mathbf{g}^+)^{-1} \mathbf{V}, \quad (4)$$

where $\mathbf{I}$ is the identity matrix. The total perturbation matrix is built from two contributions:

$$\mathbf{V} = \mathbf{V}_K + \mathbf{V}_M. \quad (5)$$

$\mathbf{V}_K$ and $\mathbf{V}_M$ account for changes in IFCs and mass between the perfect and defect-laden structures, respectively. $\mathbf{V}_{K,j\alpha,k\beta} = \frac{K'_{j\alpha,k\beta} - K_{j\alpha,k\beta}}{\sqrt{M_j M_k}}$ is computed from the differences between the second IFCs for defect-laden ($\mathbf{K}'$) and perfect ($\mathbf{K}$) structures. j, k are atom indices and α, β represent Cartesian axes. $\mathbf{V}_{M,j\alpha,k\beta} = -\frac{M'_j - M_j}{M_j} \omega^2 \delta_{jk} \delta_{\alpha\beta}$ is diagonal and nonzero only for the onsite terms of the defect. M'_j, M_j are the masses of the substitutional and host atom at the j th site, respectively.

B. Computational details

All structural information and IFCs are extracted from DFT calculations carried out using the VASP package [27], the projector augmented wave (PAW) [28] method with an energy cutoff of 500 eV and the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [29] to exchange and correlation. We employed projector augmented-wave (PAW)

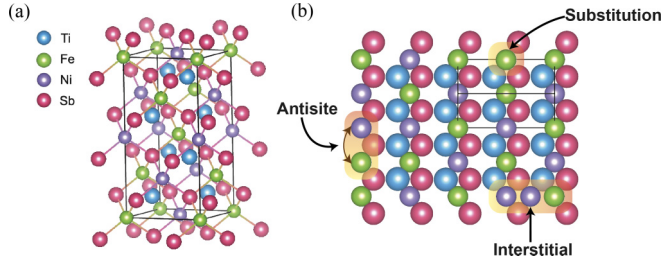


FIG. 1. (a) Crystal structure of double HH $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ belonging to space group $I\bar{4}2d$ and (b) types of point defects studied in this work.

potentials with the following explicit valence electron configurations: Ti ($3d^3 4s^1$), Fe ($3d^6 3d^7 4s^1$), Ni ($3d^6 3d^8 4s^2$), and Sb ($5s^2 5p^3$). The total energy and force convergence criteria are set to 10^{-6} eV and 0.01 eV $\text{\AA}^{-1}$, respectively. A Γ -centered Monkhorst-Pack [30] k -mesh with $13 \times 13 \times 13$ is used to sample the Brillouin zone. We considered $3 \times 3 \times 3$ supercells (containing 324 atoms) and Γ -only sampling for the calculation of IFCs of the defect-free structures. A finite-displacement method is used to obtain the second-order force constants. The supercells and the atomic displacements are created with the Phonopy code [31] with a displacement distance of 0.01 $\text{\AA}$. To calculate the third-order force constants of the pristine unit cell, we use the thirdorder.py [22] with a cutoff set to 4.2 $\text{\AA}$ thereby including third-nearest neighboring atoms. Hall coefficients were calculated with the BoltzTraP2 code [32].

Before calculating the IFCs of the defect-laden supercell, the atomic coordinates are relaxed keeping the cell volume fixed. A small random displacement of less than 0.01 $\text{\AA}$ is introduced for either the defect atom or its nearest neighbors before starting the relaxation to prevent the system from getting stuck in a symmetry-protected saddle point. The process is repeated with different initial displacements and we keep the result with the lowest energy as our best estimate of the ground-state structure of the defect. Second-order IFCs for defect-laden systems are computed using a $3 \times 3 \times 3$ supercell. As illustrated in Fig. 1(b), substitutional defects (Fe_{Ni} , Ni_{Fe}) are introduced by replacing a single Fe or Ni atom, while antisite defects are created by swapping a pair of neighboring Fe and Ni atoms, keeping the total number of atoms fixed at 324. Interstitial defects (Fe_{int} , Ni_{int}) are modeled by inserting an additional Fe or Ni atom into a vacancy-like interstitial site in the lattice. These interstitial sites correspond to the unoccupied 4d positions in the originally half-Heusler structure, which share the same local environment as the occupied 4c sites. This results in a total of 325 atoms. All defect calculations are performed using Γ -only sampling. We treat the IFC perturbations in real space, considering the localized nature of bond perturbations. We establish two cutoffs: r_{cut} and R_{cut} . The former defines the maximum distance at which changes in interactions between atom pairs are allowed, where at least one atom is a neighbor of the defect site defined by the latter. After thorough convergence tests, we selected $r_{\text{cut}} = 12$ $\text{\AA}$ and $R_{\text{cut}} = 6$ $\text{\AA}$.

To compute the defect scattering rate, Green's functions are calculated on a $12 \times 12 \times 12$ grid, using the tetrahedron

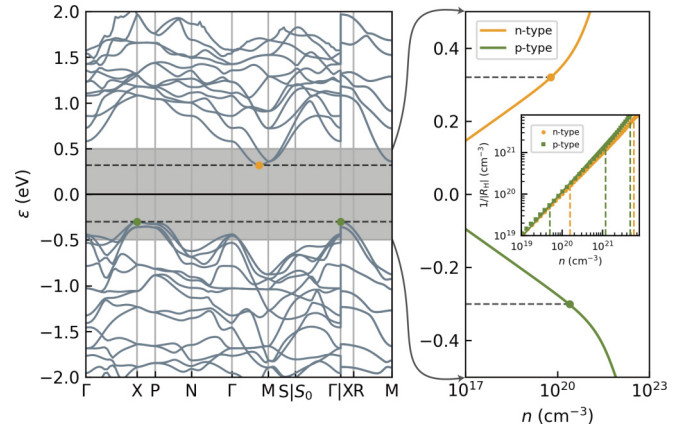


FIG. 2. Electronic properties of $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ using the PBE exchange-correlation functional within the PAW framework. The left-hand-side plot is the band structure, showing the band gap of 0.62 eV. The blue and orange points represent the CBM and VBM energy level, respectively. The right-hand-side plot is the variation in carrier concentration and Hall coefficient as a function of the chemical potential. The insert shows the relation between the calculated $1/R_H$ and the carrier concentration estimated directly from the DOS. The vertical lines show the experimentally measured Hall carrier concentrations: $4.9 \times 10^{21} \text{ cm}^{-3}$ for $\text{TiFe}_{0.6}\text{Ni}_{0.4}\text{Sb}$, $1.2 \times 10^{21} \text{ cm}^{-3}$ for $\text{TiFe}_{0.55}\text{Ni}_{0.45}\text{Sb}$, $5.0 \times 10^{19} \text{ cm}^{-3}$ for $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$, $1.6 \times 10^{20} \text{ cm}^{-3}$ for $\text{TiFe}_{0.45}\text{Ni}_{0.55}\text{Sb}$, and $6.0 \times 10^{21} \text{ cm}^{-3}$ for $\text{TiFe}_{0.4}\text{Ni}_{0.6}\text{Sb}$. See SI of Ref. [13].

method to integrate over the Brillouin-zone. A grid of $13 \times 13 \times 13$ q -point mesh is used to sample the incident phonons. In the case of interstitial defects, the pristine system and its Green's function are augmented with a noninteracting atom, which is then connected to form the defect-laden system. Calculations of scattering rates τ_{anh}^{-1} , τ_{iso}^{-1} , τ_{def}^{-1} and the final thermal conductivity are performed using a modified version of the almaBTE code [23].

III. RESULTS AND DISCUSSION

The ordered DHH $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ [Fig. 1(a)] crystallizes in the $I\bar{4}2d$ space group ($a = b = 5.924$ $\text{\AA}$, $c = 11.824$ $\text{\AA}$) [12,14]. Compared to the XYZ template for the ternary HH, the role of the Y atoms in $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ is taken by both Fe and Ni, so the tetrahedra formed by Y-Z in ternary HH are replaced by two different types of tetrahedra (Fe-Sb and Ni-Sb) in an ordered fashion. The resulting DHH compound still conforms to the 18-electron rule and therefore has an intrinsic semiconducting character. In particular, as depicted in Fig. 2, the calculated electronic band structure of $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ exhibits an indirect band gap of 0.62 eV, similar to the previously reported value (0.63 eV [14]).

The Hall coefficient is typically used to estimate the carrier concentration in doped semiconductors. In the case of the nonstoichiometric experimental samples, the measured Hall concentrations [13] indicates heavily doped semiconductors, as shown in Fig. 2. This corresponds to a carrier concentration significantly deviating from a nominal Fe/Ni 4/6 ratio and falls in the dilute limit, where defects can still be considered isolated. For the nominally stoichiometric sample,

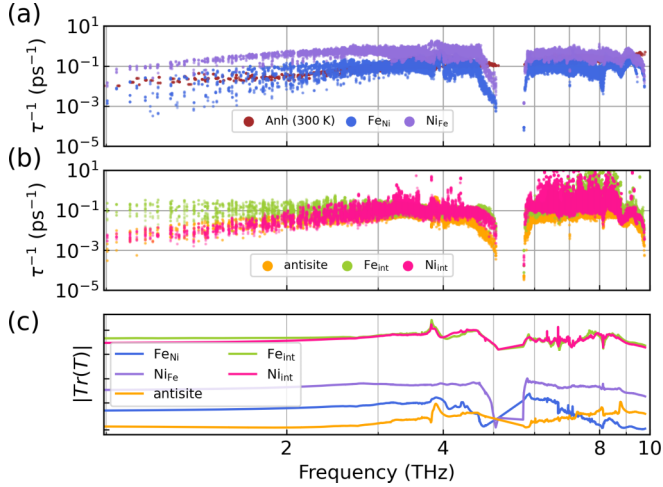


FIG. 3. (a), (b) Phonon scattering rates and (c) trace of the imaginary part of the $\mathbf{T}$ -matrix for the point defects as a function of phonon angular frequency. A defect concentration of $1 \times 10^{20} \text{ cm}^{-3}$ is assumed for enhanced graphical clarity. A variation in defect concentration would uniformly shift the scattering rates on the graph. The phonon scattering rates by these defects are compared with anharmonic scattering rates at 300 K.

TiFe_{0.5}Ni_{0.5}Sb, the Hall carrier concentration is about two orders of magnitude lower than that of the doped samples [13]. It is worth noting that complex energy bands can deviate markedly from the hypotheses of a single-parabolic-band model and Hall measurements do not directly correspond to the actual number of carriers. For this reason, we have calculated the Hall coefficient from the electronic band structure as described in the methods section. As depicted in the inset of Fig. 2, we find a very good agreement between the calculated Hall concentration and the actual carrier concentration, indicating that the measured Hall coefficients are a reliable gauge of the carrier concentration. In Figs. 3(a) and 3(b) we first present the phonon scattering rates calculated for the three distinct defect types shown in Fig. 1(b): Ni-Fe substitutional, interstitial, and antisite defects in TiFe_{0.5}Ni_{0.5}Sb compounds. The phonon-defect scattering rates are compared to the third order anharmonic scattering rates obtained at 300 K and provide clues about point-defect interactions. The scattering rates obtained for Ni_{Fe} defects are significantly larger than those of other defects. Furthermore, Fe_{int} defects exhibit large scattering rates for the low-frequency acoustic phonons (below than 3 THz), which play a crucial role in lattice thermal conductivity.

Phonon scattering by defects arises from two sources: (i) the mass difference between the impurity atom and the one it replaces, quantified by $\mathbf{V}_M$ in Eq. (5), and (ii) the local change in the IFCs, $\mathbf{V}_K$ in Eq. (5), around the impurity in response to structural relaxation and changes in the chemical environment. The large scattering rates obtained for Ni_{Fe} defects are somewhat surprising, given that the mass difference between Fe and Ni is only about three atomic mass units. A calculation including only mass differences, neglecting IFC differences, does indeed predict very similar scattering rates for Fe_{Ni} and Ni_{Fe} substitutional impurities (see Fig. S3 in the Supplemental Material [33]).

To investigate this further, we performed an analysis of the IFC perturbations in the defect-laden structures (see Fig. S4 in the Supplemental Material [33]). Our findings indicate that Ni_{Fe} defects introduce significant local lattice distortions, leading to the observed variations in phonon scattering rates. This is further supported by the Frobenius norm of the IFC perturbation matrices $\|\mathbf{V}_K\|$. Ni_{Fe} exhibits a $\|\mathbf{V}_K\|$ of 1096 eV/Å², compared to a $\|\mathbf{V}_K\|$ of 659 eV/Å² for Fe_{Ni}. These values confirm the stark contrast in scattering rates arises primarily from IFC variations. The imaginary part of the $\mathbf{T}$ -matrix, Eq. (4), determines the cross-section associated with defects for phonons at particular frequencies. It combines the variations in force constants with the Green's function, providing a comprehensive understanding of the scattering phenomena and is depicted in Fig. 3(c). The Ni_{Fe} defects exhibit significantly larger trace values of the imaginary part over the entire phonon frequency range, indicating a larger scattering cross-section for phonons and therefore a stronger contribution to thermal conductivity reduction.

For the interstitial defects, Fe_{int} and Ni_{int}, only the force constant perturbation term, $\mathbf{V}_K$, is included in the phonon scattering calculations. Since the interstitial site is initially unoccupied, $\|\mathbf{V}_K\|$ is very large, which results in very large values of the trace of the imaginary part of the $\mathbf{T}$ -matrix, Fig. 3(c). However, this trace cannot be directly used to compare the impact of the interstitials on thermal conductivity with the other defects.

First, the trace of the $\mathbf{T}$ -matrix includes diagonal terms from all phonon modes, whereas phonon scattering at a given frequency depends on the coupling of $\mathbf{T}$ -matrix with a specific incoming mode. Second, and specific for the interstitial defects, the vibrations of the unperturbed system have zero projections, Eq. (3), on the interstitial atoms, leading to inherently weak coupling between those atoms and the phonon modes.

Despite this, the difference in the $\mathbf{T}$ -matrix trace of Fe_{int} and Ni_{int} supports the observed variation in scattering rates and indicates that the IFC perturbation caused by the Fe_{int} defect is significantly larger than that caused by Ni_{int}, leading to stronger phonon scattering. This is evident in Fig. 3(c), where, in the region below 3 THz, the trace of the imaginary part of the $\mathbf{T}$ -matrix for Fe_{int} is consistently higher than that of Ni_{int}, corresponding to the difference in their scattering rates, Fig. 3(b).

A critical parameter for the quantitative evaluation of defect scattering is the concentration of defects, Eq. (3). To elucidate the effect of the defect concentrations and types in experimental samples, we calculated the TiFe_{0.5}Ni_{0.5}Sb lattice thermal conductivity at 300 K considering anharmonic scattering and the defects discussed above. The charged state of a defect can significantly influence the force constants [34]. However, in the present case our evaluation of the scattering rates for charged defects revealed that the charge state did not significantly affect the scattering rates (see Fig. S2 in the Supplemental Material [33]) and in the following we discuss the results obtained with neutral defects. In Fig. 4, we show the individual contributions of the considered point defects to the reduction in room-temperature thermal conductivity with increasing defect concentrations. As expected from the scattering rates, Fig. 3, the Ni_{Fe} substitution and

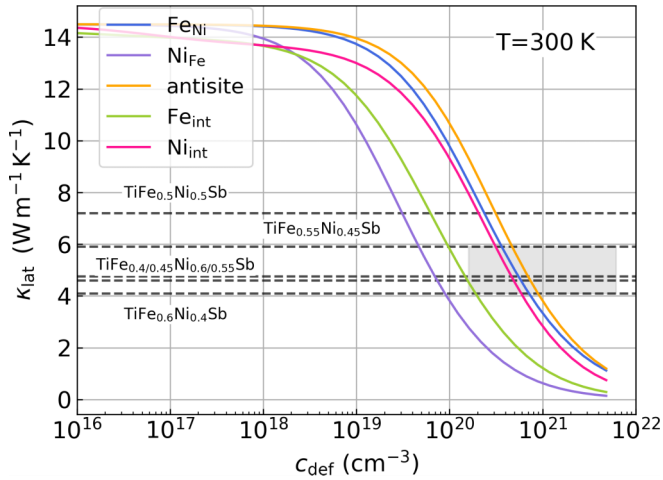


FIG. 4. Variation of the thermal conductivity with defect concentration for all point defect types considered in $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$ alloys at 300 K. The experimental lattice thermal conductivities from Ref. [13] are shown as horizontal dashed lines. The shaded region indicates the measured values for experimental samples with Fe/Ni ratios deviating from 1:1. The width of the shaded area corresponds to the range of carrier concentrations, while the height represents the range of thermal conductivities.

the Fe_{int} interstitial lead to the largest depressions of the thermal conductivity. For comparison, the measured lattice thermal conductivities are indicated with dashed horizontal lines. If, as a first approximation, we consider all impurities to be completely ionized, with each dopant contributing or capturing one electron per defect atom, the concentrations of the point defects can be expected to be of the same order of magnitude, in absolute value, as the carrier concentration. While it is not possible to pinpoint which specific defects are responsible for the scattering, in general, the lattice thermal conductivities calculated including defect scattering are consistent with the experimental values when using defect concentrations comparable to the measured Hall coefficients. It should also be pointed out that electron-phonon scattering can play an important role in heavily doped semiconductors [35–37]. Nonetheless, the analysis confirms that the discrepancy between the measured lattice thermal conductivity and that predicted when only three-phonon scattering is considered [12,14] can be attributed to additional scattering by point defects.

Considering now the nominally stoichiometric $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ we see that our calculations reproduce the deviation between the κ_{lat} calculated when only scattering from three-phonon processes ($\kappa_{\text{lat}} = 13.5 \text{ W m}^{-1} \text{ K}^{-1}$) and the experimental measurements ($\kappa_{\text{lat}} = 7.8 \text{ W m}^{-1} \text{ K}^{-1}$) that has been observed earlier [12,14]. While we observe that the strong scattering induced by Ni_{Fe} would be able to explain the deviance between the calculated and the observed lattice thermal conductivity at a defect concentration in the same order of magnitude as the Hall coefficient ($1/|R_H| = 5 \times 10^{19} \text{ cm}^{-3}$), we also point out that the measured Seebeck coefficient of these samples is positive [13] making the electron donating Ni_{Fe} defect improbable. A neutral defect like the antisite defect concentration can

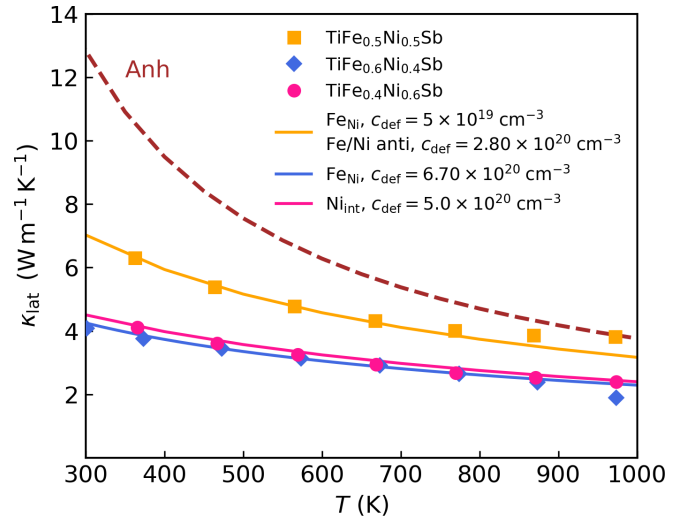


FIG. 5. Lattice thermal conductivity as a function of temperature for $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$. Lines represent the calculated thermal conductivity, both considering three-phonon scattering only and considering three-phonon, isotopic mass disorder, and phonon-defect scattering for different defect concentrations. Symbols represent experimental results from Liu *et al.* [13].

be seen to give a good agreement with experiment at a $c_{\text{def}} = 2.8 \times 10^{20} \text{ cm}^{-3}$. This can also be seen as a small disorder or alloying on the Ni-Fe sublattice of about 0.57%.

The experimentally measured lattice thermal conductivities (κ_{lat}) of $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$ ($x = 0.4, 0.5, 0.6$) are displayed in Fig. S1 in Supplemental Material [33]. Data were collected from different experimental studies [12,13,16,38]. For a given x there is good internal agreement between the experimental study and in Fig. 5 we select the thermal conductivity data from Ref. [13] as used in the rest of the paper.

In Fig. 5, we compare our calculated thermal conductivity with experimental data at all temperatures. The calculated κ_{lat} for defect-free single crystal $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ is depicted as a brown dashed line. Yellow squares represent experimental measurements for a bulk sample of $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$. Taking only three-phonon processes into account, we obtain a thermal conductivity in good agreement with previously reported DFT results [12,14], but overestimating the experimental thermal conductivity by approximately 50% [13]. Considering the carrier concentration is around $5 \times 10^{19} \text{ cm}^{-3}$, Fig. 5 demonstrates how good agreement with experiment can be obtained including scattering from $c_{\text{def}} = 5 \times 10^{19} \text{ cm}^{-3}$ of Fe_{Ni} substitutional defects combined with a concentration of $c_{\text{def}} = 2.8 \times 10^{20} \text{ cm}^{-3}$ Fe/Ni antisite defects. This observation is in line with other reports of antisite defects in HH and DHH strongly influencing the thermoelectric performance [39–41].

Additional experimental results are illustrated with blue diamonds for Fe-rich samples and pink circles for Ni-rich samples, Fig. 5. The blue diamonds represent $\text{TiFe}_{0.6}\text{Ni}_{0.4}\text{Sb}$, which displays p -type conductivity as well. Its lattice thermal conductivity is closely approximated by the model incorporating Fe_{Ni} defects, consistent with the calculated curve at a defect concentration of 1.16% ($c_{\text{def}} \approx 6.70 \times 10^{20} \text{ cm}^{-3}$). For the Ni-rich system, the pink circles denote the n -type $\text{TiFe}_{0.4}\text{Ni}_{0.6}\text{Sb}$ alloy, with its thermal conductivity fitted us-

ing Ni_{int} defects, aligning with the pink curve in the figure, when the defect concentration is set to 0.87% ($c_{\text{def}} \approx 5 \times 10^{20} \text{ cm}^{-3}$). Using the carrier concentrations for different Fe/Ni ratio in $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$ alloys reported in Ref. [13] results in a notable concordance between the calculated and the experimental thermal conductivity values across the entire temperature range in Fig. 5.

IV. CONCLUSION

We performed *ab initio* Green's function calculations of lattice thermal conductivities for three kinds of point defects in DHH compound $\text{TiFe}_x\text{Ni}_{1-x}\text{Sb}$ ($x = 0.4, 0.5, 0.6$) and found very good agreement with previous measurements. Our study suggests that intrinsic characteristics of $\text{TiFe}_{0.5}\text{Ni}_{0.5}\text{Sb}$ exhibiting *p*-type behavior are well represented by combining simulations of Fe_{Ni} point defects and antisite disorders. For Fe-rich systems, the Fe_{Ni} defects lead to a reasonable agreement with both the observed thermal conductivities and with experimental carrier concentrations. Conversely, in Ni-rich systems, Ni_{int} defects emerge as the primary scatterers responsible for the reduced thermal conductivity and *n*-type conductivity. Our analysis of the vibrational dynamics induced by each type of defect helped to elucidate the mechanisms by which these defects influence phonon behavior

in different compositional contexts. This provides an understanding of the low thermal conductivity in DHH materials and confirms that *ab initio* calculations of thermal conductivity offers a practical and reliable approach to characterize and quantify defects in materials.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [42], embargo periods may apply.

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