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# Elastic and Thermal Transport Properties of $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ at metal-insulator Transition

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**Abstract.** In a Pr-Ca-Co-O system, a metal-insulator transition (MIT) accompanied with a spin-state transition (SST) of $\mathrm{Co}^{3+}$ takes place, at which the large volume contraction is also observed because of the tilting of the $\mathrm{CoO}_6$ octahedra. To study lattice dynamics at the MI-SST, we have measured the thermal conductivity $\kappa(T)$, thermal diffusivity $\alpha(T)$, thermal dilatation $dL(T)/L$ and sound velocity $v(T)$ for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$. $\kappa(T)$ shows a drop or a kink and $\alpha(T)$ shows a dip around the MI-SST temperature, $T_{\mathrm{MI}}$. $v(T)$ gradually decreases from the higher temperature than $T_{\mathrm{MI}}$ and abruptly drops at $T_{\mathrm{MI}}$. About 50 % of the dip of $\alpha(T)$ originates from the decrease of the sound velocity at $T_{\mathrm{MI}}$. The gradual decrease in $v(T)$ above $T_{\mathrm{MI}}$ suggests that the anomaly of the lattice linked to the MI-SST starts from fairly higher temperature.

## 1. Introduction

Thermal conductivity, $\kappa(T)$, of $\mathrm{RECoO}_3$ (RE=rare earth element) strongly depends on the species of RE. For example, in $\mathrm{LaCoO}_3$, the $\kappa(T)$ shows a large peak near 35 K and rapidly decreases with increasing temperature. The $\kappa(T)$ peak originates from the spin-state transition (SST) of $\mathrm{Co}^{3+}$ from the low spin state (LS; $t_{2g}^6e_g^0$, $S$=0) to the intermediate spin (IS; $t_{2g}^5e_g^1$, $S$=1) or the high spin state (HS; $t_{2g}^4e_g^2$, $S$=2) which starts from 35 K [1, 2]. The $\kappa(T)$ for $\mathrm{PrCoO}_3$ shows a small and broad peak around 180 K, which was also attributed to the SST of $\mathrm{Co}^{3+}$ [3, 4]. For both cases, no anomaly appears in the electrical resistivity at the SST. On the other hand, a metal-insulator transition (MIT) accompanied with the SST appears in a Pr-Ca-Co-O system [5, 6, 7, 8]. At the MI-SST, the large volume contraction due to the tilting the $\mathrm{CoO}_6$ octahedra occurs [5, 6]. Such a lattice deformation would strongly affect the heat transport. In this paper, we measure the temperature dependences of the thermal conductivity $\kappa(T)$, thermal diffusivity $\alpha(T)$, thermal dilatation $dL(T)/L$ and sound velocity $v(T)$ for the $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples and discuss the origin of anomalous lattice dynamics around the MI-SST.

## 2. Experimental procedure

$(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples were prepared by a solid-state reaction method [8]. Powder X-ray diffraction patterns were taken at room temperature and the single-phase crystal structure was confirmed for all samples. The measured densities of each sample were greater than 90 % of the ideal density. Thermal conductivity, $\kappa(T)$, was measured by a steady-state heat-flow method

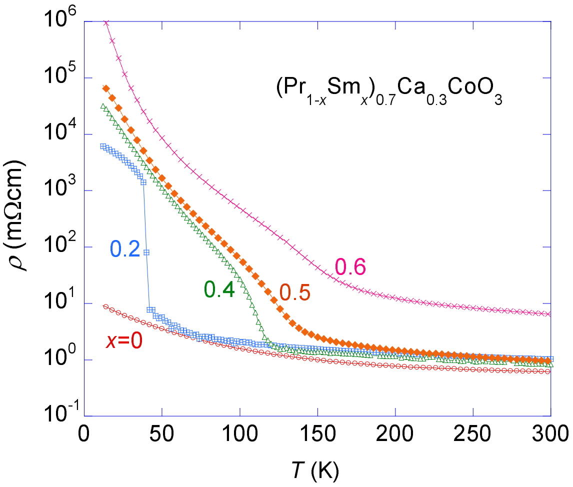

**Figure 1.** The temperature dependence of the resistivity, $\rho(T)$, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples with various $x$.

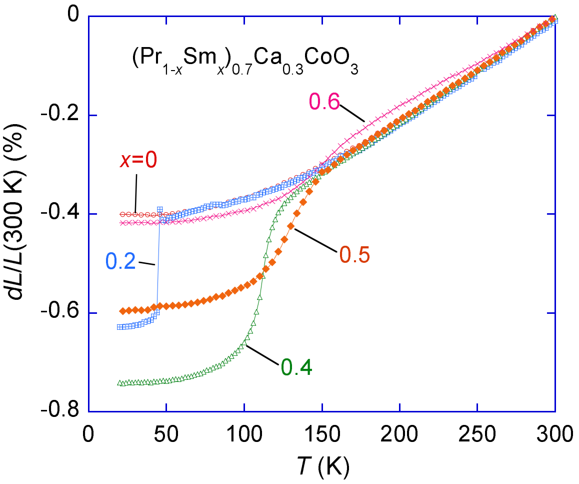

**Figure 2.** The temperature dependence of the thermal dilatation, $dL(T)/L(300\mathrm{K})$, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples with various $x$.

and thermal diffusivity, $\alpha(T)$, was measured by an arbitrary heating one under an identical experimental setup [9]. Thermal dilatation, $dL(T)/L(300\ \mathrm{K})[= (L(T) - L(300\ \mathrm{K}))/L(300\ \mathrm{K})]$, based on the sample length at 300 K, was measured using a commercial strain gauge (Kyowa KFL-1-120-C1-16). Sound velocity, $v(T)$, was measured by a pulse echo method. Electrical resistivity, $\rho(T)$, was measured by a four-probe method. All the measurements were performed by cooling runs.

## 3. Results and Discussion

Figure 1 shows the temperature dependence of the resistivity, $\rho(T)$, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples with various $x$ up to 0.6. For $x$=0, the $\rho(T)$ increases moderately with decreasing temperature. For $x = 0.2$, $\rho(T)$ shows an abrupt jump with two orders of magnitude at $T_{\mathrm{MI}}$=42 K. The $T_{\mathrm{MI}}$ increases and the width of the transition broadens with increasing $x$. The MIT was accompanied with the SST of $\mathrm{Co}^{3+}$ ions [5, 6, 7, 8].

Figure 2 shows the temperature dependence of the thermal dilatation, $dL(T)/L(300\ \mathrm{K})$, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ with various $x$. For $x$=0, the $dL(T)/L(300\ \mathrm{K})$ decreases monotonically with decreasing temperature and no anomaly appears. For $x$=0.2–0.6, the $dL(T)/L(300\ \mathrm{K})$ shows a drop at $T_{\mathrm{MI}}$, which originates from the tilting of the $\mathrm{CoO}_6$ octahedra [5, 6]. The abrupt dilatation broadens with increasing $x$ similarly to the transition in $\rho(T)$. The absolute value of the $dL(20\ \mathrm{K})/L(300\ \mathrm{K})$ for $x$=0.4 is larger than that for $x$=0.2, but that for $x$=0.5 and 0.6 decreases.

Figure 3 shows the temperature dependence of the thermal conductivity, $\kappa(T)$, of $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ for $x$=0.2 and 0.4. For $x$=0.2, $\kappa(T)$ decreases monotonically with decreasing temperature, abruptly drops at 49 K, which is somewhat higher than $T_{\mathrm{MI}}$=42 K, and then takes a broad peak at lower temperature. For $x$=0.4, $\kappa(T)$ shows a kink at 114 K, which is similar to $T_{\mathrm{MI}}$, and takes a quite moderate maximum at 40 K. The measured $\kappa$ is sum of both contributions of phonons, $\kappa_{\mathrm{ph}}$, and electrons, $\kappa_{\mathrm{el}}$. $\kappa_{\mathrm{el}}(T)$ was also shown in the figure, which was estimated using Wiedemann-Franz law ($\kappa_{\mathrm{el}} = L_0T/\rho$), where $L_0$ was Lorenz number. In both samples, the magnitude of $\kappa_{\mathrm{el}}$ is approximately 10–12 % of the measured $\kappa$ at 150 K. For $x$=0.2, the origin of the $\kappa(T)$ drop around $T_{\mathrm{MI}}$ comes from the phonons. On the other hand, for $x$=0.4,

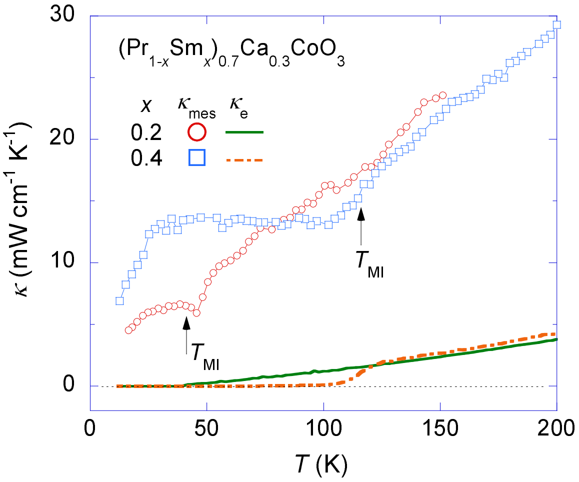

**Figure 3.** The temperature dependence of the measured and the electron thermal conductivities, $\kappa_{\mathrm{mes}}(T)$ and $\kappa_{\mathrm{el}}(T)$, respectively, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ with $x$=0.2 and 0.4.

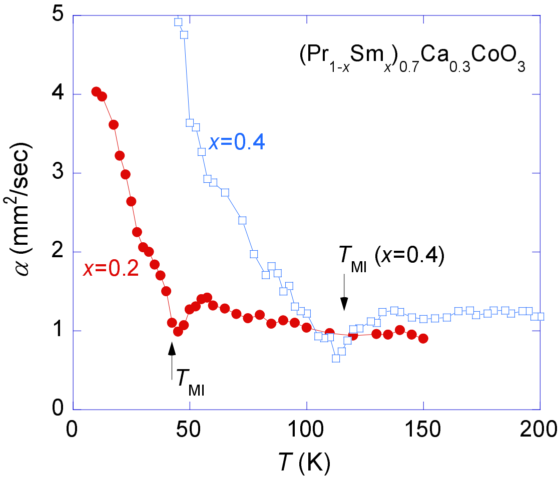

**Figure 4.** The temperature dependence of the thermal diffusivity, $\alpha(T)$, for $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ with $x$=0.2 and 0.4.

an observable small $\kappa_{\mathrm{el}}$ decrease can be seen but the measured $\kappa(T)$ anomaly around $T_{\mathrm{MI}}$ is almost due to phonons. The tilting of the $\mathrm{CoO}_6$ octahedra by the MIT gives rise to the buckling of the $\mathrm{CoO}_2$ planes, which would prevent strongly the phonon transport. In the $\kappa(T)$ peak in $\mathrm{LaCoO}_3$, we can interpret the peak in the following; at higher temperatures, Jahn-Teller (JT) active IS-$\mathrm{Co}^{3+}$ ions scatter the phonons and $\kappa(T)$ is suppressed. With decreasing temperature, the population of IS-$\mathrm{Co}^{3+}$ decreases and that of non JT active LS-$\mathrm{Co}^{3+}$ increases. As a result, the phonon scattering decreases and then $\kappa(T)$ increases and takes a maximum. For the $x$=0.2 and $x$=0.4 samples in this study, the reduction of IS-$\mathrm{Co}^{3+}$ ions enhances the $\kappa(T)$ below $T_{\mathrm{MI}}$.

Figure 4 shows the temperature dependence of the thermal diffusivity, $\alpha(T)$, of $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ for $x$=0.2 and 0.4. $\alpha(T)$ slightly increases with decreasing temperature or is almost temperature-independent at high-temperatures, shows a dip structure at around $T_{\mathrm{MI}}$ and increases rapidly with decreasing temperature. The dip in $\alpha(T)$ indicates that the sound velocity, $v(T)$, and/or the phonon mean free path, $l(T)$, decreased considering the relation, $\alpha = \frac{1}{3}vl$. Figure 5 shows the temperature dependence of the sound velocity, $\Delta v(T)/v(300\text{ K})$ [$= (v(T) - v(300\text{ K}))/v(300\text{ K})$] for $(\mathrm{Pr}_{0.6}\mathrm{Sm}_{0.4})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$. $\Delta v(T)/v(300\text{ K})$ increases with decreasing temperature, starts to decrease at 140 K, and drops discontinuously at 112 K which corresponds to $T_{\mathrm{MI}}$. The decrease in $\Delta v(T)/v(300\text{ K})$ from 140 K to 112 K is approximately 25 % of the $\Delta v(140\text{ K})/v(300\text{ K})$ value. As found in Fig. 4, the $\alpha(T)$ also started to decrease at around 137 K and took a minimum at 112 K; $\alpha(T)$=0.66 mm$^2$/sec at 112 K was about 48 % lower than $\alpha(T)$=1.28 mm$^2$/sec at 137 K. These results suggest that about 50 % of the decrease in $\alpha(T)$ around the MI-SST is caused by the change in the sound velocity. Since $\kappa$ is represented as $\kappa = C\alpha$, a part of anomaly in $\kappa(T)$ also originates from the decrease of the $v(T)$, where $C$ is the specific heat. However, to carry out the quantitative discussion, we must know the $C(T)$ for this compound. It is noteworthy that the softening of the lattice started at around 140 K, demonstrating that the anomalous lattice dynamics begins to appear at higher temperature than $T_{\mathrm{MI}}$.

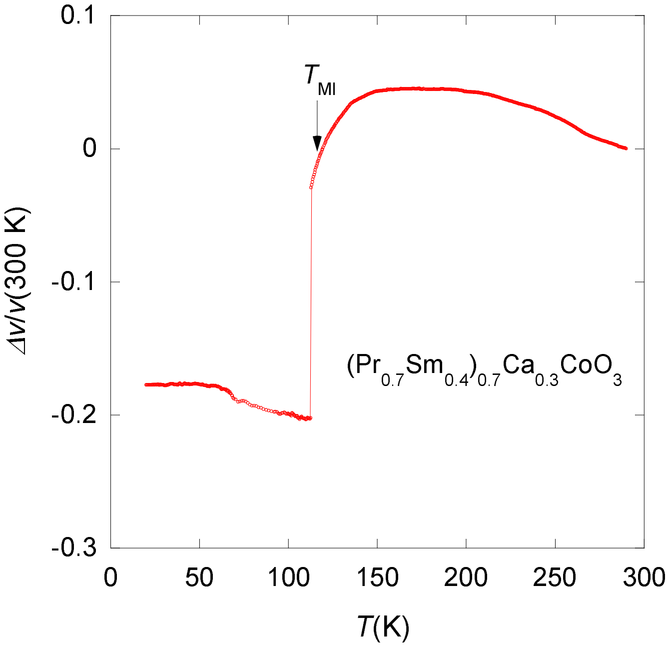

**Figure 5.** The temperature dependence of the sound velocity, $\Delta v/v(300\ \mathrm{K})$, for $(\mathrm{Pr}_{0.6}\mathrm{Sm}_{0.4})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$.

## 4. Summary

We report the thermal conductivity $\kappa(T)$, thermal diffusivity $\alpha(T)$, thermal dilatation $dL/L(300\ \mathrm{K})$ and sound velocity $\Delta v(T)/v(300\ \mathrm{K})$ at around the MI-SST for the $(\mathrm{Pr}_{1-x}\mathrm{Sm}_x)_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ samples. $\kappa(T)$ showed a drop or a kink and $\alpha(T)$ showed a dip at the MI-SST. The quite sharp drop was also found in $\Delta v(T)/v(300\ \mathrm{K})$. Comparing the magnitude of the anomalies between $\alpha(T)$ and $\Delta v(T)/v(300\ \mathrm{K})$, the change of the sound velocity $v(T)$ contributes to about 50% of the $\alpha(T)$ anomaly and affects a part of $\kappa(T)$ anomaly because of the relation of $\kappa = C\alpha$. The lattice softening occurred at rather higher temperature than $T_{\mathrm{MI}}$, which might be important to clarify the mechanism of the MI-SST.

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