Structural Parameters and Physical Quantities of Doped Manganites

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We have performed neutron powder diffraction measurement on $(Nd_{1-z}Tb_z)_{0.6}Sr_{0.4}MnO_3$ with systematically changing the averaged ionic radius r_A of the perovskite A-site. On the basis of the structural parameters, we have estimated relative variation of the one-electron bandwidth W of the e_g state. We will discuss interrelation between the geometrical W and the physical quantities, such as Curie temperature T_C , spin wave stiffness coefficient D_s and the one-electron band width W_{opt} estimated from the optical spectroscopy.

KEYWORDS: doped manganites, neutron powder diffraction, chemical pressure

§1. Introduction

The doped manganites, $R_{1-x}A_x$ MnO₃, where R and A are the trivalent rare-earth and the divalent alkalineearth ions, respectively, have a distorted perovskite structure (*Pbmn*; Z = 4) with three dimensional networks of the MnO₆ octahedra. At moderate doping level (x = 0.2 - 0.4), the system becomes ferromagnetic metallic (FM) due to the inherent double-exchange mechanism.¹⁾ Significant feature of the distorted perovskite structure is that the Mn-O-Mn angle θ can be controlled by means of the chemical substitution of the perovskite A-site (*chemical pressure*). Actually, in $R_{1/2}A_{1/2}$ MnO₃, the averaged θ -value linearly decreases with decrease of the averaged ionic radius r_A of the perovskite Asite, as $\theta = -34 + 148r_A[\text{Å}]^{(2)}$ This buckling of the MnO_6 octahedra suppresses the one-electron bandwidth $W (\propto d^{-7/2} \cos(\pi/2 - \theta/2))^{3}$ where d is the averaged Mn-O bondlength) of the e_q state. The reduced-W value has been regarded as the origin for the suppressed Curie temperature $T_{\rm C}$ in the small- r_A compounds. Recently, however, several experimental results, e.g., x-ray diffuse scattering,^{4,5)} optical absorption,⁶⁾ Raman scattering⁷⁾ and electron diffraction measurement,⁶⁾ suggest that the fluctuation of the spin-charge-orbital-lattice degree of freedoms significantly affects the physical quantities, especially near the FM-insulator phase boundary.

In this paper, we have investigated variation of the structural parameters of doped manganites $(Nd_{1-z}Tb_z)_{0.6}Sr_{0.4}MnO_3$ (z = 0.0 - 0.4), at a fixed doping level (x = 0.4). We found that the W-value (geometrical W) estimated from the structural parameters negligibly changes with $T_{\rm C}$, making a sharp contrast with other physical quantities, such as spin wave stiffness coefficient $D_{\rm s}$ and the one-electron band width $W_{\rm opt}$ estimated from the optical spectroscopy.

§2. Experimental

A series of ceramics, $(Nd_{1-z}Tb_z)_{0.6}Sr_{0.4}MnO_3$ (z = 0.0, 0.1, 0.2, 0.3 and 0.4), was synthesized by solid state reaction in an air atmosphere. Stoichiometric mixture of

commercial Nd₂O₃, Tb₄O₇, SrCO₃, and Mn₃O₄ powder was well ground and calcined two times at $1250 - 1350^{\circ}$ C for 24 h. Then, the resulting powder was pressed into a disk with a size of 20 mm $\phi \times 4$ mm and sintered at $1250 - 1350^{\circ}$ C for 24 h. Temperature variation of the magnetization M was measured under a field of 0.5 T after cooling down to 5 K in the zero field (ZFC). $T_{\rm C}$ was determined from the inflection point of the M - Tcurve.

Neutron powder diffraction data were collected on a time-of-flight (TOF) diffractometer Vega at the Neutron Science Laboratory (KENS) in the High Energy Accelerator Research Organization (KEK). The data were



Fig. 1. The whole neutron powder diffraction patterns (cross) of (Nd_{0.7}Tb_{0.3})_{0.6}Sr_{0.4}MnO₃ obtained by the TOF method at 300 K. Solid curve is the result of the two phase Rietveld refinement with the "113" main phase and the "214" secondary phase.

accumulated for ~ 3 hour. The crystal symmetry is orthorhombic (*Pbnm*; Z=4). We have analyzed the powder patterns with RIETAN-98T program with taking account of the $(R, A)_2$ MnO₄ impurity phase (1 - 4 %). Standard deviations are estimated by the conventional method. We show in Fig. 1 a prototypical example of the Rietveld refinement. Thus obtained structural pa-

Table I. Lattice constants and atomic positions for $(Nd_{1-z}Tb_z)_{0.6}Sr_{0.4}MnO_3$ determined from neutron powder profiles at 300 K. The crystal symmetry is orthorhombic (*Pbnm*; Z=4). The atomic sites are R/A $4c[x, y, \frac{1}{4}]$, Mn $4b[\frac{1}{2}, 0, 0]$, O(1) $4c[x, y, \frac{1}{4}]$, O(2) 8d[x, y, z]. The R_I -value for the main phase and the volume ratio (s) of the secondary phase is also listed.

				R/A		O(1)		O(2)				
z	a (Å)	<i>b</i> (Å)	c (Å)	x	y	x	y	x	y	z	$R_{ m I}~(\%)$	s
0.0	5.4388(2)	5.4716(2)	7.6800(3)	0.0113(9)	0.0126(8)	0.954(1)	0.488(1)	0.2332(7)	0.7717(5)	0.0278(5)	2.23	0.018
0.1	5.4393(2)	5.4646(2)	7.6822(3)	0.0116(8)	0.0170(5)	0.957(1)	0.494(1)	0.2295(6)	0.7729(6)	0.0301(4)	1.91	0.035
0.2	5.4403(1)	5.4572(2)	7.6813(2)	0.0112(7)	0.0199(4)	0.9500(8)	0.4926(9)	0.2284(5)	0.7764(6)	0.0305(4)	1.67	0.015
0.3	5.4401(2)	5.4490(2)	7.6779(2)	0.0085(8)	0.0226(4)	0.9422(8)	0.4915(8)	0.2272(6)	0.7770(6)	0.0309(4)	1.53	0.007
0.4	5.4374(2)	5.4477(2)	7.6739(2)	0.0077(8)	0.0246(4)	0.9408(8)	0.4923(7)	0.2240(6)	0.7772(6)	0.0318(4)	1.75	0.008

rameters are listed in Table I together with the $R_{\rm I}$ -value for the main phase and the volume ratio (s) of the secondary phase. The final refinements are satisfactory, in which $R_{\rm I}$ are fairly reduced ($R_{\rm I} = 1.53 - 2.23$ %).

§3. Results and discussion

Figure 2(a) and (b) shows the Mn-O bondlength dand the Mn-O-Mn angle θ calculated from the structural parameters (see Table I) against r_A . Note that



Fig. 2. Variation of (a) Mn-O bond length d, (b) Mn-O-Mn angle θ and (c) $d^{-7/2}\cos(\pi/2\cdot\theta/2)$ of $(\mathrm{Nd}_{1-z}\mathrm{Tb}_z)_{0.6}\mathrm{Sr}_{0.4}\mathrm{MnO}_3$ against the averaged ionic radius r_A of the perovskite A-site. Solid curve is the guide to the eyes. Note that the one-electron band width W is proportional to $d^{-7/2}\cos(\pi/2\cdot\theta/2)$.

there are three Mn-O bondlengths, i.e., one out-of-plane $(d_c: \text{ open squares})$ and two in-plane $(d_{ab}: \text{ open circles})$

bondlengths, and two Mn-O-Mn bond angles, i.e., out-ofplane (θ_c : open squares) and in-plane (θ_{ab} : open circles) angles, in the Pbnm setting. The d-value shows negligible variation with r_A . This makes a sharp contrast with systematic variation of the averaged θ -value with r_A from 166 ° at z = 0.0 to 161 ° at 0.4. A similar relation between r_A and θ is also reported in $R_{1/2}A_{1/2}MnO_3$ $(x = 0.5)^{2}$ and $R_{1/2}A_{1/2}$ MnO₃ $(x = 0.3)^{.3}$ We have estimated relative variation of W of the e_q state with use of the averaged d (Fig. 2(a)) and θ ((b)), and plotted them in the bottom panel of Fig. 2. The W-value smoothly decreases with decrease of r_A . Thus, the dominant chemical pressure effect on the FM doped manganites with distorted perovskite structure is reduction of the Mn-O-Mn angle, and resultant variation of the W-value. Here, we should comment that the chemical pressure on the charge-ordering transition of $R_{1/2}A_{1/2}$ MnO₃ has an aspect of orbital control,²⁾ beside the control of the Wvalue.

Now, let us compare the geometrical W with other physical quantities, such as D_s and W_{opt} . In Fig. 3(a), we plotted the geometrical W against $T_{\rm C}$. In the double exchange model,¹⁾ $T_{\rm C}$ is expected to change in proportion to W. The experimental data, however, does not obey this relation. One probable origin for this discrepancy is the polaron effect⁸⁾ due to the inherent Jahn-Teller instability of the Mn^{3+} ions. In this case, the effective bandwidth $W_{\rm eff}$ is significantly suppressed as $W \exp(-\gamma E_{\rm JT}/\hbar\omega)$, where $E_{\rm JT}$ and γ are the stabilization energy and the dimensionless parameter. Since the γ -value decreases as $E_{\rm JT}/W$ decreases, the variation of $W_{\rm eff}$ is much steeper than that of W. Of course, the other fluctuations of the spin-charge-orbital-lattice degree of freedoms, such as the CO cluster,⁶⁾ the orbital fluctuation,⁹⁾ or the charge separation instability,¹⁰⁾ are the alternative candidates for the origin of this discrepancy.

In Fig. 3(b) we plotted D_s^{11} (open circles) and W_{opt}^{12} (filled circles). D_s was estimated from low temperature specific heat. These two physical quantities changes more steeply with $T_{\rm C}$ than the geometrical W (see Fig. 3(a)). This is because these quantities are amenable to the spatial and/or temporal fluctuations of spin, charge, orbital and lattice degree of freedoms. For example, the optical transition at ~ 3 eV, from which the W_{opt} -value has been estimated,^{12,13} is directly influenced by the t_{2g} -spin fluctuation. Contrary to these quantities, the geometrical W has no relation with these



Fig.3. (a) Geometrical $W (\propto d^{-7/2}\cos(\pi/2\cdot\theta/2))$ against Curie temperature $T_{\rm C}$. (b) spin wave stiffness coefficient $D_{\rm s}$ and oneelectron bandwidth $W_{\rm opt}$ obtained from optical spectroscopy against $T_{\rm C}$. $D_{\rm s}$ and $W_{\rm opt}$ are cited from Ref. 11 and Ref. 12. Solid curve is the guide to the eyes.

fluctuations, and therefore is apparently independent of $T_{\rm C}$. Nevertheless, the geometrical W slightly changes with r_A (see Fig. 2(c)), and can cause the fluctuation of the spin-charge-orbital-lattice coupled system. Especially in the vicinity of the FM-insulator phase boundary, a slight narrowing of the W-value is expected to induce large fluctuations, and could suppress the FM phase, as observed.

§4. Summary

We have investigated variation of the structural pa-

rameters of doped manganites, $(Nd_{1-z}Tb_z)_{0.6}Sr_{0.4}MnO_3$ (z = 0.0 - 0.4), at a fixed doping level (x = 0.4). We found that the geometrical W-value negligibly changes with $T_{\rm C}$, making a sharp contrast with other physical quantities, such as $D_{\rm s}$ and $W_{\rm opt}$. This suggests an important role of the fluctuations on the physical properties near the FM-insulator phase boundary in the spin-charge-orbitallattice coupled system.

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