First-principles study of thermal transport in FeSb$_2$

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We study the thermal transport properties of FeSb$_2$, a promising thermoelectric material for cooling applications at cryogenic temperatures. A first-principles formalism based on density functional theory and ab initio lattice dynamics is applied. We calculate the electronic structure, the phonon dispersion relation, the bulk thermal expansion coefficient, and the thermal conductivity of FeSb$_2$ and compare them with other calculations and experiments. Our calculation is found insufficient to fully explain the temperature dependence of the lattice thermal conductivity of FeSb$_2$, suggesting new scattering mechanisms in this strongly correlated system. The mean free path distribution of different phonon modes is also calculated, which may provide valuable guidance in designing nanostructures for reducing the thermal conductivity of FeSb$_2$ and improving the thermoelectric figure of merit $zT$.

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I. INTRODUCTION

Thermoelectric materials are useful not only for generating electric power from heat, but also for providing cooling power by passing through an electric current [1–9]. They show an ultrahigh Seebeck coefficient ($S \approx -42$ mV/K) at very low temperatures since it was experimentally found to be $S \approx -42$ mV/K, and thus a large power factor ($PF \approx 2300 \mu\text{W} \cdot \text{K}^{-2} \cdot \text{cm}^{-1}$) at $T = 12$ K [10]. Subsequent work was done for a better understanding of this material and to improve its thermoelectric efficiency [11–18]. The origin of the high Seebeck coefficient is still under debate. FeSb$_2$ has been characterized to be a strongly correlated semiconductor [19–21], or more specifically, a Kondo insulator [22,23], where a small hybridization gap ($\sim 10$ meV) is formed at low temperatures as a result of the interaction between localized $f$- or $d$-orbitals ($d$-orbitals of Fe atoms in this case) with itinerant bands. Since $f$- and $d$-bands are in general quite flat, the resulting electronic structure is known to give large Seebeck coefficients [24]. This mechanism was recently verified in a model study of Kondo insulator nanowires using the dynamic mean field theory [25]. Tomczak et al. studied the electronic structure and the corresponding Seebeck coefficient of FeSb$_2$ in detail from first principles [26]. They obtained the electronic ground state of FeAs$_2$ and FeSb$_2$, including many-body effects using density functional theory (DFT) with GW approximation, and managed to reproduce the Seebeck coefficient that was in good agreement with experiments in the intermediate temperature range but failed to explain the large peak of Seebeck coefficient at lower temperatures for FeSb$_2$. On the other hand, Pokharel et al. [27,28] studied the correlation between the thermal conductivity and the Seebeck coefficient of FeSb$_2$ samples with different grain sizes and suggested that the phonon-drag effect should be mainly responsible for the abnormal Seebeck coefficient.

Despite its high power factor, the single-crystal FeSb$_2$ shows low $zT$ due to its high lattice thermal conductivity ($k \sim 500$ W/mK at 12 K) [10,14]. Thus, the key to improving its thermoelectric performance is to understand thermal transport in FeSb$_2$ and to reduce its thermal conductivity accordingly. Compared with the abundant investigations of its electronic properties, only a handful of work has looked into the thermal properties of FeSb$_2$. Lazarević et al. [29] calculated the phonon dispersion relation of FeSb$_2$ using density functional perturbation theory (DFPPT) and studied some specific phonon modes using Raman spectroscopy experimentally. Diakhate et al. [30] also studied the harmonic properties of phonons and the lattice heat capacity using DFPPT. No work so far, however, has been focused on the anharmonic properties of the lattice and the phonon-phonon interactions, which largely control the thermal transport properties of FeSb$_2$.

In this paper, we apply a first-principles formalism for the thermal conductivity calculation based on DFT and real-space lattice dynamics, recently developed [31,32] and verified for several realistic materials [33–38], to FeSb$_2$ to understand its intrinsic phonon-phonon interactions and, more importantly, provide the information of the phonon mean free path distribution, which is important in guiding the nanostructuring strategy for effectively reducing its thermal conductivity [3,9,11,39]. The detailed calculation procedures can be found in the references [31,32] and will only be briefly outlined here. The electronic structure is first obtained by DFT given the crystal structure, and then the interatomic forces can be calculated by DFT after directly displacing specific atoms from their equilibrium positions by a small
amount according to the crystal symmetry. Provided the atomic displacements and corresponding interatomic forces, in addition to linear constraints imposed by symmetry, a least-square fitting procedure is invoked to extract the harmonic and anharmonic force constants [31], within which the phonon harmonic and anharmonic properties are encoded. The phonon dispersion relation, the phonon-phonon scattering rates, the lattice thermal conductivity, and the mode-specific phonon mean free paths can be calculated based on the force constants information [32].

II. CALCULATION DETAILS

FeSb$_2$ crystallizes in an orthorhombic marcasite structure (space group Pn$\text{nn}$m) [19], with two iron atoms and four antimony atoms in one unit cell. Each iron atom is surrounded by six antimony atoms that are arranged in a deformed octahedron. The low symmetry of the crystal structure and the complexity of the unit cell render it a computationally challenging task to reliably attain the force constants of FeSb$_2$. We used the Quantum ESPRESSO package [40] for the DFT calculation, with norm-conserving Perdew–Zunger local density approximation pseudopotentials [41]. We chose the plane-wave cutoff energy as 120 Ryd and a $16 \times 16 \times 16$ k-mesh for the self-consistent field calculation to guarantee well-converged interatomic forces. The crystal structure was fully relaxed, and the resulting lattice parameters were $a = 5.743$ Å, $b = 6.414$ Å, and $c = 3.102$ Å, ~1% smaller than the experimental values at $T = 20$ K [19]. To obtain long-range force constants, supercells with distinct sizes ($2 \times 2 \times 2$, $1 \times 1 \times 4$, $1 \times 4 \times 1$, and $4 \times 1 \times 1$) were constructed. Specific atoms in a unit cell were displaced systematically by amounts of 0.01 Å, 0.02 Å, and 0.04 Å along different coordinate directions from their equilibrium positions, and the interatomic forces were calculated for each configuration. Several configurations with random atomic displacements were added to improve the quality of the dataset for fitting the force constants. In the least-square fitting procedure, 18 neighbor shells were included for the harmonic (second-order) force constants and 9 neighbor shells for the anharmonic (third-order) force constants, which amounted to 200 second-order and 1365 third-order independent force constants. It is worth noting that due to the low symmetry of the crystal, the 18th neighbor shell is only ~6.4 Å away from the atom at the origin, and the 9th neighbor shell goes to ~5.2 Å away. The absence of longer range interactions due to the limitation of the computing resource might contribute to the errors and uncertainties in the simulation result, as will be discussed later.

III. RESULTS AND DISCUSSION

After the harmonic force constants were extracted, the phonon dispersion relation could be calculated by solving for the eigenvalues of the dynamical matrix constructed from the harmonic force constants [32], as shown in Fig. 1. Our calculated phonon dispersion relation was in very good agreement with other calculations [29,30] using DFPT, indicating the extraction of the harmonic force constants was reliable. It is relatively harder to validate the anharmonic force constants. The mode-specific Grüneisen parameters $\gamma_{n,q} \equiv -\frac{\partial \ln \omega_{n,q}}{\partial \ln V}$, where $\omega_{n,q}$ is the frequency of a specific phonon mode and $V$ the volume of the crystal, quantify the anharmonicity of the lattice at a microscopic level and can be computed directly from the anharmonic force constants [32]. Being hard to measure in experiments, the Grüneisen parameters manifest themselves in all other measurable quantities resulting from the lattice anharmonicity, for example, the bulk thermal expansion coefficient [32,42] $\alpha = \frac{V \gamma_{10}}{\Gamma_{\text{avr}}}$, where $\Gamma$ is the averaged Grüneisen parameter weighted by the mode-specific heat capacity, $c_p$ is the total heat capacity, and $B$ is the bulk modulus. We first calculated the bulk thermal expansion coefficient and compared it with the experimental data [19], as shown in Fig. 2. Good agreement was achieved at very low temperatures, while at higher temperatures, deviations from the experimental data were observed. As discussed by Petrovic et al. [19], the

![Figure 1](image1.png)

![Figure 2](image2.png)
peak structure in the thermal expansion coefficient can be possibly attributed to the Shottky peak in the electronic specific heat associated with narrow band gap semiconductors, which cannot be captured in our simulation. Moreover, we calculated the mode-specific Gr"uneisen parameters via two different approaches and compared the results in order to check the self-consistency of our simulation. One approach was to manually scale up the size of the crystal by a small amount (0.01% in this case) and recalculate the phonon dispersion relation so that the mode-specific Gr"uneisen parameters could be computed by the finite difference method from the definition; the other approach was to compute the Gr"uneisen parameters directly from the anharmonic force constants. The result is plotted in Fig. 3. No perfect match was observed due to the absence of contributions from higher order force constants and from distant atomic layers that were not included in the simulation when calculating Gr"uneisen parameters directly from the anharmonic force constants. Especially the deviations in acoustic modes were caused by the fact that the size of the supercells that could be handled was very limited given the complexity of the unit cell. Nevertheless the general trend and the range of the dispersion of the numerical values were consistent between the two approaches, indicating that a reasonable degree of convergence in terms of the number of neighbor shells and the force constants was reached in our calculation.

Of great interest are the phonon-phonon scattering rates that can be calculated from the extracted force constants using Fermi’s golden rule [32]. The scattering rates for both normal processes and Umklapp processes at $T = 20$ K are plotted in Fig. 4. The scattering rates of acoustic modes and optical modes are plotted separately. A quadratic dependence of the normal scattering rates of acoustic phonons on frequency can be seen from the plot while the scattering rates of acoustic phonons for Umklapp processes seem to scale as $\omega^3$, a fact that is quite similar to silicon [32]. It is noticed that at $T = 20$ K, the phonon scattering rates are in general pretty low, and the phonon mean free paths can be comparable to the sample size, implying that boundary scattering should be included when calculating thermal conductivity.

A finite mesh when sampling the Brillouin zone leads to errors in calculating the lattice thermal conductivity, due to the missing contributions of phonon modes with very long wavelengths. This numerical artifact can be compensated by extrapolating the results of calculations with finite mesh of different sizes according to the following relation [32,35],

$$\frac{\kappa_n(T)}{\kappa_\infty(T)} = 1 - \frac{c(T)}{n_k} + O\left(\frac{1}{n_k^2}\right), \quad (1)$$

where the coefficient $c(T)$ can potentially depend on temperature (at higher temperatures, the phonon-phonon dominant thermal conductivity $\kappa_0(T) \sim T^{1/3}$, leading to a temperature-independent $c$ [35]; otherwise, $c(T)$ will depend on the temperature), $n_k$ is the number of sampling points.
in one dimension, \( \kappa_0 \) is the corresponding calculated lattice thermal conductivity, and \( \kappa_{\text{ex}} \) is the extrapolated lattice thermal conductivity corresponding to infinite sampling points. Calculations with \( 6 \times 6 \times 6, 8 \times 8 \times 8, \) and \( 10 \times 10 \times 10 \) sampling meshes were conducted for extrapolation. The extrapolation is illustrated in the inset of Fig. 5, where the linear relation in Eq. (1) is found to hold at different temperatures, and \( c(T = 20 \text{ K}) \) is distinct from those of higher temperatures, as expected, since the scaling \( \kappa_0(T) \sim T^{-1} \) starts at higher temperatures. The extrapolated thermal conductivity is plotted in Fig. 5 and compared with the experimental data from Bentien \textit{et al.} [10] and Sun \textit{et al.} [14]. Our calculation overestimates the thermal conductivity of FeSb\(_2\), and it is understandable and expected because at the temperature range that we are interested in, the sample boundary scattering and impurity scattering play important roles compared with the phonon-phonon scattering under investigation. We can incorporate these two effects using model relaxation times via Matthiessen’s rule. We use the Casimir model [43] for the sample boundary scattering (i.e., \( \frac{1}{\tau_{BS}} = \frac{1}{\tau} \), where \( \tau_{BS} \) is the relaxation time due to sample boundary scattering, \( \tau \) is the mode-dependent group velocity, and \( l \) is the characteristic size of the sample that we chose as a fitting parameter). We also add a Rayleigh-type term accounting for the impurity scattering [44], \( \frac{1}{\tau_{\text{imp}}} = A\omega^2 \), where \( A \) is used as another fitting parameter. The consideration of boundary scattering and impurity scattering in this manner is not \textit{first principles} and provides less essential information of phonon transport in FeSb\(_2\), since they are sample dependent, but we chose to adopt the two models for data fitting just to show it was still insufficient to explain the experimental data, even with the extra two scattering mechanisms. One such fit is shown in Fig. 5. The fitting parameter in this case is \( l = 0.5 \text{ mm} \) and \( A = 3.7 \times 10^{-41} \text{ s}^3 \). While one could bring down the calculated thermal conductivity to the experimental level at lower temperatures, the deviation at higher temperatures is still apparent. In fact, our calculation follows the typical \( T^{-1} \) trend for a phonon-phonon–dominant system quite well, whereas the experimental value falls on a \( T^{-1.7} \) fit at higher temperatures. Although exclusion of the contributions from longer range atomic interactions and higher order force constants could result in errors in our calculations, it would not alter the \( 1/T \) temperature dependence. Thus, we suspect this deviation is caused by other scattering mechanisms specific to this system, either due to electron-phonon interactions (phonon drag effect) or electron correlations. It is also worth noting that the lattice thermal conductivity was extracted from experiments by subtracting the electronic contribution from the measured total thermal conductivity, and the electronic contribution was estimated using Wiedemann–Franz law with a metallic Lorenz number \( L_0 = 2.44 \times 10^{-8} \text{ W} \Omega \text{K}^{-2} \) in both the references [10,14]. As mentioned in the references [10,14], the electronic contribution has a significant magnitude compared with phonons at temperatures above 100 K. Given the strong correlation among electrons, it is probable that the Wiedemann–Franz law or the metallic Lorenz number is no longer valid in this system. Furthermore, the strongly correlated electron dynamics could also lead to different phonon behaviors via phonon-electron interactions. These complications still require further investigations in the future.

To further examine the thermal conductivity, we decomposed the total thermal conductivity into contributions from different modes, as shown in Fig. 6. Below 50 K, the acoustic phonons dominate the thermal conduction since the population of the optical modes is very small. At higher temperatures, however, the contributions from the optical modes gradually become significant, taking up \( \sim 33\% \) at 200 K. Optical phonons typically do not contribute much to the total thermal conductivity due to their low group velocities and short mean free paths [33]. In FeSb\(_2\), the hybridization of the optical phonon bands with the longitudinal acoustic (LA) mode and, among themselves, results in significant band dispersion and higher group velocities, as can be observed in the phonon dispersion plot, which is one reason for the significant contribution from optical modes at higher temperatures.

In Fig. 7 the thermal conductivities along different crystal axes are plotted. The thermal conductivity along the \( c \) axis is

FIG. 5. (Color online) Calculated thermal conductivity (phonon-phonon scattering only and with boundary and impurity scatterings, averaged over the three crystal axes) versus experimental data. The experimental data is adapted from Bentien \textit{et al.} [10] and Sun \textit{et al.} [14]. The fitting parameters used here are \( l = 0.5 \text{ mm} \) and \( A = 3.7 \times 10^{-41} \text{ s}^3 \).

FIG. 6. (Color online) Contributions from different phonon modes to the total thermal conductivity.
FIG. 7. (Color online) Thermal conductivities along different crystal directions of FeSb$_2$.

about half of those along $a$ and $b$ axes at low temperatures, and this anisotropy diminishes at higher temperatures. The low-temperature anisotropy can be possibly attributed to two causes: the group velocity anisotropy and the phonon-phonon scattering anisotropy. The former can be ruled out by the calculated sound velocities by Diakhate et al. [30], where the average sound velocities do not show significant direction dependence. To check the latter, we present in Fig. 8 the correlation between the total relaxation time and the group velocity components of the acoustic modes that dominate the low-temperature thermal conduction. It is observed that those phonon modes with large group velocities along the $c$ axis mainly reside in the short-relaxation-time region, whereas the modes with the longest relaxation times also possess large group velocity components along the $a$, $b$, or both axes. This result confirms that the origin of the lower temperature anisotropy lies in the anisotropic phonon-phonon scattering.

Although no perfect match was achieved with the experimental data, we believe the simulation still provides valuable information on the lattice dynamics in FeSb$_2$ as a first attempt to understand the anharmonic processes from first principles of a crystal with a complex structure and possible strong electron correlations and thus could serve as a basis for future theoretical and experimental investigations. In Fig. 9 we present the accumulated thermal conductivity with contributions from phonon modes with different mean free paths due to phonon-phonon scattering alone. From Fig. 9, the phonon mean free paths are quite long at $T = 20$ K and concentrated in the range $1 \sim 200 \, \mu m$, indicating that it could be an effective way to reduce the lattice thermal conductivity of FeSb$_2$ by introducing nanostructures, such as grain boundaries and nanoinclusions, with characteristic sizes smaller than 1 $\mu m$, which has been readily verified in the work of Zhao et al. [11].

IV. CONCLUSION AND FUTURE WORK

We studied the thermal transport properties of FeSb$_2$ using a first-principles formalism based on DFT and real-space lattice dynamics. Calculations of the electronic structure, the phonon dispersion relation, the phonon-phonon scattering rates, the lattice thermal conductivity, and the phonon mean free path distribution were presented in this paper, which could be of value for future theoretical and experimental studies of FeSb$_2$. The discrepancy with the experimental data suggests that more work needs to be done in the future to better understand the thermal transport in FeSb$_2$. This could include looking into the possible effect of strong electron correlations, electron-phonon interactions, and higher order anharmonic processes on thermal transport, which has not been systematically investigated to the best of our knowledge.

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