Multitemperature crystal structures and physical properties of the partially filled thermoelectric skutterudites $M_{0.1}Co_4Sb_{12}$(M = La, Ce, Nd, Sm, Yb, and Eu)

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Partially filled skutterudites with nominal compositions of $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb; and Eu) were investigated by multitemperature (90–700 K) synchrotron radiation powder x-ray diffraction (SR-PXRD), and electrical and thermal transport property, heat capacity, and Hall effect measurements were also taken. The filling fractions, i.e., the occupancy factors of the guest atoms, were obtained from structure refinement of the SR-PXRD data, and they reflect the capacity for the individual guest atom species to fill the voids of the $CoSb_3$ structure. The filling fraction of the lanthanide guest ions correlates with their effective ionic radii and valences, and the larger the ionic radii or the lower the charge state, the larger is the occupancy. Due to the different guest atom occupancies, the doping levels vary among the samples, and they are in a good agreement with the measured charge carrier concentrations, except for the magnetic samples (Sm, Eu). Anomalously large atomic displacement parameters (ADPs) are observed for the weakly bonded guest atoms, in agreement with the "rattling" concept, but no correlation is observed between the magnitude of the ADP and the ionic radius of the guest atom. Einstein and Debye temperatures were derived from analysis of the multitemperature ADPs of guest atoms and the framework atoms, respectively, and this analysis also shows that neither the guest atoms nor the host structure atoms contain large disorder contributions to their ADPs. In ternary skutterudites without host structure substitution or disorder, partial guest filling can affect the lattice thermal conductivity (κ_L) either by direct phonon-phonon interaction or through the inherent structural disorder introduced with the partial occupancy of the voids. The present data suggest that the magnitude of the guest atom ADPs correlates with κ_L, and the larger the ADP, the lower is the κ_L.

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I. INTRODUCTION

Skutterudites and their guest atom filled forms have been the center of interest since Slack pointed out that filler species in $CoSb_3$ might lead to an additional strong phonon scattering that could bring the thermal conductivity down to values that would make the skutterudites effective thermoelectric materials.[1] A few months later, Morelli and Meisner demonstrated that the idea actually works in real samples.[2] Since then, intensive research worldwide has led to spectacular improvements in the figure of merit of these compounds, which hold potential for thermoelectric power generation applications and which are continuing to attract considerable attention.[3–6] The effectiveness of a material for thermoelectric application is determined by the dimensionless figure of merit $zT = \alpha^2 sT/\kappa$, where α is the Seebeck coefficient, σ and κ are the electrical conductivity and thermal conductivity, respectively, and T is the absolute temperature. The filled skutterudites have been suggested as examples of "phonon glass-electron crystal" (PGEC) materials,[5] and excellent thermoelectric properties have been observed, with zT reaching 1.36 in n-type $Ba_xYb_yCo_4Sb_{12}$[7] and 1.43 in $In_xCe_yCo_4Sb_{12}$.[8] Various partially filled $CoSb_3$-based skutterudites possess good electronic properties and much lower thermal conductivities than unfilled $CoSb_3$ samples.[2,7–13] However, the exact role of the guest atoms in filled skutterudites is still under discussion in the literature regarding their effects on the lattice thermal conductivity, κ_L. The guest atoms, coined "rattlers," are weakly bonded in the oversized cages formed by 12 Sb atoms and 8 Co atoms.[14] Early on, it was suggested that the rattling motion of the guest atoms in the voids interacted with a broad spectrum of lattice phonons, thus reducing their mean free paths substantially.[15] Later, the guest atoms were suggested to behave as independent Einstein oscillators, and heat capacity and inelastic neutron scattering measurements confirmed this picture.[16,17] In this picture, the reduction of the thermal conductivity is believed to be due to the Einstein oscillator modes serving as extra phonon scattering channels for the acoustic phonons of the framework, thereby efficiently impeding the heat transport. Dimitrov *et al*. used measurements of the phonon density of states by inelastic neutron time-of-flight scattering, specific heat capacity measurements, and theoretical calculations to provide evidence for the existence of Einstein modes of Yb atoms vibrating in the cage of the host lattice of $Yb_{0.2}Co_4Sb_{12}$.[18] Recently, neutron spectroscopy experiments and *ab initio* computational work on the phonon dispersion in the completely filled skutterudites $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ have shown well-defined phase relations between the guest and host dynamics, indicative of coupling between the guest atom and host lattice motion.[19] Other studies have suggested that the suppression of the lattice thermal conductivity is a result of scattering of acoustic phonons due to the resonant interaction between guest atoms and lattice phonons in filled skutterudites.[20] Koza *et al*. have shown that Ca-, Sr-, Ba-, and Yb-filled Fe_4Sb_{12} display the lattice dynamics of quasiharmonic crystals, with the filling cations forming collective hybrid modes with the Fe_4Sb_{12} matrix.[21] Inorganic clathrates (e.g., $M_8Ga_{16}Ge_{30}$) form a comparable

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host-guest system to the skutterudites.[22] In the clathrates, inelastic neutron spectroscopy has revealed that the guest atom reduces the phonon group velocity through hybridization of the guest and host modes.[23] Thus, the guest atoms do not act as specific scattering centers, decreasing the lifetime of the phonons.

Despite the uncertainty about the exact microscopic mechanisms behind the low thermal conductivity in filled skutterudites, and the fact that the guest atoms strictly speaking may not be independent oscillators, the Einstein model has been successfully applied in many studies, and it provides a specific value (the Einstein temperature) that may be compared between different samples and studies. The literature on thermoelectric skutterudites is extensive, and the thermal conductivities of these compounds are strongly reduced when guest atoms are present. It is reported that relatively larger ADPs of the guest atoms are obtained for the Ce-filled antimonide skutterudites compared with the values for arsenide and phosphide skutterudites. This correlation between the ADPs and thermal conductivity suggests that larger ADPs are crucial to lower the lattice thermal conductivity.[24,25] However, only few reports have compared the ADPs and thermal conductivities directly with respect to filling fractions and guest atom types. Furthermore, the experimental work on skutterudites tends to be quite scattered with respect to the identity of the samples and the experimental methodologies, and this makes comparison between studies problematic. Both x-ray and neutron scattering have been widely used to study the crystal structures and probe vibrational states.[5,26] In the case of thermoelectric clathrates, the measured data are more comparable, and many studies have derived Einstein and Debye temperatures from analysis of the multitemperature ADPs of guest and framework atoms.[27–30] In an earlier study, we successfully derived Einstein and Debye temperatures from analysis of ADPs for the partially filled skutterudite $La_{0.1}Co_4Sb_{12}$,[31] and here it became apparent that more homogeneous data are also desirable for the skutterudites. In the present study, we investigate a range of filled skutterudites with identical experimental methods. Einstein and Debye temperatures are obtained, and a correlation between the ADPs of the guest atoms and lattice thermal conductivities of the compounds is discussed.

The filling fraction of guest atoms is an important factor affecting the properties of skutterudites. The filling fraction limits (FFLs) for lanthanide atoms in $CoSb_3$ have been studied by *ab initio* theoretical calculations,[32] which show that the FFL decreases from La to Sm, and becomes zero from Gd to Lu, with the exception of Eu and Yb, where relatively high FFLs are predicted. Here, we characterize different lanthanide-filled $CoSb_3$ skutterudites under similar conditions and with the same nominal 10% filling fraction. Instead of studying FFLs, we analyze the occupancy factors, i.e., the actual filling fractions of the guest atoms of the partially filled $CoSb_3$ with nominal compositions of $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu), derived from refinement of synchrotron radiation powder x-ray diffraction (SR-PXRD) data. Moreover, the present work reports comprehensive electrical and thermal transport properties as well as Hall effect data.

II. EXPERIMENTAL METHODS

The details of the present experiments have been described in a previous study on $La_{0.1}Co_4Sb_{12}$.[31] In brief, the polycrystalline samples of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu) were prepared by melting stoichiometric quantities of elements in carbon-coated quartz tubes. The ampoules were slowly heated to 1200 K and maintained at this temperature for 7 hours; subsequently, they were removed from the furnace and quenched in water, followed by annealing at 900 K for 10 days. The as-synthesized materials were ground into fine powder and hot pressed in vacuum into dense pellets at a temperature of 750 K. The samples were cut into box shapes with approximate dimensions of $8 \times 2 \times 2$ mm. The physical properties were measured using a Quantum Design Physical Property Measurement System. The quasistatic method of the thermal transport option was used for measuring the Seebeck coefficient, electrical resistivity, and thermal conductivity from 2 to 380 K.[33] Hall effect measurements were done from 3 to 300 K using the AC transport measurement system option mounted on a sample rotator stick.

SR-PXRD data were collected at BL2B02 at SPring-8, Japan. The data were collected from 90 to 300 K in steps of 15 K, whereas the temperature range from 300 to 700 K was done in steps of 25 K. A homogeneous grain size was obtained by floating the crushed powder sample in ethanol several times. The wavelength ($\gamma = 0.430954$ Å) was determined from data measured on a CeO_2 standard. Sequential Rietveld refinements were carried out with the FULLPROF program.[34]

III. RESULTS AND DISCUSSION

A. Structure

Skutterudites have a cubic structure belonging to space group $Im\bar{3}$. Figure 1 shows the crystal structure of filled $CoSb_3$ in the depiction using Co_8 cubes and Sb rings, as well as the true cagelike structure formed by Co_8Sb_{12} pentagonal dodecahedron.[14] Figure 2(a) shows a typical refined diffraction pattern of the SR-PXRD data of $Eu_{0.1}Co_4Sb_{12}$ at 300 K with the resulting observed, calculated, and difference patterns. A secondary phase, $CoSb_2$, with space group $P2_1/c$, was identified in the powder diffraction pattern, with a refined concentration of 1.88 wt%. The inset shows the detailed features at higher angles (2θ from 35° to 50°), indicating the excellent data quality and good agreement between the observed data and the calculated pattern. The occupancy factor of the guest atom was refined for the 90 K data and subsequently fixed at the obtained value for all other temperatures. Refinement of occupancy factors and APDs is often difficult since they are highly correlated; however, the excellent data quality allowed such refinement at 90 K with only 50% correlation. The Co and Sb sites were fixed to full occupancy at all temperatures. A pseudo-Voigt profile function and a background modeled with linear interpolation were used for the refinement. Eighteen parameters were refined for the skutterudite phase and 82 parameters were used for the background. Table I gives a summary of the Rietveld refined parameters and reliability factors of the 300 K data for all the samples. Trace impurities such as $CoSb_2$ and MSb_2 were

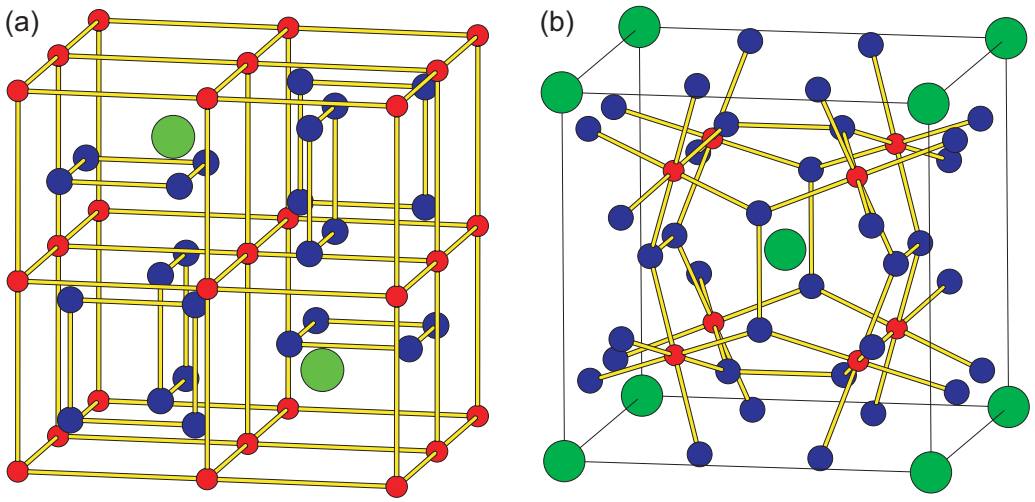


FIG. 1. (Color online) Crystal structure of filled $CoSb_3$. Co atoms are depicted in red, Sb in blue, and the guest atoms in green. (a) The structure depiction using Co_8 cubes and Sb rings. (b) The cage-like structure with a Co_8Sb_{12} pentagonal dodecahedron in a unit cell.

found, and the total impurities fraction was about 2–3 wt% for all the samples. However, in most cases, the impurities concentrations are so small that can be neglected in the refinements, and only the secondary phase $CoSb_2$ is added in the refinements of the SR-PXRD data for $La_{0.1}Co_4Sb_{12}$, $Nd_{0.1}Co_4Sb_{12}$, $Yb_{0.1}Co_4Sb_{12}$, and $Eu_{0.1}Co_4Sb_{12}$. The calculated concentrations of $CoSb_2$ are listed in Table I. The values of the lattice parameter a are ~9.04 Å for the partially filled $M_{0.1}Co_4Sb_{12}$ at room temperature. Figure 2(b) shows the temperature dependence of the lattice parameter a of $Eu_{0.1}Co_4Sb_{12}$. The lattice parameter increases roughly linearly with temperature. A simple Einstein formula is often used to model the thermal expansion,[35,36]

$$\ln\left(\frac{a}{a_0}\right) = A \times \frac{\theta}{\exp(\theta/T) - 1}, \qquad (1)$$

where a_0 is the lattice parameter at $T = 0$ K, θ is the phonon energy, and A is a scaling coefficient. The solid line in Figure 2(b) is the Einstein formula fit of the lattice parameter of $Eu_{0.1}Co_4Sb_{12}$ for with $\theta = 271$ K, $a_0 = 9.025$ Å, and $A = 1\times10^{-5}$, respectively. The other samples show similar results to $Eu_{0.1}Co_4Sb_{12}$. The structural parameters, e.g., lattice parameter a and coordinates y(Sb) and z(Sb), are quite consistent with the observed structural response to filling of the skutterudite structure as described by Chakoumakos and Sales.[37] As shown in Table I and Table II, the coordinates y(Sb) and z(Sb) basically increase with the occupancy of guest atoms in agreement with the Chakoumakos and Sales conclusion.[37]

Usually, nominal compositions are used to describe the filling fraction; however, this is not accurate because formation of impurities is difficult to avoid ($CoSb_3$ is a peritectic phase) when inserting guest atoms in the skutterudite structure. The formation of partially filled $CoSb_3$ is shown to be determined

TABLE I. Refined parameters and crystallographic details from the Rietveld analysis of the SR-PXRD data measured at 300 K. The Co $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and Sb $(0,y,z)$ sites are fixed to full occupancy at all temperatures. The occupancies of the guest atoms at (0,0,0) are refined for the 90 K data and subsequently fixed at these values at all the other temperatures.

	$La_{0.1}Co_4Sb_{12}$	$Ce_{0.1}Co_4Sb_{12}$	$Nd_{0.1}Co_4Sb_{12}$	$Sm_{0.1}Co_4Sb_{12}$	$Yb_{0.1}Co_4Sb_{12}$	$Eu_{0.1}Co_4Sb_{12}$
N_{obs}	7557	7551	7544	7543	7548	7546
N_{par} (skutterudite)	18	18	18	18	18	18
N_{Ref} (skutterudite)	1694	1650	1658	1650	1676	1721
R_P (%)	4.73	6.51	7.33	7.70	4.65	7.30
R_{WP} (%)	6.13	7.99	9.44	8.68	5.90	8.57
R_I (%)	0.797	1.35	1.36	1.34	0.798	1.14
R_F (%)	0.891	2.51	1.19	1.59	0.936	1.27
a (Å)	9.0427(1)	9.0376(1)	9.0391(1)	9.0402(1)	9.0421(1)	9.0391(1)
U_{iso}(guest) (Å^2)	0.018(2)	0.018(5)	0.035(8)	0.015(6)	0.020(1)	0.034(3)
U_{iso}(Co) (Å^2)	0.0039(1)	0.0044(1)	0.0040(1)	0.0041(1)	0.0041(1)	0.0038(1)
U_{iso}(Sb) (Å^2)	0.0055(1)	0.0058(2)	0.0055(1)	0.0057(2)	0.0054(1)	0.0052(1)
y(Sb)	0.33509(3)	0.33514(6)	0.33499(5)	0.33492(5)	0.33508(3)	0.33516(5)
z(Sb)	0.15809(3)	0.15799(6)	0.15797(5)	0.15799(5)	0.15812(3)	0.15813(5)
$CoSb_2$ (wt%)	2.00(4)		0.80(6)		3.17(4)	1.88(5)

TABLE II. Summary of room-temperature physical and transport properties of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu). See text for description of Einstein temperatures (θ_E, θ_E') and Debye temperatures (θ_D) together with the disorder factors of d_E^2, $(d_E')^2$, and d_D^2.

	$La_{0.1}Co_4Sb_{12}$	$Ce_{0.1}Co_4Sb_{12}$	$Nd_{0.1}Co_4Sb_{12}$	$Sm_{0.1}Co_4Sb_{12}$	$Yb_{0.1}Co_4Sb_{12}$	$Eu_{0.1}Co_4Sb_{12}$
Occ. guest (%)	4.9(1)	4.7(2)	3.2(3)	2.6(3)	7.6(1)	7.9(3)
ADP guest (Å^2)	0.018(2)	0.018(5)	0.035(8)	0.015(6)	0.020(1)	0.034(3)
θ_E from ADP (K)	79(3)	60(2)	54(4)	76(5)	60(1)	68(2)
d_E^2	0.004(2)	−0.008(3)	0.014(7)	0.003(4)	−0.003(1)	0.014(2)
θ_E'	80(4)	83(3)	55(3)		74(1)	74(4)
$(d_E')^2$	0.003(1)	0.003(1)	0.010(4)		0.001(1)	0.015(2)
θ_D from ADP (K)	268(1)	267(2)	267(1)	265(2)	274(1)	266(1)
d_D^2	−0.0004(1)	−0.0008(1)	−0.0008(1)	−0.0012(1)	−0.0006(1)	−0.0012(1)
θ_D from C_p (K)	280(3)	283(2)	294(3)	292(2)	281(3)	291(2)
m^*/m_0	1.78	1.55	1.41	1.31	1.75	2.30
C_p (J K mol^{-1})	400(1)	395(3)	383(5)	394(1)	407(2)	385(2)
Charge state	+3	+3	+3	+3	+2	+2
Ionic radius (Å)	1.36	1.34	1.27	1.24	1.02	1.17
ρ (10^{-5} Ω m)	2.10(1)	2.19(1)	4.06(1)	4.54(2)	1.56(1)	2.25(1)
n_{cal} (10^{20} cm^{-3})	3.7	3.5	2.4	2.0	3.8	4.0
n_{exp} (10^{20} cm^{-3})	2.3	1.9	0.9	1.3	2.0	4.9
μ (cm^2 V^{-1} s^{-1})	14.2	14.9	16.1	8.6	17.2	6.4
$\propto$ (μVK^{-1})	−152(1)	−168(1)	−204(1)	−152(1)	−177(1)	−116(1)
κ (W m^{-1} K^{-1})	4.02(6)	3.97(5)	3.28(4)	4.84(4)	3.97(5)	4.44(4)
zT	0.083(1)	0.097(1)	0.094(1)	0.031(1)	0.016(1)	0.041(1)

not only by the interaction between the guest and host atoms but also the formation of secondary phases. Shi *et al.*[38] have suggested that the reaction of the formation of the filled skutterudites can be described as

$$nM + 4CoSb_3 \rightarrow \frac{2-n}{2-y}M_yCo_4Sb_{12} + \frac{2(n-y)}{2-y}MSb_2 + \frac{4(n-y)}{2-y}CoSb_2, \quad (2)$$

where n is the nominal filling fraction, while y is the actual filling fraction. As described previously, the actual filling fractions are obtained as the occupancy factors of the guest atoms from the refinement of the SR-PXRD data at 90 K by fixing Co and Sb sites to full occupancy. Another explanation for the formation of the $CoSb_2$ impurity could be that Co defects form in the host lattice to compensate for the charge of the filler atoms. However, this should give rise to increased ADPs at the Co site in filled materials relative to unfilled materials, and this is not observed. The guest atom occupancy factors of our filled $CoSb_3$ samples are listed in Table II, together with the effective ionic radii[39,40] and the expected valences of the lanthanide ions. The results show that the occupancy of the lanthanide ions is correlated with the effective ionic radii as well as their valences. The occupancy decreases with decreasing ionic radii from La to Sm, with the exception of Yb and Eu, which have higher filling fractions. The higher filling fractions of Eu and Yb can be ascribed to their low charge state (+2) compared with the other lanthanide atoms (+3). Chen *et al.*[32,39] studied the FFLs of lanthanide guest atoms in the lattice voids of $CoSb_3$ by *ab initio* density functional calculations. Their results predict that the FFL decreases rapidly from La to Sm, and that the heavier lanthanide elements (Gd, Tb, Dy, Tm, and Lu) with relatively smaller ionic radii cannot be inserted into the lattice voids. The theoretical results show exceptions for Eu and Yb, which exhibit relatively high FFLs. For a given nominal composition of $M_{0.1}Co_4Sb_{12}$, the actual filling fraction reflects the possibility and capacity of the guest atoms to insert into the $CoSb_3$ structure, and in this point of view, our experimental results agree well with Chen's FFL calculations.

B. Atomic displacement parameters

The refined structural model included anisotropic harmonic ADPs; however, these have been converted to isotropic ADPs (U_{iso}) with the dimensions of Å^2 for convenience. U_{iso} measures the mean square displacement amplitude of the atom averaged over all directions and potentially contains contributions from static or dynamic disorder in addition to the actual thermal vibration of the atom.[27] Figure 3 shows the isotropic ADP parameters U_{iso} as a function of temperature for guest and framework atoms of the partially filled $CoSb_3$ skutterudites. The room-temperature U_{iso} values of the guest and framework atoms for different partially filled $CoSb_3$ are listed in Table I. The ADPs of the framework atoms Co and Sb are comparable to ADP values observed in other compounds, while the guest atoms exhibit unusually large ADP values. This indicates that the filler atoms are weakly bonded in the structure and vibrate strongly about their equilibrium positions and/or that they are strongly disordered.

Figure 4 shows the temperature dependence of U_{iso} of the guest atoms for the different partially filled $CoSb_3$ skutterudites. There are different factors that may affect the ADPs of the guest atoms, such as atom type, filling fraction, disorder, etc. However, few studies have probed the correlations between these factors and the ADPs of the guest atoms, mainly due

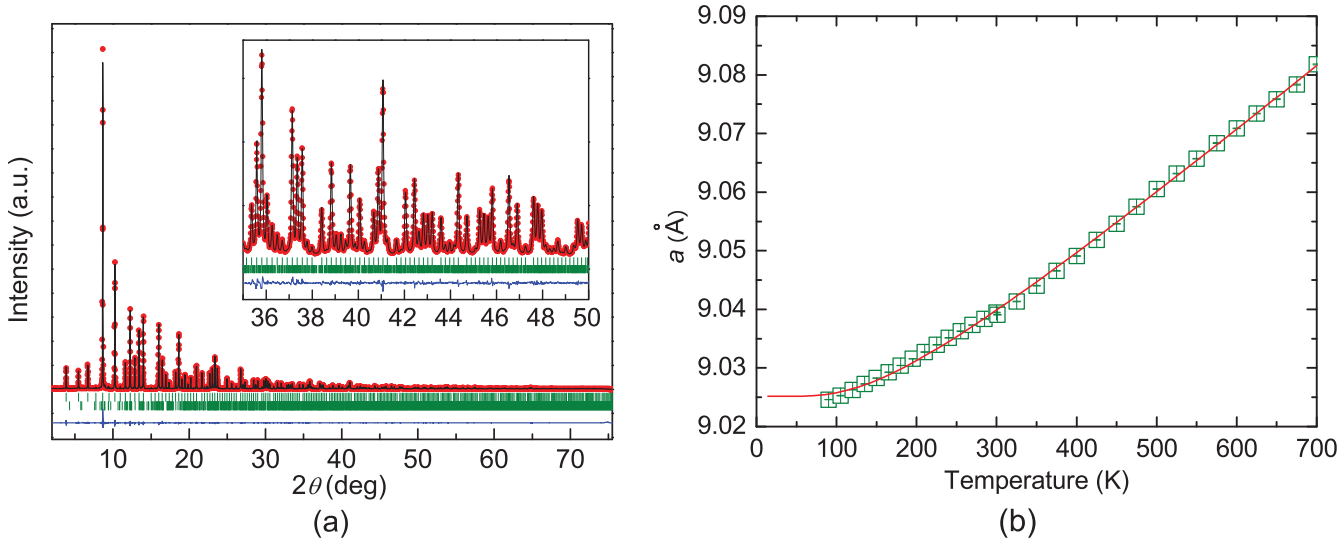


FIG. 2. (Color online) (a) Observed and calculated diffraction patterns and the difference profile of $Eu_{0.1}Co_4Sb_{12}$ at 300 K. An impurity of $CoSb_2$ is identified with a concentration of 1.88 wt%. The inset shows the detailed features at higher 2θ angles, indicating that the calculated pattern is a good fit to the observed data. (b) Lattice parameter, a, versus temperature of $Eu_{0.1}Co_4Sb_{12}$. The solid line is a fit using the Einstein formula.

to different experimental methods, low-resolution data, and problems with systematic errors. The ADPs vary with different types of filler atoms. Nd shows relative large ADPs compared with other guest atoms, while La, Ce, and Yb have similar ADPs in most of the temperature range. Chakoumakos and Sales[37] reported that the ADPs of Tl atoms vary with filling fraction; however, it is difficult to make comparison with their data, which were only measured at one temperature. If the guest atoms in skutterudites can be described as localized independent harmonic Einstein oscillators, then the ADPs of the guest atoms should not be affected by their filling fractions. In our previous study,[31] we compared the multitemperature ADPs of the La atoms in $La_{0.1}Co_4Sb_{12}$ with those of $La_{0.75}Fe_3Co_4Sb_{12}$ reported by Sales *et al.*,[5] showing that it has a comparable ADP. This agrees with the Einstein model. More evidence may be required to understand the correlations, but herein it is shown that the ADPs of the guest atoms actually correlate with the observed lattice thermal conductivities of the filled skutterudites.

Quantitative information about the "rattling" motion of the guest atom can be obtained by assuming that the obtained ADPs can be fitted using a localized harmonic oscillator model. For a quantized harmonic oscillator, the ADP in the Einstein model is given by[27,41]

$$U_{\rm iso} = \frac{h^2}{8\pi^2 m k_{\rm B}\theta_{\rm E}} \coth\frac{\theta_{\rm E}}{2T} + d_{\rm E}^2, \tag{3}$$

where $k_{\rm B}$ is the Boltzmann constant, h is the Planck constant, $\theta_{\rm E}$ is the Einstein temperature ($\theta_{\rm E} = h\nu/k_{\rm B}$), m is the mass of the rattler, and ν is the frequency of vibration. In Eq. (3), a $d_{\rm E}{}^2$ term has been added to describe possible temperature-independent disorder (or anharmonicity). From the fits of $U_{\rm iso}$ versus T by Eq. (3), the Einstein temperatures $\theta_{\rm E}$ for the different partially filled skutterudites can be estimated, and they are listed in Table II, together with the disorder factor $d_{\rm E}{}^2$. The Einstein temperature of $Nd_{0.1}Co_4Sb_{12}$ is about 54 K, which is relative low compared with the others compounds. $La_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ have much higher Einstein temperatures, with the values of 79 and 76 K, respectively. It seems that there are anharmonic contributions to the vibration at higher temperatures, and the Einstein fits for the guest atoms ADPs were therefore repeated for the low-temperature data only (except the Sm-filled sample due to the poor data quality). The fits are shown by the dashed lines in Figure 3, and the corresponding Einstein temperatures $\theta_{\rm E}'$ and disorder factors $(d_{\rm E}')^2$ are listed in Table II. The $Nd_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ samples show some disorder contributions to their ADPs, whereas the disorder parameters for the other filled samples are quite close to zero, indicating that the guest atoms in these compounds are almost fully ordered, and that anharmonicity is limited.

A true Debye solid is a monoatomic cubic structure with mass m. As an approximation, the ADPs of the framework atoms are averaged according to site occupancy fractions, and likewise an average mass (m) is used for the Debye analysis[27]

$$U_{\rm iso} = \frac{3\hbar^2 T}{m k_{\rm B}\theta_{\rm D}^2}\left[\frac{T}{\theta_{\rm D}}\int_0^{\theta_{\rm D}/T}\frac{x}{e^x-1}dx + \frac{\theta_{\rm D}}{4T}\right] + d_{\rm D}^2, \tag{4}$$

where $\theta_{\rm D}$ is the Debye temperature, and $d_{\rm D}$ is an empirical term describing temperature-independent disorder. The Debye model assumes that the unit cell has a fixed volume as a function of temperature, and using Eq. (4), we obtain the Debye temperatures $\theta_{\rm D}$ for different partially filled $CoSb_3$ (Table II). The Debye temperatures determined from the ADPs are similar for all the samples, with values around 270 K. Also for the host structure, the disorder values are close to zero, confirming that the host structures of partially filled $CoSb_3$ are fully ordered. It is, however, noteworthy that all $d_{\rm D}{}^2$ values from the Debye fits are negative. At $T \gg \theta_D$, the Debye expression becomes linear in temperature, and the negative $d_{\rm D}{}^2$ values could suggest that the host structure atoms have anharmonic contributions to their

vibration. Thus, if the ADPs values are curving upward with temperature relative to the linear expression, then the Debye fit will compensate by making $d_D{}^2$ negative.

C. Physical properties

Figure 5 shows the heat capacity at constant pressure, C_p, of the partially filled $CoSb_3$ skutterudites as function of temperature. The heat capacity at lower temperatures shown

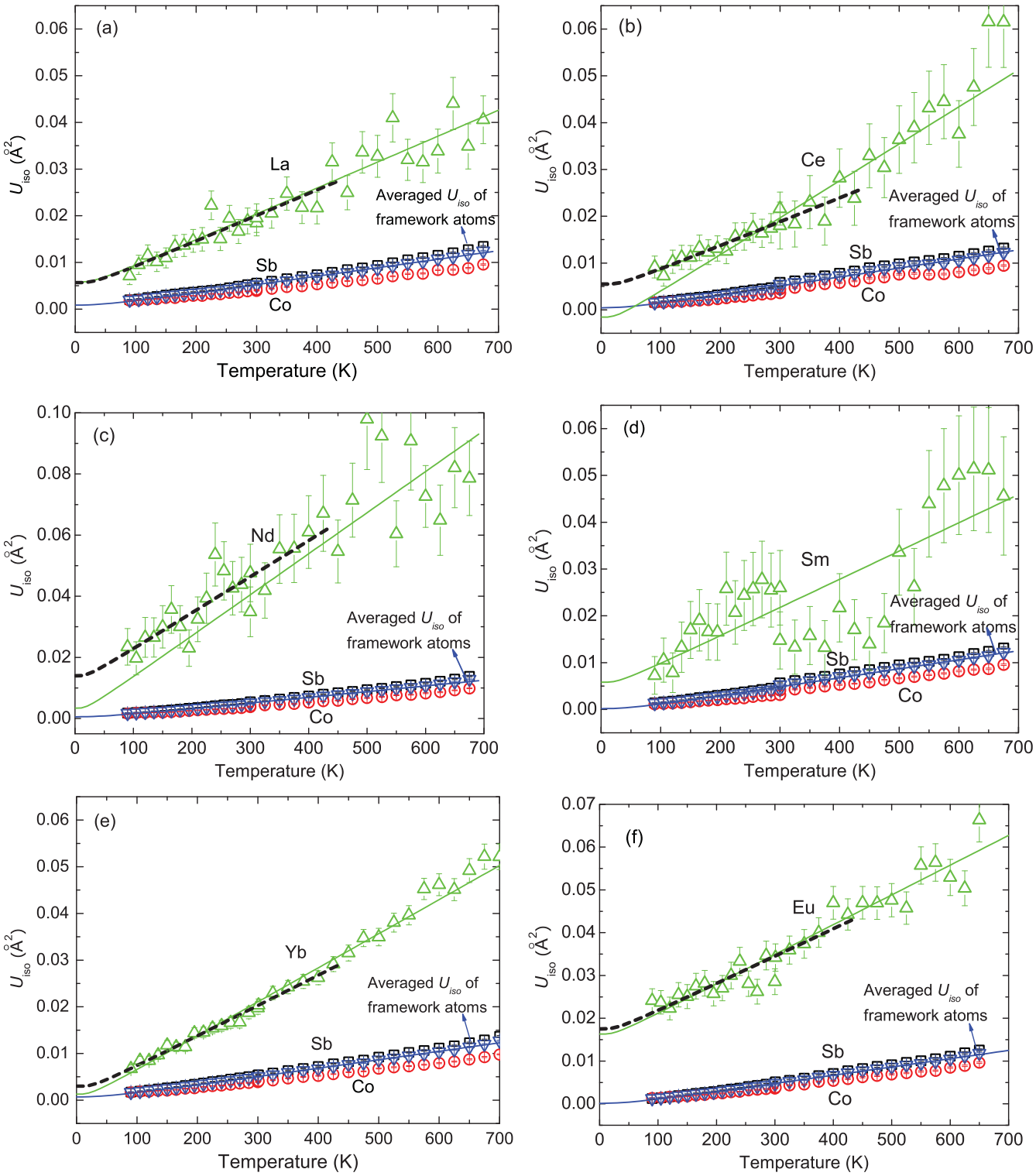


FIG. 3. (Color online) Isotropic ADPs (U_{iso}) versus temperature for M, Co, and Sb obtained from Rietveld refinement of SR-PXRD data on partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu). The solid lines represent Einstein and Debye fits for the ADPs for the whole temperature range of guest atoms and the averaged ADPs of framework atoms, respectively. The dashed lines are the Einstein fits for the ADPs of guest atoms excluding the high-temperature anharmonic part.

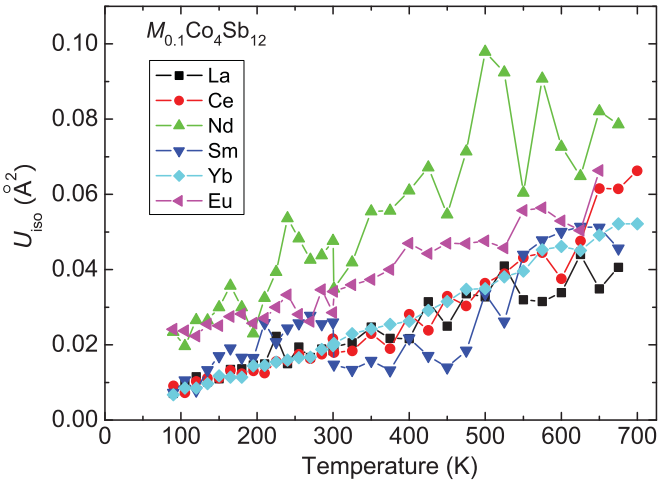


FIG. 4. (Color online) Isotropic ADPs (U_{iso}) as a function of temperature for the guest atoms of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).

in Figure 5(b) indicates that $Sm_{0.1}Co_4Sb_{12}$ has the lowest values, and this could be due to the low Sm occupancy in $Sm_{0.1}Co_4Sb_{12}$. When the foreign atoms are inserted into the $CoSb_3$ structure, the heat capacity should increase as a result of the increased occupancy of the unit cell. However, the occupancies of the guest atoms are smaller than 10%, and the contributions of the guest atoms to the total heat capacity of $M_{0.1}Co_4Sb_{12}$ are small. Hence, we reasonably derive the Debye temperature from the heat capacity. If a solid contains N atoms, the heat capacity is given by

$$C_p = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{e^x x^4}{(e^x-1)^2}dx. \quad (5)$$

By fitting the heat capacity using Eq. (5), we obtain the Debye temperatures θ_D for different partially filled $CoSb_3$, and these are also listed in Table II. The Debye temperatures determined from the heat capacity are close to the values derived from the ADPs from powder x-ray diffraction.

Some room-temperature transport properties of our partially filled $CoSb_3$ materials are listed in Table II. Figure 6 shows the electrical resistivity of the samples as function of temperature. The electrical transport properties are correlated with the structural data. As known from the SR-PXRD results, the occupancy factors of guest atoms in $Nd_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ are relatively low. As a result, the doping levels in these two compounds are low. The lower occupancy factors of guest atoms $Nd_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ cause a relative high electrical resistivity compared with other partially filled $CoSb_3$, mainly because of the reduced carrier concentrations.

The experimental temperature dependence of the carrier concentrations and the mobilities of the partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu) are shown in Figure 7(a) and 7(b)–7(c), respectively. Basically, the carrier concentration for each sample does not change with temperature below 75 K, and above this temperature, it increases due to the increased activation of carriers across the band gap. When calculating the theoretical carrier concentrations by simple charge counting of the free electrons contributed by the occupied guest atoms per cubic centimeter, which are also listed in Table II, the calculated values (n_{cal}) are slightly higher than the experimental values (n_{exp}) for most samples. This suggests that the valence electrons of the rare earth guest atoms are not completely lost to the host structure.[42] $Ce_{0.1}Co_4Sb_{12}$ has an experimental carrier concentration of 1.9×10^{20} cm^{-3} with a Ce filling fraction of 4.7% in our results. Morelli *et al.*[43] reported an experimental carrier concentration of 2.8×10^{20} cm^{-3} for a nominal composition of $Ce_{0.1}Co_4Sb_{12}$, of which the actual Ce filling fraction of 8.5% was higher than in our sample. The results show that the carrier concentrations of partially filled skutterudites change with the occupancy and charge states of the guest atoms. As listed in Table II and shown in Figure 7(a), a larger occupancy and higher charge state result in higher carrier concentration, except for the Eu filled $CoSb_3$, which shows abnormally large carrier concentration (even higher than the calculated value). The Sm-filled sample also shows anomalous behavior, with larger carrier concentration than the Nd filled

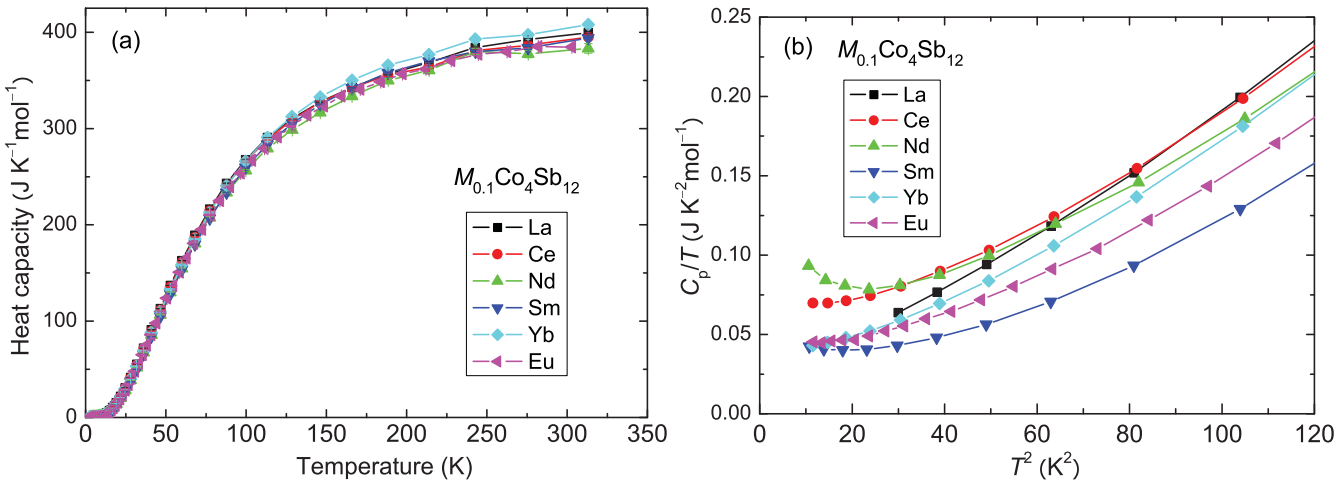


FIG. 5. (Color online) Temperature dependencies of heat capacity of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).

sample, even though the occupancy is small. The anomaly of the carrier concentration for $Eu_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ may be attributed to the magnetic ions of Eu^{2+} and Sm^{3+}. Inclusion of magnetic ions in the compounds has an influence on the charge carrier properties.[44] The carrier concentration of a magnetic compound can be influenced by a magnetic field if the ionization energies of donors or acceptors change with a magnetic field.[45]

The mobility shown in Fig. 7(b) further confirms the carrier scattering mechanisms. The carrier mobilities of all samples decrease with temperature at high temperatures, indicating acoustic phonon scattering. Figure 7(c) shows the mobility as a function of temperature in the natural logarithmic scale. The solid line with slope $k = -3/2$ is characteristic of acoustic phonon scattering, and the plot shows that $Yb_{0.1}Co_4Sb_{12}$ has the highest mobility. Due to the magnetic ions of Eu^{2+} and Sm^{3+}, the localized magnetic moments can lead to spin-disorder scattering of the charge carriers, resulting in reduction of the carrier mobilities of $Eu_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$.

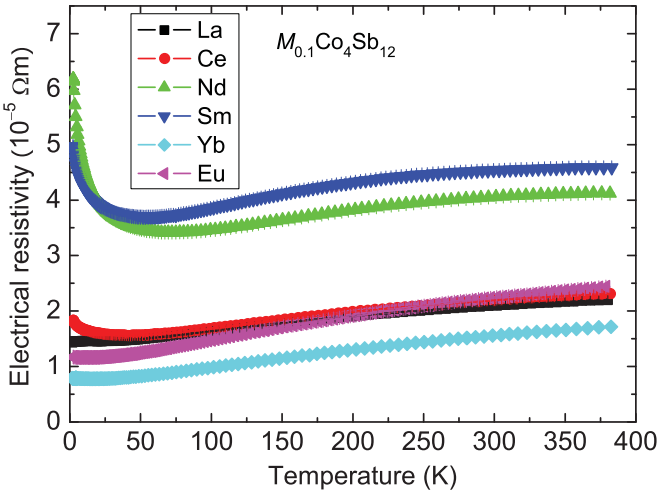
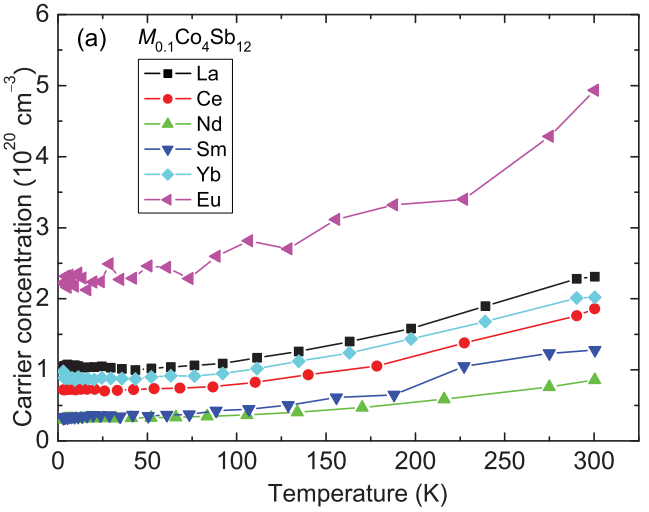
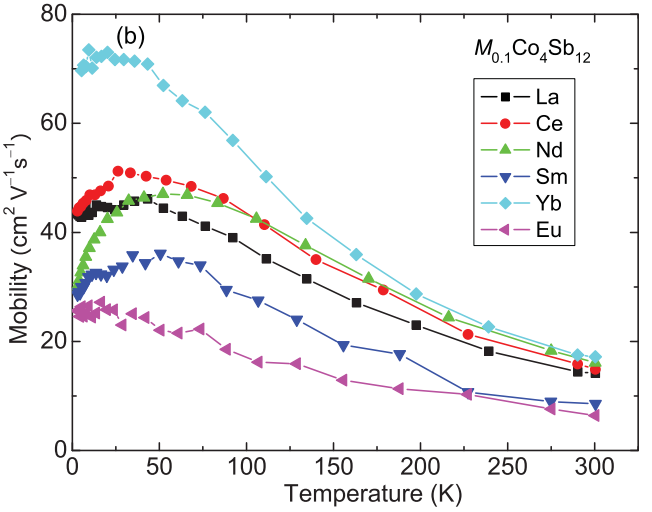


FIG. 6. (Color online) Temperature dependence of the electrical resistivity of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).





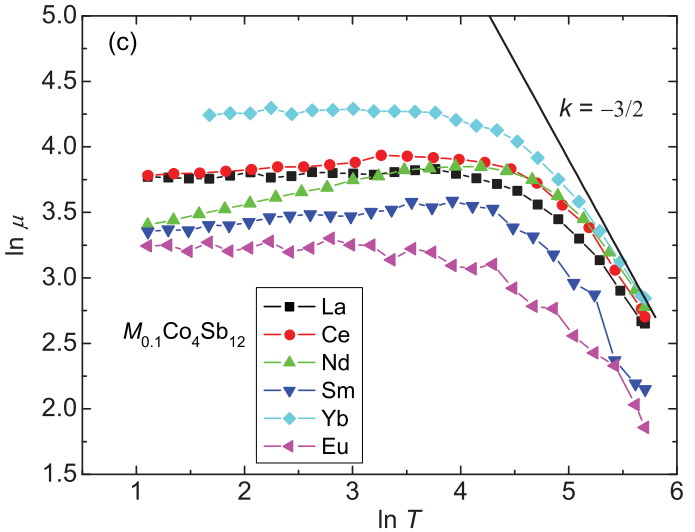


FIG. 7. (Color online) Temperature dependence of (a) carrier concentration and (b) mobility of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu). (c) Mobility as a function of temperature in the natural logarithmic scale. The solid line with slope $k = -3/2$ is characteristic of acoustic phonon scattering.

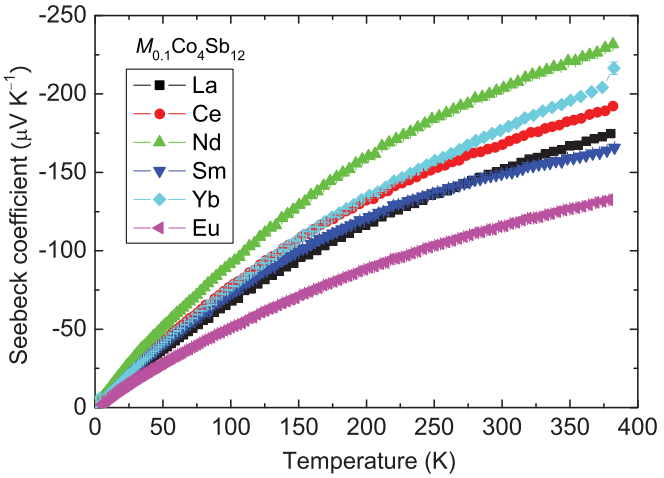


FIG. 8. (Color online) Temperature dependencies of Seebeck coefficient of $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).

Figure 8 shows the temperature dependence of the Seebeck coefficient below 380 K for each sample. All the partially filled $CoSb_3$ samples have n-type conduction, as small amounts of guest atoms added to the voids contribute additional electrons. The data show that $Nd_{0.1}Co_4Sb_{12}$ has the highest absolute Seebeck coefficient, while $Eu_{0.1}Co_4Sb_{12}$ has the lowest absolute Seebeck coefficient in this temperature range. The Seebeck coefficient is related to the effective mass, carrier concentration, and scattering mechanism through[46]

$$\alpha = -\frac{k_B}{e}\left(\frac{5}{2} + r - \ln\frac{n}{N_c}\right), \tag{6}$$

$$N_c = \frac{2(2\pi m^* k_B T)^{3/2}}{h^3}, \tag{7}$$

where N_c is the effective density of states in the conduction band, m^* is the effective mass, and r is a factor depending on the scattering mechanism. As discussed above, the scattering is dominated by acoustic phonons at temperatures above 50 K. Thus, a reasonable value of r is $-1/2$ for all the samples. The effective masses can be estimated from the equations by using the room-temperature Seebeck coefficient values and carrier concentrations, and the corresponding values are listed in Table II. The effective carrier mass is also correlated with the effective ionic radii and the valences of the lanthanide ions. Thus, the effective mass decreases with the ionic radii of guest atoms from La to Sm, while the lower valence guest atoms in $Yb_{0.1}Co_4Sb_{12}$ and $Eu_{0.1}Co_4Sb_{12}$ have higher effective masses.

The temperature dependence of the thermal conductivities is displayed in Figure 9. Note that the quasistatic thermal conductivity data are not corrected for radiation losses at high temperatures. The thermal conductivity of polycrystalline $CoSb_3$ is reported to have a value of 10 Wm^{-1} K^{-1} at room temperature and a maximum of 30 Wm^{-1} K^{-1} at 50 K.[47] All the partially filled $CoSb_3$ samples have much lower thermal conductivity compared with that of unfilled $CoSb_3$, even though the filling fractions are small. The lattice thermal conductivity (κ_L) of the samples shown in Figure 9(b) was estimated by subtracting the electronic contributions κ_c using the Wiedemann-Franz law, $\kappa_c = L_0\sigma T$, where L_0 is Lorenz number approximated by 2×10^{-8} for heavily doped semiconductors.

As described in the introduction, there is currently ongoing discussion about the microscopic mechanisms of the rapid reduction in the thermal conductivity when small amounts of guest atoms are inserted in the $CoSb_3$ voids. To a first approximation, two mechanisms can lead to the reduction in κ_L: (i) interaction between the guest atom vibrations and the host structure vibrations (i.e., phonon-phonon scattering) or (ii) disorder scattering due to the fact that the guest atom position is partially filled, which introduces disorder into the crystal lattice. If the reduction is only due to disorder, one would expect κ_L to decrease with increasing x in M_xCoSb_3 up to $x = 0.5$, and then to start increasing again up to $x = 1$. It is quite difficult to achieve a large filling fraction in skutterudites without also introducing substitution in the framework. However, in such cases, disorder scattering will increase from the framework, and the two contributions can no longer be separated. Morelli *et al.*[43] studied κ_L of skutterudites

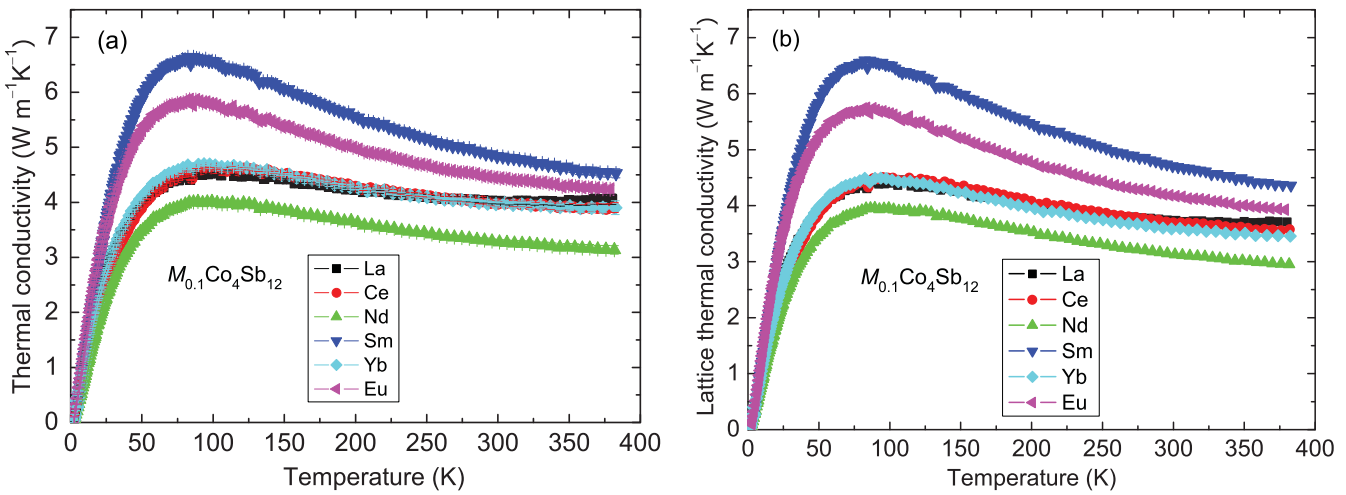


FIG. 9. (Color online) Temperature dependencies of thermal conductivity (a) and lattice thermal conductivity (b) of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).

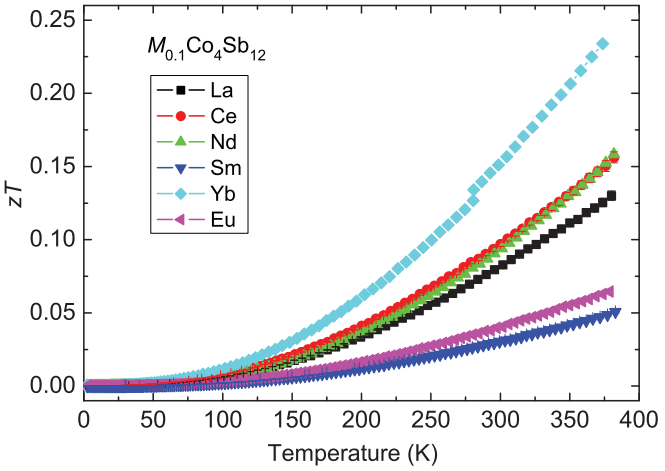


FIG. 10. (Color online) Temperature dependence of zT values of partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ (M = La, Ce, Nd, Sm, Yb, and Eu).

with different Ce filling fractions. Their results showed that only a small amount of Ce is required to produce a strong reduction in κ_L, but also that there is limited change in κ_L when the Ce content increases from $Ce_{0.05}Co_4Sb_{12}$ to $Ce_{0.2}Co_4Sb_{12}$. This suggests that the effect of the Ce guest atom is due to phonon-phonon interaction. In the same study, higher Ce filling was achieved in disordered host lattices, with the Ce content increasing from $Ce_{0.2}Fe_{3.25}Co_{0.75}Sb_{12}$ to $Ce_{1.0}Fe_{3.25}Co_{0.75}Sb_{12}$. Here, the room-temperature κ_L is almost independent of Ce filling fraction, and thus compared with the additional phonon scattering introduced upon substitution of Fe for Co, the effect of the Ce filling fraction on κ_L is small.

In the present study, the importance of the rattling motion of guest atoms on κ_L can be illustrated by comparing the ADPs and κ_L of the partially filled $CoSb_3$ skutterudites. From Figure 3 and Figure 9(b), it is seen that $Nd_{0.1}Co_4Sb_{12}$, which has the largest ADPs of the guest atoms, also shows the most reduced κ_L. Furthermore, the La-, Ce-, and Yb-filled samples, which show ADPs of the guest atoms that are almost identical, exhibit similar κ_L. This suggests that compounds that have large guest atom ADPs will exhibit low κ_L. As for the other physical properties, $Eu_{0.1}Co_4Sb_{12}$ and $Sm_{0.1}Co_4Sb_{12}$ show anomalous behavior with relatively higher κ_L compared with other samples, even though they have comparable ADPs. The origin of the anomaly of Eu- and Sm-filled $CoSb_3$ is unknown. In the Einstein model, the ADPs of the guest atoms are not expected to vary with filling fraction, and if the ADPs truly correlate with the lattice thermal conductivity, then κ_L also should not change significantly with filling fraction of guest atom. As mentioned already, this is exactly what Morelli *et al.* observed for Ce-filled skutterudites.[43] These results corroborate that the guest atoms in filled skutterudites, at least to a first approximation, can be described as Einstein oscillators. If the guest atoms can be regarded as Einstein oscillators, then increasing the filling fraction merely corresponds to increasing the density of states for the oscillator modes. If the scattering of the heat-carrying acoustic phonons is already saturated at a low density of such states, then additional filling will have limited effect on κ_L. The effect of the Einstein modes is to create an avoided crossing in the acoustic phonon dispersion, and the Umklapp phonon-phonon scattering will occur at lower temperature for the lower Einstein temperatures. It is therefore expected that the sample with the lowest Einstein temperature would have the lowest κ_L. Among the present samples, $Nd_{0.1}Co_4Sb_{12}$ does have the lowest Einstein temperature and the lowest κ_L. However, for the other filled samples, the correlation between Einstein temperature and thermal conductivity is not evident. It therefore appears that it is the specific chemical interaction between the host and the guest (the coupling) that determines the effectiveness of the rattler in lowering κ_L. As stated previously, it seems that it is the magnitude of the guest atom ADPs rather than the Einstein temperature that correlates with κ_L.

Besides the rattling motion of guest atoms, the disorder of the structure can also affect the thermal conductivity.[48] In the analysis of ADPs of partially filled $CoSb_3$ in this paper, it was found that neither the guest atoms nor the host structure atoms have significant contributions from disorder to their ADPs (only Nd and Eu show some disorder, but the contributions are limited). The structure therefore appears to be fully ordered, apart from the crystal structure disorder introduced by the partial guest atom filling. However, this crystal structure disorder does not seem to significantly affect κ_L. The skutterudites are often compared with thermoelectric clathrates such as $M_8Ga_{16}Ge_{30}$, which also contain rattling guest atoms.[26–30] In the clathrates, both the guest atoms and the host structure atoms are inherently structurally disordered.[27] In the case of the clathrates, the temperature dependence of κ_L has been strongly debated, since it has been observed that for some type I clathrate samples (e.g., n-type $Sr_8Ga_{16}Ge_{30}$, n-type $Eu_8Ga_{16}Ge_{30}$, p-type $Ba_8Ga_{16}Ge_{30}$, p-type $Ba_8In_{16}Ge_{30}$), there is no crystalline peak in κ_L at low temperature.[49,50] It appears that all skutterudite samples in the literature, which only have guest atom filling (i.e., no host structure disorder), show a normal crystal-like temperature behavior of κ_L independent of, for example, the magnitude of the ADPs or the value of the Einstein temperature. On the other hand, host structure–compensated skutterudites are able to introduce further disorder in the structure and can show a glass-like κ_L.[6,43] In analogy to this, it seems that the disorder of the structure plays an important role in the glass-like behavior of κ_L. Similarly, the glass-like behavior of κ_L in some clathrates could be related to the host structure disorder, although it could also have a different origin, such as, for example, the specific electronic band structure of the clathrate (phonon–charge carrier scattering). For the clathrates, phonon dispersion studies have cast some doubt about the validity of the Einstein model,[23] and in line with this, neither the Einstein temperatures nor the magnitudes of the ADPs of the rattlers correlate with κ_L, which seems to be largely controlled by the amount of disorder in the host structure.[28] One important difference between clathrates and skutterudites is that type I clathrates cannot be synthesized with partial "guest atom" filling, and the cations must be considered as fundamental parts of the structure. In this sense, the clathrates may not really be coined host-guest structures. It is of significant interest to further probe differences and similarities between skutterudites and clathrates to understand if the rattling behavior of the guest atoms affects the properties in the same way.

The temperature dependence of zT is shown in Figure 10. As a result of the relative high occupancy and high effective mass, Yb-filled $CoSb_3$ shows the highest zT values of the compounds studied here, indicating that the Yb guest atom is the most effective in improving the thermoelectric properties of $CoSb_3$. A zT value of 0.16 at room temperature and a maximum zT value of 0.24 at 380 K are obtained for $Yb_{0.1}Co_4Sb_{12}$, with a still increasing zT at higher temperatures, and therefore even higher values of zT can be anticipated at higher temperatures.

IV. CONCLUSION

Partially filled skutterudites $M_{0.1}Co_4Sb_{12}$ with different filling atoms (La, Ce, Nd, Sm, Yb, and Eu) were studied. The guest atoms in these filled skutterudites can be well described as Einstein oscillators. The suppression of the lattice thermal conductivity of the filled skutterudites results from scattering of acoustic phonons by the interaction between guest atom and host structure phonons. Anomalously large atomic displacement parameters (ADPs) indicate that the filling atoms are weakly bonded in the structure. Einstein and Debye temperatures derived from the analysis of multitemperature ADPs of guest atoms and the framework atoms, respectively, also reveal that neither the guest nor the host structure atoms are significantly disordered. The guest atom filling fraction is correlated to the effective ionic radii and the valences of the lanthanide ions. The filling fraction of guest atoms also affects the doping level, resulting in different electrical transport properties of the samples. A correlation is observed between the lattice thermal conductivity and the magnitude of the guest atom ADPs. The magnetic properties of Eu^{2+} and Sm^{3+} ions affect both the electrical and thermal transport properties.

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