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Lattice effects on the charge-ordering transition in $R_{0.5}$Sr$_{1.5}$MnO$_4$

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Magnetic and transport properties are investigated for single crystals of layered-type–doped manganites $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ with systematic variation of the averaged radius r_R of the trivalent rare-earth ions R^{3+}. $\mathrm{La}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ ($R=\mathrm{La}$) shows a charge-ordering (CO) transition at $T_{\mathrm{CO}}=230$ K. With a decrease of the in-plane Mn-O bond length $d_{\mathrm{Mn-O(in)}}$, T_{CO} decreases and eventually the transition disappears for $R=\mathrm{Nd}$. Such a remarkable lattice effect on the CO transition is in sharp contrast to the negligible lattice effect in the isostructural layered nickelates. [S0163-1829(97)02447-8]

Among the barely metallic 3d-electron systems, the manganese oxides are most extensively investigated because of their unusual magnetic and transport behaviors originating in the strong coupling between the e_g electrons, t_{2g} spins, Jahn-Teller (JT) instability, and e_g-orbital degree of freedom. In particular, perovskite-type compounds $R_{1-x}A_x\mathrm{MnO}_3$, where R and A are the trivalent rare-earth and divalent alkaline-earth ions, respectively, show the paramagnetic-to-ferromagnetic behaviors as well as large negative magnetoresistance[1] near above T_C. These phenomena are basically understood within the framework of double-exchange (DE) theory,[2,3] which includes only the transfer integral t of the e_g electrons and the on-site exchange interaction (Hund's-rule coupling J_H) between the itinerant e_g electrons and locarized t_{2g} spins ($S=3/2$). By contrast, in manganese oxides with a layered structure, e.g., in $\mathrm{La}_{1-x}\mathrm{Sr}_{1+x}\mathrm{MnO}_4$,[4,5] the MnO$_2$ sheets are isolated by two La(Sr)O planes. The resultant confinement of the e_g carriers in two dimensions should reduce the one-electron bandwidth W and enhance the other instabilities. One of the most prototypical examples may be the charge-ordering (CO) transition, i.e., real-space ordering of the doped carriers, observed in $\mathrm{La}_{1-x}\mathrm{Sr}_{1+x}\mathrm{MnO}_4$ ($x=1/2$) at $T_{\mathrm{CO}}=230$ K.[5] A similar CO transition is observed for other transition-metal oxides with layered structures, e.g., $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_4$ ($x=1/3$) (Ref. 6) and $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$ ($x=1/8$).[7] In particular, Cheong *et al.*[8] have reported that T_{CO} in layered nickelates is nearly independent of the ionic radius of the divalent alkaline-earth ions.

In this paper, we report a significant suppression of the CO transition in layered manganites $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ with a decrease of the average radius r_R of R^{3+} (*chemical pressure*), which makes a sharp contrast with the layered nickelates. With a decrease of r_R, T_{CO} decreases and eventually the transition vanishes for $R=\mathrm{Nd}$. We have ascribed the suppression of the transition to the increasing out-of-plane static JT distortion of the MnO$_6$ octahedra and to resultant stabilization of the $d_{3z^2-r^2}$ state. This observation suggests the important role of the orbital degree of freedom coupled with the JT instability in the CO transition for layered manganites.

Single crystals of $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ ($R=\mathrm{La}$, $\mathrm{La}_{0.5}\mathrm{Nd}_{0.5}$, $\mathrm{La}_{0.25}\mathrm{Nd}_{0.75}$, Nd, and Sm) were grown by the floating-zone method at a feeding speed of 20mm/h. A stoichiometric mixture of commercial La$_2$O$_3$, Nd$_2$O$_3$, Sm$_2$O$_3$, SrCO$_3$, and Mn$_3$O$_4$ powder was ground and calcined two times at 1300 °C for 20 h. Then the resulting powder was pressed into a rod with a size of $5\phi\times80$ mm^2 and sintered at 1350 °C for 30 h. The ingredient could be melted congruently in a flow of oxygen. Large single crystals, typically 4 mm in diameter and 20 mm in length, were obtained with two well-defined facets, which correspond to the crystallographic ab plane. Redox titaration indicates that the Mn valence is 3.50 ±0.04 for all the melt-grown crystals.[9] Powder x-ray-diffraction measurement at room temperature and Rietveld analysis[10] indicate that the crystals were single phase without detectable impurity. The crystal symmetry at 300 K is tetragonal ($I4/mmm$, $Z=4$) over the whole concentration range.

The CO transition in layered manganites shows up as a steep rise of resistivity ρ and a suppression of susceptibility χ.[5,11] Figure 1 shows the in-plane component of resistivity ρ_{ab} and magnetic susceptibility χ_{ab} ($=M_{ab}/H$; M_{ab} is in-plane component of magnetization) for a single crystal of $\mathrm{La}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ ($R=\mathrm{La}$). For four-probe resistivity measurements, the crystal was cut into a rectangular shape, typically of $3\times1\times1$ mm^3, and electrical contacts were made with a heat-treatment-type silver paint. χ_{ab} was measured under a field of $\mu_0H=0.5$ T after cooling down to 5 K in zero field (ZFC). With decreasing temperature, the ρ_{ab} value steeply increases below $T_{\mathrm{CO}}=230$ K (indicated by a downward arrow) accompanying a suppression of χ_{ab}. Thus we can monitor the CO transition with use of these anomalies observed in the ρ-T and χ-T curves. The structure of the charge- (and orbital-) ordered state of layered manganites has been investigated by several researchers. Sternlieb *et al.*[12] performed neutron-scattering measurements on a single crystal of $\mathrm{La}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ and found superlattice reflections cor-

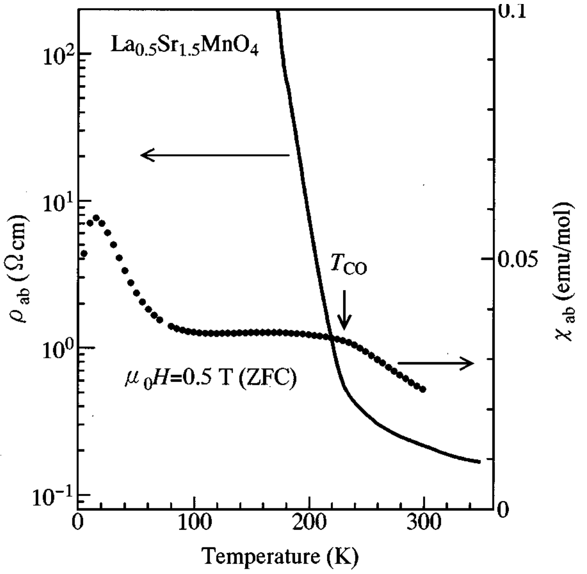

FIG. 1. In-plane component of resistivity (ρ_{ab}) and magnetic susceptibility (χ_{ab}) for a single crystal of $La_{0.5}Sr_{1.5}MnO_4$. A downward arrow indicates the charge-ordering transition.

responding to an alternating Mn^{3+}/Mn^{4+} pattern with wave vector (1/2, 1/2, 0) below T_{CO}. They further found a magnetic transition at $T_N \sim 110$ K far below T_{CO}, indicating that the spin ordering is not a main driving force of the CO transition. The electron-diffraction measurements,[5,11] however, indicate growth of fourfold modulation along the [110] and $[1\bar{1}0]$ directions below T_{CO}. Recently, Murakami *et al.*[13] performed synchrotron x-ray experiments on a single crystal of $La_{0.5}Sr_{1.5}MnO_4$ and concluded that the charge ordering with wave vector (1/2, 1/2, 0) accompanies an orbital ordering, i.e., an alternating e_g-orbital pattern, with wave vector (1/4, 1/4, 0).

Lattice constants were obtained by Rietveld analysis of powder- x-ray-diffraction patterns and are listed in Table I together with the ratio of the lattice constant c/a. With decreasing r_R, $d_{\text{Mn-O(in)}}$ ($\equiv 2/a$) steeply decreases from 1.932 Å for R=La to 1.916 Å for R=Sm. Accordingly, the ratio c/a increases from ≈ 3.218 for R=La to ≈ 3.230 for R=Sm, suggesting the increasing static JT distortion of the MnO_6 octahedra along the c axis. To determine the magnitude of the JT distortion, neutron powder-diffraction measurements were performed at 300 K for $La_{0.5}Sr_{1.5}MnO_4$ and $Nd_{0.5}Sr_{1.5}MnO_4$ with a high-efficiency powder diffractomater with the 150 detector system HERMES installed at the JRR-3M reactor in Japan Atomic Energy Research Institute, Tokai, Japan. Neutrons with wavelength 1.819 Å were obtained by the (331) reflection of Ge monochromater and a combination 12′-Blank-Sample-18′ collimator. Melt-grown crystals were crushed and sealed in a vanadium capsule with helium gas. Results of the Rietveld analysis are summarized in Table II. Substitution of the smaller Nd^{3+} ions for larger La^{3+} ions increases the out-of-plane bond length $d_{\text{Mn-O(out)}}$ and hence increases the static out-of-plane JT distortion ($\Delta \equiv d_{\text{Mn-O(out)}}/d_{\text{Mn-O(in)}}$) from $\Delta \approx 1.04$ for R=La to ≈ 1.05 for R=Nd. Note that these Δ values are much smaller than that for $LaMnO_3$ [$\Delta \approx 1.09$ (Ref. 14)]. A similar chemical pressure effect is observed in the double-layered manganites $R_{1.2}Sr_{1.8}Mn_2O_7$,[15] in which the Δ value increases from ≈ 1.02 for R=La to ≈ 1.03 for R=Nd. The chemically induced static JT distortion and resultant stabilization of the $d_{3z^2-r^2}$ state are expected to influence the magnetic and transport properties for layered manganites.

TABLE I. Lattice constants for $R_{0.5}Sr_{1.5}MnO_4$ at 300 K.

R	a (Å)	c (Å)	a/c
La	3.8632(6)	12.430(1)	3.2175
$La_{0.5}Nd_{0.5}$	3.8524(3)	12.4097(5)	3.2213
$La_{0.25}Nd_{0.75}$	3.8490(3)	12.4080(3)	3.2237
Nd	3.8405(3)	12.3955(6)	3.2275
Sm	3.8309(2)	12.3751(5)	3.2303

TABLE II. Typical bond lengths for $R_{0.5}Sr_{1.5}MnO_4$ at 300 K.

R	$d_{\text{Mn-O(in)}}$ (Å)	$d_{\text{Mn-O(out)}}$ (Å)	$d_{\text{Mn-O(out)}}/d_{\text{Mn-O(in)}}$
La	1.9316(3)	2.00(1)	1.04
Nd	1.9203(2)	2.01(1)	1.05

We show in Fig. 2 the temperature dependence of resistivity up to ~ 500 K for single crystals of $R_{0.5}Sr_{1.5}MnO_4$: Solid curves are for the in-plane component (ρ_{ab}) and broken curves the out-of-plane component (ρ_c). At room temperature, all the compounds show insulating behaviors with an activation energy of $E_a \sim 100$–110 meV (~ 140–150

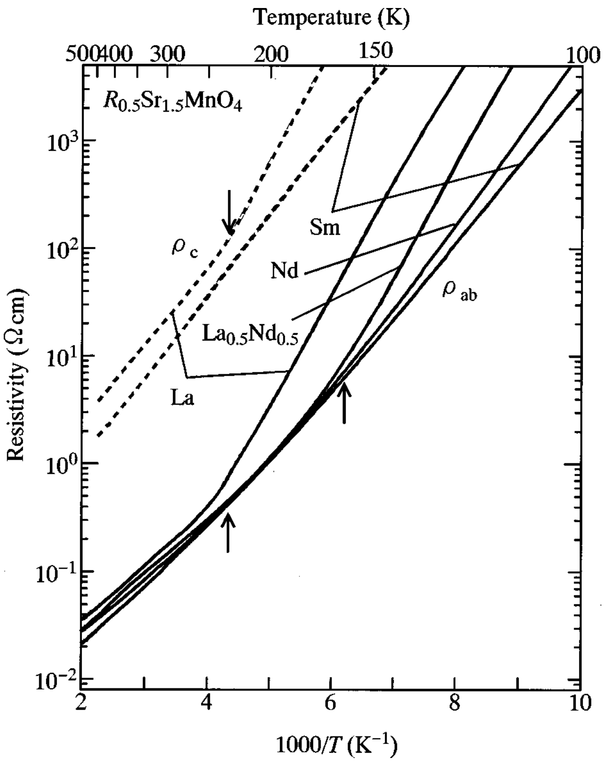

FIG. 2. Temperature dependence of resistivity for $R_{0.5}Sr_{1.5}MnO_4$ with variation of the trivalent rare-earth ion R^{3+}. Solid curves are for the in-plane component (ρ_{ab}) and broken curves for out-of-plane component (ρ_c). Arrows indicate the charge-ordering transition.

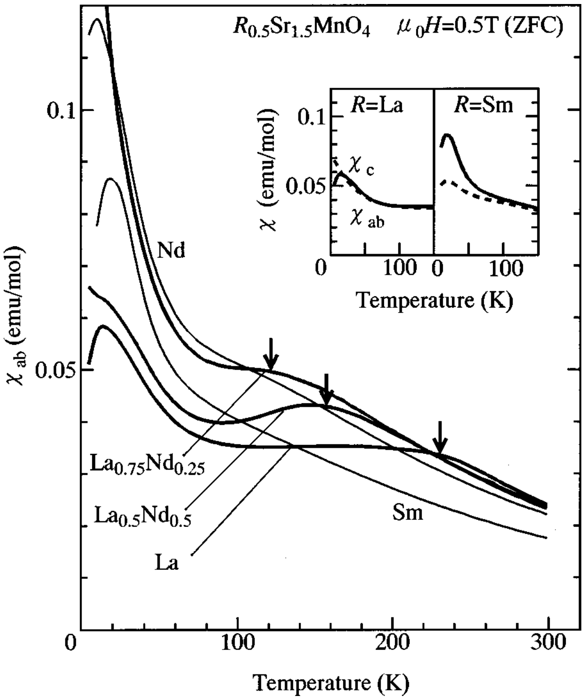

FIG. 3. Temperature dependence of in-plane component of susceptibility (χ_{ab}) for $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ with variation of the trivalent rare-earth ion R^{3+}. Arrows indicate the charge-ordering transition. The inset shows the anisotropy of susceptibility for R = La and Sm. The susceptibility data were measured under a field of $\mu_0 H = 0.5$ T after cooling down to 5 K in zero field (ZFC).

meV) for ρ_{ab} (ρ_c). In $\mathrm{La}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ (R = La), the resistivity steeply increasing below $T_{\mathrm{CO}} = 230$ K (indicated by an arrow) and then the magnitude of E_a jumps up to ~200 meV (~210 meV) for ρ_{ab} (ρ_c). A similar anomaly is observed in the ρ_{ab}-T curve for $R = \mathrm{La}_{0.5}\mathrm{Nd}_{0.5}$ at ≈160 K,[16] indicating that chemical substitution fairly suppresses the CO transition. The absence of thermal hysteresis in the resistivity anomaly suggests the second-order nature of the transition. In the case of $\mathrm{Nd}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ (R = Nd) and $\mathrm{Sm}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ (R = Sm), no trace of the CO transition is observed. We further measured the temperature dependence of [001] electron-diffraction patterns for R = Nd and confirmed that no traces of the superlattice reflections are observed down to 77 K.

Now let us proceed to the magnetic properties for $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$. Figure 3 shows the temperature dependence of the in-plane component χ_{ab} of susceptibility measured under a field of $\mu_0 H = 0.5$ T after cooling down to 5 K in zero field. For R = La, the χ_{ab}-T curve increases with decreasing temperature and then becomes nearly temperature independent below $T_{\mathrm{CO}} \approx 230$ K. The suppression of χ_{ab} below T_{CO} has been ascribed to the weakened DE interaction due to locarization of the e_g carriers.[5] Partial substitution of the smaller Nd^{3+} ions for larger La^{3+} ions shifts T_{CO} toward the low-temperature side from ≈230 K for R = La and ≈160 K for $R = \mathrm{La}_{0.5}\mathrm{Nd}_{0.5}$ to ≈120 K for $R = \mathrm{La}_{0.25}\mathrm{Nd}_{0.75}$, as indicated by downward arrows. For R = Nd and Sm (thin curves in Fig. 3), the χ_{ab}-T curves monotonically increase down to ~20 K, indicating the absence of the CO transition. The inset of Fig. 3 shows the anisotropy of χ for R = La and Sm. In the case for R = La, χ is nearly isotropic except for the low-temperature region (≤20 K). A similar behavior is observed for $R = \mathrm{La}_{0.5}\mathrm{Nd}_{0.5}$ and $\mathrm{La}_{0.75}\mathrm{Nd}_{0.25}$ (not shown). These make a sharp contrast with Sm compound, in which significant enhancement of χ_{ab} is observed as compared to χ_c. Plotted in Fig. 4 are the thus obtained critical temperatures for CO transition for $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ as a function of $d_{\mathrm{Mn-O(in)}}$. With decreasing $d_{\mathrm{Mn-O(in)}}$, the CO state (the hatched region) is suppressed and finally disappears around $d_{\mathrm{Mn-O(in)}} \approx 1.922$ Å. This observation indicates that the repulsive interaction between the e_g electrons (or the small polarons) is not the dominant driving force of the CO transition since such an interaction is expected to enhance with a decrease of the intersite distance.

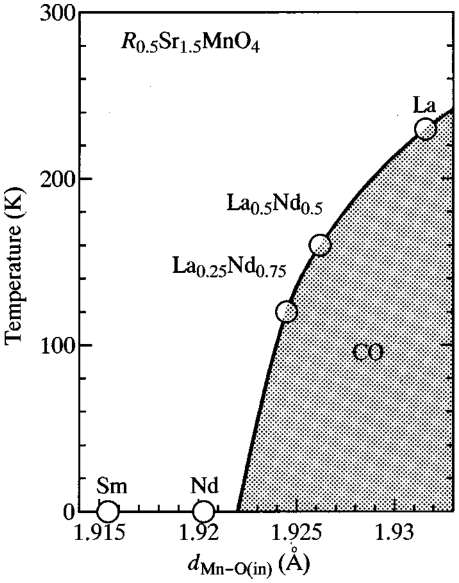

FIG. 4. Electronic phase diagram for $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ as a function of the in-plane Mn-O bond length $d_{\mathrm{Mn\text{-}O(in)}}$. The solid curve is a guide to the eye. Hatching represents the charge-ordering state.

The suppression of T_{CO} with decreasing $d_{\mathrm{Mn-O(in)}}$ implies that the e_g-orbital degree of freedom plays an important role in the transition since the increasing static out-of-plane JT distortion of the MnO_6 octahedra stabilizes the $d_{3z^2-r^2}$ state and changes the character of the e_g orbital. In the case of doped manganites, the orbital degree of freedom of barely mobile e_g carriers strongly couples with the JT distortion. In an extreme case, e.g., in $\mathrm{La}_{1/2}\mathrm{Ca}_{1/2}\mathrm{MnO}_3$,[17] the charge and orbital ordering take place at $T_{\mathrm{CO}} \approx 155$ K from the ferromagnetic state accompanying a large structural change originating in the cooperative JT distortion. Then it is probable that the charge-ordered state in layered manganites is stabilized by concomitant cooperative JT distortion within the MnO_2 sheet or, equivalently, the orbital ordering. Murakami *et al.*[13] proposed that the charge ordering of the layered manganites accompanies an orbital ordering with wave vector (1/4, 1/4, 0). According to this scenario, the observed suppression of the CO transition (see Fig. 4) is interpreted as follows. For R = La with smaller static JT distortion along the c axis, the charge- and orbital-ordered states are easily realized with a slight modification of the in-plane oxygen positions. With decreasing $d_{\mathrm{Mn-O(in)}}$, however, the orbital-ordered state within the MnO_2 sheet is difficult to realize since the e_g electrons are dominated by the $d_{3z^2-r^2}$ character. This is why the CO state is destabilized in the small-$d_{\mathrm{Mn-O(in)}}$ compounds. Consistently with this, Mizokawa and Fujimari[18] have performed an unrestricted Hartree-Fock calculation on the multiband *p*-*d* model and found that a decrease of the JT distortion destabilizes the charge- and orbital-ordered states for $R_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$.

Finally, it should be mentioned that lattice effects on the CO transition is negligible in layered nickelates $\mathrm{La}_{5/3}A_{1/3}\mathrm{NiO}_4$ ($A=$Ca, Sr, and Ba),[8] in which the Ni^{2+} (or Ni^{3+}) ions are free from the JT instability. By contrast, the charge-ordering phenomenon of the e_g carriers (or the small polarons) in layered manganites is strongly coupled with the e_g-orbital degree of freedom mediated by the strong JT instability inherent to the Mn^{3+} (d^4) ions.

In conclusion, we have observed a significant suppression of the CO transition in $\mathrm{La}_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ with the substitution of the smaller Nd^{3+} (or Sm^{3+}) ions for La^{3+} ions. We have ascribed the suppression to destabilization of the orbital ordering within the MnO_2 sheet due to the increasing out-of-plane static JT distortion. Our observation suggests that the character of the e_g electrons can be controlled by the application of the chemical pressure, which will lead us to *orbital physics*.

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[1] For example, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).

[2] P. W. Anderson and H. Hasagawa, Phys. Rev. **100**, 675 (1955).

[3] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

[4] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).

[5] Y. Moritomo, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B **51**, 3297 (1995).

[6] C. H. Chen, S.-W. Cheong, and A. S. Cooper, Phys. Rev. Lett. **71**, 2461 (1993).

[7] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **337**, 561 (1995).

[8] S.-W. Cheong, H. Y. Hwang, C. H. Chen, B. Batlogg, L. W. Ruppa Jr., and S. A. Carter, Phys. Rev. B **49**, 7088 (1994).

[9] The charge-ordering temperature T_{CO} for $\mathrm{La}_{1-x}\mathrm{Sr}_{1+x}\mathrm{MnO}_4$ is insensitive to the hole concentration x (see Ref. 11).

[10] F. Izumi, in *The Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford, 1993), Chap. 13; Y.-I. Kim and F. Izumi, J. Ceram. Soc. Jpn. **102**, 401 (1994).

[11] W. Bao, C. H. Chen, S.-W. Cheong, and S. A. Carter, Solid State Commun. **98**, 55 (1996).

[12] B. J. Sternlieb, J. P. Hill, U. C. Wildgruber, G. M. Luke, B. Nachumi, Y. Moritomo, and Y. Tokura, Phys. Rev. Lett. **76**, 2169 (1996).

[13] Y. Murakami *et al.* (unpublished).

[14] G. Matsumoto, J. Phys. Soc. Jpn. **29**, 606 (1970).

[15] J. M. Mitchell, D. N. Argyriou, J. D. Jorgensen, D. G. Hinks, C. D. Potter, and S. D. Bader, Phys. Rev. B **55**, 63 (1997); J. F. Mitchell. D. N. Argyriou, C. D. Potter, J. D. Jorgensen, D. G. Hinks, and S. D. Bader, Proceedings of MRS, 1997, in press.

[16] In a preliminary [001] electron diffraction measurement on $(\mathrm{La}_{0.5}\mathrm{Nd}_{0.5})_{0.5}\mathrm{Sr}_{1.5}\mathrm{MnO}_4$ [S. Mori *et al.* (unpublished)], fourfold modulation along the [110] and $[1\bar{1}0]$ directions appears below ~190 K.

[17] P. G. Radaelli, D. E. Cox, M. Marezio, and S.-W. Cheong, Phys. Rev. B **55**, 3015 (1997).

[18] T. Mizokawa and A. Fujimori, Phys. Rev. B **56**, 6669 (1997).