# Thermal Conductivity Anomalies of RECoO₃ (RE = La–Nd) Related to Valency and Spin State of Co Ion

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The thermal conductivities $\kappa(T)$ of Co- and La-site-substituted $LaCoO_3$ were measured and the origin of the $\kappa(T)$ peak was investigated. The sharp $\kappa(T)$ peak at approximately 30 K is strongly suppressed by the introduction of a small amount of Jahn–Teller (JT)-active $Co^{4+}$ ions because of Co-site substitution by divalent ions such as $Ni^{2+}$ and $Cu^{2+}$, similarly to the La-site substitution by $Sr^{2+}$. In contrast, the $\kappa(T)$ peak of samples with the Co-site substituted by tetravalent ions such as $Sn^{4+}$ and $Zr^{4+}$, which introduce $Co^{2+}$ ions, moderately decreased. The temperature at which a small and broad $\kappa(T)$ peak in the Pr-containing $RECoO_3$ [rare-earth (RE) = $La_{1-y}Pr_y$ and $Pr_{1-z}Nd_z$] is also observable shifts from 110 K for RE = $La_{0.5}Pr_{0.5}$ to 180 K for RE = Pr and $Pr_{0.5}Nd_{0.5}$, which corresponds to the spin-state transition temperature of $Co^{3+}$ ions.

## 1. Introduction

The perovskite oxide $LaCoO_3$ has been studied intensely during the last 40 years because of its unique magnetic behavior and the related insulator–metal transition. The ground state is known to be nonmagnetic, corresponding to a low-spin (LS) state of $Co^{3+}$ ions ($t_{2g}^6 e_g^0$, $S = 0$). With increasing temperature, a paramagnetic state appears at about $T = 80$–120 K and another magnetic state takes place at $T = 400$–600 K with an insulator-to-metal transition. The low-temperature magnetic transition was originally interpreted in terms of the gradual increase of the population of the $Co^{3+}$ high-spin (HS) state ($t_{2g}^4 e_g^2$, $S = 2$).[1] Another interpretation was proposed in the second half of the 1990s, in which the low-temperature magnetic transition was attributed to a transition from an LS state to an intermediate-spin (IS) state ($t_{2g}^5 e_g^1$, $S = 1$).[2] This interpretation was supported by descriptions in many papers.[3–6] However, no studies have definitively shown that the excited state is the IS state. Recent measurements indicate that it might still be the HS state,[7–10] and the mechanism and even the spin state of the excited state remain controversial. For the $RECoO_3$ system (RE: rare-earth) with a smaller $RE^{3+}$ ion such as $Pr^{3+}$ or $Nd^{3+}$, the LS state of $Co^{3+}$ is stabilized up to higher temperatures, as confirmed by the extrinsic pressure effect using $LaCoO_3$[11] and the chemical pressure effect using $(La_{1-y}Pr_y)CoO_3$.[12]

Yan *et al.* reported the temperature dependence of the thermal conductivity $\kappa(T)$ and the magnetic susceptibility $\chi(T)$ for single crystals of $RECoO_3$ (RE = La, Pr, Nd).[13] The $\kappa(T)$ of $LaCoO_3$ has a sharp peak at approximately $T = 20$ K and decreases rapidly with increasing temperature. The sharp $\kappa(T)$ peak was shown to result from the spin-state transition from LS to IS (or HS) in $Co^{3+}$ ions; i.e., the IS (or HS) $Co^{3+}$ ions introduced a local lattice distortion in the LS $Co^{3+}$ network because of the larger ionic radius than that of the LS $Co^{3+}$ ions. Because the IS $Co^{3+}$ ions are Jahn–Teller (JT)-active ions, phonon scattering might be further en-

hanced by their introductions. The $\kappa(T)$ of $PrCoO_3$ resembles that of $LaCoO_3$ with a sharp suppression at temperatures greater than 30 K, and that of $NdCoO_3$ shows a $1/T$ temperature dependence, which originates from a phonon–phonon scattering mechanism, as can be sometimes seen in ordinary solids. Because the spin-state transition from LS to IS (or HS) was estimated to be at 180 K for $PrCoO_3$, the $\kappa(T)$ peak of $PrCoO_3$ is not related to a spin-state transition. At present, the origin of the $\kappa(T)$ peak has not been clarified for $PrCoO_3$. Furthermore, the influences of the $Co^{4+}$ and $Co^{2+}$ ions on phonon scattering in perovskite cobaltites such as $RE_{1-X}Sr_XCoO_3$ and $RECoO_{3-\delta}$ have not been investigated systematically. It is necessary to investigate the origin of the $\kappa(T)$ peak in $RECoO_3$ and the influence of the JT-active ion on the phonon scattering.

In the present study, we systematically investigate the effect of the valency and/or the spin state of Co ions on the phonon thermal conductivity $\kappa(T)$ in perovskite cobaltites. First, we measure the $\kappa(T)$ of $LaCoO_3$ and $La(Co_{0.98}M_{0.02})O_3$. The effect of substitution at the Co site by various valence cations M is examined, including phonon scattering by the substituted cation M itself, to determine whether they are JT-active ions or not. Second, we measure the $\kappa(T)$ of $RECoO_3$ with various ionic radii for samples with Pr contained in the RE site (RE = $La_{1-y}Pr_y$ and $Pr_{1-z}Nd_z$). The relation between the $\kappa(T)$ anomaly and the spin-state transition of the $Co^{3+}$ ions is systematically investigated.

## 2. Experimental Procedure

All the samples used in this study are polycrystals prepared by a solid-state reaction. In $LaCoO_3$ and $La(Co_{0.98}M_{0.02})O_3$ (M: $Ni^{2+}$, $Cu^{2+}$, $Ga^{3+}$, $Cr^{3+}$, $Zr^{4+}$, $Sn^{4+}$), mixtures of raw powders of $La_2O_3$, $Co_3O_4$, and the respective oxides containing M ions were calcined at 1000 °C for 24 h in air, pressed into pellets, and then sintered at 1400 °C for 8 h in air.[14] In addition, $RECoO_3$ (RE = $La_{1-y}Pr_y$ and $Pr_{1-z}Nd_z$) and $La_{1-X}Sr_XCoO_3$ ($0.005 \leq X \leq 0.02$) were fabricated using the same procedure. The measured densities of the samples were about 90% of the ideal values. X-ray

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diffraction analyses at room temperature confirmed the single phase in the crystal structure for the samples except for $La_{0.5}Pr_{0.5}CoO_3$, which mostly comprised the orthorhombic *Pnma* phase but also contained a small amount of the rhombohedral $R\bar{3}c$ phase, as suggested in ref. 12. Thermal conductivity $\kappa(T)$ was measured using a steady-state heat-flow method. To detect the spin-state transition, a linear thermal expansion, $dL(T)/L(20\,K) = [L(T) - L(20\,K)]/L(20\,K)$, based on the sample length $L$ at 20 K, or a thermal expansion coefficient $\alpha(T)$, which was defined as the temperature derivative $dL(T)/L(20\,K)$, was determined using a strain-gauge method (Kyowa KFL-1-120-C1-16). Measurements of $\kappa(T)$ and $dL(T)/L(20\,K)$ were performed using a GM cycle helium refrigerator. Magnetization $M(T)$ was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) under a field of 0.5 T after zero-field cooling.

## 3. Results and Discussion

### 3.1 Effect of La-site substitution in LaCoO₃ on thermal conductivity κ(T)

Figure 1(a) shows the temperature dependence of the thermal conductivity $\kappa(T)$ of $(La_{1-X}Sr_X)CoO_3$ and $(La_{0.98}M_{0.02})CoO_3$ (M = $Pr^{3+}$, $Nd^{3+}$) samples. Because all the samples measured in this study are insulators, the heat is carried by acoustic phonons ($\kappa = \kappa_{ph}$). The $\kappa(T)$ of $LaCoO_3$ has a large peak of 80 mW/(cm·K) at approximately 30 K, drops sharply to a low value with increasing temperature, and subsequently increases slightly up to 300 K. The sharp $\kappa(T)$ peak was strongly suppressed by the substitution at only 0.5% of the La site by $Sr^{2+}$ and was completely removed by 2% substitution. In general, crystal disorder is introduced in a lattice by element substitution. As a result, the thermal conductivity is suppressed in the entire temperature range. However, it is difficult to infer that the reduction of the $\kappa(T)$ peak in $La_{0.995}Sr_{0.005}CoO_3$ results from the lattice disorder, because the $\kappa(T)$ peak of the samples in which 2% of La sites were substituted by $Pr^{3+}$ and $Nd^{3+}$ was not reduced. Either LS or IS $Co^{4+}$ ions are introduced, both of which have different ionic radii from that of $Co^{3+}$, when the $Sr^{2+}$ ions are substituted at the $La^{3+}$ site depending on the amount of $X$ in $La_{1-X}Sr_XCoO_3$. The disappearance of the $\kappa(T)$ peak suggests the existence of a powerful phonon-scattering center that is only effective at low temperatures. The scattering center as above must be large, because the phonon wavelength is also large at low temperatures. Phelan *et al.* suggested the existence of $Co^{4+}$(LS)–$6Co^{3+}$(IS) clusters from the results of an elastic neutron scattering study on $La_{1-X}Sr_XCoO_3$.[15] $Co^{4+}$(LS) ions with the $t_{2g}^5 e_g^0$ configuration are also JT-active in the $t_{2g}$ level and might be accompanied by a local lattice distortion. Moreover, the lattice distortion might be strongly enhanced because of the cluster nature. For these reasons, the cluster model is a possible explanation for the powerful phonon scattering.

Figure 1(b) shows the temperature dependence of the thermal expansion coefficient $\alpha(T)$ of $La_{1-X}Sr_XCoO_3$. For the $LaCoO_3$ sample, an anomalous thermal expansion takes place at $T > 35\,K$, which results from the spin-state transition of $Co^{3+}$ ions from LS to IS (or HS) with increasing temperature. Because the spin-state transition involves electron transfer from a $t$ orbital to an $e$ orbital and causes an
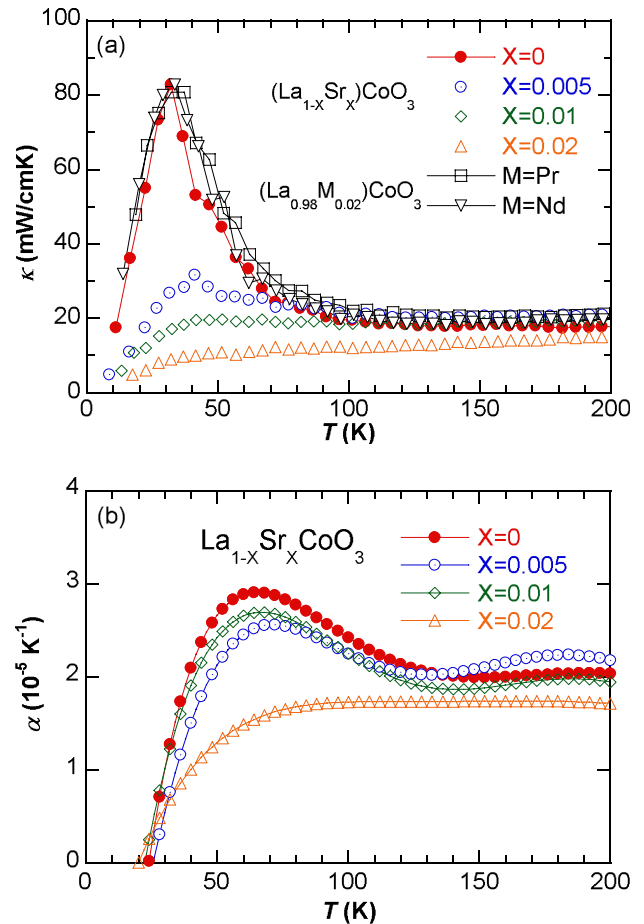


Fig. 1. (Color online) (a) Temperature dependence of the thermal conductivity $\kappa(T)$ of $La_{1-X}Sr_XCoO_3$ ($0 \leq X \leq 0.02$) and $La_{0.98}M_{0.02}CoO_3$ (M = $Pr^{3+}$, $Nd^{3+}$). (b) Temperature dependence of the thermal expansion coefficient $\alpha(T)$ of $La_{1-X}Sr_XCoO_3$ ($0 \leq X \leq 0.02$).

ionic size change of the octahedral-site $Co^{3+}$ ion; the ionic radius of LS $Co^{3+}$ was reported to be 0.545 Å, whereas IS and HS $Co^{3+}$ have larger radii of 0.56 and 0.61 Å, respectively.[16] For $X = 0.005$ and 0.01, a clear enhancement of $\alpha(T)$ was also observed at temperatures greater than 35 K because of the LS → IS (or HS) spin-state transition, and the transition becomes broad for $X = 0.02$. Asai *et al.* measured the temperature dependence of the lattice constant for $La_{1-X}Sr_XCoO_3$ ($X = 0$, 0.08).[17] For the $X = 0$ sample, an abrupt increase in the lattice constant took place above 50 K. Similar results for the values of $\alpha(T)$ were also reported by Zobel *et al.*[18]

### 3.2 Effect of Co-site substitution effect in LaCoO₃ on thermal conductivity κ(T)

The explanation in the preceding subsection demonstrated that the $\kappa(T)$ peak in $LaCoO_3$ is strongly suppressed by the introduction of the $Co^{4+}$ LS (or IS) ions because of the La-site substitution by $Sr^{2+}$. In this subsection, the measured thermal conductivity of $La(Co_{0.98}M_{0.02})O_3$ with various valence cations of M is reported and the influence of the introduction of various valence Co ions on $\kappa(T)$ is discussed. Figures 2(a) and 2(b) respectively show the thermal conductivity $\kappa(T)$ and the magnetization $M(T)$ of $La(Co_{0.98}M_{0.02})O_3$ (M: $Ni^{2+}$, $Cu^{2+}$, $Ga^{3+}$, $Cr^{3+}$, $Zr^{4+}$, $Sn^{4+}$). The $\kappa(T)$ peak was maintained upon the Co-site
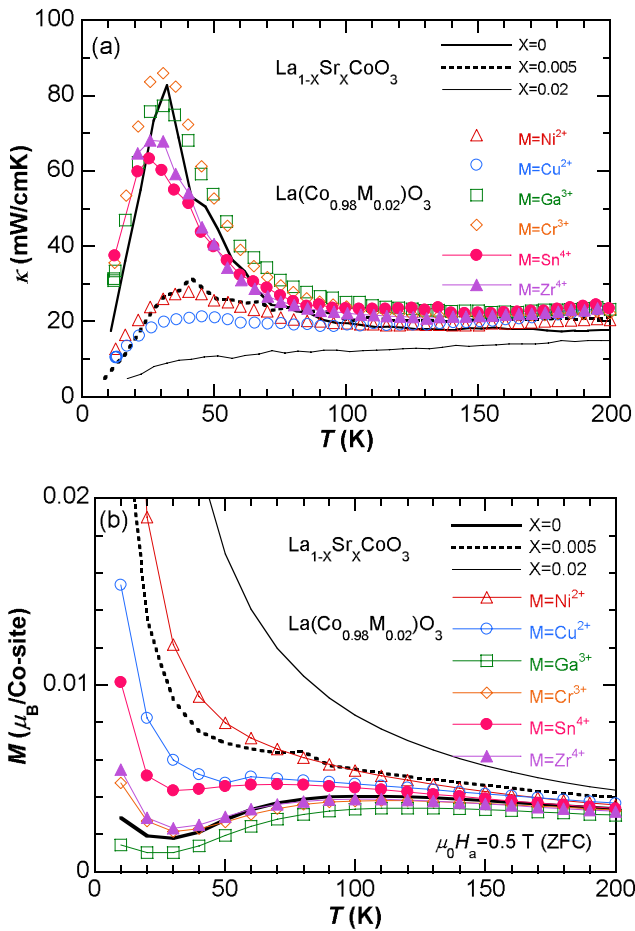
Fig. 2. (Color online) Temperature dependence of the (a) thermal conductivity $\kappa(T)$ and (b) magnetization $M(T)$ of $La(Co_{0.98}M_{0.02})O_3$ for various M ions (M = $Ni^{2+}$, $Cu^{2+}$, $Ga^{3+}$, $Cr^{3+}$, $Sn^{4+}$, $Zr^{4+}$) under an applied field of $\mu_0 H_a = 0.5$ T after zero field cooling. For comparison, the $\kappa(T)$ and $M(T)$ of $La_{1-X}Sr_XCoO_3$ ($X = 0$, 0.005, and 0.02) are also shown.

substitution by M = $Ga^{3+}$ and $Cr^{3+}$, and $M(T)$ showed similar behavior to that of $LaCoO_3$. These results suggest that the lattice disorder attributable to the 2% Co-site substitution by the trivalent ions in $LaCoO_3$ does not influence the behaviors of $\kappa(T)$ and $M(T)$ and that the $Co^{3+}$ LS state is maintained. Regarding the $\kappa(T)$ behavior of $La(Co_{0.98}Cr_{0.02})O_3$, it is possible that the Cr ions are substituted for Co ions as $Cr^{4+}$ ($t_{2g}^2 e_g^0$; non-JT) and that, as a result, HS-$Co^{2+}$ ions ($t_{2g}^5 e_g^2$; non-JT; $S = 3/2$) are created, which would explain the unchanged $\kappa(T)$ peak. However, the behavior of $M(T)$ cannot be explained using this scenario. Consequently, the Cr ion should be substituted at the Co site as $Cr^{3+}$. For the divalent-ion substitution of M = $Ni^{2+}$ and $Cu^{2+}$, the magnitude of the $\kappa(T)$ peak markedly decreases to the level of $\kappa(T)$ in $La_{0.995}Sr_{0.005}$-$CoO_3$. In this case, the $Co^{4+}$ ions might be created by the 2% divalent M ion substitution, similarly to the La-site substitution by $Sr^{2+}$, causing the scattering of the phonons. It is noteworthy that the $\kappa(T)$ peak is more strongly suppressed by $Cu^{2+}$ than by $Ni^{2+}$ in the Co-site substituted sample. In fact, $Cu^{2+}$ ($t_{2g}^6 e_g^3$) is a JT-active ion, and the phonon scattering might be further enhanced. However, we cannot quantitatively explain why the effect of 2% substitution by $Ni^{2+}$ or $Cu^{2+}$ is comparable to that of 0.5% substitution by

$Sr^{2+}$; the amount of $Co^{4+}$ is four times larger in the former than in the latter.

For M = Sn and Zr, which take various valences in an ionic state, the $\kappa(T)$ peak reduction is less pronounced, possibly because of the formation of $M^{4+}$. Upon $M^{4+}$ cation substitution, the $Co^{2+}$ ion is expected to appear because of the charge neutrality. In our previous study, the sign of the Seebeck coefficient of the samples was reported to be negative, which strongly indicated that Sn and Zr ions were tetravalent species in $La(Co_{0.98}M_{0.02})O_3$[14] and, as a result, the $Co^{2+}$ ion was created. The moderate suppression of the $\kappa(T)$ peak in $La(Co_{0.98}M^{4+}_{0.02})O_3$ might be a characteristic feature of phonon scattering by $Co^{2+}$ ions, of which the spin state is reported to be HS ($t_{2g}^5 e_g^2$, $S = 3/2$).[19] These results are the first report for the phonon scattering by $Co^{2+}$ ions, as far as we know. The determination of the reason is in progress, why the suppression by $Co^{2+}$ is so moderate in comparison with that by $Co^{4+}$.

A qualitative understanding of the phononic heat transport can be obtained from the relation $\kappa \sim Cvl$, where $C$, $v$, and $l$ respectively denote the specific heat, the sound velocity, and the mean free path of the phonons. The reported specific heat $C(T)$ of the $LaCoO_3$ crystal increases with increasing temperature and shows no anomaly at 20–100 K.[20] The low-temperature spin-state transition from LS to the excited state is not clearly reflected in the heat capacity. The temperature dependence of the sound velocity $v(T)$ of $LaCoO_3$ was measured by Naing *et al.*[21] $v(T)$ decreased slightly with decreasing temperature, then increased by 15% below 50 K and saturated at 10 K. From these results of $C(T)$ and $v(T)$, the large $\kappa(T)$ peak in $LaCoO_3$ originates mainly from the enhancement of the phonon mean free path $l(T)$ at low temperatures because of the disappearance of strong phonon scattering.

### 3.3 Thermal conductivity of $RECoO_3$

Figure 3(a) shows the temperature dependence of the thermal conductivity $\kappa(T)$ of $(La_{1-y}Pr_y)CoO_3$ and $(Pr_{1-z}Nd_z)$-$CoO_3$ samples. The $\kappa(T)$ peak of the $(La_{1-y}Pr_y)CoO_3$ samples decreases for $y = 0.2$ without a temperature shift of the $\kappa(T)$ peak. The reduction of the $\kappa(T)$ peak results from the lattice disorder caused by the substitution of $Pr^{3+}$ ions with a different ionic radius at the La site. However, for the $(La_{0.5}Pr_{0.5})CoO_3$ sample, the $\kappa(T)$ peak increased and the temperature at which the peak appears decreases. The $\kappa(T)$ peak of the $y = 1$ sample ($PrCoO_3$) was greatly enhanced to 200 mW/(cm·K) at 15 K. Because the LS → IS (or HS) spin-state transition in $PrCoO_3$ was reported to take place at 180 K,[13] a different mechanism should exist causing the sharp $\kappa(T)$ peak other than the spin-state transition. The $\kappa(T)$ peak of $(Pr_{1-z}Nd_z)CoO_3$ increases with decreasing ionic radius of the element at the RE site, and the temperature at which the $\kappa(T)$ peak appears increases slightly. For $NdCoO_3$, $\kappa(T)$ shows $1/T$ temperature dependence, which is conventional $\kappa(T)$ behavior in ordinary solids.

Yan *et al.* reported a small and broad $\kappa(T)$ peak at 180 K in $PrCoO_3$, which was closely related to the spin-state transition of $Co^{3+}$ ions from LS to IS.[13] We measured the $\kappa(T)$ of the Pr-containing $RECoO_3$ sample, and the relation between the small and broad $\kappa(T)$ peak and the spin-state transition of the $Co^{3+}$ ions was investigated. Figure 3(b)
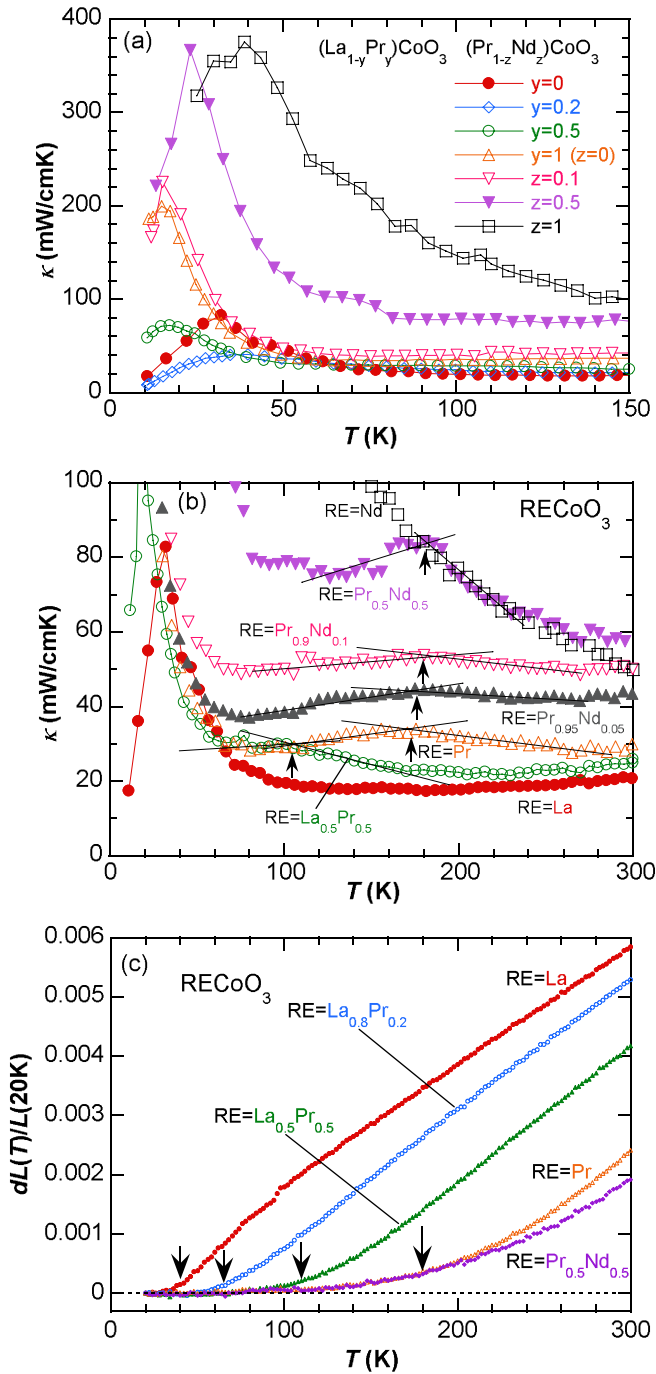
Fig. 3. (Color online) (a) Temperature dependence of the thermal conductivity $\kappa(T)$ of $(La_{1-y}Pr_y)CoO_3$ and $(Pr_{1-z}Nd_z)CoO_3$. (b) Magnification of $\kappa(T)$ around the second peak in $RECoO_3$ with RE ions of various ionic radii (see text). (c) Temperature dependence of the linear thermal expansion $dL(T)/L(20\,K)$ for $RECoO_3$ with RE ions of various ionic radii.

shows $\kappa(T)$ around the small peak in $RECoO_3$ with the Pr-containing RE site. Hereafter, we refer to the small $\kappa(T)$ peak as the second peak. This peak appears for RE = $La_{0.5}Pr_{0.5}$ at $T(2nd) = 110\,K$, and $T(2nd)$ approaches $180\,K$ for the RE = Pr and RE = $Pr_{0.5}Nd_{0.5}$ samples. The second peak of the RE = $Pr_{0.5}Nd_{0.5}$ sample is more clearly observable and $\kappa(T)$ is clearly suppressed at an intermediate temperature range of $20$–$180\,K$. In addition, a further reduction in $\kappa(T)$ also occurs at $T > 180\,K$ because of the spin-state transition. For a smaller RE ion such as RE = Nd, the second peak was obscured by the large phonon–phonon

$\kappa(T)$ peak as shown in Fig. 3(b). It should be noted that all the samples that have a second peak in $\kappa(T)$ contain Pr ions. The second peak might be a characteristic feature of the Pr-containing $RECoO_3$ samples. The strong energy overlap of the outer-lying $4f$ orbital of $Pr^{3+}$ with the neighboring oxygen $2p$ levels of $PrBa_2Cu_3O_{7-\delta}$ results in a characteristically mixed or fluctuating valence.[22] In the $RE_{1-X}$-$AE_XCoO_3$ system (AE = Ba, Sr, Ca), the insulator–metal transition, which is related to a spin-state transition, can be observed only in the $Pr_{1-X}Ca_XCoO_3$ system.[23,24] Consequently, novel characteristics in the Pr-containing perovskite cobaltites are reported. The behaviors of $\kappa(T)$ for $PrCoO_3$ and Pr-containing $RECoO_3$ might be related to the characteristic electron configuration of Pr ions.

Figure 3(c) shows the temperature dependence of the linear thermal expansion $dL(T)/L(20\,K)$ for $RECoO_3$ with elements of various ionic radii at the RE site. For $(La_{1-y}Pr_y)CoO_3$, the temperature at which the anomalous thermal expansion takes place increases and the change in $dL(T)/L(20\,K)$ becomes moderate with increasing $y$. For example, $T = 110\,K$ for RE = $La_{0.5}Pr_{0.5}$ and $T = 180\,K$ for RE = Pr. These results suggest that the LS state of the $Co^{3+}$ ion becomes stable at low temperatures with decreasing effective ionic radius at the RE site and that the transition becomes more gradual. The characteristic temperatures shown with arrows in Fig. 3(c) are nearly equal to the values of $T(2nd)$ shown in Fig. 3(b). It is noticeable that the small and broad second peak of $\kappa(T)$ for the Pr-containing $RECoO_3$ is related to the spin-state transition of $Co^{3+}$.

## 4. Summary

The thermal conductivities $\kappa(T)$ of $LaCoO_3$, and La- and Co-site-substituted $LaCoO_3$ and $RECoO_3$ samples (RE: $La_{1-y}Pr_y$, $Pr_{1-z}Nd_z$) have been measured and the origin of the $\kappa(T)$ peak in $LaCoO_3$ has been investigated by comparison with the valence and spin state of Co ions. The important experimental results and conclusions are summarized as follows.

1) A sharp $\kappa(T)$ peak of $LaCoO_3$ at approximately $30\,K$ is strongly suppressed by the introduction of a small amount of $Co^{4+}$ ions because of Co-site substitution by divalent cations such as $Cu^{2+}$ and $Ni^{2+}$, in addition to La-site substitution by $Sr^{2+}$. A large-scale lattice distortion such as a $Co^{4+}(LS)$–$6Co^{3+}(IS)$ cluster with JT-active ions is a possible candidate for the strong phonon-scattering centers. The $\kappa(T)$ peak of $LaCoO_3$ was not influenced by the 2% substitution of $RE^{3+}$ at the La site or by the substitution of $M^{3+}$ at the Co-site, which suggests that the ionic radius mismatch does not influence the phonon scattering.

2) The $\kappa(T)$ peak is moderately suppressed in the $La(Co_{0.98}M^{4+}_{0.02})O_3$ sample (M = $Sn^{4+}$, $Zr^{4+}$). The $\kappa(T)$ suppression might be a characteristic feature of phonon scattering by $Co^{2+}$ ions, which is first reported in this study. A detailed study to understand the reason why the suppression by $Co^{2+}$ is so moderate in comparison with that by $Co^{4+}$ is in progress.

3) In Pr-containing $RECoO_3$, a small and broad $\kappa(T)$ peak appears in $(La_{0.5}Pr_{0.5})CoO_3$ at $T = 110\,K$. The temperature at which the $\kappa(T)$ peak appears increases and approaches $180\,K$ in $PrCoO_3$ and $Pr_{0.5}Nd_{0.5}CoO_3$.

These temperatures correspond to those at which the anomaly of the linear thermal expansion $dL(T)/L(20\,K)$ is detected. The $\kappa(T)$ anomaly is closely related to the spin-state transition in $Co^{3+}$ ions, which is obscured by the large phonon–phonon peak for the $NdCoO_3$ system with a smaller RE ion and by the large $\kappa(T)$ peak at 30 K for the $LaCoO_3$ system with a larger RE ion.

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