EFFECT OF *A*-SITE CATION SIZE MISMATCH ON FIRST-ORDER-LIKE FERROMAGNETIC TRANSITION IN PEROVSKITE MANGANITES*

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The effect of the A-site cation radius variation σ^2 on the ferromagnetic (FM) and metal–insulator (M–I) transition in ${R^{3+}}_{0.75}{M^{2+}}_{0.25}MnO_3$ mixed crystals has been studied by measuring the magnetization $M(T)$, electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$. With increasing σ^2, the first-order-like character of FM and M–I transition observed in $La_{0.75}Ca_{0.25}MnO_3$ is promptly suppressed in mixed crystals in spite of the same tolerance factor Γ value kept constant to that of $La_{0.75}Ca_{0.25}MnO_3$.

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1. Introduction

A series of carrier-doped perovskite manganites with the formulae $RE_{1-X}AE_XMnO_3$ (RE=lanthanide: AE=alkaline earth) exhibit a variety of novel physical properties and have been the subject of recent revived researches [1,2]. The novel properties originate from competitions and cooperations of various interactions of nearly equal importance, *i.e.*, the double exchange, superexchange, charge and orbital order, Jahn–Teller (J–T) effect due to Mn^{3+} ions, A- and B-site cation radii mismatch in the ABO_3 perovskite lattice, *etc.* The characterisitc metal–insulator (M–I) transition concomitant with the ferromagnetic (FM) order cannot be explained by the double exchange mechanism only, and the importance of the lattice effect is widely admitted. The lattice effect is enhanced through the J–T effect and A–B cation radius mismatch. In a previous paper [3], we reported an anomalous first-order-like ferromagnetic M–I transition in mixed crystals, $(La_{1-Y}Pr_Y)_{0.75}$ $(Ca_{1-Z}Sr_Z)_{0.25}$ MnO_3. The anomalous transition did not involve hysteresis and took place for the average A-cation radius,

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1.195Å$<r_A<$1.212Å(r_A in 9-hold coodination). The most clear and typical first-order-like behavior was exhibited by $La_{0.75}Ca_{0.25}MnO_3$ (LCMO) with r_A=1.207Å. The r_A value determines the lattice distortion from the cubic form through the tolerance factor Γ ($=(r_A+r_O)/(\sqrt{2}(r_B+r_O))$, r_B and r_O being the ionic radii of Mn and oxygen). The single electron energy bandwidth W becomes wider as the Γ value approaches 1 and, resultantly, the FM metal (FM–M) phase is more strongly stabilized in a nearly cubic lattice. Rodoriguez *et al.* [4] and Sundaresan *et al.* [5] pointed out that not only the r_A value but also its variance σ^2 significantly affect the FM and M–I transition in the manganite systems. In this paper, we investigate the effect of σ^2 on the FM–M phase transition, with special emphasis on the first-order-like behavior, by monitoring the magnetization M(T), electrical resistivity $\rho(T)$ and the thermal conductivity $\kappa(T)$.

2. Experimental

$RE_{1-X}AE_XMnO_3$ samples (RE: La, Pr, Nd, Sm and $La_{0.50}Sr_{0.50}$, AE: Ca, Sr, Ba and thier mixtures) were prepared by a solid-state reaction method. The mixtures of raw powders were calcined at 1000°C for 24h in air, pressed into pellets and sintered at 1500°C for 8h in air. The mixing ratios of AE ions were selected so as to keep the average A-site cation radius constant (r_A=1.207Å, Γ=0.917) and the hole concentration at X=0.25. The mixing ratios, the sample symbols used in the text and the values of σ^2 are summarized in Table 1. The radius variance is given by $\sigma^2=\Sigma y_i r_i^2 - r_A^2$, where y_i is the fractional occupancy of the A-site species and r_i is its ionic radius. For calculation, tabulated radii r_i with 9-hold coordination [6] were used. The magnetization M(T) was measured using a SQUID magnetometer. The thermal conductivity $\kappa(T)$ was measured by a steady-state heat flow method in a Gifford-McMahon (GM) cycle helium refrigerator.

TABLE I

Sample compositions and σ^2 values

Sample	Symbol	σ^2
$La_{0.75}Ca_{0.25}MnO_3$	LCMO	0.0006
$(La_{0.50}Pr_{0.50})_{0.75}(Ca_{0.573}Sr_{0.427})_{0.25}MnO_3$	(LaPr)(CaSr)	0.0015
$Pr_{0.75}(Ca_{0.146}Sr_{0.854})_{0.25}MnO_3$	Pr(CaSr)	0.0030
$Nd_{0.75}(Sr_{0.819}Ba_{0.181})_{0.25}MnO_3$	Nd(SrBa)	0.0068
$Sm_{0.75}(Sr_{0.237}Ba_{0.763})_{0.25}MnO_3$	Sm(SrBa)	0.0180

3. Results and discussion

Figure 1(a) shows M(T) of respective samples under the field of 0.5 T. With decreasing temperature T, M(T) of LCMO ($\sigma^2 = 0.0006$) jumps up step-like just below T_c, which is a characteristic feature of the first-order-like transition. The step-up-like M(T) is somewhat obscured for (LaPr)(CaSr) ($\sigma^2 = 0.0015$) and M(T) becomes completely second-order-like for larger σ^2 values. For Sm(SrBa) with the largest σ^2 value (=0.0180), the FM saturation moment in the low T region is remarkably reduced. Figure 1(b) presents $\rho(T)$ for the same samples as in Fig. 1(a). A very sharp drop of $\rho(T)$ is noticed for LCMO and (LaPr)(CaSr), while it exhibits gentle variations at T_c for the larger σ^2. The $\rho(T)$ behaviors are all metallic below the FM transition temperature T_c except for Sm(SrBa).

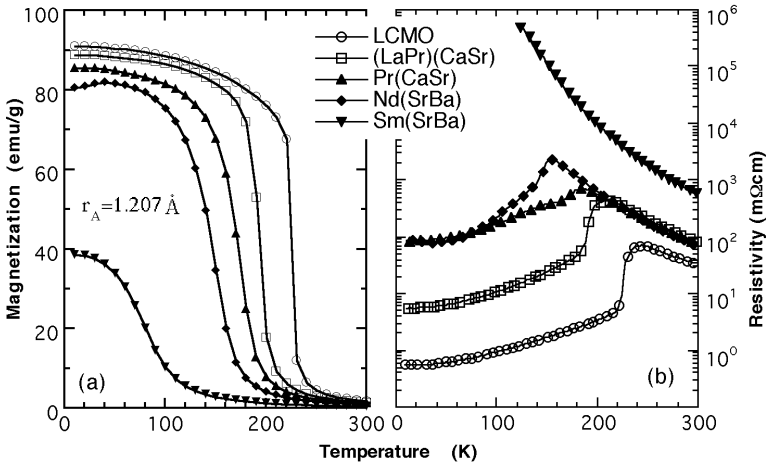

Fig. 1. (a) M(T) and (b) $\rho(T)$ for the samples given in Table I.

Figure 2(a) shows $\kappa(T)$, which is contributed overwhelmingly by phonons ($\kappa \simeq \kappa_{ph}$) in the present samples. For LCMO, $\kappa(T)$ shows a step-like rise just below T_c with decreasing temperature and then is gradually enhanced with further decrease of T. In (LaPr)(CaSr), the $\kappa(T)$ jump just near T_c and the gradual enhancement become pretty moderate. In contrast, $\kappa(T)$ of Pr(CaSr), which shows the second-order-like M–I transition, does not show such anomalous behaviors. Figure 2(b) presents T_c *vs* σ^2. T_c decreases with increasing σ^2. It is worthwhile to notice that the perovskite manganite system with the hole concentration $X = 0.25$ and the tolerance factor $\Gamma = 0.917$ is transformed to a FM-insulator by the large σ^2 values (Sm(SrBa)).

In summary, the A-site cation radius variance σ^2 vitally affects the ferromagnetic and the metal-insulator transition in the perovskite manganite system. In the mixed crystals, the first-order-like FM and M–I transition

promptly disappeared with increasing σ^2 in spite of the constant tolerance factor $\mathit{\Gamma}(= 0.917)$ and the constant hole concentration $X = 0.25$. The behavior of the thermal conductivity $\kappa(T)$ was also heavily influenced by the σ^2 value.

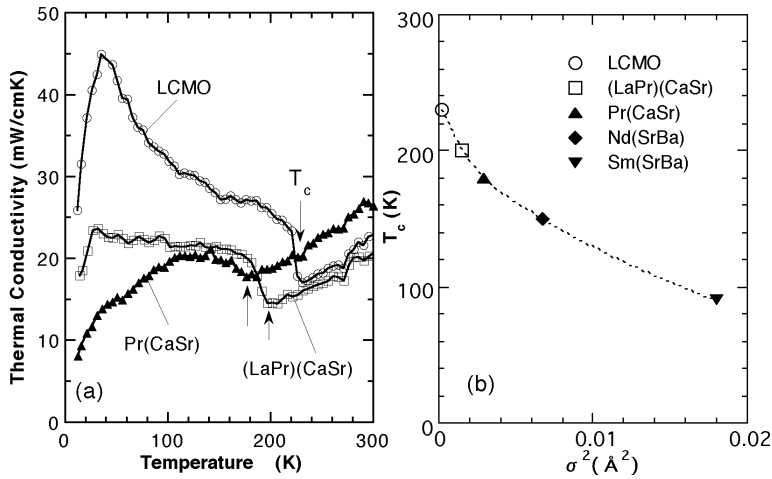

Fig. 2. (a) $\kappa(T)$ for the LCMO, (LaPr)(CaSr) and Pr(CaSr) samples and (b) T_c *vs* σ^2 for the samples given in Table I. The specimens denoted by open symbols show the first-order-like transitions.

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