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Physica B 359–361 (2005) 1360–1362
PHYSICA B
www.elsevier.com/locate/physb

Anomalous phonon scattering by Jahn–Teller active Co intermediate spins in $LaCoO_3$ and doped $LaCoO_3$

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Abstract

Thermal conductivity $\kappa(T)$, Seebeck coefficient $S(T)$, and magnetization $M(T)$ have been measured on $LaCo_{0.98}M_{0.02}O_3$ doped with various valence cations M. A sharp and strong $\kappa(T)$ peak of pristine $LaCoO_3$ around 30 K is suppressed for 2+ dopants. Jahn–Teller active Co^{4+}(IS) · $6Co^{3+}$(HS) clusters introduced concomitantly with the hole doping may act as the powerful phonon scattering centers at low temperatures.

PACS: 75.30.Hx; 72.15.Eb; 72.10.Di

Keywords: Phonon scattering; Jahn–teller distortion; Co-spin state transition; Cation doping effect

1. Introduction

$LaCoO_3$ has attracted renewed interest recently. A main controversy is concerned with Co^{3+} spin state transitions, i.e., the role of the intermediate spin (IS) configuration $t_{2g}^5e_g^1$ and the high spin (HS) configuration $t_{2g}^4e_g^2$ thermally excited from the sea of Co^{3+} low spins (LS) with t_{2g}^6 configuration. The hole doped cobaltites such as $La_{1-x}Sr_xCoO_3$ 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 Co^{3+}(IS) and Co^{4+}(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 $LaCoO_3$, $La_{0.98}Sr_{0.02}CoO_3$ and $LaCo_{0.98}M_{0.02}O_3$ ($M: Ni^{2+}$, Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, Zr^{4+}, Sn^{4+}). The phonon scattering mechanism in the hole doped cobaltites is discussed.

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doi:10.1016/j.physb.2005.01.411

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 κ(150 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

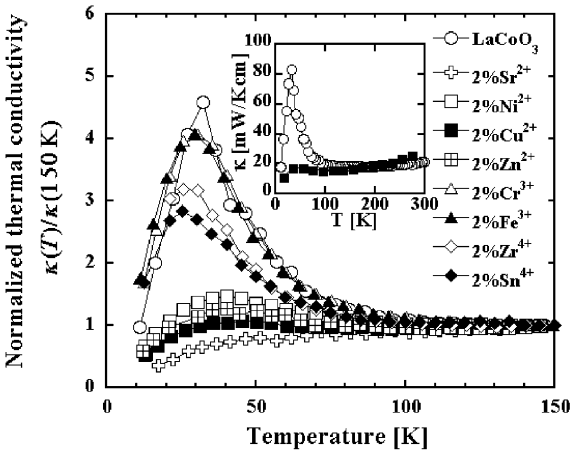

Fig. 1. The normalized thermal conductivity $\kappa(T)/\kappa$(150 K) for $LaCoO_3$, $La_{0.98}Sr_{0.02}CoO_3$ and $LaCo_{0.98}M_{0.02}O_3$. The $\kappa(T)$ for $LaCoO_3$ and 2%Cu^{2+}-doped sample is shown in the inset.

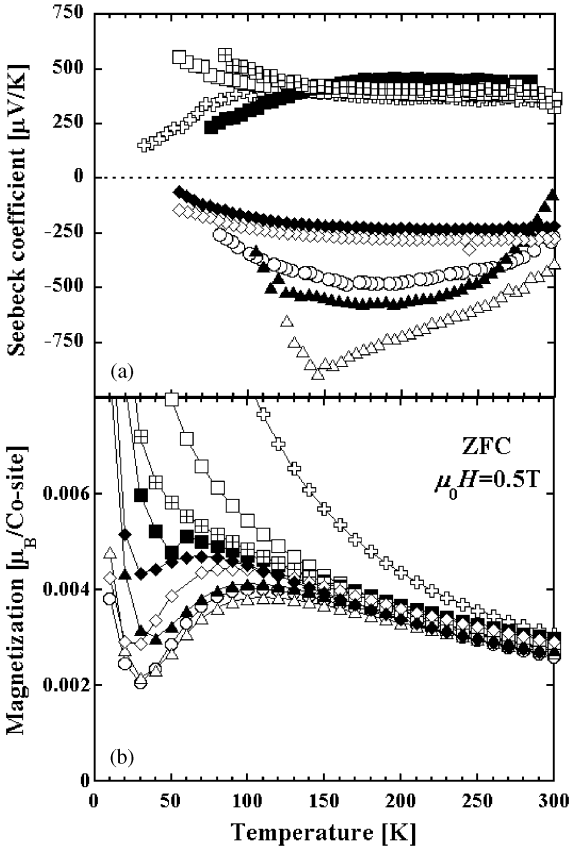

Fig. 2. (a) The Seebeck coefficient $S(T)$ and (b) the magnetization $M(T)$ in the field of 0.5 T for the respective samples. Symbols are the same as Fig. 1.

to be very efficient in phonon scattering [2]. The intact κ peak of the G1 group demonstrates that the 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 ($T \leqslant 50\,K$). 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 $Co^{4+}(IS) \cdot 6Co^{3+}(HS)$ clusters upon hole doping. The $Co^{4+}(IS)$ ions with $t_{2g}^4 e_g^1$ configuration are also Jahn–Teller active and should accompany the local lattice distortion. Moreover, the lattice distortion around Co^{4+} becomes large-scaled because of the cluster nature. Thus $Co^{4+}(IS) \cdot 6Co^{3+}(HS)$ clusters can be the powerful phonon scattering centers, enhancing $M(T)$ in Fig. 2(b) as well. Upon 4+ cation doping, the appearance of $Co^{2+}(LS)$ is expected because of the charge neutrality. The Jahn–Teller active $Co^{2+}(LS)$ ions with $t_{2g}^6 e_g^1$ 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 $LaCoO_3$ and doped $LaCoO_3$. The characteristic peak around 30 K of the phonon thermal conductivity of $LaCoO_3$ 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 Co^{4+} forming $Co^{4+}(IS) \cdot 6Co^{3+}(HS)$ clusters is the most probable candidate for the strong phonon scattering.

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