First-order-like ferromagnetic transition in (La$_{1-y}$Pr$_y$)$_{1-x}$(Ca$_{1-z}$Sr$_z$)$_x$MnO$_3$ ($x \sim 0.25$)

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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 = 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 magneto-resistance, 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$_x$MnO$_3$ system exhibits a first-order-like PM to FM transition at the Curie temperature $T_c$ for $0.25 \leq x \leq 0.30$, 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$_3$ ($0 \leq y \leq 0.2$) and La$_{0.75}$(Ca$_{1-z}$Sr$_z$)$_{0.25}$MnO$_3$ ($0 \leq z \leq 0.3$).

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

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PII: S 0 9 2 1 - 4 5 2 6 ( 9 9 ) 0 0 8 8 9 - 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$_{0.75}$Pr$_{0.25}$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$_{0.75}$Pr$_{0.25}$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 ($y=0.2$, $z=0$), ($y=0$, $z=0.2$) and ($y=0$, $z=0.4$) 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 $1.345 < r_{RA} < 1.362$ 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.

**References**