Anomalous phonon scattering by Jahn–Teller active Co intermediate spins in LaCoO₃ and doped LaCoO₃

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Abstract
Thermal conductivity $\kappa(T)$, Seebeck coefficient $S(T)$, and magnetization $M(T)$ have been measured on LaCo₀.₉₈M₀.₀₂O₃ doped with various valence cations M. A sharp and strong $\kappa(T)$ peak of pristine LaCoO₃ around 30 K is suppressed for 2+ dopants. Jahn–Teller active Co⁴⁺ (IS) · 6Co⁴⁺ (HS) clusters introduced concomitantly with the hole doping may act as the powerful phonon scattering centers at low temperatures.

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1. Introduction
LaCoO₃ has attracted renewed interest recently. A main controversy is concerned with Co³⁺ spin state transitions, i.e., the role of the intermediate spin (IS) configuration $t_{2g}^3e_g^1$ and the high spin (HS) configuration $t_{2g}^4e_g^2$ thermally excited from the sea of Co³⁺ low spins (LS) with $t_{2g}^6$ configuration. The hole doped cobaltites such as La₀.₉₈Srₐ.₀₂CoO₃ also exhibit unusual physical properties which have not yet been fully understood. A variety of the physical properties of the cobaltites may partly originate from the enhanced spin–lattice interaction through the Jahn–Teller effect of Co³⁺ (IS) and Co⁴⁺ (IS). We report the effect of the doped cation valence in the phonon thermal conductivity $\kappa(T)$, Seebeck coefficient $S(T)$, and the magnetization $M(T)$ of LaCoO₃, La₀.₉₈Sr₀.₀₂CoO₃ and LaCo₀.₉₈M₀.₀₂O₃ (M : Ni²⁺, Cu²⁺, Zn²⁺, Cr³⁺, Fe³⁺, Zr⁴⁺, Sn⁴⁺). The phonon scattering mechanism in the hole doped cobaltites is discussed.
2. Experimental

The polycrystalline cobaltites were prepared by a solid state reaction method. $\kappa(T)$ and $S(T)$ were measured by a steady heat flow method. $M(T)$ was recorded using a SQUID magnetometer under a field of 0.5 T.

3. Results and discussion

Fig. 1 shows the temperature dependence of $\kappa(T)$ normalized by the value of $\kappa(150 \text{ K})$. The electrical resistivity $\rho(T)$ of all the present cobaltites is semiconductive and very high and $\kappa(T)$ can be regarded entirely due to phonons. The behavior of $\kappa(T)$ can be classified into three groups. $\kappa(T)$ of the first group (G1) shows a characteristic peak around 30 K. Non-doped LaCoO$_3$ and 2%Cr- and Fe-doped samples belong to this group. The characteristic peak of $\kappa(T)$ is almost completely suppressed for the second group (G2), to which La$_{0.98}$Sr$_{0.02}$CoO$_3$ and 2%Zn-, Cu- and Ni-doped samples belong. The third group (G3) consists of 2%Sn$^{4+}$- and Zr$^{4+}$-doped specimens, whose $\kappa(T)$ peak is lightly reduced.

Fig. 2(a) shows the temperature dependence of the Seebeck coefficient $S(T)$ for the respective samples. $S(T)$ of the G2 samples is positive, suggesting the hole doping and the valencies of the G2 cations should be 2+ . $S(T)$ of the G1 samples remains negative and the valencies of Cr and Fe are inferred to be 3+ similarly to Co$^{3+}$. $S(T)$ of Sn$^{4+}$- and Zr$^{4+}$-doped specimens is also negative but the $S$ values are somewhat smaller than those of G2 ions. Fig. 2(b) shows the magnetization $M(T)$. It can be seen that the $M(T)$ of the G2 samples is enhanced in comparison to pristine LaCoO$_3$.

The sharp $\kappa(T)$ peak of LaCoO$_3$ is not attributable by usual phonon–phonon scattering, but it is attributable to the phonon scattering due to thermally excited Jahn–Teller active Co$^{3+}$ ions with IS configuration [1]. The local Jahn–Teller distortion (static or dynamic) has been confirmed.
to be very efficient in phonon scattering [2]. The intact $\kappa$ peak of the G1 group demonstrates that the $\text{Co}^{3+}$ spin-state transition is hardly affected by the $3^+$ cation doping.

The disappearance of the $\kappa(T)$ peak for the $2^+$ dopants suggests the appearance of a very powerful phonon scattering center effective at low temperatures ($T \leq 50\,\text{K}$). At low temperatures, effective phonon scattering centers must be of rather large size because the phonon wavelength is also large. On the basis of the exact diagonalization method, Tsutsui et al. [3] predicted the formation of $\text{Co}^{4+}(\text{IS})\cdot 6\text{Co}^{3+}(\text{HS})$ clusters upon hole doping. The $\text{Co}^{4+}(\text{IS})$ ions with $t^6_e e^1_g$ configuration are also Jahn–Teller active and should accompany the local lattice distortion. Moreover, the lattice distortion around $\text{Co}^{4+}$ becomes large-scaled because of the cluster nature. Thus $\text{Co}^{4+}(\text{IS})\cdot 6\text{Co}^{3+}(\text{HS})$ clusters can be the powerful phonon scattering centers, enhancing $M(T)$ in Fig. 2(b) as well. Upon $4^+$ cation doping, the appearance of $\text{Co}^{2+}(\text{LS})$ is expected because of the charge neutrality. The Jahn–Teller active $\text{Co}^{2+}(\text{LS})$ ions with $t^6_e e^1_g$ configuration may possibly be responsible for the moderate reduction of the $\kappa(T)$ peak observed for the G3 specimens.

In summary, we discussed the phonon scattering mechanism in $\text{LaCoO}_3$ and doped $\text{LaCoO}_3$. The characteristic peak around $30\,\text{K}$ of the phonon thermal conductivity of $\text{LaCoO}_3$ is rapidly suppressed by the introduction of holes caused by the $2^+$ cation doping. The relatively large-scale lattice distortion around Jahn–Teller active intermediate $\text{Co}^{4+}$ forming $\text{Co}^{4+}(\text{IS})\cdot 6\text{Co}^{3+}(\text{HS})$ clusters is the most probable candidate for the strong phonon scattering.

References