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# First-order-like ferromagnetic transition in $(La_{1-y}Pr_y)_{1-x}(Ca_{1-z}Sr_z)_xMnO_3$ $(x \sim 0.25)$

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**Abstract**

The magnetization $M(T)$, electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ have been measured for the manganese oxides, $R_{0.75}A_{0.25}MnO_3$ ($R = La_{1-y}Pr_y$: $A = Ca_{1-z}Sr_z$) ($0 \leqslant y \leqslant 1.0, 0 \leqslant z \leqslant 1.0$). Two types of the first-order-like ferromagnetic transition have been verified; the transition shows no hysteresis for $1.345 \leqslant r_{RA} \leqslant 1.362$ Å ($r_{RA}$ = average ionic radius of R–A site), while it accompanies hysteresis for $1.320 < r_{RA} < 1.345$ Å. For $r_{RA} > 1.362$ Å and $r_{RA} < 1.320$ Å, the ferromagnetic transition is of the second order. The order of the transition may be closely correlated with the strength of the electron–phonon coupling as Millis et al. have predicted. 

*Keywords:* Manganese oxides; Ferromagnetic order; First-order–like transition; Electron–phonon coupling

Perovskite-based manganese oxides, $(R_{1-x}A_x)MnO_3$ (R = trivalent rare-earth ions such as La, Pr: A = divalent alkaline-earth ions such as Sr, Ca) display a variety of physical properties such as the paramagnetic (PM) to ferromagnetic (FM) transition synchronized with the insulator-to-metal (I–M) transition and the colossal magnetoresistance, etc. [1,2]. The novel physical properties of this system are greatly influenced by the hole concentration $x$ and the average ionic radius $r_{RA}$ of (R–A) site ions. The effect of the difference in the ionic radius can be systematically interpreted in terms of the tolerance factor $f$ [3]. The $La_{1-x}Ca_xMnO_3$ system exhibits a first-order-like PM to FM transition at the Curie temperature $T_c$ for $0.25 \leqslant x \leqslant 0.30$, showing an almost discontinuous increase of the magnetization [4,5], though no trace of hysteresis is seen. The electrical resistivity also shows a sharp drop at $T_c$. Generally, the FM transition is of the second order, but a first-order FM transition may be possible in case of a strong magneto–elastic or electron-phonon coupling [4,6]. In this note, we investigate the magnetization $M(T)$, electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ of $(La_{1-y}Pr_y)_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ samples. The hole concentration $x$ is fixed at 0.25, because $La_{0.75}Ca_{0.25}MnO_3$ shows the most typical first-order-like transition. $r_{RA}$ is changed by varying $y$ and $z$ values. The ranges of $y$ and $z$, where the first-order-like ferromagnetic transition is observable, have been determined.

$La_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ and $(La_{1-y}Pr_y)_{0.75}Ca_{0.25}MnO_3$ samples were prepared by a solid-state reaction method. The mixtures of raw powders were calcined at 1000°C for 24 h in air, pressed into pellets and sintered at 1500°C for 8 h in air. $\rho(T)$ was measured by a standard four-point probe method and M(T) was measured using a SQUID magnetometer under a magnetic field of 0.5 T after zero-field cooling. $\kappa(T)$ was automatically measured by a continuous heat-flow method.

Fig. 1 shows the temperature dependence of the magnetization $M(T)$ of $(La_{1-y}Pr_y)_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ samples. $T_c$ increases with increasing average ionic radius $r_{RA}$ ($r_{Pr} < r_{La}$ and $r_{Ca} < r_{Sr}$). The step-like $M(T)$ anomaly around $T_c$ can be observed for the samples of $(La_{1-y}Pr_y)_{0.75}Ca_{0.25}MnO_3$ $(0 \leqslant y \leqslant 0.2)$ and $La_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ $(0 \leqslant z \leqslant 0.3)$.

Fig. 2 shows the temperature dependence of the resistivity $\rho(T)$. $\rho(T)$ decreases below $T_c$ and shows the

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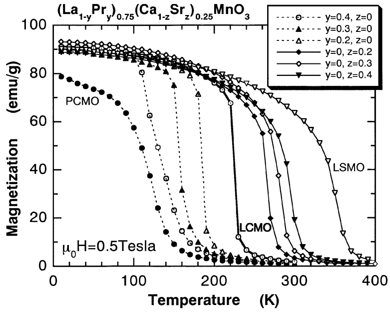


Fig. 1. The temperature dependence of the magnetization $M(T)$ of $(La_{1-y}Pr_y)_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ samples.

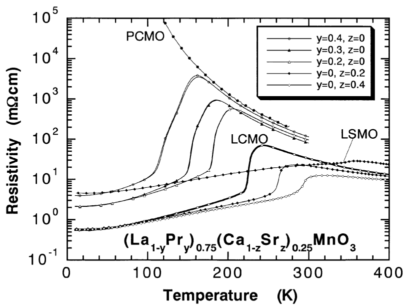


Fig. 2. The temperature dependence of the resistivity $\rho(T)$ of the samples.

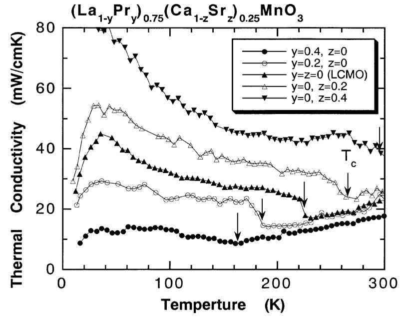


Fig. 3. The temperature dependence of the thermal conductivity $\kappa(T)$ for typical samples.

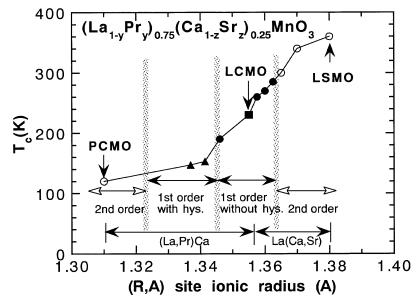


Fig. 4. The average ionic radius of (R–A) site ions $r_{RA}$ versus the ferromagnetic transition temperature $T_c$ determined using the results in Figs. 1–3.

metallic behavior at low temperatures except for $Pr_{0.75}Ca_{0.25}MnO_3$. A step-like decrease of $\rho(T)$ without hysteresis is observed just below $T_c$ for the samples in which the step-like $M(T)$ anomaly is observable. $\rho(T)$ of $(La_{1-y}Pr_y)_{0.75}Ca_{0.25}MnO_3$ ($y = 0.3$ and 0.4) shows a hysteresis around $T_c$ which suggests the first-order nature of the transition. The observation of a similar hysteresis in $\rho(T)$ was also reported by other authors [7]. The absolute value of $\rho$ decreases with increasing average ionic radius $r_{RA}$. For $La_{0.75}Sr_{0.25}MnO_3$, however, the $\rho$ value increases again, which is somewhat contradictory to our anticipation.

Fig. 3 shows the temperature dependence of the thermal conductivity $\kappa(T)$ for several samples. For the sample of $(La_{1-y}Pr_y)_{0.75}(Ca_{1-z}Sr_z)_{0.25}MnO_3$ ($y = 0.4$, $z = 0$) with smaller $r_{RA}$, $\kappa(T)$ shows a local minimum around $T_c$. A step-like anomaly (without hysteresis) of $\kappa(T)$ at $T_c$ can be seen for the ($y = 0.2$, $z = 0$), ($y = 0$, $z = 0$) and ($y = 0$, $z = 0.2$) samples. For the ($y = 0$, $z = 0.4$) sample with larger $r_{RA}$, the step-like anomaly of $\kappa(T)$ disappears again.

Fig. 4 shows $r_{RA}$ versus the ferromagnetic transition temperature $T_c$ for the present samples using the results in Figs. 1–3. $r_{RA}$ is calculated from the tabulated radii of (R–A) site cations with 12-fold coordination ($La^{3+} = 1.36$ Å, $Pr^{3+} = 1.30$ Å, $Sr^{2+} = 1.44$ Å, $Ca^{2+} = 1.34$ Å) [8]. $T_c$ is scaled by $r_{RA}$ as reported for the other fixed values of the hole concentration [7]. We classify the first-order-like FM transition into two groups, i.e., with and without hysteresis. The range of $r_{RA}$, where the first-order-like FM transition shows no hysteresis, is $1.345 \leqslant r_{RA} \leqslant 1.362$ Å and that where it shows hysteresis is $1.320 < r_{RA} < 1.345$ Å. The second-order-like FM transition occurs beyond both ends of these $r_{RA}$ regions.

It is not unreasonable to anticipate that the strength of the effective electron–phonon coupling is correlated with $r_{RA}$ and because of increasing internal stress acting on Mn–O–Mn bonds, the coupling may become stronger for the smaller $r_{RA}$. Millis et al. theoretically predicted that a first-order transition may be possible between PM insulator and FM metal phases for an intermediately strong electron–phonon coupling [6]. The experimental results of this study may exemplify a typical case of the first-order-like FM transitions which is in accord with the prediction.

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