

Structure dependence of the ferromagnetic transition temperature in rhombohedral $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Na, K, Rb, and Sr}$)

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Structure analysis and measurement of resistivity under both isostatic pressure smaller than 1.1 GPa and magnetic field of 1 T were carried out for rhombohedral $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Na, K, Rb, and Sr}$). A close relationship was confirmed to hold between T_c and the bond distance of Mn-O. The application of the isostatic pressure up to 1.1 GPa decreased the resistivity more than 60% below T_c but this effect was smaller above T_c . This pressure dependency was explained by the decrease in bond distance of Mn-O under pressure. Magnetic resistance for $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ was found to be $-10\%/T$, which is the same order of the previous reports for $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Ca, Sr, Ba}$).

The electronic states of transition-metal ions in the complex oxides have attracted much attention after the superconductivity was found in cupric oxides. Before the discovery of the high-temperature superconductivity in cupric complex oxides, metal-nonmetal transition has been mainly focused on 3d single-element oxides, V_2O_3 , Ti_2O_3 , and VO_2 . Recently, Zaanen, Sawatzky, and Allen^{1,2} (ZSA) have shown a general framework of classification of oxides, metallic or insulative oxides. Based on this framework, Torrance *et al.*³⁻⁵ succeeded to explain the metallic and insulative oxides in more general and in detail. According to the ZSA picture, two types of gaps are possible. One is Mott-Hubbard gap and the other is charge-transfer gap. Oxides in an earlier group in 3d transition metals such as V_2O_3 , Ti_2O_3 , and VO_2 are known to show the metal-insulator transition due to the Mott-Hubbard gap, and the oxides in the later 3d transition metals such as RNiO_3 ($R = \text{lanthanide ions}$) show the transition due to the charge-transfer gap. Torrance *et al.* clearly explained the electronically induced structural changes in RNiO_3 ($R = \text{La, Nd, Sm}$). At the metal-insulator transition in these systems, a small volume change, a small change in Ni-O distance, and a small change in the Ni-O-Ni angle are observed. A close relationship has been suggested to exist between the Ni-O-Ni angles and the transition temperature but clear relation between the structural parameters and the metal-nonmetal transition temperature has not been observed.

Properties of perovskite-type complex oxides, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Ca, Sr, Ba, and Pb}$) (Refs. 6 and 7) is of interest because these compounds show a ferromagnetic transition accompanied by the metal-nonmetal transition which is originating from the double exchange interaction.⁸ The relation between the substituted amount x and ferromagnetic transition temperature or saturated magnetization has been known in these materials, but no simple relation between T_c and structural parameters has not been found. Since the giant magnetic resistance (GMR) effect has been quite recently found for these compounds,⁹⁻¹² it is necessary to find out the relationship between the structural parameters and ferromagnetic transition temperature in the manganese perovskite. In this paper, we report a systematic study of the

metal-nonmetal transition and magnetic phase transition mainly in alkali-substituted $\text{La}_{1-x}\text{A}_x\text{Mn}_2\text{O}_3$ in order to grasp the behaviors of the ferromagnetic phase transition originating from the double-exchange interaction so that we can better understand their interrelationships and the physical origins.

Samples of $\text{La}_{1-x}\text{A}_x\text{Mn}_2\text{O}_3$ were synthesized by the conventional solid-state reaction technique. Stoichiometric mixture of powders of MnO_2 (4N), $\text{MnCO}_3\cdot\text{H}_2\text{O}$ (analytical grade), La_2O_3 (4N), Na_2CO_3 (3N), K_2CO_3 (3N), Rb_2CO_3 (3N), SrCO_3 (3N) were calcined in air at 1293 K. After pulverizing, the powder was pressed into pellets at a pressure of 160 MPa and sintered at 1393 K and furnace cooled in an oxygen gas flow. This pulverizing and sintering process was repeated once. Some of the samples were quenched from 1393 K into liquid nitrogen. Identification of the phase and structural analysis were carried out by the powder x-ray-diffraction technique using MAC Science MXP18 HF x-ray diffractometer equipped with graphite monochromator. High-purity silicon powder was used as an internal standard for the lattice parameter determination. Structural analysis was carried out using the Rietveld structural refinement program, RIETAN,¹³ for the data measured at conditions of 0.02° step scanning, accumulating for 1 s, the accelerating voltage 50 kV, and the current 300 mA. The metal content in the sintered sample was determined by the induced coupled plasma (ICP) spectroscopy and the valence of manganese ions was determined by the redox titration technique. Atomic absorption analysis was carried out for the sample containing Rb. Magnetic susceptibility was measured using both a Quantum Design MPMS2 SQUID magnetometer and a Shimadzu MB-2 magnetic balance in the temperature ranges $T < 350$ K and $300 < T < 1000$ K, respectively. Measurement of resistivity under high pressure was carried out using a clamp-type piston cylinder below 1.1 GPa under the magnetic field between 0 and 1 T.

Table I summarizes the results of chemical analysis and magnetic susceptibility measurements. All the samples were found to have the rhombohedral symmetry of the space group $R\bar{3}c$ and almost constant valency between 3.24 and 3.45. It is clear that alkali metal evaporated during sintering

TABLE I. Summaries of chemical analysis and determination of valence of manganese ions, and magnetic susceptibility measurements.

Composition	Valence manganese ions	T_c (K)
$\text{La}_{0.95}\text{Mn}_{0.93}\text{O}_3$	3.36(3)	185
$\text{La}_{0.93}\text{Na}_{0.04}\text{Mn}_{0.96}\text{O}_3$	3.31(3)	219
$\text{La}_{0.88}\text{Na}_{0.09}\text{Mn}_{0.96}\text{O}_3$	3.40(3)	286
$\text{La}_{0.90}\text{Na}_{0.09}\text{Mn}_{0.97}\text{O}_3^a$	3.29(2)	274
$\text{La}_{0.84}\text{Na}_{0.12}\text{Mn}_{0.97}\text{O}_3$	3.45(3)	336
$\text{La}_{0.82}\text{Na}_{0.16}\text{Mn}_{1.00}\text{O}_3$	3.38(3)	308
$\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$	3.40(3)	270
$\text{La}_{0.90}\text{K}_{0.06}\text{Mn}_{0.99}\text{O}_3^a$	3.26(2)	260
$\text{La}_{0.82}\text{K}_{0.14}\text{Mn}_{1.02}\text{O}_3$	3.41(3)	330
$\text{La}_{0.91}\text{Rb}_{0.06}\text{Mn}_{0.94}\text{O}_3$	3.41(3)	234
$\text{La}_{0.94}\text{Rb}_{0.06}\text{Mn}_{0.99}\text{O}_3^a$	3.24(2)	222
$\text{La}_{0.86}\text{Sr}_{0.09}\text{Mn}_{0.96}\text{O}_3$	3.42(3)	246
$\text{La}_{0.78}\text{Sr}_{0.18}\text{Mn}_{0.97}\text{O}_3$	3.37(3)	326
$\text{La}_{0.70}\text{Sr}_{0.28}\text{Mn}_{0.99}\text{O}_3$	3.37(3)	376

^aQuenched from 1393 K into liquid nitrogen.

although starting composition was aimed $\text{La}_{1-x}\text{A}_x\text{MnO}_3$. A small amount of evaporation of manganese during sintering was also confirmed. There is no clear correlation between the substituted amount and valence, i.e., the control of valency of manganese ions was not possible using the sintering condition in this study. Similar phenomena has been reported for the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ system by Takeda *et al.*¹⁴ Using the compositions and the valency of manganese ions in the sample, all the samples should have excess oxygens, i.e., interstitial oxygens. However, we represent all the samples by the formula $\text{La}_y\text{A}_x\text{Mn}_u\text{O}_3$ with no interstitial oxygen since Tofield and Scott¹⁵ and Roosmalen *et al.*¹⁶ reported that cation vacancies exist both in A and B sites instead of oxygen interstitials by the neutron technique. Figure 1 shows the plot of T_c versus valence of manganese ions. Surprisingly, we could not find a clear relationship between the valence of manganese ions and T_c although the amount of substitution or valence of manganese ions could be variables for the change in T_c in the previous reports.^{1,2} Figure 2 shows the variation of T_c with the change in bonding angle of Mn-O-Mn and the bond distance of Mn-O determined by the Rietveld analysis. We can recognize a tendency that T_c tends to increase when the Mn-O-Mn bond angle increases although the scatter of the data and the estimated error are fairly large. On the contrary, we can recognize a clear relation between T_c and Mn-O distance, i.e., the data show a quadratic dependence. Since the value of spin moment S is almost constant in this system, the quadratic increase in T_c with the bond distance is caused by the increase in exchange integral J . As easily expected from the theory of the double-exchange interaction, shorter Mn-O distance in this structure, which corresponds to the larger Mn-O-Mn bonding angle (namely, being close to 180°), leads to a stronger interaction, giving the higher T_c and lower resistivity.

Figure 3 shows the pressure dependence of the resistivity for $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ under 0 and 1 T of the magnetic field. All the data shown in this figure have been normalized to show the resistivity at constant pressures since pressure

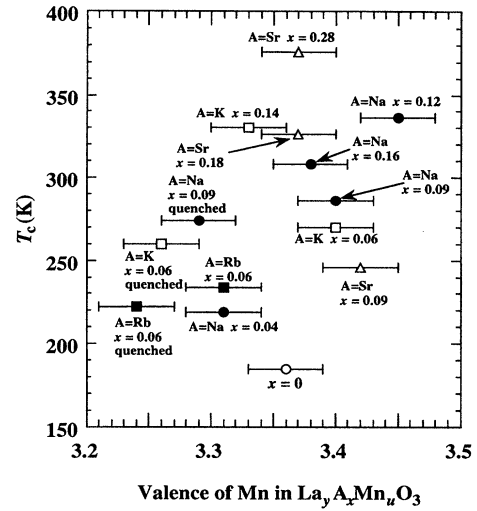


FIG. 1. Plot of ferromagnetic transition vs mean valence of manganese ions in $\text{La}_y\text{A}_x\text{Mn}_u\text{O}_3$. Values of x show the analytical values.

decrease with a temperature decrease cannot be avoidable using the clamp-type piston cylinder. It is clear that T_c increase at the rate $+15 \text{ K/GPa}$ ($d \ln T_c / dp = 0.056/\text{GPa}$) and resistivity decreases with an increase in pressure. We have carried out the measurement of ac susceptibility under high pressure and found that the small hump of the resistivity corresponds to T_c and the T_c increases at a rate 15 K/GPa ($d \ln T_c / dp = 0.056/\text{GPa}$). Referring to Fig. 2, the increase in T_c of 15 K corresponds to the decrease in the bond distance $6 \times 10^{-4} \text{ nm}$, where these two parameters are not independent of each other. It is easily expected that T_c would increase by applying pressure because the isostatic compression tends to decrease the bond distance and to increase the

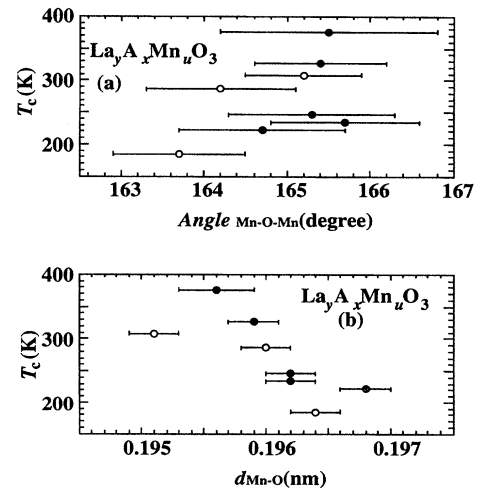


FIG. 2. Plot of magnetic transition temperature as a function of (a) Mn-O-Mn and (b) Mn-O distance in $\text{La}_y\text{A}_x\text{Mn}_u\text{O}_3$. Open circles are the data for $\text{A}=\text{Na}$ and $x=0$, solid circles are for $\text{A}=\text{Sr}$, and hatched circles are for $\text{A}=\text{Rb}$.

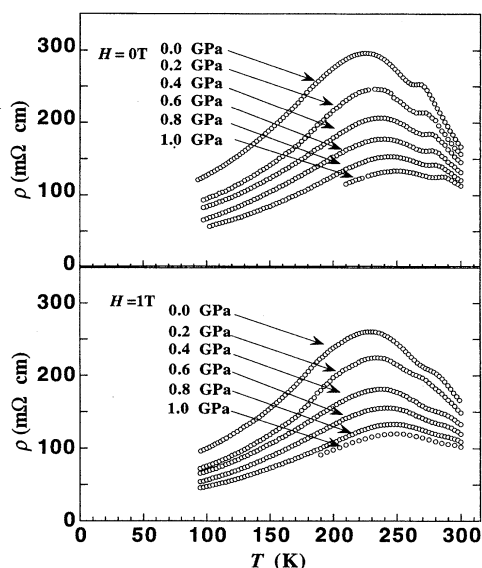


FIG. 3. Pressure dependence of the resistivity for $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ measured under 0 and 1 T magnetic field.

bond angle. Since we do not have the compressibility data for $\text{La}_y\text{A}_x\text{Mn}_z\text{O}_3$, we roughly estimate the linear compressibility as follows. Using the value of the volume compressibility for SrTiO_3 ,¹⁷ $6 \times 10^{-12}/\text{Pa}$ and assuming the isostatic compression under 1 GPa, a linear compression of $6 \times 10^{-3} \times 1 \times 10^9/3 = 2 \times 10^{-3} = 0.2\%$ is expected. Applying this value to $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$, we obtain the linear shrinkage of 4×10^{-4} nm for Mn-O distance. Since the compressibility of $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ cannot be same as that of SrTiO_3 , we can say that experimental and calculated values agree with each other, as a first approximation, and the effect of shrinkage in the bonding distance by all means contributes to the variation of T_c with pressure. In the double-exchange interaction, the transfer of electrons between the adjacent sites is given by the relation $\tilde{t} = t_0 \cos(\Delta\theta/2)$ where $\Delta\theta$ is the cant angle among the localized spin moments.¹⁸ Near T_c , isostatic pressure may help the direction of t_{2g} spins to align parallel to each other. We have already measured the pressure dependence of T_c and resistivity for SrRuO_3 which has T_c at 160 K. The decreases of the resistivities below and above T_c at 1 GPa and the pressure dependence of T_c for SrRuO_3 are -2% (130 K) and -5% (200 K), and -8 K/GPa ($d \ln T_c / dp = -0.05/\text{GPa}$),¹⁹ respectively. Therefore, the effect of the pressure for the resistivity of $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ is abnormally large, as shown in Fig. 3, about 1 order of

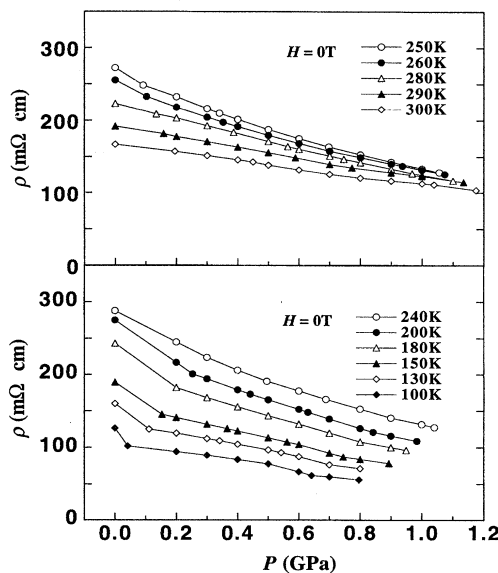


FIG. 4. Pressure dependence of resistivity at various temperatures.

magnitude higher compared to SrRuO_3 and the sign of pressure dependence of T_c of these two compounds is completely opposite. The effect of the magnetic field for the resistivity of $\text{La}_{0.87}\text{K}_{0.06}\text{Mn}_{0.97}\text{O}_3$ was found to be of the magnitude of $-10\%/T$ in the ferromagnetic state, which is consistent with results in the previous studies.⁹⁻¹²

Figure 4 shows the pressure dependence of resistivity at constant temperatures. It is apparent that the decrease in resistivity is larger in the ferromagnetic state compared to the paramagnetic state and this is explained by the difference in the scattering of charge by the localized spin moment in t_{2g} orbital. These behaviors are also considered to be correlated to a change in the compressivity of the crystal due to the rhombohedral-orthorhombic phase transition at lower temperatures.²⁰

As a conclusion, a clear relationship was not observed between T_c and mean valence of manganese ions or substituted amount for $\text{La}_y\text{A}_x\text{Mn}_z\text{O}_3$ ($A = \text{Na}, \text{K}, \text{Rb}, \text{Sr}$). However, a close relationship between T_c and the Mn-O distance was clearly shown to exist in this study. This is qualitatively correlated to the strength of the double-exchange interaction. More quantitative discussion will be carried out based on the results obtained by the other experimental techniques.

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