Structural Order-Disorder Transitions and Phonon Conductivity of Partially Filled Skutterudites

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I. Details of cluster expansions

To fit the effective cluster interactions (ECI) of the cluster expansion (CE), we calculated the total energy of 28 Ba-vacancy configurations over the void sites (BCC sublattice) of CoSb\(_3\) using density functional theory (DFT) as implemented in the Vienna \textit{ab initio} Simulation Package (VASP) calculations. In the total energy calculations all atomic positions as well as the unit cell dimensions were fully relaxed. The ECI were fit to reproduce the formation energies (\(\Delta E_f\)) of Ba\(_{x}\)Co\(_4\)Sb\(_{12}\), defined as

\[
\Delta E_{f,i} = E_{x,i} - [(1-x)E_{V,i} + xE_{Ba}],
\]

where \(E_{x,i}\) is the total energy of the crystal with Ba atoms (concentration \(x\)), \(E_{V,i}\) is the total energy of the crystal without any Ba (i.e., CoSb\(_3\)), and \(E_{Ba}\) is the total energy of the crystal when all Ba sites are filled (i.e., BaCo\(_4\)Sb\(_{12}\)). Figure S1 shows the DFT formation energies \(\Delta E_f\) as well as those predicted by the CE. The CE was also used to predict energies of other Ba-vacancy configurations not considered with DFT. The ground-state structures are those that lie on the convex hull. These are stable ordered phases that should be stable at low temperature. The weighted cross validation (CV) score, an estimate of the predictive error of the CE, is about 6 meV, which is considered reasonably small.

![Figure S1. Convex hull of Ba\(_x\)Co\(_4\)Sb\(_{12}\) compounds computed through the formalism of CE. Formation energies predicted from the CE and calculated from DFT as a function of Ba composition. The large orange circles indicate ground-state atomic structures and are confirmed by the DFT calculations.](image-url)
II. Phonon calculation with CRs and DFT methods

In order to obtain the empirical molecular dynamics (MD) potentials of compounds in the intermediate concentration, we used the combinative rules (CRs) with the empty CoSb$_3$ and fully-filled BaCo$_4$Sb$_{12}$ potentials from [1]. The Morse potential is useful for covalent bonds and is
\[
\phi(r_{ij}) = \phi_0 \{1 - \exp(-a(r_{ij} - r_0))\}^2 - 1
\]
where $\phi_0$ is the depth of the potential energy minimum, $a$ is a parameter related to the depth and width of the potential well, and $r_0$ is the equilibrium bond length. For the Morse parameters for A-B compounds (e.g., half-filled, $x = 0.5$), we used the Lorentz-Berthelot mixing rules [2-4]. The A-B structural parameters ($\phi_0$, $a$, and $r_0$) are assumed to have the form of
\[
\phi_{AB} = (\phi_A + \phi_B)/2, \quad r_{AB} = (r_A + r_B)^{1/2}, \quad a_{AB} = (a_A a_B)^{1/2},
\]
where A and B are denoted as an empty ($x = 0$) and fully-filled structure ($x = 1$), respectively. In our CRs method, the GULP program was used for the prediction of the phonon properties.

The DFT method directly calculates the force field using the VASP [5] and PHONON [6] codes. The total energy and Hellmann-Feynman (HF) forces were found with a supercell optimization process. It is required that the largest absolute value of the HF force is less, or much less than 0.001 eV/Å. This ab initio calculation of the HF forces begins by the displacement of the Co, Sb, and Ba atoms along the $x$, $y$, and $z$ directions, $\pm 0.03$ Å. For the case of $x = 0.25$ ground-state structures, each displaced configuration generates $2 \times 3 \times 65 = 390$ components of the HF forces. The calculated HF forces for quarter-filled structure and used in the PHONON. Figure S2 shows the phonon branches for $x = 0.25$ (ground-state, $\gamma$-phase) from using CRs and from DFT methods. The three acoustic branches have similar trends (on the average). Comparison of the total phonon density of states (DOS) $D(\omega)$ from two methods is shown in Figs. S3(a) to (d). Figure S3 (a) and (b) are the total phonon DOS of $x = 0.25$ (ground-state, $\gamma$-phase) compounds with respect to frequency. Also, the integrated phonon DOS is given in Figs. S3 (c) and (d). The integrated phonon DOS is defined by
\[
N(\omega) = \int_0^\omega D(\omega)d\omega.
\]

Even though there are some apparent deviations for the group velocity and the energy along the $\Gamma$-$N$ direction, the results show the overall sound speed and specific heat capacity (includes all the modes) would agree well between the two methods calculation.

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Figure S2. Calculated phonon dispersions of the Ba$_{0.25}$Co$_4$Sb$_{12}$ compounds using empirical potentials (with the CRs) and DFT (VASP and PHONON codes). Most optical phonon branches are omitted.
III. Construction of two-phase mixture atomic structures

In the two-phase regime (0.25 < x < 0.5), the atomic structures used in MD calculations, are divided into CoSb$_3$ host and Ba filler atoms. We use two steps to set up the mixture, first we construct a full-atomic configuration 14 × 2 × 2 supercells (system volume ∼ 86,700 Å$^3$) of α-phases. And then, we modify the Ba atom' positions to reach a composition (e.g., for x = 0.38, mixture is made first half with x = 0.25 and then second half with x = 0.5), keeping the desired Ba positions of the x = 0.25 and x = 0.5 in the CoSb$_3$ host structures. Then in the MD simulations of these mixture structures we use the empirical potentials from CRs. All MD two-phase structures have a single two-phase interface and periodic boundary conditions in all three directions.
IV. Details of molecular dynamics simulations and $\kappa_L$ calculations

The lattice thermal conductivity tensor $\kappa_L$ is determined using the equilibrium MD results and the Green-Kubo heat current autocorrelation function (HCACF) decay [1, 7], i.e.,

$$\kappa_L = \frac{1}{k_B T^2 V} \int_0^\infty \langle q(t)q(0) \rangle dt,$$

where $t$ is time, $k_B$ is the Boltzmann constant, $V$ is the MD volume, $T$ is the temperature, $\langle q(t)q(0) \rangle$ is the HCACF tensor. The heat current vector $(q)$ can be expressed

$$q = \frac{d}{dt} \sum_i E_i r_i = \sum_i E_i u_i + \frac{1}{2} \sum_{i,j} (F_{ij} \cdot u_i) r_{ij},$$

where $E_i$, $r_i$, and $u_i$ are the energy, position vector, and velocity vector of particle $i$, and $r_{ij}$ and $F_{ij}$ are the interparticle separation vector and force vector between particle $i$ and $j$. To minimize computation time and size effects, the MD simulations were mostly performed on systems consisting of many conventional unit cells ($\sim 3600$ atoms). While $\kappa_L$ results are for a specific direction for each atomic configuration, we verified that the phonon transport in that direction is not noticeably affected by the small dimensions in the other two directions. We also checked that the size effects were minor when using the supercell system consisting of $\sim 3600$ atoms [1]. The Verlet leapfrog algorithm with the Nose-Hoover thermostat and the Berendsen barostat were used in $NpT$ ensemble for 200 ps and then in $NV E$ for 100 ps to reach the equilibrium. Then 3000 ps raw data were obtained for the calculation of heat current vector. The resultant HCACFs were then directly integrated and the $\kappa_L$ was set as the average value in the stable regime of the integral.

![Figure S4. Various atomic structures (configurations) of Ba$_x$Co$_4$Sb$_{12}$ compounds. For Ba$_x$Co$_4$Sb$_{12}$, the green large spheres represent the Ba atoms, the small blue spheres represent the Co atoms, and the small brown spheres represent Sb atoms. (a) Empty ($x = 0$), (b) $\gamma$-phase (ground-state of $x = 0.25$), (c) $\alpha$-phase (ground-state of $x = 0.5$), and (d) fully-filled structure ($x = 1$).](image)

According to the results of thermodynamic calculations [Fig. 1(a) and Fig. S1], we used five different atomic configurations as input structures of MD simulations at 300 K: empty ground-state [$x = 0$, Fig. S4(a)], solid-solution ($x = 0.03$ and 0.14), $\gamma$-phase ground-state [$x = 0.25$, Fig. S4(b)], two-phase mixture...
(x = 0.33, 0.38, and 0.44), and α-phase ground-state [x = 0.5, Fig. S4(c)]. When temperature increased to 800 K, all configurations of different Ba concentrations were obtained from solid-solution structure (Monte Carlo snapshot). During the MD simulation time of 3000 ps, these atomic structures were very stable and confirmed with MD movie.

V. Analytical phonon conductivity models for partially-filled compounds

The Cahill-Pohl thermal conductivity assumes all phonons have a mean free path equal to one-half of their wavelength and is assumed to give the thermal conductivity of the amorphous phase. So, it is designated as the minimum phonon conductivity $\kappa_{min}$ of solid-state materials. The thermal conductivity in this model is given by

$$\kappa_{min} = \left( \frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \sum_{i=1}^{3} u_{p,g,i} \left( \frac{T}{T_{D,i}} \right)^2 \int_{0}^{T_{D,i}/T} \frac{x^3 e^x}{(e^x - 1)^2} \, dx.$$  

When $T > T_D$, above equation reaches its classical limit,

$$\kappa_{min} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \sum_{i=1}^{3} u_{p,g,i} = 0.4 k_B n^{2/3} (u_{p,g,L} + 2u_{p,g,T}),$$

where $n$ is atomic number density, $u_{p,g,L}$ is longitudinal and $u_{p,g,T}$ is transverse phonon speed [8, 9]. This gives $\kappa_{min} \approx 0.37 \text{ W/m-K}$ using CoSb$_3$ properties and this $\kappa_{min}$ result is also shown in Fig. 2(a).

Starting with $\kappa_L$ of CoSb$_3$ dominated by phonon-phonon scattering, we consider phonon-point defects scattering and two-phase scattering for the compounds. In Regime I, we considered only point-defects scattering. Using the Matthiessen rule [7], the overall $\kappa_L$ with the inclusion of phonon-point defects scattering is $1/\kappa_L(x) = 1/\kappa_L(0) + 1/\kappa_{L,d}$. Here $\kappa_L(x) = \kappa_L(0)/(1 + c(x)[x(1-x)]^{1/2})$, where $c(x)$ is the coefficient for point-defects scattering with respect to $x$ [10-14], and the results are shown in Fig. 2(a) predicting a significant phonon scattering in Regime I. For $\kappa_{L,d}$, we start with mass fluctuation scattering parameter $\Gamma$ is given by

$$\Gamma = \sum x(1-x)[\frac{M(Ba)}{M}]^2,$$

where $M$ is the mass of an average ternary cluster (Ba$_x$Co$_4$Sb$_{12}$), $M = 4M(\text{Co}) + 12M(\text{Sb}) + xM(\text{Ba})$ with $0 < x < 1$. The phonon conductivity limited by the point-defects scattering $\kappa_{L,d}$ is

$$\kappa_{L,d} = \frac{k_B}{4\pi u_{p,g,L} a_1 CT} \left( \frac{M(Ba)}{M} \right)^{1/2},$$

where $CT$ is the relaxation time for interphonon scattering. The $CT$ can be estimated from the $\kappa_L$ of empty CoSb$_3$ [$\kappa_L(0) = 7.9 \text{ W/m-K}$ from MD simulation], i.e.,

$$CT = \left( \frac{6n}{2\pi^{4/3} \kappa_L(0)} \right)^{1/3},$$

where $n$ is the atomic number density. This yields $CT = 4.758 \times 10^{-16} \text{ s}$. The parameter $a_1$ is the coefficient for the Rayleigh point-defects scattering rate, which is given by

$$a_1 = \frac{V_c \Gamma}{4\pi u_{p,g,L}},$$

where $V_c$ is the unit cell volume. The data are summarized in Table S1, and for example, $\Gamma(x = 0.5)$ is 1.513 $\times 10^{-3}$. This value matches that in reference [11] $\Gamma(x = 0.5) = 1.5464 \times 10^{-3}$. $\kappa_L(0) = 7.9 \text{ W/m-K}$ is the average of MD results ($x = 0$). The analytical model results for point defects scattering are shown in Fig. 2(a).
Table S1. Data used in the analytical model of Regime I (point-defects scattering) for various Ba concentrations.

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<th>$x$</th>
<th>$M$</th>
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<th>$a_1$</th>
<th>$\kappa_{L,d}$</th>
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In the two-phase mixture ($0.25 < x < 0.5$, Regime II), the mixture of two ordered phases ($\gamma$ and $\alpha$) creates significant two-phase scattering. Using the Matthiessen rule,

$$\frac{1}{\kappa_L(\text{two-phase})} = \frac{x_\gamma}{\kappa_{L,\gamma}} + \frac{1 - x_\gamma}{\kappa_{L,\alpha}} + \frac{1}{\kappa_{L,d}},$$

where $x_\gamma$ is the fraction of $\gamma$-phase in a $\gamma$-$\alpha$ mixture [10, 12, 13]. This overall two-phase resistivity [$\kappa_L(\text{two-phase})$] considers each phase resistivity ($\kappa_{L,\alpha}$ and $\kappa_{L,\gamma}$) and the interfacial resistivity ($\kappa_{L,d}$) simultaneously. So, we denoted this as two-phase scattering. In this calculation, both phase phonon conductivities, $\kappa_{L,\alpha}$ and $\kappa_{L,\gamma}$, are from the MD simulations. The thermal resistivity due to the interfacial two-phase scattering is derived from $CT = 4.578 \times 10^{-16}$ s, $\Gamma \approx 0.0953x(1-x)$, $u_{p,g,A} = 2934$ m/s [10], $a_1 = 2.326 \times 10^{-40}$, and $1/\kappa_{L,d} = 0.888[x_\gamma(1-x_\gamma)]^{1/2}$ (m-K/W).

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