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Thermal diffusivity of $La_{1-X}Ca_XMnO_3$ up to 1200 K

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Abstract

The thermal diffusivity $\alpha(T)$ and the normalized specific heat $C(T)/C(300\,\mathrm{K})$ of the colossal magnetoresistive manganite, $La_{1-X}Ca_XMnO_3$ (LCMO; $0 \leqslant X \leqslant 1.0$), were measured in the temperature range from 10 to 1200 K. At high temperatures above 300 K, the temperature differential of the diffusivity, $d\alpha/dT$, changes from negative to positive with increasing Ca concentration X. The positive $d\alpha/dT$ coefficient is not standard and a possible origin correlated with the local distortion around the Jahn–Teller active Mn^{3+} ions is proposed. The phase diagram of the LCMO system is completed up to 1200 K using the anomalies of $\alpha(T)$, $C(T)$ and other physical quantities.

Keywords: Thermal diffusivity; $La_{1-X}Ca_XMnO_3$; Specific heat; Phase diagram; Laser flush method

$La_{1-X}Ca_XMnO_3$ (LCMO) is a typical material which exhibits colossal magnetoresistance (CMR) and undergoes a paramagnetic insulator (PM-I) to a ferromagnetic metal (FM-M) transition for the Ca concentration regime $0.2 < X < 0.5$ [1]. For the high doping range, $X \geqslant 0.5$, the ground state is an antiferromagnetic insulator (AFM-I) accompanied with the charge ordering (CO) and a canted antiferromagnetic (CAF) order also takes place at $0.82 \leqslant X \leqslant 1.0$ [2]. We have noticed that the thermal diffusivity α ($= \kappa/C$; κ is the thermal conductivity and C the specific heat) of the $X = 0.25$ sample, for example, abruptly increases just below the FM transition temperature $T_c = 232$ K and then continues to increase gradually with decreasing temperature T. We have also noticed that, for $T > T_c$, $\alpha(T)$ slightly increases with increasing temperature up to room temperature [3]. In ordinary insulators, $\alpha(T)$ is mainly contributed by phonon heat conduction and is expected to decrease monotonously or remains constant with increasing temperature ($d\alpha/dT \leqslant 0$). This is because α_{ph} is given by $v_s l_{ph}/3$ (v_s: sound velocity, l_{ph}: phonon mean free path), and $l_{ph}(T)$ limited by the phonon–phonon scattering should be a decreasing function of T or approach constant because of saturation at high temperatures. The positive gradient, $d\alpha/dT > 0$ for $T > T_c$, suggests that the phonon scattering is actually enhanced on approaching T_c from higher temperatures. It should be interesting to measure the thermal diffusivity $\alpha(T)$ above room temperature and to discuss the origin of the positive $d\alpha/dT$. In this paper, we investigate the thermal diffusivity $\alpha(T)$ of the $La_{1-X}Ca_XMnO_3$ system for a wider Ca concentrations X ($0 \leqslant X \leqslant 1.0$), extending the temperature range up to 1200 K.

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The samples used in this study were the polycrystal of which the densities are higher than 85% of the ideal ones [4]. Below 300 K, $\alpha(T)$ was measured by the arbitrary heating method by the use of the measuring system of our own making [5]. The heat pulse was applied to the slender-shaped sample and the thermal diffusivity was calculated from the heat pulse propagation speed. Above room temperature, $\alpha(T)$ and the normalized specific heat $C(T)/C(300\,\mathrm{K})$ were measured by the laser flush method (SINKU-RICO Inc., TC-7000) up to 1200 K using the disk-shaped samples.

Figs. 1(a)–(c) show the temperature dependence of the thermal diffusivity $\alpha(T)$ of the typical samples. According to an estimation based on the Wiedemann–Franz law, the heat conduction is overwhelmingly due to phonons in this system. For $X = 0$ sample, $\alpha(T)$ increases with decreasing temperature below 300 K, showing a slight kink around the Néel temperature $T_N = 120$ K. Two anomalies at T_{S1} and T_{S2} are observable above 300 K; the one at $T_{S1} = 530$ K is related with the phase transition between the cooperatively Jahn–Teller (JT) distorted orthorhombic phase (O-phase) and the octahedron rotated orthorhombic phase (O*-phase) and the other at $T_{S2} = 805$ K may probably come from the structure transition between the O*-phase and the rhombohedral phase (R-phase) [6,7]. The transition temperature T_{S1} decreases to ~ 300 K for $X = 0.10$ and disappears for higher X samples. The temperature differential of the diffusivity, $\mathrm{d}\alpha/\mathrm{d}T$, changes at T_{S1} from negative to positive upon heating. The diffusivity at T_{S2} shows a distinct and sharp upturn on heating for $X = 0$ and 0.10, but the anomaly reduces to a faint kink around T_{S2} for $X \geqslant 0.25$. T_{S2} gradually decreases with increasing X up to 0.25 and, in turn, increases for higher X samples.

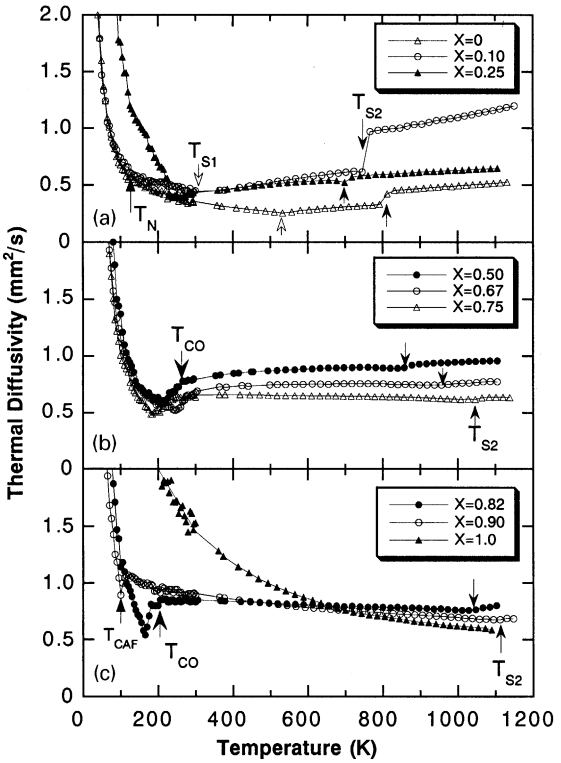

Fig. 1. Temperature dependence of the thermal diffusivity $\alpha(T)$ of $La_{1-X}Ca_XMnO_3$ system for (a) $X = 0-0.25$, (b) $X = 0.50-0.75$ and (c) $X = 0.82-1.0$.

For $X = 0.50$ (Fig. 1(b)), where the AFM and CO state is stable below $T_{CO} = 230$ K, an anomalous decrease of $\alpha(T)$ is observed just below T_{CO}. The rather gradual reduction of $\alpha(T)$ below T_{CO} is a common and characteristic feature in the CO state, as is shown for $X = 0.67$ and 0.75 samples. For $X = 0.82$ and 0.90 samples, where a canted AFM order takes place below T_{CAF} [8], $\alpha(T)$ shows a sharp dip around T_{CAF}. At high temperatures, where the crystal structure belongs to the O*- or R-phase, the gradient $\mathrm{d}\alpha/\mathrm{d}T$ changes systematically from negative to positive with increasing X. $X = 0.67$ is the critical concentration for this $\mathrm{d}\alpha/\mathrm{d}T$ change. The systematic change of $\mathrm{d}\alpha/\mathrm{d}T$ suggests that the lattice dynamics of this system become rather normal with the decrease of the JT ion (Mn^{3+}) density. The change of $\mathrm{d}\alpha/\mathrm{d}T$ with X may be understood as follows. As we have pointed out in our previous papers [3,4,9], phonon scattering by randomly distributed local JT distortions is vital to limit the phonon thermal conductivity κ_{ph}. The anomalous positive $\mathrm{d}\alpha/\mathrm{d}T$ occurs for $X \leqslant 0.67$ where the density n of the JT active Mn^{3+} ($n = 1 - X$, nominally) is pretty large. In the higher temperature region where the lattice oscillation amplitudes become large owing to increasing number of phonons, the local JT

distortions may be obscured and may become less effective in phonon scattering. Thus the existence of the JT active ions may be the main origin for the anomalous positive $d\alpha/dT$. For $X = 1.0$ sample, where the Mn^{3+} ions are nominally absent, the absolute value of $\alpha(T)$ and the negative diffusivity gradient is very large. It is also worthwhile to notice that in the cooperatively (and coherently) JT distorted O-phase of $LaMnO_3$ ($X = 0$), $d\alpha(T)/dT$ is again negative and normal.

Fig. 2 shows the specific heat $C(T)/C(300\,K)$ normalized to the room temperature value for the typical samples. For $X = 0$ sample, two specific heat anomalies were observed at $T_{S1} = 530\,K$ and $T_{S2} = 803\,K$. It should be noticed that the anomaly at T_{S2} becomes sharp at $X = 0.06-0.25$, where $\alpha(T)$ abruptly enhances upon heating, and then becomes broad for higher X samples. The structural phase transition at T_{S2} for $X \leqslant 0.25$ is not of the simple first-order but of the second-order-like.

Fig. 3 shows the phase diagram of the LCMO system determined by the anomalies of $\alpha(T)$ and $C(T)/C(300\,K)$ together with those of other physical quantities such as magnetization $M(T)$ and the sound velocity $v_s(T)$ [10]. The phase boundaries between O- and O*-phases and between O*- and R-phases have been clearly determined in this work. The obtained phase diagram is consistent with that proposed by Uehara et al. [11].

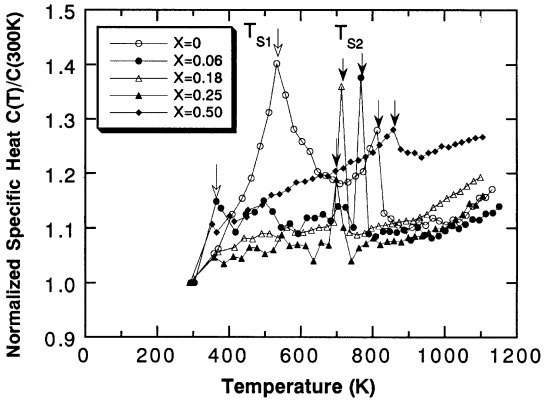

Fig. 2. Temperature dependence of the specific heat $C(T)/C(300\,K)$ normalized by the room temperature value for typical LCMO samples.

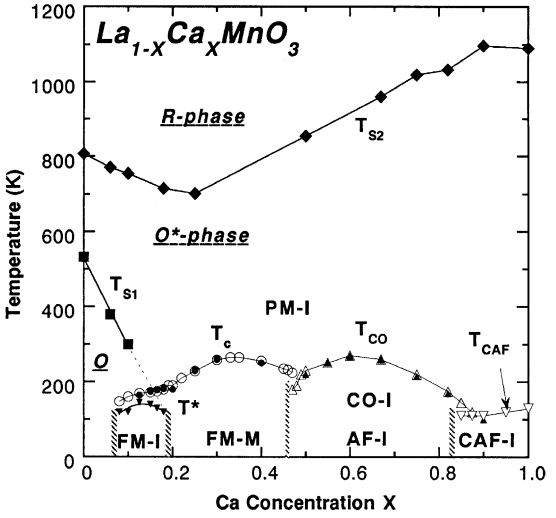

Fig. 3. The determined phase diagram of the LCMO system. ■ and ◆ represent the phase transition temperature T_{S1} between the O- and O*-phases and T_{S2} between the O*- and R-phases, respectively (see the text).

In summary, we measured thermal diffusivity $\alpha(T)$ of $La_{1-X}Ca_XMnO_3$ ($0 \leqslant X \leqslant 1.0$) in the temperature range from 10 to 1200 K. At high temperatures and in the octahedron rotated O*- and R-phases, we confirmed the anomalous positive temperature dependence of the diffusivity $\alpha(T)$ for the Ca concentration $X \leqslant 0.67$. The origin of the possible $d\alpha/dT$ has been attributed to the strong phonon scattering by the incoherent local JT distortions around Mn^{3+} ions, which becomes less effective with increasing phonon amplitude at higher temperatures. The phase diagram of the LCMO system was completed utilizing the anomalies in various physical quantities such as $\alpha(T)$, $C(T)/C(300\,K)$, $M(T)$ and $v_s(T)$.

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