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Effect of oxygen content variation on phonon heat transport in $La_{0.75}Ca_{0.25}MnO_{3+\delta}$

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Abstract

The thermal conductivity $\kappa(T)$, thermal dilatation $dL(T)/L$, magnetization $M(T)$ and the electrical resistivity $\rho(T)$ of $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ have been measured for various oxygen off-stoichiometry δ. The phonon thermal conduction, the electrical conduction and the order of the ferromagnetic phase transition were found to be strongly depending on δ. The scattering of phonon by small ($T > T_C$) and large ($T < T_C$) Jahn–Teller polarons was found to be of main importance to limit the phonon thermal conduction of this system.

Keywords: Thermal conductivity; Oxygen off-stoichiometry; Thermal dilatation; Manganese oxides

As recent revived studies have demonstrated, hole-doped $(RE_{1-X}AE_X)MnO_3$-type manganites (RE = trivalent rare-earth ions, AE = divalent alkaline-earth ions) with the perovskite-based structure show a variety of dramatic phenomena such as the colossal magnetoresistance (CMR) and the metal-insulator (M−I) transition [1]. Besides the double exchange mechanism, the electron–phonon interaction enhanced by the Jahn–Teller (J−T) effect of the Mn^{3+} ions has been widely recognized to be essential [2]. Another important key factor influential to the lattice effect is the ionic radius matching (or mismatching) between the $(RE_{1-X}AE_X)$ and Mn ions, which eventually determines the Mn 3d electron band width (e_g). The mobility and the band filling of the doped holes mainly determine the electronic properties of the strongly correlated manganite systems.

The ionic radii of La^{3+} and Ca^{2+} are not much different and the fundamental structure of $La_{1-X}Ca_XMnO_{3+\delta}$ (LCMO) remains orthorhombic over the entire Ca concentration X. LCMO is a ferromagnetic metal (FMM) below the Curie temperature T_C for $0.18 \leqslant X \leqslant 0.47$ [3,4] and it exhibits a characteristic first-order-like FMM transition around $X = 0.25$ [5]. The first-order-like transition was found to be critically related to the $(RE_{1-X}AE_X)$ and Mn ionic radius matching. However, also the oxygen off-stoichiometry is to crucially affect the magnetic and transport properties of the manganite systems [6] through the change of the effective band-filling n_e ($= X + 2\delta$, nominally). In this report, we present the effect of the oxygen off-stoichiometry δ on the phonon thermal conduction and on the first-order-like phase transition in $La_{0.75}Ca_{0.25}MnO_{3+\delta}$.

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The $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ samples were prepared by a standard solid-state reaction method. The sintering temperature was 1500°C. The δ values were determined by iodine titration. The precision of the iodine titration was estimated to be $\Delta\delta \leqslant \pm 0.005$. The structure of all of the present samples was confirmed to be a single orthorhombic phase by X-ray diffraction analysis. The thermal conductivity $\kappa(T)$ was measured by a steady-state heat flow method between 10 and 300 K using a Gifford–MacMahon cycle He refrigerator as a cryostat. The magnetization $M(T)$ was measured by a SQUID magnetometer. The thermal dilatation $dL(T)/L$ was measured by a strain gauge method.

In this study, the oxygen content $3+\delta$ was controlled by heat-treating the as-sintered starting sample in Ar–H_2 (Ar:H_2 = 10:1) atmosphere at various temperatures. From the analyses of iodine titration, the oxygen off-stoichiometry δ of the present $La_{1-X}Ca_XMnO_{3+\delta}$ samples was determined to be, 0.040, 0.032, 0.010 and 0.001 for as-sintered, heat-treated at 450°C, 500°C and 520°C, respectively. Fig. 1 shows the magnetization $M(T)$ as a function of temperature T for these four samples. $M(T)$ of the as-sintered ($\delta = 0.040$) sample increases almost discontinuously at and just below T_C, which is indicative of the first-order FM transition. However, hysteretic behavior, which is another characteristic feature of the first-order phase transition could not detected. The FM transition becomes gradual and of typical second-order with decreasing δ as can be seen in the figure.

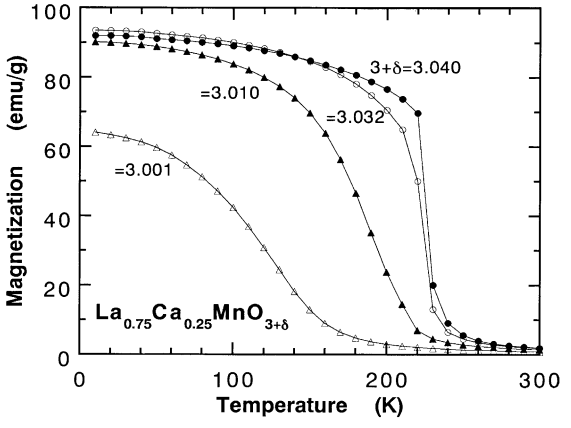

Fig. 1. The magnetization $M(T)$ of $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ for $\delta = 0.040$, 0.032, 0.010 and 0.001 under the field of $\mu_0 H = 0.5$ T. $M(T)$ rises very sharply for $\delta = 0.040$ and 0.032 just below T_C.

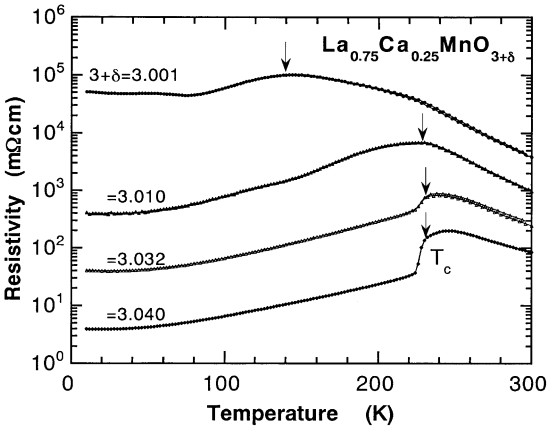

Fig. 2. The electrical resistivity $\rho(T)$ as a function of temperature T. The samples are the same as those in Fig. 1.

Fig. 2 shows the temperature dependence of the electrical resistivity $\rho(T)$. The $\rho(T)$ values of the $\delta = 0.040$ sample show a sizable reduction at T_C with decreasing temperature and clear metallic behavior can be seen below T_C. The $\rho(T)$ reduction is smaller for the $\delta = 0.032$ sample and disappears for the $\delta = 0.010$ and 0.001 samples. For $T > T_C$, $\rho(T)$ of all the samples behave semiconductive and the electrical conduction is due to the hopping of small polarons [7,8] accompanied with local J–T lattice distortions. For $\delta = 0.040$ and 0.032 and for $T < T_C$, the metallic conduction is probably due to much mobile large polarons accompanied with locally reduced and spatially somewhat extended J–T distortions.

Fig. 3 shows the thermal dilatation $dL(T)/L$ as a function of T. For $\delta = 0.040$, $dL(T)/L$ exhibits almost discontinuous contraction with decreasing temperature. This sharp contraction may reflect the relaxation of the local J–T lattice distortion associated with the increase in the mobility and with the change of the charge carrier characters (i.e., from the small to large polarons). The contraction becomes very small for $\delta = 0.010$ and disappears for $\delta = 0.001$. It is noticed that

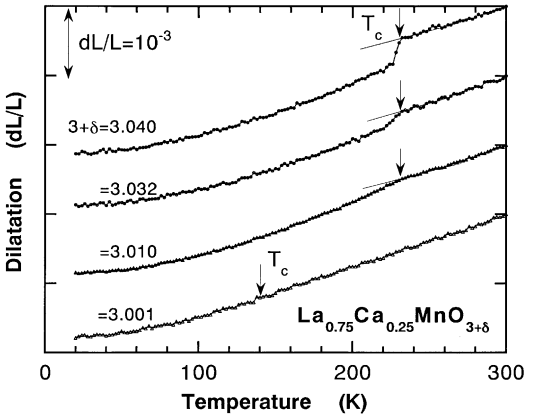

Fig. 3. The temperature dependence of the thermal dilatation $dL(T)/L$. The arrow indicates the Curie temperature T_C.

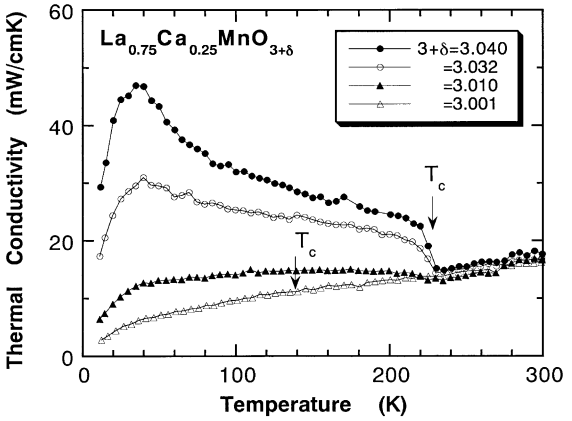

Fig. 4. The thermal conductivity $\kappa(T)$. $\kappa(T)$ above T_C is small and almost equal for all the samples. Below T_C, $\kappa(T)$ is enhanced in metallic samples ($\delta = 0.040$ and 0.032).

$\rho(T)$ of the $\delta = 0.001$ sample remains very large even for $T < T_C$ and that the small-polaron-like electrical conduction dominates over the entire temperature range.

Fig. 4 presents the thermal conductivity $\kappa(T)$ for the respective samples. Based on the Wiedemann–Franz law, the electronic contributions to κ are very small even in the metallic state, and $\kappa(T)$ is overwhelming due to phonons for all the present $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ samples. For $T > T_C$, the $\kappa(T)$ values of all the samples are almost the same and very small. At $T \approx T_C$, $\kappa(T)$ of the $\delta = 0.040$ and $\delta = 0.032$ almost jumps up, continues to be enhanced with decreasing temperature and takes a maximum at around $T \approx 40$ K. The magnitude of the $\kappa(T)$ jump and the enhance is more conspicuous for $\delta = 0.040$ than for $\delta = 0.032$. The $\kappa(T)$ enhance at $T \approx T_C$ is barely discernible for $\delta = 0.010$ and is completely wiped out for $\delta = 0.001$. The X dependence of $\kappa(T)$ clearly corresponds to those of $\rho(T)$ and $dL(T)/L$. For $T > T_C$, where the electrical conduction is due to the small J−T polarons, $\kappa(T)$ is small due to strong phonon scattering by the large and random J−T local distortions. For $T < T_C$ and in the samples of $\delta = 0.040$ and 0.032, the phonon scattering is progressively reduced with decreasing temperature as the local J−T distortion is relaxed with increasing mobility of the large J−T polarons. In the $\delta = 0.010$ and 0.001 samples, where $\rho(T)$ is large even below T_C and the small polaron hopping characters of charge carriers survive even in the ferromagnetic phase, the strong phonon scattering by the random local J−T distortions remains over the entire temperature range of this study.

In summary, we studied the effect of the oxygen off-stoichiometry on the FM phase transition by measuring the thermal conductivity $\kappa(T)$, electrical resistivity $\rho(T)$ and thermal dilatation $dL(T)/L$. The first-order-like FM transition in as-sintered $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ ($\delta = 0.040$) promptly disappeared with decreasing δ and the transition became typical of second-order in $La_{0.75}Ca_{0.25}MnO_{3+\delta}$ ($\delta = 0.010$). Thus not only the mismatch of the ionic radius between ($La_{0.75}Ca_{0.25}$) and Mn ions but also the band filling of holes critically affects the FM transition of the $La_{1-X}Ca_XMnO_3$ system. The main phonon scatters in this system are the local J−T distortions around Mn^{3+} ions. The relaxation of the J−T lattice distortions associated with the change of the charge carrier characters from the small to large polaron causes the observed $\kappa(T)$ enhancement for the metallic $\delta = 0.040$ and 0.032 samples below T_C.

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