Anomalous expansion and phonon damping due to the Co spin-state transition in $R$CoO$_3$ with $R = \text{La, Pr, Nd and Eu}$

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Abstract. We present a combined study of the thermal expansion and the thermal conductivity of the perovskite series $R$CoO$_3$ with $R = \text{La, Nd, Pr and Eu}$. The well-known spin-state transition in LaCoO$_3$ is strongly affected by the exchange of the $R$ ions due to their different ionic radii, i.e. chemical pressure. This can be monitored in detail by measurements of the thermal expansion, which is a highly sensitive probe for detecting spin-state transitions. The Co ions in the higher spin state act as additional scattering centers for phonons, therefore suppressing the phonon thermal conductivity. Based on the analysis of the interplay between spin-state transition and heat transport, we present a quantitative model of the thermal conductivity for the entire series. In PrCoO$_3$, an additional scattering effect is active at low temperatures. This effect arises from the crystal field splitting of the $4f$ multiplet, which allows for resonant scattering of phonons between the various $4f$ levels.

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1. Introduction

Cobalt compounds are of particular interest due to the possibility that Co ions can exhibit different spin states and hence the occurrence of temperature-driven spin-state transitions. The most prominent example is LaCoO$_3$, which has been intensively studied and controversially debated for more than fifty years, see e.g. [1,2,3,4,5,6,7,8,9]. The Co$^{3+}$ ions in LaCoO$_3$ feature a $3d^6$ configuration which in principle can occur in three different spin states: a nonmagnetic low-spin (LS) ($t^6_{2g}e^0_{g}$, $S = 0$), an intermediate-spin (IS) ($t^5_{2g}e^1_{g}$, $S = 1$) and a high-spin (HS) state ($t^4_{2g}e^2_{g}$, $S = 2$). It is generally agreed that the Co$^{3+}$ ions in LaCoO$_3$ realize the LS state at low temperatures. Above approximately 25 K a higher spin state, either IS or HS, becomes thermally populated affecting various physical properties, e.g. the magnetic susceptibility $\chi$ or the thermal expansion $\alpha$, which both exhibit pronounced maxima in their temperature dependencies [10,11]. The susceptibility is obviously affected because the excited spin state, either IS or HS, induces a strong increase of the magnetization above 25 K. The thermal expansion is affected due to the different ionic radii of the smaller LS-Co$^{3+}$ with empty and the larger IS- or HS-Co$^{3+}$ ions with partially filled $e_g$ orbitals. The spin-state transition can be well described in a LS – IS scenario, i.e. the excited spin state is the IS state, with a constant energy gap of $\Delta_{Co} = 185 K$ [10,11]. However, more recent investigations show, that a LS/HS model including spin-orbit coupling is more reasonable [12,13,14]. A consequence of the latter model is a temperature-dependent energy gap $\Delta_{Co}(T)$, which strongly increases with increasing temperature [13].

The spin-state transition in LaCoO$_3$ is strongly affected by both, heterovalent and isovalent doping on the La site. The former possibility causes hole doping and chemical pressure and suppresses the spin-state transition due to the implementation of Co$^{4+}$ ions [15,16]. The latter one, i.e. chemical pressure without changing the Co valence, is usually realized by introducing trivalent rare-earth ions $R^{3+}$. In RCoO$_3$ the spin-state transition is not suppressed but its onset is shifted to higher temperature. The energy gap between the LS and the excited spin state increases from about $\Delta_{Co} = 185 K$ for $R =$ La to $\gtrsim 2000 K$ for $R =$ Eu [11]. Moreover, due to the decreasing ionic radius of the lanthanide series, the structure changes from rhombohedral in LaCoO$_3$ to orthorhombic for $R =$ Pr, Nd and Eu. Recently, it has been reported, that the low-temperature thermal conductivity of LaCoO$_3$ is also very anomalous [17,18]. This behaviour has been qualitatively attributed to the onset of the spin-state transition. However, a quantitative analysis of the anomalous thermal conductivity of LaCoO$_3$ has not been presented yet.

The aim of this paper is to develop a consistent picture of the influence of the spin-state transition on the thermal conductivity. Therefore, we measured the thermal conductivity $\kappa(T)$ of the series RCoO$_3$ with $R =$ La, Pr, Nd and Eu. Moreover, we studied the thermal expansion $\alpha(T)$, which is a very sensitive probe to investigate spin-state and also crystal-field transitions and their coupling to the lattice. In the quantitative analysis of our data, we will consider both models of the spin-state transition, which are favoured for LaCoO$_3$ in the literature, i.e. we will consider the LS – IS scenario with a constant $\Delta_{Co}$ and the more recently proposed spin-orbit coupled HS (SOcHS) model with a temperature dependent energy gap $\Delta_{Co}(T)$.
Table 1. Characteristic properties of the investigated crystals. Here, $T_{on}$ denotes the onset temperature of the spin-state transition, $\Delta_{Co}$, the energy gap between the LS ground state and the excited spin state (either IS or HS) and $\gamma$ is related to their ionic radii difference (see text). Due to the large $T_{on}$ of EuCoO$_3$ we can only give lower limits for the values of $\gamma$ and $\Delta_{Co}$, as it was also the case in the related analysis of the magnetic susceptibility [11]. The last three columns give the room-temperature values of the thermopower $S_{RT}$, which for the LaCoO$_3$ crystals have been taken from [18], and the crystal dimensions (sample cross section $A$ and sample length $L$) which are important for the measurements of $\kappa$ (the cross section of S5 is an approximate value, since it is not of rectangular shape).

| Sample     | $T_{on}$ (K) | $\Delta_{Co}$ (K) | $\gamma$ (%) | $S_{RT}$ ($\mu$V/K) | $A$ (mm$^2$) | $L$ (mm) |
|------------|--------------|-------------------|--------------|---------------------|-------------|----------|
| LaCoO$_3$ (S1) | 25           | 185               | 0.7          | -700                | $0.8 \times 1.5$ | 3.7      |
| LaCoO$_3$ (S2) | 1000         | 1200              | 2.8          | -400                | $1.0 \times 3.8$ | 2.5      |
| LaCoO$_3$ (S3) | 1000         | 1200              | 4.8          | -400                | $1.7 \times 2.0$ | 2.8      |
| LaCoO$_3$ (S4) | 1000         | 1200              | $\geq 10$    | -500                | $0.3 \times 0.85$ | 2.0      |

2. Experiment

All RCoO$_3$ crystals have been grown in a floating-zone image furnace. We examine five different LaCoO$_3$ crystals identical to those used in [18], where details of the sample preparation and characterization are given. For EuCoO$_3$ this information can be found in [11]. The NdCoO$_3$ and PrCoO$_3$ single crystals have been grown in the same way as those of LaCoO$_3$ and EuCoO$_3$. Characteristic properties of all crystals are listed in table 1. The thermal conductivity measurements have been performed by a standard steady-state method using a differential Chromel-Au+0.07 % Fe-thermocouple [19]. The thermal expansion below $\approx 200$ K was measured using a home-built high-resolution capacitance dilatometer [20], whereas the high-temperature measurements $135$ K $\leq T \leq 670$ K were performed using commercial inductive dilatometer (TMA 7, Perkin-Elmer).

3. Results and Discussion

3.1. Thermal Expansion

In figure 1(a) we show the thermal-expansion coefficients $\alpha(T) = 1/L \cdot \partial L / \partial T$ of RCoO$_3$. The low-temperature results of LaCoO$_3$ and EuCoO$_3$ were already discussed in detail in [10, 11]. The thermal expansion consists of a phononic part and a Schottky contribution, caused by the thermal population of the $e_g$ orbitals of the Co$^{3+}$ ions, i.e. $\alpha = \alpha_{Ph} + \alpha_{Sch}$. The latter contribution causes the large maximum at $\approx 50$ K in LaCoO$_3$. To further analyze the data we subtract $\alpha_{Ph}$, which we estimate using a Debye function with the Debye temperature $\Theta_D = 600$ K of LaCoO$_3$ [21]. Here, we used the same $\Theta_D$ for the various cobaltates, but sample-dependent prefactors determined by scaling the Debye function to the low-
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Figure 1. (a) Thermal expansion of \( \text{RCoO}_3 \) with \( \text{R} = \text{La}, \text{Pr}, \text{Nd} \) and \( \text{Eu} \). The solid line is the estimated phonon contribution of \( \text{NdCoO}_3 \) (see text). (b) Anomalous part of the thermal expansion obtained by subtracting the phononic background. For clarity the different data sets are offset by \( 10^{-5}/\text{K} \) with respect to each other. The arrows signal the approximate onset temperature of the spin-state transition and the solid circles denote the metal-insulator transition temperature estimated from resistivity measurements for each compound. The solid lines are fits of the respective Schottky anomalies, see equations (1) and (2), assuming a constant energy gap \( \Delta_{\text{Co}} \) between the different spin states of \( \text{Co}^{3+} \). The dashed line for \( \text{LaCoO}_3 \) is a similar fit using \( \Delta_{\text{Co}}(T) \) obtained from the magnetic susceptibility (see text).

temperature data of each compound. As an example, we show \( \alpha_{\text{ph}} \) for \( \text{NdCoO}_3 \) in figure 1(a); \( \alpha_{\text{ph}} \) of \( \text{EuCoO}_3 \) (\( \text{PrCoO}_3 \); not shown) is slightly larger (smaller). Since a clear separation of \( \alpha_{\text{ph}} \) and \( \alpha_{\text{Sch}} \) is not possible for the low-temperature data of \( \text{LaCoO}_3 \), we used \( \alpha_{\text{ph}} \) of \( \text{EuCoO}_3 \) also for \( \text{LaCoO}_3 \). The resulting \( \alpha_{\text{Sch}} \) of all crystals are shown in figure 1(b). We note that, in particular for \( \text{PrCoO}_3 \) and \( \text{NdCoO}_3 \) the spin-state transition is seen much better in the thermal-expansion data than in the magnetic susceptibility. The reason is that \( \alpha_{\text{ph}} \) is rather small compared to the total thermal expansion, whereas \( \chi \) is dominated by the large contribution of the 4\( f \) moments of the \( \text{Pr}^{3+} \) and \( \text{Nd}^{3+} \) ions, respectively, which makes a further analysis rather uncertain. The insulator-metal transitions occurring above about 500 K, see e. g. [11, 22] also cause anomalies in \( \alpha(T) \). The solid circles in figure 1(b) signal the transition temperatures \( T_{\text{MI}} \), which have been determined from resistivity measurements on our crystals (not shown).

Within the LS/IS scenario with a constant \( \Delta_{\text{Co}} \), \( \alpha_{\text{Sch}}(T) \) is given by [10]

\[
\alpha_{\text{Sch}}(T) = \frac{\gamma \Delta_{\text{Co}}}{T^2} \frac{\nu \exp(-\Delta_{\text{Co}}/T)}{(1 + \nu \exp(-\Delta_{\text{Co}}/T))^2},
\]

(1)

where \( \nu = 3 \) is the degeneracy of the excited spin state and \( \gamma \) is a measure of the ionic radius difference of the \( \text{Co}^{3+} \) in the LS and the excited spin state. Moreover, \( \gamma \) is related to the uniaxial pressure dependence of \( \Delta_{\text{Co}} \) via \( \gamma = k_B/V_{fu} \cdot \partial \Delta_{\text{Co}}/\partial p_{\alpha} \), where \( k_B \) is Boltzmann’s constant, \( V_{fu} \approx 56 \, \text{Å}^3 \) the volume per formula unit and \( p_{\alpha} \) means uniaxial pressure along the direction of which \( \alpha \) is measured [23, 24]. To get the hydrostatic pressure dependence one has to use the volume expansion which in the case of the twinned \( \text{RCoO}_3 \) single crystals is given by 3\( \alpha \). The corresponding fit of \( \alpha \) of \( \text{LaCoO}_3 \) (already presented in [10]) is shown by the solid
line in figure 1(b). The fit parameters are $\Delta_{Co} = 185$ K and $\gamma = 0.007$ giving a hydrostatic pressure dependence $\partial (\ln \Delta_{Co}) / \partial \text{hydr} \approx 45$ %/GPa, in agreement with the increase of $\Delta_{Co}$ of $\approx 42$ % obtained from measurements of $\chi$ under $\approx 1.1$ GPa [25].

For the SOcHS model one has to consider the temperature dependence of $\Delta_{Co}$ [13], which can be calculated from the measured $\chi(T)$ [11]. For LaCoO$_3$, this yields a linear increase $\Delta_{Co}^{HS}(T) = \Delta_{Co}^{0} + a \cdot T$ with $\Delta_{Co}^{0} = 135$ K and $a = 1.66$ in the temperature range almost up to the MI transition. Using this $\Delta_{Co}^{HS}(T)$ in the partition sum, equation (1) modifies to

$$\alpha_{Sch}(T) = \gamma^{HS} \frac{\Delta_{Co}^{0}}{T^2} \frac{\nu \exp(-(\Delta_{Co}^{0} + a \cdot T)/T)}{(1 + \nu \exp(-(\Delta_{Co}^{0} + a \cdot T)/T))}$$

(2)

The corresponding fit of $\alpha_{Sch}$ with $\gamma^{HS}$ as the only free parameter gives the dashed line in figure 1(b). Obviously, both fits hardly differ because the modified $\Delta_{Co}^{HS}$ is compensated by a larger value of $\gamma^{HS} = 0.02$. We note, however, that this does not necessarily correspond to a larger pressure dependence of $\Delta_{Co}^{0}$, because $\alpha_{Sch}$ of equation (2) is determined by the pressure dependencies of $\Delta_{Co}^{0}$ and that of the slope $a$; see e.g. the discussions in [23, 26, 27]. In view of the small differences between both fits for LaCoO$_3$, and since there are no indications for a temperature-dependent $\Delta_{Co}$ from other physical quantities, the fits of $\alpha_{Sch}$ of the other RCoO$_3$ crystals have been done for constant energy gaps only. Since equations (1) and (2) are identical for $a = 0$, this analysis is not able to distinguish between both models. The obtained values of $\Delta_{Co}$ and $\gamma$ are given in table 1. As expected, $\Delta_{Co}$ strongly increases with decreasing radius of the $R^{3+}$ ions and therefore the spin-state transition monotonically shifts to higher temperature. The onset temperature $T_{on}$ of the spin-state transition for each compound, $T_{on} \approx 25, 175, 230$ and 400 K for $R = \text{La, Pr, Nd and Eu}$, respectively, are marked by arrows in figure 1(b).

### 3.2. Thermal conductivity

Figure 2(a) displays the thermal-conductivity data of RCoO$_3$. As has been already found in previous studies on LaCoO$_3$ [17, 18], the overall shape and qualitative behaviour of $\kappa(T)$ is rather unusual. First of all, $\kappa$ is rather low in the whole temperature range and its temperature dependence clearly deviates from the typical behaviour expected for a conventional phononic heat conductor. The thermal conductivity of LaCoO$_3$ exhibits a maximum around 20–30 K. Towards higher temperatures $\kappa$ rapidly drops and features a minimum around 150 K instead of the expected $1/T$-decrease (see also [18]). Qualitatively, this minimum can be traced back to the spin-state transition of LaCoO$_3$, which sets in close to the maximum of $\kappa$. The thermal population of the Co $e_g$ levels induces a certain fraction of Co$^{3+}$ ions with a larger ionic radius compared to the LS Co$^{3+}$ ions. These randomly distributed larger Co$^{3+}$ ions do not only cause the huge anomaly in $\alpha(T)$, but also lead to additional disorder in the lattice and therefore act as additional scattering centers for phonons. Hence, the thermal conductivity is additionally suppressed. A quantitative description will be given below.

Since the spin-state transition shifts to higher temperature when La$^{3+}$ is replaced by smaller $R^{3+}$ ions, the above scenario suggests that the onset of the suppression of $\kappa(T)$ of RCoO$_3$ systematically shifts towards higher temperature with decreasing radius of the $R^{3+}$...
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Figure 2. (a) Thermal conductivity of $RCoO_3$ with $R = La$, Pr, Nd and Eu; the solid line is a fit via equation (3). (b) Thermal conductivity of five different LaCoO$_3$ single crystals S1 – S5 (note the different scale). The inset shows the maximum values of the thermal conductivity $\kappa_{\text{max}}$ of these crystals vs. the saturation values of the magnetization $M_{\text{sat}}$ measured at 2 K. As shown by the solid line, we find an approximate proportionality $\kappa_{\text{max}} \propto 1/M_{\text{sat}}$ (see text).

Let us first consider the data of EuCoO$_3$, which is the compound with the smallest $R^{3+}$ ion and the largest $\Delta_{Co} \gtrsim 2000$ K [11]. Hence, the spin-state transition should not affect the thermal conductivity below room temperature and, indeed, the thermal conductivity of EuCoO$_3$ exhibits much larger values than in LaCoO$_3$. Its low-temperature maximum exceeds that of LaCoO$_3$ by about one order of magnitude. Moreover, the temperature dependence of $\kappa$ of EuCoO$_3$ meets the expectation of a purely phononic heat conductor.

The thermal conductivity of NdCoO$_3$ is lower than $\kappa$ of EuCoO$_3$ in the entire temperature range and, at a first glance, its overall temperature dependence seems to be consistent with a conventional phononic picture, too. A closer inspection of the data yields, however, a slight slope change towards a somewhat steeper decrease of $\kappa(T)$ at $\approx 230$ K, i.e. close to the onset temperature of the spin-state transition, see figure 1 (b). This slope change supports the above proposed explanation that the spin-state transition causes additional scattering centers.

PrCoO$_3$ also exhibits an unusual temperature dependence of $\kappa$, which appears somewhat similar to that of LaCoO$_3$. Above the low-temperature maximum, $\kappa(T)$ rapidly decreases to a small value of $\approx 3.5$ W/Km and remains almost temperature independent between about 80 K and 175 K. Above this temperature a further decrease of $\kappa$ sets in. Since this decrease starts again at the onset of the spin-state transition (see figure 1(b)), it is natural to attribute it to the additional scattering due to the presence of Co$^{3+}$ ions in different spin states. In contrast, the anomalous temperature dependence of $\kappa(T)$ at lower temperature is not related to the spin-state transition and, as will be discussed separately in section 4.2, this anomalous feature is related to the crystal-field splitting of the 4$f$ shell of Pr$^{3+}$.

Summarizing the presented data so far, we observe in all crystals with $T_{\text{on}} < 300$ K that this onset coincides with an additional suppression of $\kappa$. Since $\Delta_{Co}$ strongly increases with decreasing $R^{3+}$ radius [11, 22], $T_{\text{on}}$ also shifts towards higher temperature and the additional
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suppression of the thermal conductivity is less obvious, because at higher temperature the usual suppression of $\kappa$ due to phonon-phonon Umklapp scattering becomes more and more dominant. However, the data in figure 2(a) also show, that $\kappa$ is not only suppressed at temperatures above $T_{\text{on}}$. Instead, with increasing size of $R^{3+}$ a monotonic decrease of $\kappa$ in the entire temperature range is found (here we have neglected the additional suppression of $\kappa$ in Pr$CoO_3$). If the spin-state transition would be the only effect causing additional disorder scattering, $\kappa(T)$ should approach the 'bare' phononic value below $T_{\text{on}}$. Taking Eu$CoO_3$ with stable LS Co$^{3+}$ ions up to above room temperature as a rough measure for this 'bare' phononic heat conduction, it becomes clear that this expectation is not observed in our data.

In general, the magnitude of the low-temperature maximum of $\kappa$ depends on the sample quality, which determines the maximum free path. Thus, the different values within the $RCoO_3$ series could arise from different sample qualities. However, there is no indication for a systematic increase of the crystal quality with decreasing $R^{3+}$ ion radius. In order to study a possible influence of the crystal quality, we measured $\kappa$ of five different La$CoO_3$ single crystals. As shown in figure 2(b) the high-temperature behaviour is essentially the same for all crystals, but the low-temperature maxima differ considerably. Nevertheless, all of them remain much lower than that of Eu$CoO_3$. We relate the low-temperature maxima of $\kappa$ to the defect concentrations by considering the low-temperature magnetization, since a really pure La$CoO_3$ with all Co$^{3+}$ ions in the LS state would be non-magnetic (apart from core dia- and van Vleck paramagnetism). At $\approx 2$ K we measured magnetization up to 14 Tesla in order to reach its saturation $M_{\text{sat}}$, which is a measure of the content of magnetic impurities. The inset of figure 2 displays the low-temperature maxima of $\kappa(T)$ vs. $M_{\text{sat}}$, which indeed roughly follow a $1/M_{\text{sat}}$ dependence as shown by the solid line.

The most likely source for magnetic impurities in La$CoO_3$ is a weak oxygen nonstoichiometry, which changes the average valence from Co$^{3+}$ towards Co$^{2+}$ or Co$^{4+}$. Due to the odd number of $3d$ electrons, the latter are magnetic in all possible electronic configurations, but in most cases Co$^{2+}$ and Co$^{4+}$ realize $t^5_2 e^2_0$ and $t^5_2 e^0_0$ states with spin $S = 3/2$ and $S = 1/2$, respectively. Experimental evidence for a weak charge-carrier doping in nominally pure La$CoO_3$ stems from the large values of different signs of the room-temperature thermopower for the different La$CoO_3$ crystals; cf. table [1] and the discussion in [18]. From magnetization data on Sr-doped La$CoO_3$ it is known that low doping concentrations induce so-called high-spin polarons with effective spin values up to $S = 16$ [28]. Such polarons are formed around the doping-induced Co$^{4+}$ ions, which cause a spin-state transition in the adjacent Co$^{3+}$ ions. Most probably, this is a transition from the LS to an IS state, because the electronic configuration $t^5_2 e^1_1$ of Co$^{3+}$ is favourable for the hopping of the $e_g$ electron for both kinds of neighbours, Co$^{4+}$ with $t^5_2 e^0_0$ and Co$^{2+}$ with $t^5_2 e^2_2$. Other possible configurations often only allow a $t^3_2$ hopping or may cause the so-called spin-blockade effect [29, 30].

§ One may speculate that the low-temperature maximum of $\kappa$ is also influenced by twinning. All these single crystals are twinned, but it seems plausible that the average size of the twin domains increases from La$CoO_3$ to Eu$CoO_3$, because the deviation from the cubic symmetry increases. However, the observed correlation between $\kappa_{\text{max}}$ and the magnetic impurity concentration for the different La$CoO_3$ crystals, makes it rather unlikely to explain the different low-temperature maxima of $\kappa$ in terms of different domain sizes.
formation of high-spin polarons will depend on $\Delta_{Co}$ between the LS ground state and the excited spin state of Co$^{3+}$. Since $\Delta_{Co}$ strongly increases with decreasing $R^{3+}$ radius, the occurrence of such polarons in the $R$CoO$_3$ series should get more and more unlikely for smaller $R^{3+}$ ions. Unfortunately, the presence of high-spin polarons in PrCoO$_3$ and NdCoO$_3$ cannot be studied by magnetization measurements because of the strong magnetism of the partially filled 4$f$ shells of Pr$^{3+}$ and Nd$^{3+}$. For EuCoO$_3$ such an analysis is again easier, because Eu$^{3+}$ only exhibits van Vleck paramagnetism and, in fact, the impurity contribution to the magnetic susceptibility in EuCoO$_3$ is one order of magnitude smaller than in LaCoO$_3$ [11].

Moreover, the magnetic impurity contribution of the La$_{1-x}$Eu$_x$CoO$_3$ series systematically decreases with increasing $x$, i.e. with decreasing average ionic size on the La site and with increasing $\Delta_{Co}$ [11]. These observations strongly support the above idea that the systematic dependence of the low-temperature thermal conductivity of $R$CoO$_3$ on the ionic size of $R^{3+}$ is related to phonon scattering by high-spin polarons, whose formation depend on a weak oxygen-nonstoichiometry and on $\Delta_{Co}$.

4. Quantitative analysis of the thermal conductivity

For a quantitative analysis of the thermal conductivity we use an extended Debye model [31]

$$\kappa(T) = \frac{k_B T^3}{2\pi^2 \hbar v_s} \int_0^{\theta_D/T} \tau(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (3)$$

Here, $\Theta_D$ denotes the Debye temperature, $v_s$ the sound velocity, $\omega$ the phonon frequency, $x = \hbar \omega/k_BT$ and $\tau(x, T)$ the phonon relaxation time. The scattering rates of different independent scattering mechanisms sum up to a total scattering rate

$$\tau^{-1}(x, T) = \tau_{bd}^{-1} + \tau_{pt}^{-1} + \tau_{um}^{-1} = \frac{v_s}{L} + P \omega^4 + U T \omega^3 \exp(\frac{\Theta_D}{uT}). \quad (4)$$

The three terms on the right-hand side refer to the typical scattering rates for phonon heat transport in insulators, namely boundary ($\tau_{bd}$; $L = 1$ mm is the characteristic length scale of the sample [32] and was kept fixed for all crystals), point defect ($\tau_{pt}$) and phonon-phonon Umklapp scattering ($\tau_{um}$). Since the lattice spacing is a natural lower limit for the mean-free path, $\kappa(T)$ is expected to approach a minimum value at higher temperatures. In order to model this, $\tau(x, T)$ in equation (4) is replaced by $\max(\tau_{\Sigma}(x, T), \ell_{min}/v_s)$ with the minimum mean-free path $\ell_{min}$ being of the order of the lattice constant; compare the discussion in [33].

As shown by the solid line in figure 2, the thermal conductivity data of EuCoO$_3$ can be reproduced reasonably well by equation (3). In order to reduce the number of adjustable parameters, we used $\Theta_D = 600$ K and $v_s = 3900$ m/s determined for LaCoO$_3$ [21, 34]. The other parameters have been adjusted to fit the experimental data. We obtain $P = 3.7 \cdot 10^{-43}$ s$^3$, $U = 4.9 \cdot 10^{-31}$ s$^2$/K and $u = 7.6$; $\ell_{min}$ is not reached in EuCoO$_3$ up to 300 K.

4.1. Scattering related to the spin-state transition

In the following analysis we consider the thermal conductivity of EuCoO$_3$ as the bare phononic heat conductivity that is not influenced by the spin-state transition. For the other
members of the \( RCoO_3 \) series we introduce an additional scattering mechanism arising from
the thermal occupation of the \( Co^{3+} \) \( e_g \) shells, which causes additional lattice disorder due to
the presence of smaller and larger \( Co^{3+} \) ions in the LS and the excited spin state, respectively.
Considering the \( Co^{3+} \) ions of different sizes as point-like defects, we assume an \( \omega^4 \) frequency
dependence for this additional scattering rate (cf. equation (4))

\[
\tau_{\text{dis}}^{-1} = C \cdot f(T) \cdot \omega^4, \tag{5}
\]

where \( C \) is an adjustable parameter describing the scattering strength and \( f(T) \) models the
temperature dependence of the additional lattice disorder.

The unknown functions \( C \cdot f(T) \) for \( LaCoO_3 \), \( PrCoO_3 \) and \( NdCoO_3 \) can be calculated
from the experimental data in the following way: we use equation (4) with all the parameters
obtained from the fit of \( \kappa \) of \( EuCoO_3 \) kept fix and add \( \tau_{\text{dis}}^{-1} \). Then the total \( \tau \) is used in
equation (3) and the values of \( C \cdot f(T) \) at each temperature are determined point by point
from the measured \( \kappa(T) \). The resulting \( C \cdot f(T) \) curves for all three \( RCoO_3 \) samples are shown by
the open symbols in figure 3. In order to avoid additional complications arising from the
aforementioned high-spin polarons, we restrict the analysis to the temperature range above
\( \approx 25 \text{ K} \). For \( LaCoO_3 \) the resulting \( C \cdot f(T) \) has a pronounced maximum around \( 100 \text{ K} \), and
strongly resembles the temperature dependence of the magnetic susceptibility of \( LaCoO_3 \).
Here, we have used Sample S2 which exhibits the highest value of the low-temperature
maximum of \( \kappa \), i.e. the sample which is least affected by impurity scattering. We note,
however, that in the considered temperature range above \( 25 \text{ K} \) the resulting \( C \cdot f(T) \) is not
very different for the other \( LaCoO_3 \) crystals. For \( PrCoO_3 \), \( C \cdot f(T) \) features a clear maximum
followed by a slope change around \( 175 \text{ K} \). The obtained values of \( C \cdot f(T) \) for \( NdCoO_3 \) are
much lower than those of \( LaCoO_3 \) and \( PrCoO_3 \) and there is no maximum, but again a clear
slope change around \( T_{\text{on}} \approx 230 \text{ K} \). Thus, we find in all three \( RCoO_3 \) compounds either an
increase of \( C \cdot f(T) \) or a slope change towards larger values at temperatures close to the
respective onset temperatures of the spin-state transition; see figure 1.

In order to model the additional scattering rate we use the so-called Nordheim rule [35],
which is a successful approach to describe \( \kappa \) in disordered mixed alloys. There, the additional
scattering rate is proportional to \( x(1 - x) \), with \( x \) being the fraction of one of the constituents.
In the present case this corresponds to the fractions \( n_{\text{HS/LS}} \) of \( Co^{3+} \) ions in the higher and
\( n_{\text{LS}} = (1 - n_{\text{HS/LS}}) \) in the LS state. Thus, the temperature dependence of the additional scattering
rate of equation (5) is expected to be given by (see equations (1) and (2))

\[
f(T) = \frac{\nu \exp(-\Delta_{Co}(T)/T)}{(1 + \nu \exp(-\Delta_{Co}(T)/T))^2}. \tag{6}
\]

The solid line in figure 3(a) corresponds to a calculation of \( C \cdot f(T) \) via equation (6)
using the temperature-independent \( \Delta_{Co} = 185 \text{ K} \) of the LS–IS scenario. Here, \( C \) is the
only adjustable parameter, and for \( C = 5.9 \cdot 10^{-40} \text{ s}^3 \) this model yields a good description
of the experimental data in the temperature range from 30 K to 150 K. The dashed line shows
the corresponding fit (yielding \( C = 11 \cdot 10^{-40} \text{ s}^3 \)) for the same temperature range based on
the SOcHS scenario with a temperature-dependent \( \Delta_{Co}(T) \), which is in reasonable agreement
with the data, too. Obviously, both models are not able to describe the decrease of \( f(T) \) above
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Figure 3. Open symbols denote the experimentally obtained additional scattering rates $C \cdot f(T)$, which are needed to suppress $\kappa$ from a hypothetical bare phonon heat conductivity represented by $\kappa$ of EuCoO$_3$ to the measured values of $\kappa$ of LaCoO$_3$, PrCoO$_3$ and NdCoO$_3$ (see text for details). In all three $\text{RCO}_3$ an additional scattering sets in above the respective onset temperature $T_{on}$ (marked by the arrow in each panel) of the spin-state transition. The lines show the expected additional scattering rates due to the spin-state transition for a LS/IS scenario (solid) and for the SOcHS model (dashed); see equations (5) and (6). In panel (a) the scattering strengths $C$ for each model have been adjusted by fitting the lines to the experimental data in the temperature range below 150 K. These values have been kept fixed to calculate the lines in panels (b) and (c), and, as shown by the solid symbols, the additional scattering above $T_{on}$ completely vanishes, when these lines are subtracted from the experimental $C \cdot f(T)$.

150 K. This disagreement does, however, not contradict the models, because for $T \gtrsim 150$ K the measured $\kappa$ of LaCoO$_3$ is already close to its minimum value arising from the aforementioned lower limit of the mean-free path. For $C \cdot f(T)$ of PrCoO$_3$ and NdCoO$_3$, we keep the values of $C$ fixed and use the gap values $\Delta_{\text{Co}} = 1200$ K and $\Delta_{\text{Co}} = 1700$ K obtained from the analysis of $\alpha(T)$, cf. table 1. The corresponding curves, which for the different models only differ in the scattering strengths, are shown as solid and dashed lines in Figs.3(b) and (c). When we subtract these lines from the experimental data, the slope changes around $T_{on}$ completely vanish, as is shown by the solid symbols in Figs.3(b) and (c). This gives further evidence that the spin-state transition is indeed responsible for the suppression of the thermal conductivity of PrCoO$_3$ and NdCoO$_3$ as it is the case for LaCoO$_3$.

Encouraged by this finding we tried to fit the thermal conductivity of LaCoO$_3$ via equation (3) including the additional scattering rate given by equations (5) and (6) in equation (4). Again, we restrict our analysis to $T \gtrsim 25$ K and keep most of the fit parameters fixed to their values as obtained from the Debye fit of the bare phononic $\kappa$ of EuCoO$_3$. From these parameters, we only readjust the prefactor $P$ of the point-defect scattering term in equation (4), because the number of point defects varies in different crystals, and point-defect scattering also reduces $\kappa$ at high temperatures. In addition, the scattering strength $C$ is readjusted, but changes only little (to $C = 6 \cdot 10^{-40}$ s$^3$ and $12 \cdot 10^{-40}$ s$^3$ for the LS/IS and the SOcHS model, respectively), and we consider the minimum mean-free path $\ell_{\text{min}}$. The results for the LS–IS as well as the SOcHS model are displayed in figure 4. Both models describe...
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Figure 4. Thermal conductivity (symbols) of LaCoO$_3$ with fits based on equation (3) assuming (a) the LS–IS or (b) the SOcHS model for the spin-state transition. The dashed (solid) lines are obtained when a minimum mean-free $\ell_{\text{min}}$ is (is not) taken into account (see text).

the thermal conductivity well over a large temperature range of about 200 K, in particular, when the minimum mean-free path is taken into account. As was already seen in figure 3 the quality of the fits based on the different models hardly differs. Therefore, the analysis of the thermal conductivity of RCoO$_3$ does not allow to judge, whether the LS/IS or the SOcHS scenario is preferable.

4.2. Scattering related to crystal-field excitations

Next we consider the additional suppression of $\kappa$ of PrCoO$_3$ below $T_{\text{on}}$, which is not related to the spin-state transition. As can be seen in figure 1 the thermal expansion of this compound also exhibits an additional anomaly at lower temperatures. This anomaly arises from the crystal-field splitting of the 4$f$ shell of the Pr$^{3+}$ ions. In an orthorhombic crystal field the $^3H_4$ multiplet of the free Pr$^{3+}$ ion splits into nine singlets. We are not aware of experimental investigations of the crystal-field splitting in PrCoO$_3$, but it is known that the crystal-field levels of other orthorhombic PrA$_3$O$_3$ are very similar [36, 37, 38]. Only the lower levels slightly depend on the exact orthorhombic distortion, which is mainly characterized by the $A-O-A$ canting angle. The energy splitting between the crystal-field ground state and the first excited level in PrCoO$_3$ can be determined from a fit of the low-temperature thermal expansion by a Schottky anomaly. As shown in figure 5(a), such a fit for two non-degenerate levels (setting $\nu = 1$ and replacing $\Delta_{\text{CF}}$ by $\Delta_{\text{CF}}$ in equation (1)) describes the experimental data well and yields $\Delta_{\text{CF}} = E_1 = 70$ K and $\gamma = 0.056 \%$. For the higher-lying energy levels we use the values $E_2 = 151$ K, $E_3 = 174$ K, $E_3 = 235$ K, ... of PrNiO$_3$ [38], which has almost the same $A-O-A$ canting angle as PrCoO$_3$. We note here that the thermal population of these higher-lying levels may contribute to $\alpha(T)$ at higher temperatures, but below about 50 K the two-level system used is sufficient to model the experimental data.

The most likely source for the suppression of the thermal conductivity of PrCoO$_3$ in the intermediate temperature range is resonant scattering between different 4$f$ crystal-field
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Figure 5. Low-temperature (a) thermal expansion and (b) thermal conductivity of PrCoO$_3$. The thermal-expansion data (symbols) in panel (a) are well described by a Schottky anomaly (line) of a two-level system with non-degenerate levels with energy splitting $E_1 - E_0 = 70$ K. The lines F01, F02 and F12 in panel (b) are fits for $T > 20$ K to the thermal conductivity data (symbols) including either the resonant scattering process $E_0 \leftrightarrow E_1$, $E_0 \leftrightarrow E_2$ or $E_1 \leftrightarrow E_2$, respectively. A sketch of the energy levels is also included [38].

levels, as it is also known from e.g. rare-earth garnets [39]. In such a resonant scattering process a phonon is absorbed by inducing a transition between different energy levels and then re-emitted in an arbitrary direction (see e.g. [40, 41]), causing an additional thermal resistance. A mechanism based on random volume changes as discussed above for the spin-state transition of Co$^{3+}$ is unlikely because the 4$f$ orbitals are inner shells. This difference is directly reflected in the magnitudes of the Schottky peaks, which are mainly determined by the underlying volume change. The low-temperature peak in $\alpha$ of PrCoO$_3$ is e.g. one order of magnitude smaller than that of LaCoO$_3$; see figure 1 and [1].

In order to model $\kappa(T)$ in the low-$T$ range we include the rate

$$\tau_{\text{res}}^{-1} = R \frac{4\omega^4 \Delta_{\text{CF}}^4}{(\Delta_{\text{CF}}^2 - \omega^2)^2} \cdot (N_i + N_j)$$

in equation (4) describing a direct resonant scattering process [40, 42]. Here, $\Delta_{\text{CF}} = |E_i - E_j|$ is the energy difference between the two levels, and $N_i, N_j$ denote their population determined by the partition sum. For the fit we keep again $\Theta_D = 600$ K and $v_s = 3900$ m/s, while $P, U, u$ and $R$ are adjusted with respect to the data. The fits have been restricted to $T \geq 20$ K, since other processes may become dominant at very low temperatures.

In a first attempt, resonant scattering between $E_0$ and the first excited level $E_1$ is considered, yielding the fit labelled F01 in figure 5(b). This fit only reproduces the data for $T \geq 100$ K but totally misses the low-temperature maximum in $\kappa(T)$. Basically the same result is achieved by considering the process $E_0 \leftrightarrow E_2$ (curve F02 in figure 5(b)). A much better description of the data is obtained, however, for the process $E_1 \leftrightarrow E_2$ (curve F12; with parameters $P = 5 \cdot 10^{-43}$ s$^3$, $U = 4.85 \cdot 10^{-18}$ s$^2$/K, $u = 5$ and $R = 3.8 \cdot 10^{-40}$ s$^3$). Hence, the
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transition $E_1 \leftrightarrow E_2$ appears to be the dominant scattering channel of the phonons in PrCoO$_3$ at intermediate temperatures.

5. Summary

In this paper we have presented measurements of the thermal-expansion coefficient and the thermal conductivity of $RCoO_3$, with trivalent $R =$ La, Pr, Nd and Eu. As a consequence of the chemical pressure due to the decreasing ionic radius from $R =$ La to Eu, the energy gap between the LS ground state and the first excited spin state of the Co$^{3+}$ ions increases drastically and the temperature-induced spin-state transition of the Co$^{3+}$ ions is systematically shifted towards higher temperature. This strong pressure dependence is also reflected in pronounced Schottky anomalies in the thermal-expansion coefficients, making this quantity a sensitive probe to analyze spin-state transitions. The microscopic origin of the pressure dependence is the volume change due to the partial occupation of the $e_g$ levels of the Co$^{3+}$ ions in the excited spin state in contrast to the empty $e_g$ levels of LS Co$^{3+}$ ions. Another consequence of this volume difference is a strong suppression of the phonon heat transport, which sets in above the onset temperature of the spin-state transition, because the random occupation of the Co sites with Co$^{3+}$ ions in different spin states, i.e. of different sizes, causes additional lattice disorder. By considering this disorder as point-like defects, our analysis clearly shows this effect in the temperature dependence of the corresponding scattering rates of LaCoO$_3$, PrCoO$_3$ and NdCoO$_3$, where the spin-state transition sets in below room temperature, in contrast to EuCoO$_3$ which exhibits a stable LS state up to about 400 K.

Quantitatively, the temperature dependence of the additional scattering due to the spin-state transition can be described in a model based on the Nordheim rule, which is usually applied to describe scattering in disordered mixed alloys. For the cobaltates, this means that the temperature dependence of this additional scattering rate is given by the product of the occupation numbers of the LS and of the excited spin states. Moreover, we find that the scattering strength is constant for LaCoO$_3$, PrCoO$_3$ and NdCoO$_3$. Our analysis does, however, not allow to distinguish between the different models discussed for the spin-state transition in LaCoO$_3$, namely a LS – IS scenario with a temperature-independent energy gap or the more recently proposed model based on a spin-orbit coupled high-spin state with a temperature-dependent energy gap.

The above described model explains a damping of the phonon heat transport above the onset temperature of the spin-state transition. Experimentally, however, we find that as a function of increasing size of the $R^{3+}$ ions the thermal conductivity decreases also in the temperature range below the respective onset of the spin-state transition. By studying five different LaCoO$_3$ single crystals, we could show that the low-temperature thermal conductivity inversely scales with the amount of magnetic impurities. Most likely, these impurities arise from a weak oxygen nonstoichiometry giving rise to a certain amount of Co$^{2+}$ or Co$^{4+}$ ions. Since it is known that these magnetic Co ions tend to form so-called high-spin polarons by inducing a spin-state transition in the neighbouring Co$^{3+}$ ions, our data suggest that the phonon damping at low temperature arises from such a doping-induced spin-
state transition. The drastic increase of the energy gap to the excited spin state of Co$^{3+}$ for decreasing $R^{3+}$ ionic radii makes the formation of spin polarons more and more unlikely, and thus can naturally explain the systematic increase of the thermal conductivity in the temperature range below the temperature-induced spin-state transition.

Additional low-temperature features have to be considered in PrCoO$_3$, because the thermal expansion exhibits another Schottky anomaly and there is an additional suppression of the thermal conductivity. Both effects are not related to the temperature-dependent spin-state transition of Co$^{3+}$, but stem from the crystal-field splitting of the ground-state multiplet of the 4$f$ shell of Pr$^{3+}$. Our analysis demonstrates that the Schottky anomaly of the thermal expansion arises from a thermal occupation of the first excited crystal-field level, whereas the phonon damping is a consequence of resonant phonon scattering between the first two excited crystal-field levels.

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