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Low-temperature thermal properties of n-type partially filled calcium skutterudites

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Abstract

The low temperature thermal properties of polycrystalline $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ skutterudite samples have been investigated between 10 and 300 K for different x contents. The compounds were synthesized via solid-state reactions. The lattice thermal conductivity is found to decrease drastically with the increasing content of Ca at any temperature considered. Our theoretical analysis puts forward that this reduction can be explained by phonon-point defect scattering due to both mass fluctuations and strain field scattering on the $2a$ crystallographic position and also to phonon resonance scattering.

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Introduction

Skutterudites have gained renewed attention last years because of their unusual transport and magnetic properties but also of their promising thermoelectric properties and potential for device applications [1-4]. Among the nine binary skutterudite compounds, much effort has been directed towards the cobalt triantimonide CoSb_3 in the context of solid-state energy conversion. CoSb_3 crystallizes in the bcc structure (space group Im-3 , 32 atoms per unit cell) and is a narrow band-gap semiconductor.

A good thermoelectric material has to possess a large dimensionless figure of merit $ZT = S^2T/\rho\lambda$, where S is the thermoelectric power, ρ the electrical resistivity, λ the thermal conductivity and T the absolute temperature. The binary skutterudite compound CoSb_3 has a moderate power factor (S^2/ρ) but a quite high thermal conductivity (~ 10 W/mK at 300 K) compared to state-of-the-art thermoelectric materials (~ 1.5 W/mK at 300 K) [5]. Various strategies were attempted to improve their thermoelectric properties, including partial filling of the voids of the crystallographic structure ($2a$ site) [6-19], doping by appropriate substitutions on the transition metal or pnictogen sites [20-25], forming of isoelectronic solid solutions [20, 26-27], nanostructuring [28],... Among all these various approaches, filling the voids of the structure was found to be the most efficient. The presence of a filler element leads to a drastic reduction of the thermal conductivity of the binary CoSb_3 and affects also its electrical properties. The decrease of the thermal conductivity is believed to be due to resonant scattering of phonons via localized low frequency vibrations of the guest atoms. This can be thought of as due to the rattling of the trapped elements in their oversized cage. Understanding the phonon scattering mechanisms in skutterudites is important namely for the technical implications as well as with respect to its intriguing physical background.

We investigated the electronic structure of partially filled $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ compounds recently [29]. The results were valuable for understanding the role of calcium on the electrical and magnetic properties. One important result was that the presence of Ca ions modifies the band structure of CoSb_3 near the Fermi level and adds electrons to the framework. In fact, these results are not unique to calcium but were also noted with other filler ions. As a consequence of the perturbation of the electrical properties, these skutterudite materials based on CoSb_3 cannot be classified as true phonon glass electron crystals (PGEC) as it was proposed at the outset [30]. Indeed, in the concept of PGEC edited by Slack [30], the electrical properties of the framework are supposed to stay unmodified by the addition of rattlers.

In this work, we pursued our studies on this interesting system by investigating its thermal conductivity at low temperature. Altering the Ca filling fraction was found to deeply impact the thermal conductivity. The role of the Ca fillers in affecting the lattice thermal conductivity is analyzed using the approach first proposed by Callaway [31].

Experimental techniques

Polycrystalline samples of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ with $x = 0, 0.03, 0.05, 0.08, 0.20$ (composition determined par electron probe microanalysis) were fabricated using a combination of solid-liquid reactions, grinding processes, annealing and finally hot pressing. A description of the synthesis as well as of the electronic and magnetic properties of these partially-filled calcium skutterudites is given in detail elsewhere [29, 32].

Measurements of the thermal conductivity were conducted from 10 to 300 K in an automated closed-cycle refrigerator system using a steady-state technique, on bar

shaped samples of typical dimensions $2 \times 2 \times 10 \text{ mm}^3$. One end of the sample was glued (with silver paste) to a copper block that served as a heat sink, while a calibrated chip resistor was glued to the other end. The temperature difference along the sample was controlled to be less than 1.5 K and was measured with fine chromel-constantan thermocouples. The accuracy on the thermal conductivity is estimated to be 10%.

As samples display different densities (ranging from 81 to 92% of the theoretical density), the experimental thermal conductivity data were corrected for porosity using the effective medium percolation theory [33] in order to make a more appropriate comparison.

Results and discussion

The temperature dependences of the corrected thermal conductivity of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ skutterudites are shown in figure 1. In non-magnetic solids, the total thermal conductivity λ can be expressed as the sum of lattice (λ_L) and electronic (λ_E) terms:

$$\lambda = \lambda_L + \lambda_E. \quad (1)$$

We estimated the electronic contribution using the Wiedemann-Franz law:

$$\lambda_E = L_0 T / \rho, \text{ where the Lorenz number } L_0 \text{ was taken equal to } 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}.$$

Due to the high electrical resistivity of the $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ compounds [29], it is found that the contribution of λ_E to λ is the highest for the most conducting sample ($x = 0.20$). This contribution is less than 3% below 150 K and reaches 5% at room temperature. In other words, the temperature dependences of the thermal conductivities reported in figure 1 are essentially representative of those of the phononic part.

The results obtained for CoSb_3 are in good agreement with those of the literature [34-35]. The behavior corresponds to that expected for a dielectric crystal. The value of

the dielectric maximum (~ 60 W/mK at $T \sim 35$ K) is nevertheless significantly lower than that obtained for single crystalline CoSb_3 (> 1000 W/mK [36]) because of phonon scattering at the grain boundaries.

The insertion of calcium in the binary CoSb_3 skutterudite compound drastically decreases its lattice thermal conductivity (Figure 1). The reduction is more marked at low temperature where the dielectric maximum is strongly depressed. Moreover, the weak temperature dependence is characteristic of the scattering of phonons due to the rattling of the Ca ions in the constitutional voids of the skutterudite structure, similarly to what has also been observed with e.g. Ce ions [6] and La ions [37]. The insertion of very few calcium ions is sufficient to produce an effective scattering. These results are similar to those encountered in other crystalline materials exhibiting localized vibration modes, like for instance in KCl:Li crystals [38]. The decrease of the lattice thermal conductivity can also be due, apart from the dynamic disorder induced by the Ca ions, to mass fluctuations on the $2a$ crystallographic site. This point of view, proposed independently by Nolas et al. [37] and Meisner et al. [39], is based on the argument that a random distribution of ions in their cage (partial filling) should be more effective in diffusing the phonons than an arrangement in which all the cages are filled (filling up to 100%). The fact that the lattice thermal conductivity in the $\text{Ce}_x\text{Fe}_y\text{Co}_{4-y}\text{Sb}_{12}$ [39], $\text{La}_x\text{Co}_4\text{Sn}_y\text{Sb}_{12-y}$ [37], $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$ [10] and $\text{Sr}_x\text{Co}_4\text{Sb}_{12}$ [19] systems shows a minimum for a value x different from unity supports the proposition of Nolas et al. [37] and Meisner et al. [39]. In our compounds, the lattice thermal conductivity diminishes at $T = 300$ K when the Ca content increases, but the solubility limit is too weak so that it is difficult to draw any conclusion on the existence of this minimum (Figure 2). In this figure are also summarized the results obtained for various other partially filled

$R_x\text{Co}_4\text{Sb}_{12}$ skutterudites, for different filler atoms R. The values of the thermal conductivity obtained with the Ca partially filled skutterudites are very close to those reported for partial filling with other alkaline earths, Sr [19] or Ba [10]. They remain however relatively high compared to those achieved by a partial filling with rare earth atoms (R = La [37], Ce [6], Nd [14], Yb [11]) or other elements (R = Tl [9], Sn [40]) for which the values of the atomic displacement parameter (ADP) have been found to be higher than that of calcium (ADP = 0.68 Å² [32]). Nevertheless, all these values are still far above the theoretical minimum of the lattice thermal conductivity estimated to be 0.3 W/mK at $T = 300$ K for CoSb_3 [37].

In order to gain a deeper understanding of the influence of calcium insertion on the phonons scattering mechanisms and on the origin of the significant decrease of the lattice thermal conductivity, we performed theoretical modelling of the temperature dependent behaviour of the lattice thermal conductivity for all $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples, using the Debye model. In this model, λ_L may be given by [31, 41]:

$$\lambda_L(T) = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (2)$$

where x is a dimensionless parameter, the phonon frequency, k_B the Boltzmann constant, \hbar the reduced Planck constant, θ_D the Debye temperature, v the average velocity of sound, and τ the phonon scattering relaxation time. The overall phonon relaxation rate, τ^{-1} , has been considered to result from four scattering mechanisms of the phonons, and is expressed as:

$$\tau^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T e^{-\theta_D/3T} + \frac{C\omega^2}{(\omega_0^2 - \omega^2)^2} \quad (3)$$

where the grain size L , the resonance frequency, and the A , B , C coefficients are adjustable parameters.

The four terms on the right-hand side of Eq. 3 represent respectively: (i) grain boundary scattering, (ii) point-defects scattering (Rayleigh type scattering), (iii) phonon-phonon Umklapp scattering, this term having been used previously to describe successfully semiconductors [34, 42-44], and (iv) resonant scattering resulting from the interactions between the normal modes of the structure and the localized modes of the Ca fillers described as Einstein type oscillators. This last term, derived for a simple mechanical oscillator, has been used in the past to describe the thermal properties of KCl crystals containing small concentrations of KNO_2 [45] and more recently those of clathrate or skutterudite materials [34, 46]. The prefactor C is supposed to be proportional to the concentration of the oscillators.

Taking the Debye temperature = 287 K and the velocity of sound $v = 2934$ m/s from Refs. [36] and [21], respectively, the experimental data of the thermal conductivities have been fitted using Eqs 2 and 3, by varying the adjustable parameters for each x Ca content. The results of the fits are reported as solid lines together with the experimental data in figure 3, and the values of the corresponding fitting parameters in table 1. It can be seen that the fits are in very good agreement with the experimental temperature dependent behaviours in the whole temperature range investigated, except near room temperature for the $x = 0.03$ and 0.05 compounds for which the experimental values are slightly superior to those issued from the modelling. The discrepancies may be attributed to radiation losses.

The grain size L (table 1) determined from the fits is on the order of the micrometer except for the parent binary compound ($x = 0$) for which it is one order of magnitude greater. These values agree fairly well with the grain size observations made on our samples from scanning electron microscopy images. The coefficient A , representing Rayleigh scattering, increases significantly with the calcium amount inserted in the cavities. The same result was obtained by Yang et al. [34] in Yb-filled skutterudites. The prefactor A can be further analysed as [47]:

$$A = \frac{\Omega_0 \Gamma}{4\pi \nu^3} \quad (4)$$

where Ω_0 is the unit cell volume and Γ is the scattering parameter which depends both on mass fluctuations and strain field scattering. For a single lattice site on which impurity with relative concentration α can be present, Γ is given by [48]:

$$\Gamma = \alpha(1 - \alpha) \left[\left(\frac{\Delta M}{\bar{M}} \right)^2 + \varepsilon \left(\frac{\Delta \delta}{\bar{\delta}} \right)^2 \right] \quad (5)$$

where ΔM is the difference between the mass of the impurity and that of the host, $\Delta \delta$ the difference in ionic radius of the two species, and the weighted averages of the mass and the radius on this lattice site and ε a phenomenological parameter.

According to Eq. 5 and refs. [39] and [49], we can derive an expression for $\Gamma(\text{Ca}_x\text{Co}_4\text{Sb}_{12})$:

$$\Gamma(\text{Ca}_x\text{Co}_4\text{Sb}_{12}) \approx x(1 - x) \frac{1}{17} \left(\frac{40.08}{102.16} \right)^2 \left[1 + \varepsilon \left(\frac{\Delta \delta}{\bar{\delta}} \right)^2 \right]. \quad (6)$$

If we plot A versus $x(1-x)$, we can note that the changes of A follow quite well a linear law, in good agreement with the predictions of Eqs (4) and (6) (Fig. 4a). The slope of the line is close to $5.2 \times 10^{-41} \text{ s}^3$. If we consider only mass fluctuations between the non-

occupied and Ca-occupied sites in the cages of the skutterudite structure, the previous analysis predicts a slope of $2.0 \times 10^{-41} \text{ s}^3$. This deviation with regard to the experimental data suggests that point defect scattering cannot be only attributed to mass fluctuation. Strain field scattering has certainly to play a role at least as important as mass fluctuation scattering in $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ compounds.

Concerning the coefficient B , reflecting Umklapp processes, the values obtained from the fit procedure are of the same order of magnitude whatever the composition is (table 1). As B depends on many factors such as the Debye temperature, the Grüneisen constant and the average number of atoms in the unit cell [42, 43] which are not expected to vary crucially with x the obtained results are representative of this matter of fact.

On the other hand, as the coefficient C is proportional to the concentration of the local oscillators, it should linearly increase with x . Our data support quite well this picture, as it can be seen in Fig. 4b. The resonance frequency is in the order of some tera-Hertz (table 1), in very good agreement with the results of the literature [34, 46]. Thus, the rattling motion of Ca in the voids of the skutterudite structure is conveniently described by the use of a resonant scattering term.

Conclusion

Thermal transport properties of polycrystalline $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ skutterudite compounds were measured between 10 and 300 K for different x contents. It was found that the lattice thermal conductivity of the CoSb_3 binary compound can be strongly reduced by the insertion of even small amounts of Ca in the constitutional voids of the skutterudite structure. Our theoretical modelling fits very well the temperature

dependent behaviours of the thermal conductivity in the whole temperature range studied and for any Ca content. The most consequent effects of the increasing calcium content on the lattice thermal conductivity are to enhance: (i) phonon-point defect scattering through both mass fluctuations and strain field scattering on the $2a$ crystallographic site and (ii) phonon resonance scattering.

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Table captions

Table 1: Fitting parameters determined following Eqs 2 and 3 for the theoretical analysis of the lattice thermal conductivity of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ polycrystalline compounds. See text for details.

x	L (μm)	A (10^{-43} s^3)	B (10^{-18} sK^{-1})	C (10^{33} s^{-3})	ω_0 (THz)
0	13	5.7	3.2	0	-
0.03	1.1	29	1.4	3.5	5.8
0.05	1.4	30	2.1	5.0	6.1
0.08	1.3	41	1.7	4.3	5.6
0.20	1.3	68	2.4	11	4.4

Figure captions

Figure 1: Temperature dependence of the total thermal conductivity of different $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ polycrystalline skutterudites.

Figure 2: Lattice thermal conductivity of partially R-filled skutterudites at 300 K, as a function of the filling fraction x .

Figure 3: Temperature dependence of the lattice thermal conductivity: symbols are experimental data and solid curves correspond to fits to the data for different $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ polycrystalline compounds. For symbols legend see Fig. 1.

Figure 4: (a) Coefficient A versus $x(1-x)$ for point defect scattering. The theoretical expected variation due to mass fluctuations is represented by the grey line. (b) Coefficient C versus x for phonon resonance scattering.

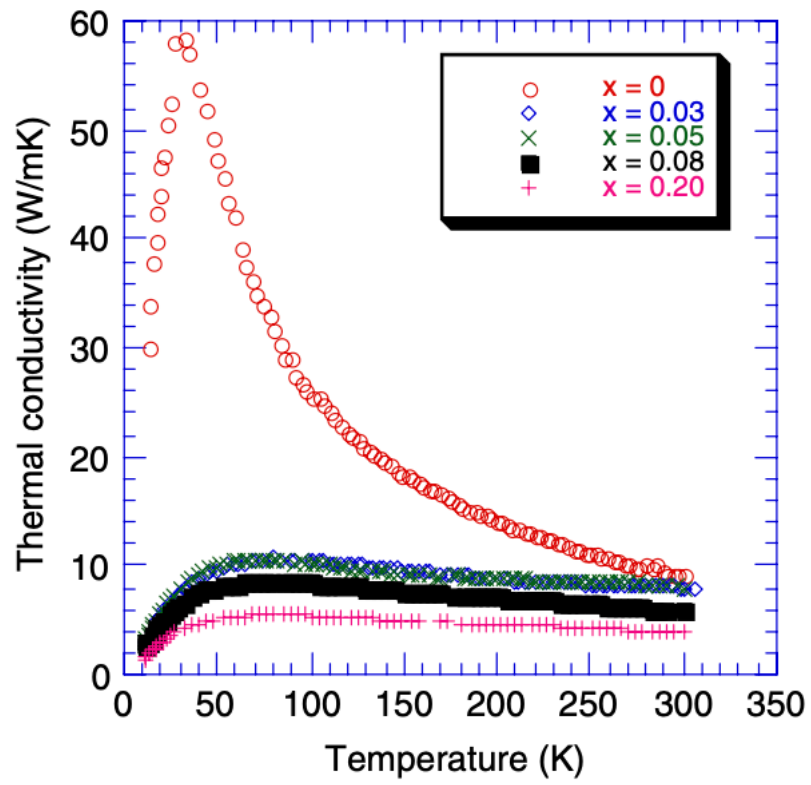


Figure 1

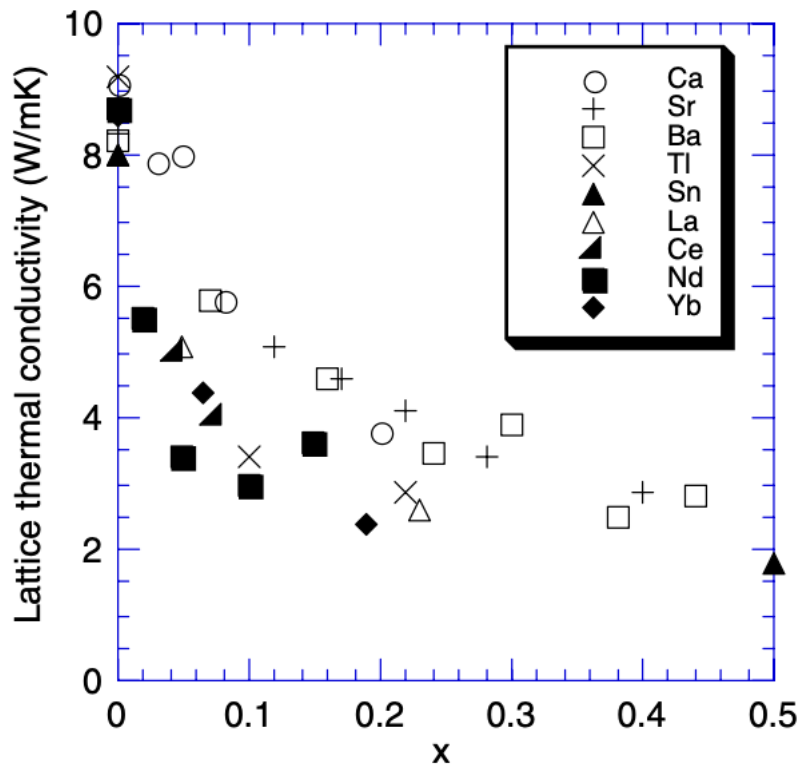


Figure 2

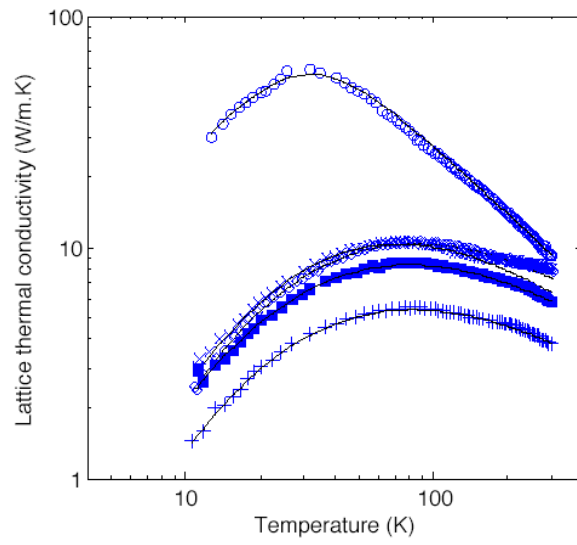


Figure 3

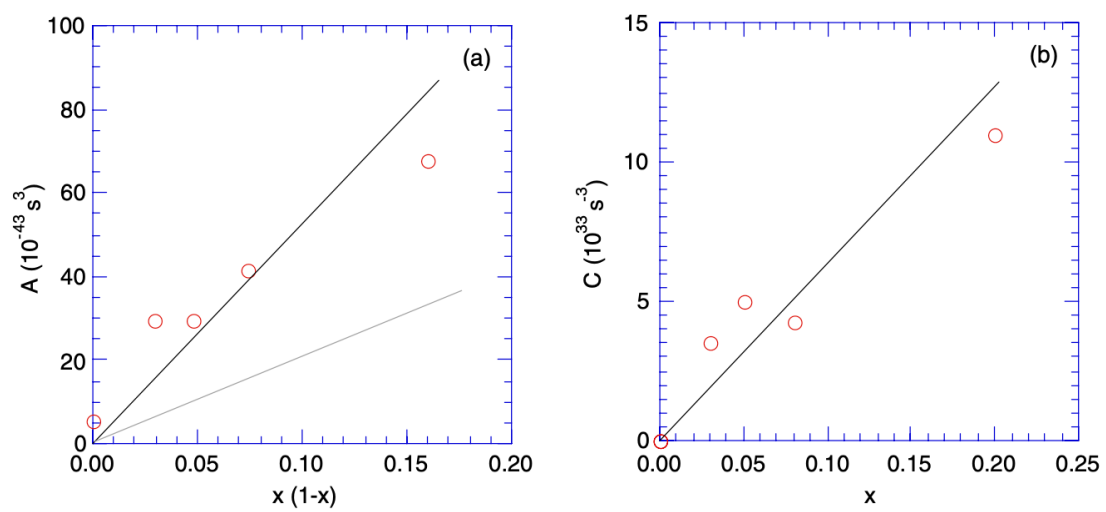


Figure 4