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Electronic and Magnetic Properties of Perovskite Manganites Including Rare Earth Metal Ions

Tomoyuki Terai, Tomoyuki Kakeshita, Takashi Fukuda, Masahiko Yamamoto,
Toshio Saburi*, Hiroki Kitagawa**, Koichi Kindo**, and Makoto Honda***

Department of Materials Science and Engineering, Graduate School of Engineering,
Osaka University, Suita, Osaka 565-0871, Japan, e-mail: terai-t@mat.eng.osaka-u.ac.jp
* Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan
** Research Center for Materials Science at Extreme Conditions, Osaka University,
Toyonaka, Osaka 560-8531, Japan
***Department of Physics, Faculty of Science, Naruto University of Education,
Naruto, Tokushima, 772-8502, Japan

Electronic and magnetic properties of perovskite manganites of $(La_{1-x}R_x)_{0.7}A_{0.3}MnO_3$ (R=Gd, Dy, Ho, Er ; A=Ca, Sr) have been studied by measuring electrical resistivity and magnetic susceptibility in order to know the relations between their electronic and magnetic properties and two parameters; tolerance factor, t (geometrical index), and the variance, σ^2 (the second moment), of A-site ion radii distribution. We found: (i) Curie temperature, T_C, where metal-insulator transition occurs, decreases with decreasing t. (ii) At the constant t, T_C also decreases with increasing σ^2. (iii) when t is smaller than 0.908 and σ^2 is larger than $2.0\times10^{-5}nm^2$, the compounds show spin-glass insulator state below T_g. Considering these results, we conclude that electronic and magnetic properties of manganites depend not only on t but also on σ^2.

Key words: perovskite, rare earth metal ions, metal-insulator transition, Curie temperature, tolerance factor

1. INTRODUCTION

Perovskite manganites with 20-40% of trivalent rare-earth ions of R^{3+} replaced by divalent alkaline-earth metal ions of A^{2+}, $R_{1-x}A_xMnO_3$, are found to show remarkable phenomena such as metal-insulator transition and colossal magnetoresistance (CMR) and are expected to be applied to electronic devices. Therefore, perovskite manganites have been extensively studied from the 1950s. According to the studies[1-3], electronic and magnetic properties of those manganites are mainly explained by double-exchange interaction, ferromagnetic interaction between Mn^{3+} and Mn^{4+} that is caused by the hopping of e_g electrons between the two partially filled d shells with strong on-site Hund's coupling[4].

Hwang *et al.*[5] have investigated $(La_{1-x}R_x)_{0.7}Ca_{0.3}MnO_3$ ($R=Pr^{3+}$, Y^{3+}) systematically while keeping the Mn^{3+}/Mn^{4+} ratio fixed at 7/3. They found that T_C decreases with increasing the content of Pr^{3+} and/or Y^{3+}. Considering these results, they concluded that the electronic and magnetic states of these compounds depend on tolerance factor, t. Incidentally the tolerance factor, a geometrical index, is defined as $t=(r_A+r_O)/\sqrt{2}\,(r_{Mn}+r_O)$, where r_A is the average ionic radius of R^{3+} and Ca^{2+}, r_O is the ionic radius of O^{2-}, and r_{Mn} is the average ionic radius of Mn^{3+} and Mn^{4+}.

However, recently, Rodriguez-Martinez and Attfield[6] speculated that the difference in size among A-site ions also influences electronic and magnetic properties of manganites. In order to quantify such a difference, they introduced the variance, σ^2 (the second moment), of the A-site ions radii distribution. Incidentally, σ^2 is defined as $\sigma^2=\sum y_i r_i^2-\langle r_i\rangle^2$, where i is difference of the kinds of A-site ions, r_i is the radius of each A-site ion, y_i is its fractional occupancy ($\sum y_i=1$), and $\langle r_i\rangle$ is the average radius of A-site ions. In the present study, therefore, we have investigated the relation between these parameters (t, σ^2) and electronic and magnetic properties of, $(La_{1-x}R_x)_{0.7}A_{0.3}MnO_3$ (R=Gd, Dy, Ho, Er; A=Ca, Sr).

2. EXPERIMENTAL

$(La_{1-x}R_x)_{0.7}A_{0.3}MnO_3$ compounds were prepared by conventional solid state reaction processing in air (calcined at 1273K for 12h, sintered at 1623K for 48h). t was determined by using ionic radii reported by Shannon[7]. Powder X-ray diffraction measurement was made at room temperature. Resistivity and magnetic susceptibility were measured by the standard four-probe method and by vibrating sample magnetometer (VSM), respectively.

3. RESULTS

3.1 X-ray diffraction measurement

From X-ray measurement, most compounds used show a single phase with a cubic structure at room temperature. These lattice constants change from 0.773 nm (t=0.916) to 0.763 nm (t=0.898) with decreasing t.

3.2 Resistivity measurements

We made resistivity measurements for the compounds with the cubic structure. Typical results of $(La_{1-x}Dy_x)_{0.7}Ca_{0.3}MnO_3$ are shown in Fig. 1, where metal-insulator transition temperature, T_{MI}, indicated with a single arrow, is observed. As known from the figure, T_{MI} decreases with decreasing t and goes to below 1.5K for t=0.898. It should be noted in the figure that resistivities of t=0.911, 0.908 and 0.907 increase again below temperatures indicated with double arrows, which correspond to the temperature of a spin-glass transition, which will be described later. Similar behavior of the electrical resistivity as a function of temperature are observed in the other compounds replaced by the other rare earth metal ions (Gd^{3+}, Ho^{3+}, Er^{3+}).

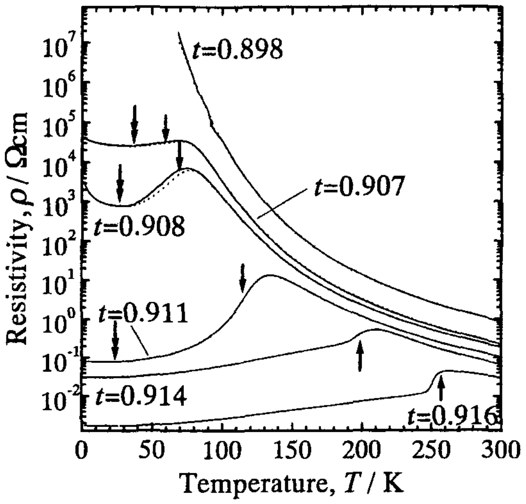

Fig.1 Temperature dependence of resistivity for $(La_{1-x}Dy_x)_{0.7}Ca_{0.3}MnO_3$.

3.3 Magnetic susceptibility measurements

We made magnetic susceptibility measurements on the two conditions; one is the zero-field-cooled (ZFC) run and the other is field-cooled (FC) run at H=0.01T. A typical result of the compounds including Dy^{3+} ions is shown in Fig. 2, where solid and dotted curves represent the results of ZFC and FC runs, respectively.

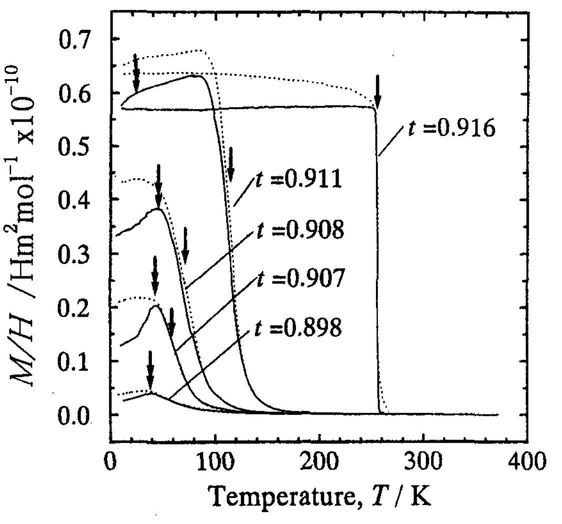

Fig.2 M/H-T curves of $(La_{1-x}Dy_x)_{0.7}Ca_{0.3}MnO_3$.

As known from the figure, Curie temperature, T_C, indicated with a single arrow, decreases with decreasing t. It should be noted that M/H-T curves of t=0.911, 0.908, 0.907 and 0.898 obtained by ZFC runs are different from those obtained by FC runs below temperatures indicated with double arrows. Similar temperature dependence of M/H-T curves were observed for $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$[8] and Fe-Au[9] and they were confirmed to show spin-glass states by neutron diffraction measurements. Therefore, the different behavior between ZFC and FC runs in the present compounds is believed to be due to a spin-glass transition. According to the previous studies[8,9], the transition temperature, T_g, is defined as a temperature where M/H-T curve of ZFC run yields to a cusp, in cases that T_C and T_g are close each other or identical. This situation holds for the compound of t= 0.908, 0.907 and 0.898 and, therefore, T_g, is determined as a temperature of the observed cusp, which is shown in each M/H-T curve with the double arrow. On the other hand, for the compound of t=0.911, M/H-T curve under a ZFC run has two cusps, being quite similar to that of a compound that becomes a typical reentrant spin-glass at low temperatures[9]. In this case, T_g is determined as a temperature where the second cusp appears (indicated with a double arrow in the figure).

4. DISCUSSION

Figure 3 shows T_C and T_g of the present $(La_{1-x}R_x)_{0.7}Ca_{0.3}MnO_3$ as a function of t. The figure also show T_C of the previous $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ obtained by Hwang *et al.*[5] In the figure, electronic and magnetic states in the present compounds are also shown by using notations derived previously[5,8]; that is, paramagnetic insulator (PMI), ferromagnetic metal (FMM), and spin-glass insulator (SGI).

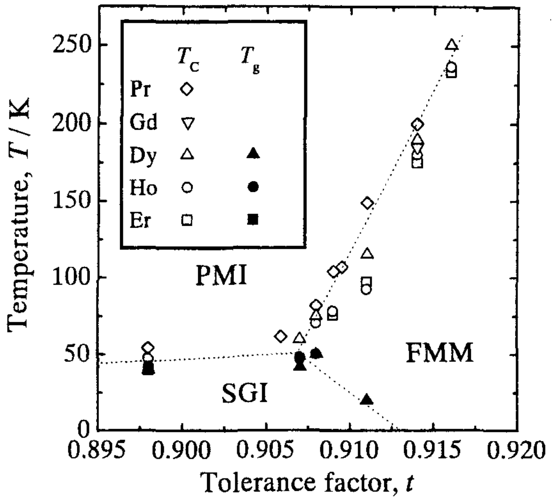

Fig.3 Elecronic and magnetic phase diagram of $(La\text{-}R)_{0.7}Ca_{0.3}MnO_3$.

It is noted from the figure, when t is larger than 0.913, T_C decreases with decreasing t, being similar to the previous study by Hwang *et al.*[5] However, when t takes values between 0.913 and 0.907, FMM state and reentrant spin-glass insulator state appears below T_C and T_g, respectively and when t is smaller than 0.907, SGI state appears, being different from the previous study by Hwang *et al.*[5] It should be also noted that T_C of present compounds are smaller than those of previous compounds although t takes the same value. These results suggest that electronic and magnetic states of these compounds does not depend on t only. Then, we plot the relation between T_C and σ^2 in order to know the influence of σ^2 on electronic and magnetic properties of manganites, as suggested by Lodriguez-Martinez and Attfield.

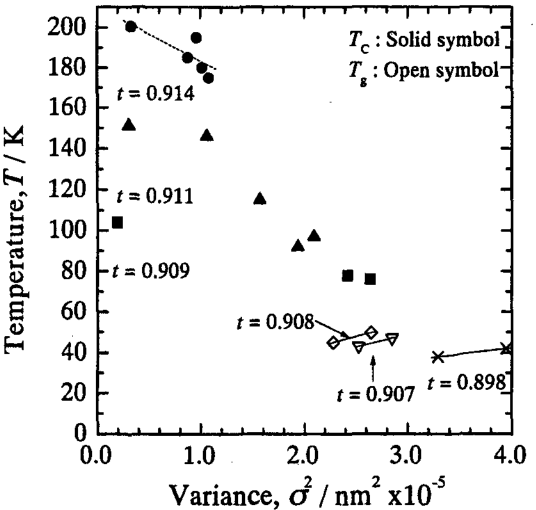

Fig. 4 The relations between σ^2 - T_C or T_g.

The relations between σ^2-T_C or Tg is shown in Fig. 4, where T_C decreases with increasing σ^2 even when t takes the same value. It is also noted that when σ^2 is larger than about 2.0×10^{-5} nm^2 and t is larger than 0.908, the ground state changes to SGI state, meaning that σ^2 also influences the electronic and magnetic properties of manganites. Such influences of t and σ^2 on electronic and magnetic properties of manganites are speculated as follows. That is, with decreasing t, Mn-O-Mn bond angles decreases; i.e., transfer integer b decreases[4]. This causes the decrease of T_C. On the other hand, with increasing σ^2, the randomness of Mn-O-Mn bond angles distribution increases; i.e., the compounds are inhomogeneous magnetically. This causes the SGI state consisting ferromagnetic and antiferromagnetic region. Thus, we conclude that electronic and magnetic properties of manganites depend not only on t but also on σ^2.

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