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Alkali-metal-filled $CoSb_3$ skutterudites as thermoelectric materials: Theoretical study

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The crystal structures, filling fraction limits (FFLs), electronic structures, and electrical transport properties for alkali-metal-filled $CoSb_3$ skutterudites are studied using density functional band-structure calculations. The calculated FFLs in $CoSb_3$ are more than 60% for Na and K, 25% for Rb, and zero for Li and Cs, at 1000 K. The reasons for these unusual FFLs of alkali atoms are discussed. Based on the calculated electronic structures, the electrical transport properties of $CoSb_3$ are likely to be retained upon Na and K fillings, which was also confirmed by our calculated electrical transport properties of these materials. Furthermore, excellent thermoelectric properties are expected for Na-filled $CoSb_3$ skutterudites.

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I. INTRODUCTION

Filled skutterudite materials have been widely studied in recent years due to their potential applications for thermoelectric power generation.[1,2] The dimensionless figure of merit ZT is used to evaluate the performance of a thermoelectric material for either power generation or refrigeration application, and is given by $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, T the temperature, κ the total thermal conductivity, and σ the electrical conductivity. According to the concept of phonon-glass-electrical-crystal introduced by Slack,[3] various atoms[4–14] (Ce, La, Nd, Eu, Yb, Tl, Sn, Ge, Ga, Sr, Ba, etc.) have been filled into the large lattice voids of $CoSb_3$ to form filled skutterudites. The weakly bound filler atoms rattle inside the lattice voids, scatter low frequency acoustic phonons, significantly reduce lattice thermal conductivity, and, thus, lead to substantial improvement of thermoelectric performance. People, thus far, have mainly focused on the rare-earth-filled skutterudites, since it is believed that heavy atoms are more effective in scattering phonons than the light ones.[15] Experimentally, only a few fractions of the voids, however, can be filled by rare earth (La, Ce, Nd, Eu, Yb, etc.) without charge compensation,[4–8] which limits the reduction of thermal conductivity as well as the tuning space of electrical transport properties. Because of the significant influence of filling fraction on the thermoelectric performance of filled $CoSb_3$,[4–14] much effort has been spent on searching for new fillers with relatively high filling fraction limits (FFLs) in $CoSb_3$ to obtain better n-type thermoelectric materials.

In the past, alkali atoms have not attracted much attention as candidate void fillers, since it is unknown whether they can be filled into $CoSb_3$ and they are considered to be too light to be good rattlers. Our recent density functional calculations,[16] however, showed that K has an ultrahigh filling fraction limit (more than 60%) in $CoSb_3$. $ZT=1$ at 800 K for $K_{0.38}Co_4Sb_{12}$ was later achieved experimentally.[17] Although alkali metal fillings do not reduce thermal conductivity more than alkali-earth or rare-earth fillings, K-filled $CoSb_3$ possess a relatively large Seebeck coefficient and, therefore, a reasonably high power factor ($S^2\sigma$).[17] Until now, the FFLs of other alkali metals, and the effect of alkali metal filling on the electronic band structures and electrical transport properties of $CoSb_3$, are not yet well understood. Based on the simple selection rule proposed by Shi *et al.*,[18] alkali metals besides K may also have high FFLs in $CoSb_3$. Filling $CoSb_3$ with low valence state fillers seems to be a different approach to improve the thermoelectric performance of $CoSb_3$-based materials.

A number of theoretical studies have been done to investigate the electronic structures and various properties of skutterudite-type materials. Singh and co-workers have calculated various properties of $IrSb_3$, $CoSb_3$, $CoAs_3$, CoP_3, $LaFe_4P_{12}$, and $(La,Ce)Fe_4Sb_{12}$ by the linearized augmented plane wave method.[19–21] Løvvik and Prytz and L. Chaput *et al.* have investigated the thermodynamic stabilities and some electrical properties of CoP_3- and $CoSb_3$-based filled skutterudites.[22,23] Recent work on combining the classical Boltzmann transport equation and relaxation time approximation to calculate electrical transport properties for several types of thermoelectric materials has also been quite successful.[21,23–25] In this paper, we systematically investigate the FFLs for all alkali atoms (Li, Na, K, Rb, and Cs) in $CoSb_3$ by *ab initio* density functional calculations. Detailed electronic structures for Na- and K-filled $CoSb_3$ skutterudites are presented. We have also studied the electrical transport properties of Na- and K-filled $CoSb_3$ by using the Boltzmann equation and constant relaxation approximation as implemented in the Vienna *ab initio* simulation package (VASP).

II. COMPUTATIONAL METHOD

Density functional calculations within the generalized gradient approximation (GGA), as implemented in VASP, were utilized in this study.[26,27] Perdew-Burke-Ernzerhof GGA[28] for the exchange-correlation potential was used for all the calculations. Projector augmented plane-wave method was used to span out the electron density.[29,27] A plane-wave cutoff energy of 320 eV and an energy convergence criterion

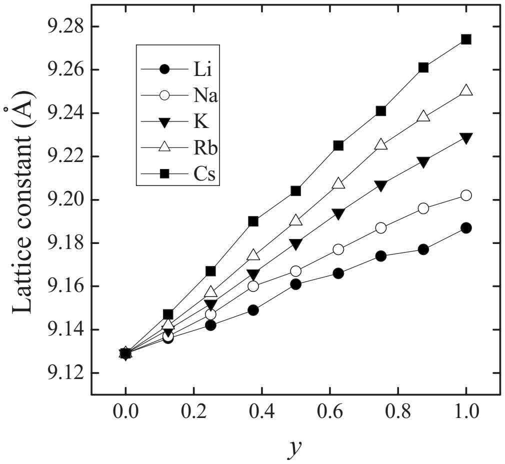

FIG. 1. Calculated lattice constant as a function of filling fraction (y) for alkali-metal-filled $CoSb_3$ skutterudite.

of 10^{-4} eV for electronic structure self-consistency were used in all calculations. All calculations of filled-$CoSb_3$ skutterudites were carried out on a supercell ($2\times2\times2$ primitive cell) with a total of 128 atoms and 8 voids of pure $CoSb_3$. Only gamma point was used for the electronic structure self-consistency for the relatively large supercell, and convergence has been shown to be good (see Ref. 35 for details). A $6\times6\times6$ Monkhorst-Pack[30] k-point sampling was employed for the other compounds, e.g., the secondary phases. The partial occupancy for each wave function is evaluated based on the Fermi smearing method for calculations.

Structure relaxations have been performed by using the residual minimization scheme by direct inversion in iterative subspace implementation of the quasi-Newton method.[31] The ionic coordinates were considered relaxed when all the Hellmann-Feynman forces exerted on atoms were less than 10^{-2} eV/Å. The unit cell sizes were also optimized to obtain the most stable structure free of internal stress. A single calculation of high accuracy was performed after the completion of structure relaxation to obtain the total free energy.

III. RESULTS AND DISCUSSION

A. Crystal structure and filling fraction limits

1. Crystal structure

In all calculations, the structure relaxation scheme allows the unit cell to change size and ionic positions. For the partially filled $CoSb_3$, it was found that the structures with the same filling fraction but different filling configurations exhibit the same lattice constant. Generally, lattice constant increases with increasing filling fraction. This is shown in Fig. 1, where the cubic cell lattice constant is plotted as a function of filling fraction y for all alkali metals. The lattice expansion due to alkali filling is very close to linear. In addition, the lattice expansion seems to be closely correlated to the ionic radius of the filler.

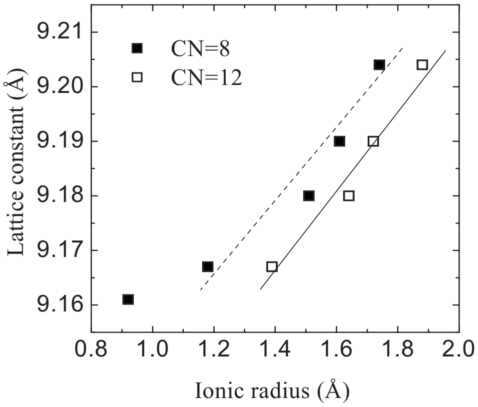

FIG. 2. Correlation between the calculated lattice constant and alkali ionic radius for 50% alkali-metal-filled $CoSb_3$ skutterudite. The ionic radii of alkali ions (Ref. 32) with both 8 coordinations (CN=8, filled squares) and 12 coordinations (CN=12, unfilled squares) are plotted. Note that Li ion has only the 8-coordination data. Trend looks similar by using the 8-coordination or 12-coordination ionic radius for ions. The dashed and solid lines are used for guiding the eyes.

Though different alkali atoms may have different filling fractions in $CoSb_3$, we take the 50% filled $CoSb_3$, i.e., ICo_8Sb_{24} (I represents an alkali impurity atom), to analyze the effect of ionic size on the $CoSb_3$ lattice expansion by plotting the correlation between the calculated lattice constant of filled $CoSb_3$ and the alkali ionic radius at $y=0.5$ (see Fig. 2). Note that the inserted ion in the Sb cage of $CoSb_3$ may be considered to have 12 Sb nearest neighbors. In principle, 12-coordination (CN=12) ionic radius is probably a more reasonable approach. Unfortunately, only the 8-coordination (CN=8) Li-ion radius could be found in Ref. 32. Therefore, the correlation between expanded lattice constant and ionic radius of CN=8 (Li, Na, K, Rb, and Cs) and of CN=12 (Na, K, Rb, and Cs) are all presented in Fig. 2 for comparison. Generally speaking, the data for CN=8 and CN=12 show a similar trend.

The lattice constant increases in an approximately linear way from Na-, K-, Rb-, to Cs-filled $CoSb_3$. In fact, the ionic radius of Cs (1.88 Å for CN=12) (Ref. 32) is comparable to the void radius of $CoSb_3$ (1.89 Å, estimated by Nolas *et al.*[15]). We expect that the lattice strain due to Cs filling would be too large to form stable Cs-filled $CoSb_3$ compounds. Note that the lattice for the Li-filled $CoSb_3$ does not fall on the trend line linking Na, K, and Cs ions based on either the 8-coordination or 12-coordination data (see Fig. 2). The calculated lattice constant of the 50% Li-filled $CoSb_3$ is 9.16 Å, much larger than the extrapolated value 9.13 Å (CN=12) or 9.14 Å (CN=8) based on the linear trend shown in Fig. 2. Two reasons are expected. First, Li donates exactly the same number of extra free electrons to bands as Na, therefore, Li-induced lattice expansion due to the changed electron filling, mostly on Sb-Sb bonds, is expected to be similar to that from Na although Li introduces less strain. Such an electron filling effect may introduce a low limit to the impurity-induced lattice expansion. Second, because of the relatively small ionic radius of Li (0.92 Å for Li^+),[32] in comparison with the lattice void size in $CoSb_3$, the inserted Li atom does not exactly occupy the center position of the void, and thus, exhibits a relatively large static disorder in the cage which would result in extra lattice expansion. The lattice expansion

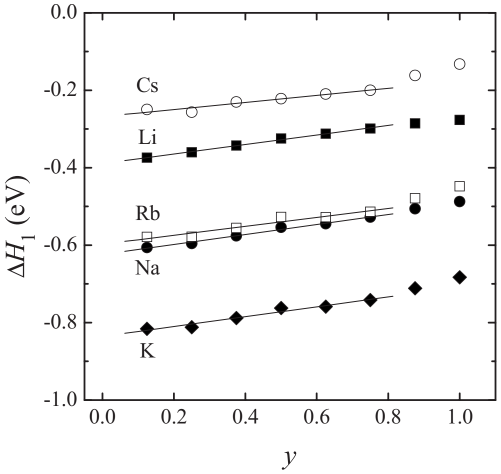

FIG. 3. Formation enthalpy (per impurity atom) as a function of filling fraction y for the alkali-metal-filled $CoSb_3$ skutterudites. The symbols are calculated data. The lines are the best linear fits to the data.

of $CoSb_3$ due to Li filling is very small, even much smaller than that of Yb filling. According to our previous study,[33] Li atom would be too small to form a stable filled skutterudite structure, which will be verified in the later part of filling fraction limit calculations.

2. Filling fraction limits for alkali atoms in $CoSb_3$

The formation of stable filled skutterudite materials is a complicated process which usually includes two main chemical reactions. First, the formation of a filled $CoSb_3$ by filling an impurity I into the lattice voids of $CoSb_3$ can be described by $yI+4CoSb_3 \rightarrow I_yCo_4Sb_{12}$, and the reaction of forming the filled system owes a formation enthalpy ΔH_1 (per impurity I) as described in detail in Ref. 18. Figure 3 plots the calculated formation enthalpy ΔH_1 as a function of y for all alkali atoms. Our previous research has demonstrated that the FFL is determined by the competition between the formation of a filled skutterudite phase and that of secondary phases.[18] Since the alkali metals are chemically very active and easily reactible with antimony, the second reaction, which is the formation of secondary phases, happens in practice and can be described as $I+CoSb_3 \rightarrow ISb+CoSb_2$. This reaction has a formation enthalpy ΔH_2, and the detailed calculation procedure is given in Ref. 18. Table I lists the space group, relaxed lattice constant, and formation enthalpy ΔH_2 for all possible secondary phases during the formation of alkali-metal-filled $CoSb_3$ skutterudites. The most thermodynamically stable secondary phases for Li, Na, K, Rb, and Cs at 0 K are Li_3Sb, Na_3Sb, KSb, RbSb, and CsSb, respectively. By considering the fact that it is normally Sb rich while Na tends to vaporize before reaction could take place during sample synthesis,[17] the formation of the secondary phases for Na should be changed to $3Na+CoSb_3+2Sb \rightarrow 3NaSb+CoSb_2$. The corresponding formation energy is −0.589 eV, lower than that for Na_3Sb (−0.511 eV). Therefore, NaSb is taken as the most stable secondary phase for Na in this work. Similar effect of excessive Sb on other alkali atoms was also considered. ISb turns out to be the most stable form of the secondary phase for Na, K, Rb, and Cs, but I_3Sb for Li.

By combining the aforementioned two reactions, the actual chemical reaction could be expressed as $nI+4CoSb_3 \rightarrow [(4-n)/(4-y)]I_yCo_4Sb_{12}+[4(n-y)/(4-y)]ISb+[4(n-y)/(4-y)]CoSb_2$. At a finite temperature, the corresponding Gibbs formation energy per impurity is[18]

$$\Delta G_3 = \frac{4(n-y)}{n(4-y)}\Delta H_2 + \frac{(4-n)y}{n(4-y)} \times \left\{ \Delta H_1(y) + kT\left[\ln y + \frac{1-y}{y}\ln(1-y) \right] \right\},$$

TABLE I. Space group, measured and calculated lattice constants, and formation enthalpy of possible secondary phases during the formation of alkali-filled $CoSb_3$. All measured lattice constants and angles are from the Inorganic Compound Structure Database (Ref. 40).

	Space group	Measured lattice constants (a,b,c) (Å)	Measured lattice angles (α,β,γ) (deg)	Calculated lattice constants (a,b,c) (Å)	ΔH_2 (eV)
$CoSb_2$	*P*121/*C*1	6.505, 6.383, 6.541	90, 117.65, 90	6.531, 6.407, 6.578	
Li_3Sb	*FM*-3*M*	6.559, 6.559, 6.559	90, 90, 90	6.573, 6.573, 6.573	−0.771
Li_2Sb	*P*-62/*C*1	7.946, 7.946, 6.527	90, 90, 90	7.943, 7.943, 6.490	−0.748
Na_3Sb	*P*63/*MMC*	5.355, 5.355, 9.496	90, 90, 120	5.378, 5.378, 9.555	−0.511
NaSb	*P*121/*C*1	6.800, 6.340, 12.480	90, 117.60, 90	6.829, 6.417, 12.571	−0.434
K_3Sb	*P*63/*MMC*	6.025, 6.025, 10.693	90, 90, 120	6.093, 6.093, 10.805	−0.479
KSb	*P*121/*C*1	7.072, 6.879, 13.207	90, 115.20, 90	7.332, 7.068, 13.562	−0.652
KSb_2	*C*12/*M*1	14.055, 4.233, 7.053	90, 95.02, 90	14.302, 4.304, 7.152	−0.446
Rb_3Sb	*P*63/*MMC*	6.283, 6.283, 11.18	90, 90, 120	6.420, 6.420, 11.371	−0.407
RbSb	*P*212121	7.315, 7.197, 12.815	90, 90, 90	7.421, 7.321, 13.005	−0.629
Cs_3Sb	*FM*-3*M*	9.180, 9.180, 9.180	90, 90, 90	9.326, 9.326, 9.326	−0.367
CsSb	*P*212121	7.575, 7.345, 13.273	90, 90, 90	7.812, 7.571, 13.473	−0.692

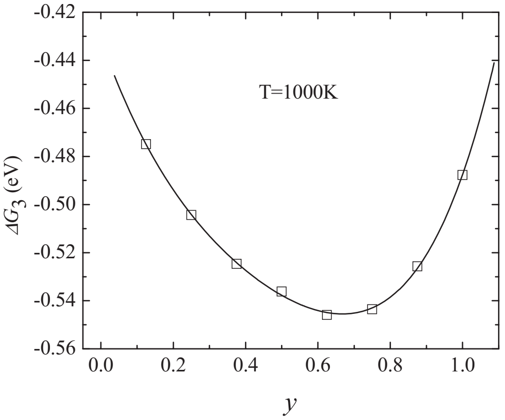

FIG. 4. Gibbs free energy ΔG_3 for filling Na into $CoSb_3$ at $T=1000$ K. The solid line is a polynomial fit to the calculated data (open symbols).

where k is the Boltzmann constant and T the absolute temperature. The $kT[\ln y+[(1-y)/y]\ln(1-y)]$ term comes from the configurational entropy due to the random distribution of alkali atoms in the lattice voids.[34] By minimizing ΔG_3 with respect to y, the FFL can be obtained in terms of ΔH_1 and ΔH_2. Figure 4 plots the Gibbs free energy ΔG_3 for Na-filled $CoSb_3$ skutterudite as a function of y at $T=1000$ K. A polynomial fit to ΔG_3 determines the maximum filling fraction as 65%. FFLs for other alkali atoms in $CoSb_3$ can be obtained in the same way.

Figure 5 shows the FFLs for all alkali atoms (Li, Na, K, Rb, and Cs) in $CoSb_3$ at 1000 K. Our calculations show that the FFLs for Na and K in $CoSb_3$ are 65% and 60%, respectively. They are much higher than those of rare-earth or alkali-earth atoms. These results were validated in K-filled $CoSb_3$ synthesis,[16,17] where the experimental filling fraction for K was found to be above 50%. In addition, the experimental results showed that the K-filling improves the electrical transport properties of $CoSb_3$ and leads to a reasonably good thermoelectric performance.[17] Recent ongoing experimental work has shown the possibility of about 60% FFL for Na in $CoSb_3$. We expect that Na-filled skutterudites should also have good thermoelectric properties. Our calculation also shows that Li and Cs cannot be filled into the voids of $CoSb_3$ to form a stable filled skutterudite structure.

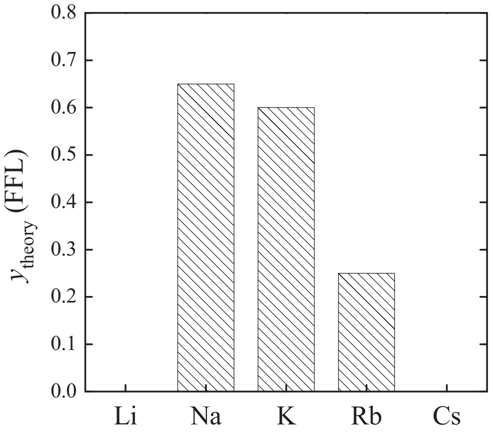

FIG. 5. Calculated FFLs for alkali atoms in $CoSb_3$. The FFLs for Li and Cs in $CoSb_3$ are zero.

TABLE II. Calculated ΔE_1, ΔE_2, ΔH_2, ΔE_s, and ΔE_b for alkali-filled $CoSb_3$, in the unit of eV per impurity. See text for the explanation of the corresponding parameters.

	ΔE_1	ΔE_2	ΔH_2	ΔE_s	ΔE_b
$Li_yCo_4Sb_{12}$	−0.39	0.12	−0.77	0.03	−0.42
$Na_yCo_4Sb_{12}$	−0.62	0.13	−0.43	0.08	−0.70
$K_yCo_4Sb_{12}$	−0.84	0.13	−0.65	0.18	−1.02
$Rb_yCo_4Sb_{12}$	−0.60	0.12	−0.63	0.26	−0.86
$Cs_yCo_4Sb_{12}$	−0.27	0.09	−0.69	0.38	−0.65

3. Factors determining the filling fraction limits for alkali atoms in $CoSb_3$

Figure 3 may give us some hints on why some alkali atoms have high FFLs in $CoSb_3$ structure. ΔH_1 varies almost linearly with y for all alkali atoms when $y\leqslant 0.75$, while similar linear behavior is only sustained when $y\leqslant 0.5$ for other fillers studied.[18] According to our previous work, $\Delta H_1(y)$ can be expressed as $\Delta H_1(y)=\Delta E_1+y\Delta E_2$, where ΔE_1 represents the formation energy of an isolated filler that is determined by the interaction between the filler and its neighboring host atoms; and ΔE_2 describes the effective interaction between the impurity atoms. From Fig. 3, we obtained the values of ΔE_1 and ΔE_2, which are listed in Table II. By assuming a screened Coulomb interaction between impurity atoms, the impurity-impurity interaction energy ΔE_2 can be related to the impurity valence charge q_I by $\Delta E_2 \propto q_I^2/R$, where R is the distance between the nearest filler atoms. Based on the ΔE_2 values, q_{I} of these alkali ions can be estimated.[18] Table III lists the calculated effective charge of all alkali ions in $CoSb_3$ structure, together with those of some alkali-earth (AE) and rare-earth (RE) ions for comparison. The effective valence charge q_{I} for alkali ions in $CoSb_3$ is close to +1, the typical charge state for alkali atoms in compounds. In fact, the values of repulsive interaction energies ΔE_2 for alkali-filled $CoSb_3$ are much lower than those for AE- or RE-filled $CoSb_3$, e.g., 0.68 eV for Ba and 0.50 eV for Yb. Lower repulsive interaction energy ΔE_2 due to the low effective charge state of alkali ions can partially explain why Na and K have such high FFL values in $CoSb_3$. Valence charge state is a critical factor in determining the FFL for impurities in $CoSb_3$.

The zero FFL for Li and Cs in the $CoSb_3$ structure seems to contradict the above analysis. In fact, it is $\Delta E_1-\Delta H_2$ that determines whether or not a selected impurity can be filled

TABLE III. Effective charge q_I for impurities in $CoSb_3$ structure estimated by first-principles calculation. See text for the explanation of the effective charges.

	Li	Na	K	Rb	Cs	Sr	Ba	La
q_{I}	0.84	0.88	0.88	0.84	0.73	1.94	2	2.63

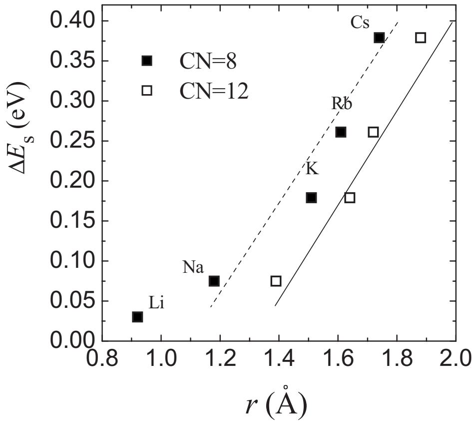

FIG. 6. Correlation between the lattice strain energy ΔE_s for the filled $CoSb_3$ and the corresponding filler ionic radius (r). The ionic radii of alkali ions (Ref. 32) with both 8 coordinations (CN=8, filled squares) and 12 coordinations (CN=12, unfilled squares) are plotted. Note that Li ion has only the 8-coordination data. The trend looks similar by using the 8-coordination or 12-coordination ionic radius for ions. The dashed and solid lines are used for guiding the eyes.

into the lattice voids of $CoSb_3$.[33] Our previous study also shows that the ionic radius of an impurity has a strong effect on its FFL in $CoSb_3$. In the case of rare-earth-filled skutterudites, a filled skutterudite structure does not form for small size fillers because the antimony cage is too large for necessary RE-antimony bonding. The same explanation can also be applied to Li filling in $CoSb_3$. As to Cs filling, the ionic radius is too large in comparison with the void radius. Cs filling would introduce large strain in the $CoSb_3$ structure and make the whole system unstable. Further analysis of the isolated impurity formation energy ΔE_1 showed that it could be divided into two parts: $\Delta E_1 = \Delta E_b + \Delta E_s$, where the first term ΔE_b is attributed to the chemical bonding between an impurity and host atoms, and ΔE_s corresponds to the strain energy that comes from the local lattice strain due to impurity filling. The technical details on how to determine ΔE_s and ΔE_b can be found elsewhere.[35] The calculated strain energy ΔE_s and bonding energy ΔE_b are also listed in Table II. Bonding energy ΔE_b for Li filling is much higher (lower in absolute value) than those of other alkali-filled $CoSb_3$, indicating a weak bonding between Li and its neighboring atoms, and thus, leading to an unstable filled skutterudite structure. This is the main reason why Li cannot be filled into the $CoSb_3$ structure, consistent with our previous conclusion.[33]

Filling a metal atom into the voids of $CoSb_3$ expands the crystal structure and, hence, increases the total energy of the filled system. Figure 6 plots the relationship between the calculated ΔE_s and the corresponding ionic radius. For alkali-filled skutterudites, the strain energy is primarily determined by the ionic size. A good linear trend in Fig. 6 is observed for Na-, K-, Rb-, and Cs-filled $CoSb_3$. Li-filled $CoSb_3$ obviously does not follow this trend. Since the ionic size of Li is relatively small, the lattice expansion due to Li filling is lower in comparison with other alkali ions. The oversized Cs ion inevitably causes a large crystal lattice expansion, and thus, increases the total energy of the filled $CoSb_3$ system. When the formation energy for filling an isolated impurity into $CoSb_3$ is larger than those of secondary phases, the FFL for this atom becomes zero. That is the case for Cs.

B. Electronic structure calculations

1. Electronic structures for Na- and K-filled $CoSb_3$

The band structure and electronic density of states (DOS) are critical to evaluate whether a material is promising for thermoelectric applications or not. A number of theoretical studies have investigated the electronic structure of $CoSb_3$-based materials.[19,36,37] Our electronic structure calculations are performed in the framework of density functional theory using the projector augmented plane-wave method of VASP. We are mostly interested in heavily doped $CoSb_3$ skutterudites with the Fermi level lying above the conduction-band edge. Spin-orbit coupling effect is neglected.[23] Our calculated band structure of $CoSb_3$ is similar to those previously reported in the literature,[19,36,37] and the band gap is 0.168 eV, in good agreement with the value calculated by Sofo and Mahan.[36]

Our calculations show that Na and K filling have little effect on the near-edge DOS of $CoSb_3$, except for moving the Fermi level up into the conduction band. Figure 7 shows the band structures of pure $CoSb_3$ and 50% Na- and K-filled $CoSb_3$. Here, we can clearly see that alkali filling moves the Fermi level upward into the conduction band. Meanwhile, several bands that previously belonged to the conduction band are now crossing the Fermi level from above. In addition, the Fermi level of $Na_{0.5}Co_4Sb_{12}$ crosses the lower conduction bands at several points (see Fig. 7), leading to an increased DOS at the Fermi level, consistent with our DOS analysis. In general, the qualitative properties of the band structures close to the conduction-band edges, especially the areas below Fermi level for filled systems [see Figs. 7(b) and 7(c)], are essentially not changed much, so the main effect of adding alkali atoms is to increase the carrier concentration when filling fraction is not extremely high. Our recent work on the carrier effective masses of filled $CoSb_3$ also indicates that filling $CoSb_3$ with different atoms has only a slight influence on band-edge structures.[38] It should be mentioned that the relatively high-energy conduction bands do shift and split as seen in Figs. 7(b) and 7(c) due to the slight impurity-induced structure distortion and the new impurity bands. However, the overall similarity in the conduction-band-edge areas for the systems with and without impurity filling is still obvious. We, thus, expect that the Na- and K-filled $CoSb_3$ could retain the relatively high Seebeck coefficient of $CoSb_3$.

2. Electrical transport properties

By combining the Boltzmann transport theory and the relaxation time approximation, an *ab initio* approach based on band-structure information has been shown to be quite successful in predicting the thermoelectric performance of several materials.[21,23–25] We have also implemented this method in our laboratory and used it to evaluate the electrical transport properties, together with the VASP package. The imple-

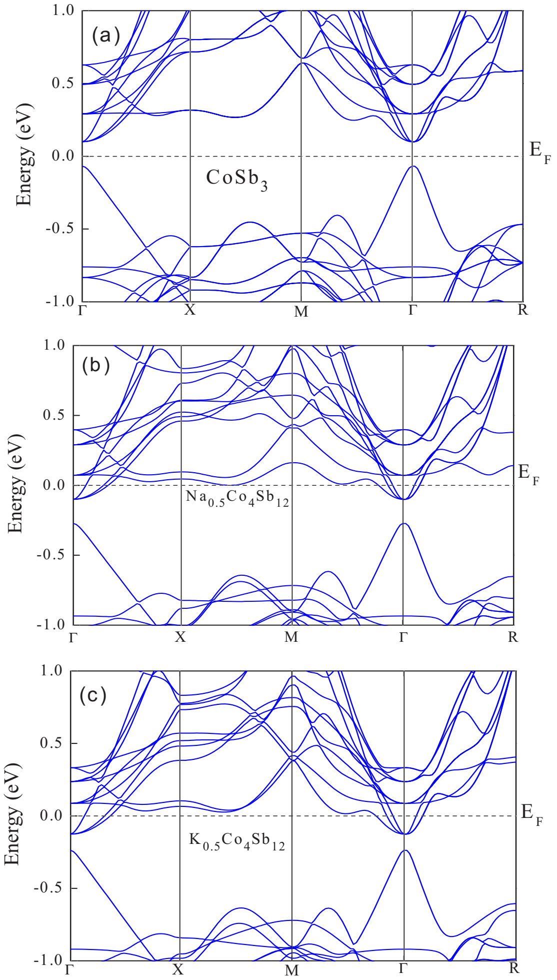

FIG. 7. (Color online) The band structures for (a) $CoSb_3$, (b) $Na_{0.5}Co_4Sb_{12}$, and (c) $K_{0.5}Co_4Sb_{12}$ around the Fermi level E_F. The energy is in eV relative to E_F.

mentation methods are simply described as follows. More details will be presented elsewhere. Using relaxation time approximation, the electrical transport properties of a compound, such as the Seebeck coefficient S and the electrical conductivity σ can be written as

$$\boldsymbol{\sigma} = e^2 \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) \Xi(\varepsilon),$$

$$\boldsymbol{S} = e k_B \boldsymbol{\sigma}^{-1} \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - E_F}{k_B T},$$

where E_F and f denote the Fermi level and Fermi function, respectively; e denotes the electronic charge, k_B Boltzmann's constant, and T the temperature. All the material-dependent properties in the two equations above are related to the so-called transport distribution function $\Xi(\varepsilon) = \Sigma_k \tau(k,\varepsilon_k) \vec{v}_k \vec{v}_k \delta(\varepsilon - \varepsilon_k)$, where k is the wave vector, $\tau(k,\varepsilon_k)$ the relaxation time, $\vec{v}_k$ the group velocity, and $\delta(\varepsilon - \varepsilon_k)$ the delta function. In this approach, E_F determines and is also determined by carrier concentration. The bands, and hence, $\Xi(\varepsilon)$, are fixed (thus "the rigid band approximation"). Therefore, only one band-structure calculation needs to be performed per compound to evaluate its theoretical electrical transport properties. The relaxation time τ is treated as a constant in this approach. This is believed to be a reasonable approximation for the electrical transport properties of materials such as $CoSb_3$ with isotropic cubic lattices and relatively simple band-edge structures. The validity of this approach has been tested earlier[23–25] and actually turns out to be a good approximation for isotropic bulk materials systems like skutterudites. In the following part, we focus on the transport properties of Na- and K-filled $CoSb_3$.

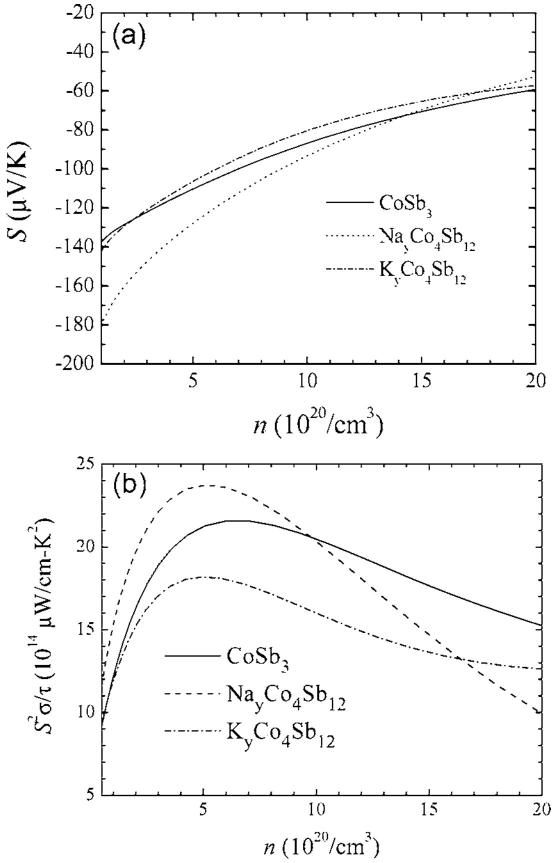

FIG. 8. The calculated electrical transport properties for $CoSb_3$, $Na_yCo_4Sb_{12}$, and $K_yCo_4Sb_{12}$ at 300 K: (a) Seebeck coefficient as a function of electron concentration and (b) $S^2\sigma/\tau$ as a function of electron concentration. A constant electron relaxation time is assumed for all the transport calculations.

For n-type filled $CoSb_3$ skutterudites, the free carriers are mainly electrons lost by impurities after being inserted into the voids of $CoSb_3$. The free electrons are all in the conduction bands. Using the calculated electronic structures, we can mimic impurity filling by shifting the Fermi level using the rigid band approximation. For a certain Fermi level E_F, the corresponding electron concentration can be estimated by $n = \int_{E_{CB}}^{E_F} f(E) g(E) dE$, where CB represents the conduction-band edge, $f(E)$ is the Fermi distribution, and $g(E)$ is the density of states. Seebeck coefficient and power factor are calculated in the framework of the Boltzmann transport theory with a constant relaxation time. Figure 8 shows the calculated Seebeck coefficient and power factor with respect to scattering time as a function of electron concentration between $n = 1$

$\times 10^{20}$ cm^{-3} and $n=2\times 10^{21}$ cm^{-3}. The Seebeck coefficients S for $CoSb_3$, $Na_yCo_4Sb_{12}$, and $K_yCo_4Sb_{12}$ decrease with increasing electron concentration. $Na_yCo_4Sb_{12}$ has a higher S than pure $CoSb_3$ and $K_yCo_4Sb_{12}$ when the electron concentration n is between 1×10^{20} and 1.4×10^{21} cm^{-3}. It is possibly due to the relatively sharp increase of the DOS around the Fermi level for $Na_yCo_4Sb_{12}$. High Seebeck coefficient and electrical conductivity of Na-filled $CoSb_3$ result in high power factor values. For both Na- and K-filled $CoSb_3$, the maximum power factor is achieved when $n\cong 5\times 10^{20}$ cm^{-3}. Recently, Pei *et al.* have synthesized Na- and K-filled $CoSb_3$ skutterudites and characterized their thermoelectric performance.[17,39] Experimental results show that at room temperature, $Na_yCo_4Sb_{12}$ and $K_yCo_4Sb_{12}$ achieve the largest power factor when their electron concentrations are around 3.8×10^{20} cm^{-3} (Ref. 39) and 5.32×10^{20} cm^{-3},[17] respectively, very close to our theoretically estimated values.

If we assume that the free electrons of filled $CoSb_3$ come mainly from the contribution of impurity atoms, the electron concentration of alkali-metal-filled $CoSb_3$ can be estimated by $q_I y/\mathrm{V}$, where q_I is the effective charge of alkali ions in $CoSb_3$ (see Table III), y the filling fraction, and V the volume of the unit cell. The room-temperature optimal filling fraction y for maximum power factor is estimated to be 22.4% and 22.1% for Na- and K-filled $CoSb_3$, respectively. Based on the synthesized samples and characterized thermoelectric performance of the Na- and K-filled $CoSb_3$ skutterudites,[17,39] at room temperature, $Na_yCo_4Sb_{12}$ and $K_yCo_4Sb_{12}$ achieve the largest power factor when y is around 0.23 (Ref. 39) and 0.38,[17] respectively. The measured filling fraction corresponding to room-temperature maximum power factor for Na-filled systems seems to be very close to our theoretical estimation, but that for K-filled $CoSb_3$ somehow deviates from our calculation. Similar estimations are also carried out for both Ba- and Eu-filled $CoSb_3$, and the corresponding filling fractions obtained from theory and experiments all show a reasonable agreement. It has been conjugated that the deviation for K-filled systems may come from Sb rich phases due to the extra Sb introduced in the process of sample synthesis. Detailed composition characterization is in process now. Based on our calculations, the relative magnitudes of $S^2\sigma/\tau$ for Na- and K-filled systems are shown in Fig. 8. Notice that the Na-filled samples have higher power factors than those of the K-filled $CoSb_3$. If Na filling has a similar effect on the thermal conductivity of $CoSb_3$ as K filling, the optimal thermoelectric performance for $Na_yCo_4Sb_{12}$ is expected to be better than that of K-filled $CoSb_3$.

IV. CONCLUSIONS

The *ab initio* density functional calculations are used to investigate the filling fraction limits of alkali atoms in the $CoSb_3$ structure. Our calculations show that Na and K atoms have more than 60% FFL, which can be attributed to the low valence charge states for alkali metals. Li and Cs atoms, however, cannot be filled into $CoSb_3$ to form a stable filled $CoSb_3$ skutterudite structure. Too small or too large ionic radius introduces unstable bonding and large strain, respectively, in the filled $CoSb_3$, making the whole system unstable. Electronic structures and electrical transport properties of Na- and K-filled $CoSb_3$ are computed. The calculated dependence of the Seebeck coefficient and power factor on free carrier concentration leads to estimated optimal doping levels for Na and K in $CoSb_3$ for achieving the maximum power factors. The calculated optimal carrier concentration at 300 K for filled $CoSb_3$ skutterudite is around 5×10^{20} cm^{-3}, which is in agreement with experimental results. Based on the calculated power factors, Na-filled $CoSb_3$ skutterudites are expected to show reasonably good thermoelectric performance and could be taken as an additional skutterudite thermoelectric material.

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