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Properties of alkaline-earth-filled skutterudite antimonides: $A(\mathrm{Fe},\mathrm{Ni})_4\mathrm{Sb}_{12}$ (A=Ca, Sr, and Ba)

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Properties of alkaline-earth-filled skutterudite antimonides based on Fe and Ni are studied using first-principles calculations and Boltzmann transport theory. We find heavy conduction bands and a light-band-heavy-band mixture in the valence bands. The thermopower at high temperature is high for high carrier concentrations up to 0.2 per unit cell for both p type and n type. The results suggest experimental investigation of these materials as potential thermoelectrics.

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I. INTRODUCTION

The performance of thermoelectric materials is generally characterized by a dimensionless figure of merit, $ZT=\sigma S^2T/\kappa$, where T is the temperature, S is the thermopower, σ is the electrical conductivity, and κ is the thermal conductivity, which is generally a sum of electronic and lattice contributions, $\kappa=\kappa_e+\kappa_l$. Thermoelectric performance therefore depends on a balance of properties: high S, high σ, and low κ. However, high S is essential. This is because of the Wiedemann-Franz relation, $\kappa_e=L\sigma T$, which results in $ZT=rS^2/L$, where L is the Lorentz number and $r=\kappa_e/\kappa\leq 1$. There is no known upper bound on ZT but materials that have ZT higher than unity are rare.[1]

Filled skutterudites are a very promising class of thermoelectric materials.[2] The thermoelectric compositions are semiconductors, with general formula $R_xT_4\mathrm{Sb}_{12}$, where R is a rare earth, mixture of rare earths or a mixture of rare earths with other elements, and T is Fe, Co, or a mixture of these elements. These compounds occur in a body-centered-cubic structure, space group $Im3$. This structure may be visualized as an expanded simple cubic lattice of T (Fe or Co) atoms with the centers of three quarters of the resulting transition-metal cubes filled by nearly square Sb_4 rings perpendicular alternately to the Cartesian x, y, and z directions and the remaining one quarter filled or partially filled with R atoms. In fact, the filled skutterudite structure exists for a large number of compositions with alkali metal, alkaline earth, rare earth, and actinide fillers, Fe, Co, Ni, Ru, Rh, Os, and Ir metal (T) atoms, and P, As, and Sb ligands, and it additionally admits partial substitutions on different sites.[3] Some of these phases exhibit remarkable physical properties including unconventional superconductivity[4] and quantum critical magnetism.[5] Here we focus on thermoelectricity.

These filled skutterudite thermolectrics are based on the unfilled skutterudite CoSb_3, which has the same structure, except that the R sites are empty. This compound is a very narrow gap semiconductor with a nonparabolic near linear dispersing valence band and multiple heavy conduction bands.[6,7] The effect of filling is to strongly reduce the thermal conductivity due to anharmonic interactions between the rare earth and antimony atoms[2,8–13] and to modify the band structure.[14,15] The compositions may be understood in relation to the electronic structure using a Zintl concept. The semiconducting composition is at CoSb_3. Insertion of an electropositive element into the filling site raises the electron count, which then may be compensated by replacing part of the Co by Fe so that, for example, $\mathrm{LaFe}_3\mathrm{CoSb}_{12}$ is a nominally semiconducting composition. In practice, the filling is less than 100% and in addition there may be compensating defects so that additional Co is needed to bring the Fermi energy up to the gap.

The lattice thermal-conductivity reduction upon filling plays an important role in the high ZT of filled skutterudites. Recently, a number of authors have shown further improvement of the properties, especially for n-type material by filling with mixtures of rare earth or rare earth and Ba atoms. This presumably works by scattering phonons over a range of phonon frequencies rather than a more narrow phonon frequency band.[16–23]

The changes in the band structure are important for p-type material but less so for n type. This is because the multiple heavy conduction bands are already favorable for thermoelectric performance while the single light near linear dispersing valence band is not. Specifically, the valence-band shape of CoSb_3 gives a low S with a weaker dependence on carrier concentration than a normal parabolic band.[6,7] This dispersive valence band has primarily Sb p character involving orbitals directed toward the filling site. As such, these states will be pulled down by filling of that site with a cation and in the case of a rare earth, there can also be a lowering due to hybridization with the unoccupied rare-earth states. The result is a valence-band structure with a gap and a mixture of heavy and light bands that is favorable for thermoelectric performance.[14] This is sensitive to details so that, for example, qualitatively different band structures are found for the arsenides and phosphides.[6,24] Furthermore, in a partially filled system the disorder on the R site may be expected to give strong scattering of the carriers in the light hole band for p-type material. On the other hand the heavy bands at the conduction-band edge, which are important for obtaining a high thermopower for n-type material are less affected by the filling. This asymmetry in the electronic structure and its response to filling between the valence and conduction bands may be the reason why the best reported thermoelectric performance for filled n-type skutterudites is significantly higher than for the best p-type filled skutterudites, which are inferior. Therefore, better performance p-type compositions would be particularly helpful for thermoelectric applications, which require couples of p-type and n-type materials.

In this regard, Wee *et al.*[25] recently reported interesting theoretical results for fully and partially alkaline-earth-filled

$CoSb_3$, i.e., $A_xCo_4Sb_{12}$ with A=Ca, Sr, and Ba and various x from 0.25 to 1.0. These are n type. For this composition range they report a weak gap opening when filling with Sr, larger gap opening with Ca filling, and a gap closing with Ba filling. The results indicate that gaps can be opened with A filling. Here we examine the properties of fully alkaline-earth-filled skutterudites with compositions around the semiconducting composition, including virtual-crystal calculations and some ordered cells based on Fe-Ni mixtures to obtain the needed electron count.

II. APPROACH

Our electronic-structure calculations were performed with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE),[26] using the general potential linearized augmented plane wave (LAPW) method[27] (also known as the full potential LAPW method) as implemented in the WIEN2K code.[28] The calculations were done with well-converged basis sets, including local orbitals for the semicore states of the alkaline-earth and transition-element atoms.[29,30] Here we used the standard LAPW linearization, matching values and derivatives of the wave functions as opposed to the more efficient but slightly less flexible APW+LO method.[31] The LAPW sphere radii were $2.4a_0$ for the A atoms and $2.35a_0$ for the transition-element and Sb atoms. We used the experimental cubic lattice parameters of $CaFe_4Sb_{12}$, $SrFe_4Sb_{12}$, and $BaFe_4Sb_{12}$, which are 9.1634 Å, 9.181 Å, and 9.202 Å, respectively. These are rather close, reflecting the rigidity of the skutterudite framework, which may be expected to lead then to a rather soft potential for the small Ca^{2+} ion. The internal atomic coordinates were relaxed using energy minimization. These calculations were done in a scalar relativistic approximation, except for the thermopower, where spin orbit was included.

One may note that these compounds contain Fe and Ni. Oxides of Fe and especially Ni are often strongly Coulomb correlated. For example, NiO is a prototypical Mott insulator. This is clearly seen in electronic spectroscopies, which show a band gap of ~4 eV between O p valence bands and an upper Hubbard band of Ni d character, in contrast to density-functional calculations which predict a very small band gap of d-d character.[32] However, this does not seem to be the case in skutterudites. In particular, spectroscopic experiments show that the d density of states has a shape and position in accord with density-functional predictions.[33,34] The behavior of these skutterudite antimonides is therefore similar to that of the iron pnictide superconductors, which are also found to be weakly to moderately correlated.[35–38] As such, we use the band structures as obtained from first principles in the transport calculations.

Transport properties were calculated within Boltzmann theory based on the first-principles electronic structures from the LAPW calculations and making use of the constant scattering time approximation.[39,40] The BOLTZTRAP code was used for the needed integrals.[41] The constant scattering time approximation, which is commonly applied to metals and degenerately doped semiconductors, is particularly useful in studying thermoelectric materials. It consists in taking the scattering time, τ as independent of energy at fixed temperature and doping level. It does not involve any assumptions regarding the possibly strong doping and temperature dependence of τ. With this approximation the thermopower $S(T)$ can be calculated directly from the electronic structure without adjustable parameters. This has led to a number of successful applications to thermoelectric materials, including conventional materials and oxides.[14,40,42–49] Finally, because transport is sensitive to the details of the band structure, we additionally performed calculations of the thermopower including spin orbit. The effect of spin orbit in these materials is a minor reduction in the thermopower particularly for low-doping levels.

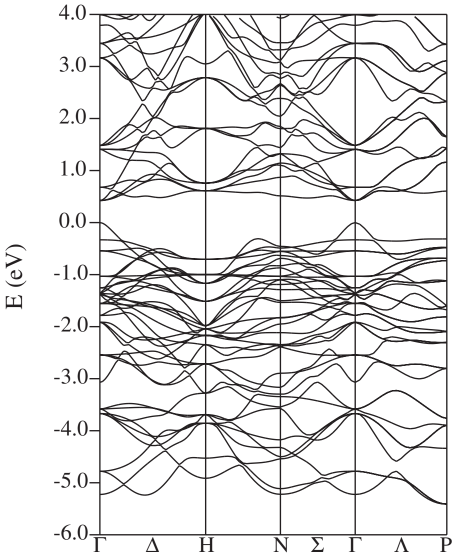

FIG. 1. Virtual-crystal band structure of $SrFe_3NiSb_{12}$ as obtained in a scalar relativistic approximation (see text).

The vibrational properties were calculated using a frozen phonon method, as implemented in the FROPHO code.[50] The needed forces were obtained using the projector augmented wave method in the VASP code.[51] We used the PBE GGA with a basis set cutoff energy of 460 eV. The calculations were done using ordered cells of composition AFe_3NiSb_{12} again following relaxation of the internal coordinates as well as the lattice parameters. The relaxed lattice parameters were a=9.192 Å, 9.218 Å, and 9.245 Å for A=Ca, Sr, and Ba, respectively. These relaxed lattice parameters for the supercells are within 0.5% of the experimental values for the pure compounds that we used in the electronic-transport calculations.

III. ELECTRONIC STRUCTURE

We begin with the virtual-crystal electronic structures for CaT_4Sb_{12}, SrT_4Sb_{12}, and BaT_4Sb_{12} for the semiconducting stoichiometry $T=Fe_{0.5}Co_{0.5}$ or equivalently $T=Fe_{0.75}Ni_{0.25}$ (see below). The calculated band structures for the three cases are rather similar. The band structure for the Sr compound is shown in Fig. 1 and a comparison of the density of states (DOS) of the three cases is shown in Fig. 2.

As may be seen these compounds are modest gap semiconductors with a singly degenerate light valence-band

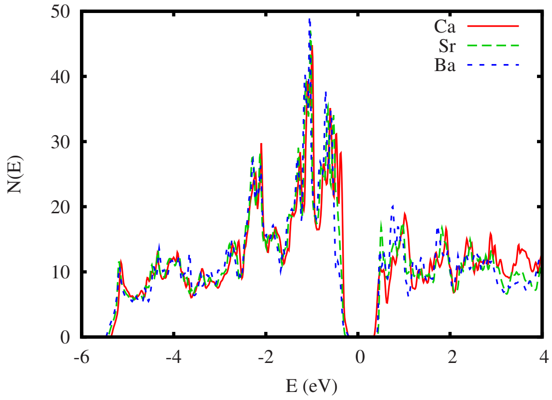

FIG. 2. (Color online) Comparison of the scalar relativistic electronic densities of states for virtual-crystal $A\mathrm{Fe}_3\mathrm{NiSb}_{12}$, A=Ca, Sr, and Ba (see text).

maximum at Γ. This band intersects much heavier bands at higher binding energy. This is similar to $\mathrm{LaFe}_4\mathrm{Sb}_{12}$ with the exception that the distance between the valence-band edge and the heavy-band onset is larger. There are multiple heavy conduction bands similar to other skutterudites. The calculated PBE-GGA band gaps are 0.37 eV for Ca, 0.42 eV for Sr, and 0.36 eV for Ba. These values are ~0.1 eV larger than the values that were found by Wee *et al.*[25] for filled CoSb_3. Also it should be noted that these are density-functional calculations, and so it is possible that the band gaps are underestimated. We are not aware of experimental data for comparison. However, the effect of a band gap underestimate would be an overestimate of the amount of bipolar conduction. Therefore if the band gap is underestimated, the actual values of the thermopower at low doping and high temperature may be higher in magnitude than those that we calculate.

Importantly, the shape of the density of states near the band edges for the three compounds is very similar. The implication is that the scattering due to disorder on the alkaline-earth site that would result from alloying Ca, Sr, and Ba would not be as strong as that due to rare-earth disorder or disorder due to partial rare-earth filling. This suggests that the electrical properties of these compounds with optimized p-type doping could be superior to p-type rare-earth-filled skutterudites especially since mixed alkaline-earth compositions may have higher mobility than the multiple rare-earth-filled materials. However, obtaining a thermoelectric composition in this way requires charge balancing based on transition-element alloying. Conventionally, this is done in skutterudite thermoelectrics using alloys of Fe and Co. Since alkaline earths are divalent, the use of an alkaline earth for the filling atom rather than a trivalent rare earth would require a higher Co concentration to obtain the semiconducting composition. On the other hand, it is known that skutterudites based on Fe-Ni alloys can be made and that these can be semiconducting similar to CoSb_3 provided that the electron count is maintained.[52,53] This may be advantageous because each Ni contributes two additional electrons relative to Fe as compared to one for Co, and so a lower concentration of Ni would be needed, perhaps reducing the amount of alloy scattering. Furthermore, Ni is significantly less expensive than Co. This might be of importance in thermoelectric applications where materials cost is a factor. We compared calculations for ordered cells of composition $\mathrm{SrFe}_3\mathrm{NiSb}_{12}$ and $\mathrm{SrFe}_2\mathrm{Co}_2\mathrm{Sb}_{12}$ in order to determine whether this is a possibility. In both cases the cells were constructed from the primitive 17-atom-filled skutterudite structure and the internal atomic coordinates were fully relaxed. Figure 3 shows the densities of states of these ordered cells in comparison with the virtual-crystal result. As may be seen Ni filling causes only very small distortion of the DOS in the valence bands while there is a larger but still not large distortion at the conduction-band edge. This is not to say that the Fe d and Ni d electronic states are coherent. In fact the occupied Fe d states occur at the onset of the heavy bands below the valence-band edge while the Ni d states are mainly located at higher binding energy between −3.5 and −1.5 eV, relative to the valence-band edge, as shown in Fig. 4. In any case, this mild distortion of the DOS indicates that $\mathrm{SrFe}_3\mathrm{NiSb}_{12}$ may be a good thermoelectric material provided that the lattice thermal conductivity is low as in other filled skutterudites and that doping levels that yield high thermopowers can be

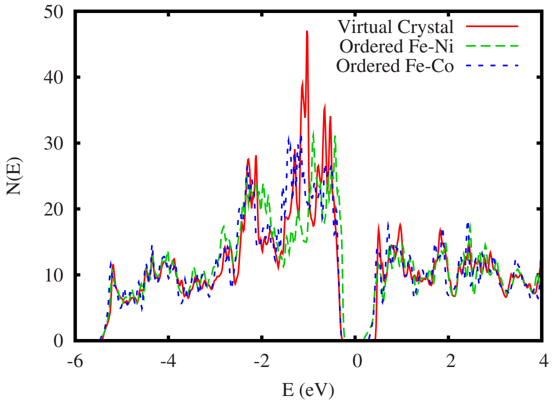

FIG. 3. (Color online) Comparison of the scalar relativistic electronic densities of states for ordered cells of composition $\mathrm{SrFe}_3\mathrm{NiSb}_{12}$ and $\mathrm{SrFe}_2\mathrm{Co}_2\mathrm{Sb}_{12}$ with a virtual-crystal calculation. All internal coordinates were relaxed. Note that the very low DOS due to the light valence band extending up to 0 eV is not seen on this scale.

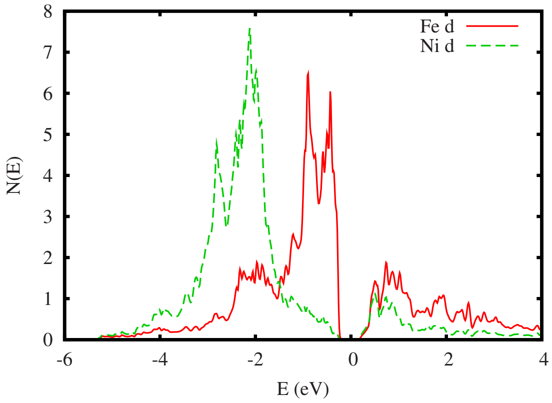

FIG. 4. (Color online) Fe d and Ni d projections of the scalar relativistic DOS for an ordered cell of $\mathrm{SrFe}_3\mathrm{NiSb}_{12}$, shown on a per atom basis.

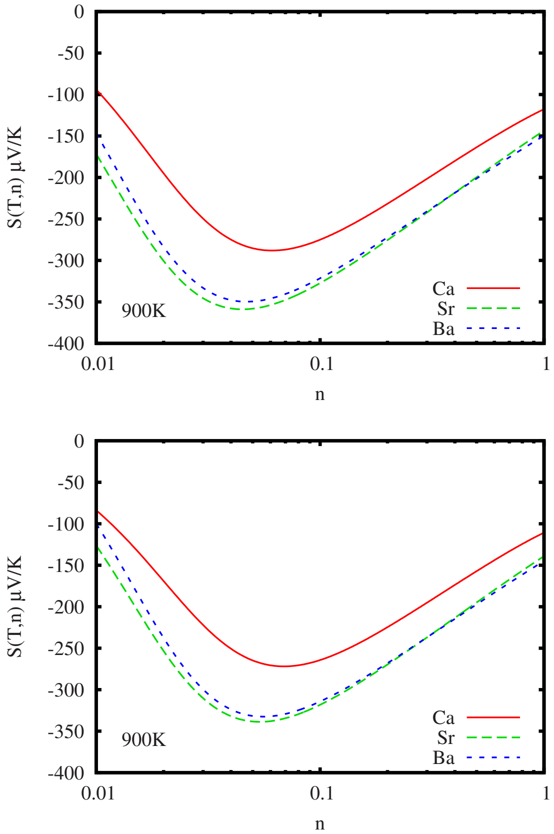

FIG. 5. (Color online) Calculated thermopower as a function of carrier concentration at 900 K for n-type $A\mathrm{Fe_3NiSb_{12}}$, A=Ca, Sr, and Ba (see text). The top panel is based on the scalar relativistic electronic structure while the bottom panel includes spin orbit. The carrier concentrations are in units of carriers per unit cell.

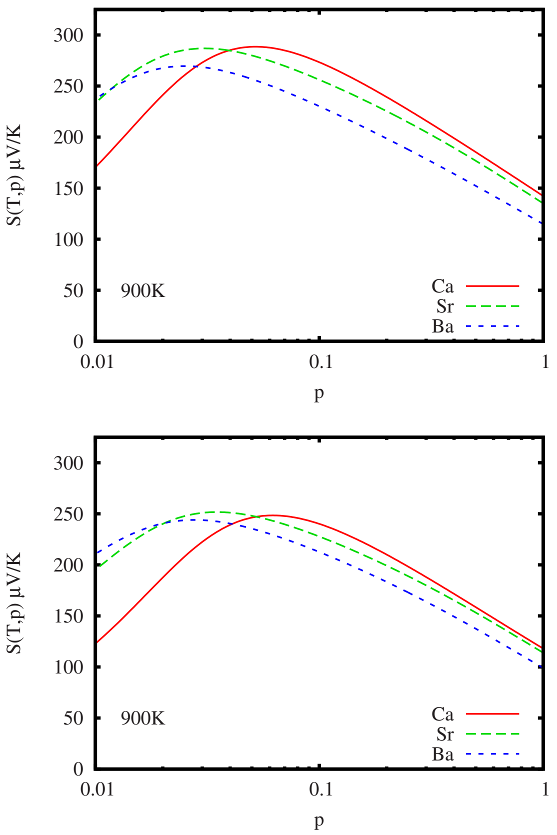

FIG. 6. (Color online) Calculated thermopower as a function of carrier concentration at 900 K for p-type $A\mathrm{Fe_3NiSb_{12}}$, A=Ca, Sr, and Ba (see text). The top panel is based on the scalar relativistic electronic structure while the bottom panel includes spin orbit. The carrier concentrations are in units of carriers per unit cell.

found. We did Boltzmann transport calculations to evaluate this.

IV. TRANSPORT CALCULATIONS

The thermopower, $S(T)$ was calculated for the three alkaline-earth-filled skutterudites as a function of carrier concentration and temperature using the virtual-crystal electronic structures. The calculated $S(T)$ as a function of carrier concentrations is shown at 900 K for n type and p type in Figs. 5 and 6, respectively. The top and bottom panels of these figures show results with the scalar relativistic band structure and the relativistic band structure including spin orbit, respectively. As may be seen the effect of spin orbit is a minor reduction in the thermopower particularly at low-doping levels. The n-type thermopowers can have very high magnitudes, ~ -300 μV/K for Sr and Ba filling and ~ -200 μV/K for Ca, over a range of carrier concentrations from n=0.03 to n=0.2/f.u. (0.1/f.u. is $\sim 2.6\times 10^{20}$ cm^{-3}). Below this range the thermopower is reduced by bipolar conduction, which is negative for thermoelectric performance. These high thermopowers at high carrier concentrations are consistent with experimental data and prior calculations for other n-type skutterudites.[45,54,55] Based on this, if the mobility and thermal-conductivity behave similarly to other filled skutterudites, the optimum carrier concentration for power generation using n-type material would be $n\sim 0.1-0.5$ per unit cell (higher doping if the mobility is lower or the lattice thermal conductivity is higher). Remarkably the thermopower for both n type and p type remains high up to very high carrier concentration. For Sr and Ba filling, the n-type thermopower is larger in magnitude than -200 μV/K up to $n\sim 0.5$/unit cell and for p type, thermopowers in excess of 200 μV/K are found up to $p\sim 0.2$/unit cell for Ca and Sr filling. In contrast, the doping levels for conventional thermoelectric materials such as PbTe are typically 0.01 or lower per formula unit. The behavior for the skutterudite is reminiscent in this respect of the oxide thermoelectric $\mathrm{Na_xCoO_2}$.[56] In that material high thermoelectric performance is found for $p\sim 0.3$ per Co, an even higher doping than for the n-type case here (note that the skutterudite has four transition element atoms per cell). The origin is the same—flat transition-metal bands at the band edge leading to high thermopowers at high-doping levels.[57]

In connection with this, Puyet *et al.*[54] reported that the addition of a small amount of Ni to $\mathrm{Ca_yCo_4Sb_{12}}$ leads to increased conductivity, presumably due to a higher carrier concentration, without degrading the thermopower, and it was also reported that the thermal conductivity of $\mathrm{CoSb_3}$ is strongly reduced upon Ca or Sr filling.[58,59]

Turning to the p-type case, we also find high thermopowers, S(900 K)$\sim$200 μV/K in the concentration range p

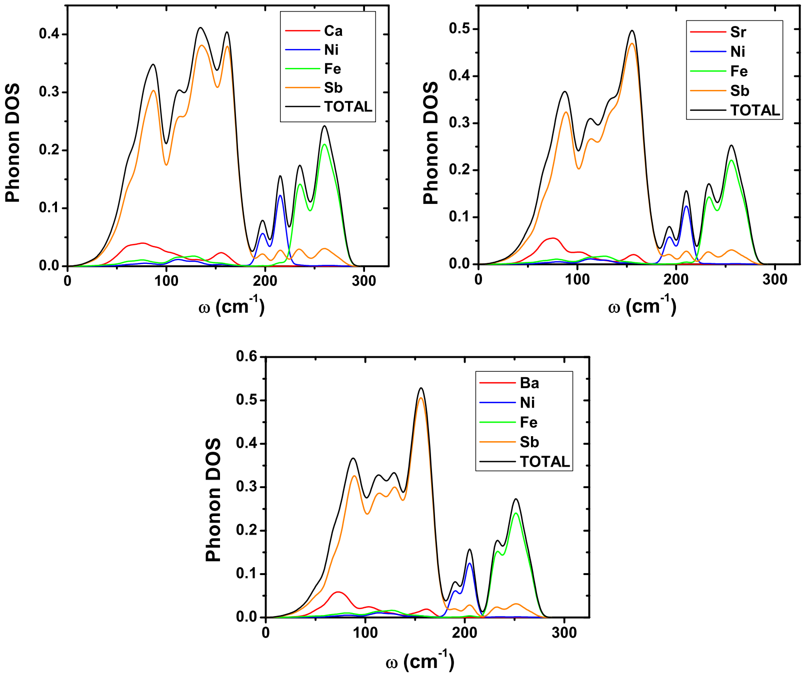

FIG. 7. (Color online) Calculated vibrational density of states and site projections for ordered AFe$_3$NiSb$_{12}$ cells, A=Ca (top left), A=Sr (top right), A=Ba (bottom).

$=0.02-0.1$ per unit cell. While this is similar to the range for high S in the n-type case, for p-type it involves the combination of heavy bands with a light band, which is a very favorable case for enhanced mobility as such the p-type thermoelectric performance for optimum carrier concentration is expected to be higher than the n-type case. This heavy-band, light-band combination is also reflected in the low carrier-concentration regime, where one may note that the reduction in the thermopower due to bipolar conduction is weaker than for n type. This is because for a given carrier concentration the Fermi energy will be further from the band edge in the p-type case due to the light band at the valence-band maximum.

V. VIBRATIONAL PROPERTIES

Frozen phonon calculations were done for ordered cells of AFe$_3$NiSb$_{12}$. The vibrational densities of states and site projections are shown in Fig. 7. Figure 8 shows a comparison of the phonon density of states for BaFe$_3$NiSb$_{12}$ at the relaxed supercell lattice parameter of 9.245 Å, as in Fig. 7, with that at 9.202 Å, which is the experimentally based lattice parameter used in the transport calculations. As expected, only small changes are found especially in the region below 150 cm^{-1}, which is thought to be the region most important for heat transport.[9] Remarkably, even though Ca, Sr, and Ba have very different masses, the main vibrational peaks associated with the filling atoms are at very similar frequencies of ∼80 cm^{-1} in the three compounds. This is similar to what was found by Wee *et al.*[25] for A-filled CoSb$_3$. The reason is that while Ca has a much lower mass than Ba, it is also smaller. The rigidity of the skutterudite framework around the filling site then leaves it more room to vibrate (i.e., a softer potential). The Shannon radii of 12 coordinate Ca^{2+}, Sr^{2+}, and Ba^{2+} are 1.48 Å, 1.58 Å, and 1.75 Å, respectively, which corresponds to a range of 0.27 Å. On the other hand, the nearest-neighbor A-Sb distances in the optimized virtual-crystal structures are 3.402 Å, 3.427 Å, and 3.455 Å for A=Ca, Sr, and Ba, respectively. This is a range of only ∼0.05 Å.

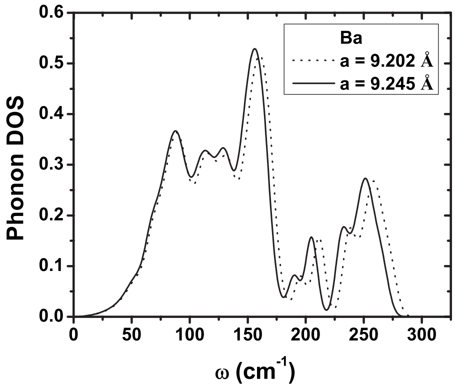

FIG. 8. Comparison of the vibrational density of states of BaFe$_3$NiSb$_{12}$ supercells at lattice parameters a=9.245 and 9.202 Å.

As mentioned, the lattice thermal-conductivity reduction in filled skutterudites relative to the unfilled compounds is thought to be mostly a result of anharmonic interactions between the filling atom and the surrounding Sb atoms.[2,9–13] A key observation was the finding of two distinct peaks associated with rare-earth vibrations, even though in a cubic material only one vibrational peak associated with the single rare-earth site might be anticipated.[60] This two-peak structure was explained as arising from the mixing of rare earth and Sb vibrational modes due to the interaction between the filler and the neighboring Sb sites.[9,10,12] We find a similar mixing here for the A fillers, reflected in the width of the A peaks in vibrational DOS. Even though the main filling atom frequencies are similar for the different A's, it may be seen from the different shapes of the projected phonon DOS that the amount of mixing depends on the specific filling atom. This is because of the different interaction strengths for the different *A*'s reflecting their different sizes as discussed above. As such, there may be an opportunity to lower the thermal conductivity of *A* filled skutterudites using the disorder that comes from alloying with mixtures of *A* fillers.

VI. SUMMARY AND CONCLUSIONS

Calculations of the electronic structure, thermopower, and vibrational properties of $A\mathrm{Fe}_3\mathrm{NiSb}_{12}$ are reported. We find high thermopowers at high carrier concentrations, reflecting heavy conduction bands and mixture of a light and very heavy valence bands. The other properties are consistent with good thermoelectric performance, including for *p*-type doping. An advantage of these compositions for some applications is the fact that alkaline earths are inexpensive and much more available than heavy rare earths, and that Ni is less expensive than Co, and furthermore a semiconducting composition can be reached with less Ni than Co.

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