On the basis of the neutron structural analysis, lattice effect on the charge/orbital-ordering transition of doped manganites has been reconsidered. We have investigated the stability of the respective $e_g$ orbitals by a Madelung potential calculation, and have found a close correlation between the orbital stability and the charge-ordering transition. This observation indicates that the chemical pressure has an aspect of orbital control, besides the control of the transfer integral $t$ between the neighboring Mn sites.

Perovskite-type doped manganites $R_{1-x}A_x$MnO$_3$ where $R$ and $A$ are trivalent rare-earth and divalent alkaline-earth ions, respectively, have three-dimensional networks of the MnO$_6$ octahedra. Variation of the averaged ionic radius $\langle r_A \rangle$ of the perovskite $A$ site modifies the Mn-O-Mn angle, bond length, and so on, and affects the magnetotransport properties. Among the lattice structural changes induced by chemical pressure, the variation of the Mn-O-Mn angle $\Theta$ has been focused. This is because suppression of the Curie temperature $T_C$ with decrease of $\langle r_A \rangle$ has been ascribed to the reduced transfer integral $t [\propto \sin(\Theta/2)]$ between the Mn sites. Radaelli et al. 1 have experimentally confirmed this trend at a fixed $x (=0.3)$. On the other hand, a chemical pressure effect for the layered manganites $(R,A)_{n+1}$Mn$_n$O$_{3n+1}$ ($n = 1,2$) is different from that for the cubic perovskite. Moritomo et al. 2 have observed suppression of the charge/orbital-ordering temperature of single-layer La$_{0.5}$Sr$_{1.5}$MnO$_4$ with substitution of the Nd$^{3+}$ ions for La$^{3+}$ ions, and have ascribed it to the elongated MnO$_6$ octahedra and resultant unstabilized $d_{3z^2-r^2}/d_{3z^2-r^2}$ orbital alternation. Akimoto et al. 3 have found a correlation between the orbital stability at room temperature and magnetic structures in the structure-controlled bilayer manganites at a fixed $x (=0.4)$. These experimental observations indicate that the chemical pressure effects in the layered manganites have an aspect of the orbital control.

The charge-ordering transition of the cubic manganites, e.g., Nd$_{1/2}$Sr$_{1/2}$MnO$_3$, 4 accompanies an antiferromagnetic spin ordering with the CE-type structure, 5-7 as well as the $d_{3z^2-r^2}/d_{3z^2-r^2}$ orbital alternation. Such an orbital-ordered state has been observed by anisotropy of the tensor of susceptibility scattering measurement in Nd$_{1/2}$Sr$_{1/2}$MnO$_3$ (Ref. 8) as well as by the electron microscope in La$_{1/2}$Ca$_{1/2}$MnO$_3$. 9 The chemical pressure effect on the charge-ordering transition has been regarded as control of $t$ with change of $\langle r_A \rangle$; the smaller $t$ becomes, the more stable the charge-ordered state becomes. 10 However, we know a serious exception on this trend. In (Nd$_{1-x}$Sm$_x$)$_{1/2}$Sr$_{1/2}$MnO$_3$, 11 the charge-ordering temperature $T_{CO}$ is $\sim 150 \text{K}$ at $y = 0 (\langle r_A \rangle = 1.355 \text{Å})$, but the transition disappears at $y = 0.84 (\langle r_A \rangle = 1.342 \text{Å})$ even though the value of $t$ is fairly suppressed. Judging from the fact that the charge-ordering transition accompanies the orbital alternation, variation of the orbital stability induced by the chemical pressure should affect the charge-ordering transition. Here, we have investigated stability of the respective $e_g$ orbitals by means of Madelung potential calculations based on the structural data at room temperature obtained by neutron powder diffraction experiments. We have found a close correlation between the orbital stability at room temperature and the ground state, indicating that the orbital stability governs the charge-ordering transition of the half-doped manganites.

A series of ceramics compounds $R_{1/2}A_{1/2}$MnO$_3$ ($R = \text{La, Pr, Nd, Nd}_{1/2}\text{Ta}_{1/2}$, and $A = \text{Sr}$ and $\text{Ca}$), was synthesized by solid-state reaction in air atmosphere. Stoichiometric mixture of commercial La$_2$O$_3$, Pr$_2$O$_3$, Nd$_2$O$_3$, Tb$_2$O$_3$, SrCO$_3$, CaCO$_3$, and Mn$_2$O$_4$ powder was well ground and calcined two times at 1250–1350°C for 24 h. Then, the resulting powder was pressed into a disk with a size of 20 mm $\phi \times 4 \text{ mm}$ and sintered at 1250–1350°C for 24 h. Rietveld analysis 12 of neutron powder patterns indicates that investigated compounds were single phase without detectable impurities. The crystal symmetry is orthorhombic ($Pbnm; Z = 4$) except for La$_{1/2}$Sr$_{1/2}$MnO$_3$, (La$_{1/2}$Nd$_{1/2}$)$_{1/2}$Sr$_{1/2}$MnO$_3$, Pr$_{1/2}$Sr$_{1/2}$MnO$_3$, and Nd$_{1/2}$Sr$_{1/2}$MnO$_3$ ($Ibmm; Z = 4$). Neutron powder diffraction measurements were performed with the Kinken powder diffractometer for high efficiency and high-resolution measurements 13 (HERMES) installed at the JRR-3M reactor at the Japan Atomic Energy Research Institute, Tokai, Japan. Neutrons with wavelength 1.8196 Å were obtained by the 331 reflection of the Ge monochromator, and 12’-x-Sample-22’ collimation.
Table I. Lattice constants and atomic positions for $R_{1/2}A_{1/2}\text{MnO}_3$ determined from neutron powder profiles at room temperature. $g$ means oxygen occupancy determined by Rietveld analysis. The crystal symmetry is orthorhombic [Ibmm, $Z=4$ for $La_{1/2}Sr_{1/2}\text{MnO}_3$, ($La_{1/2}Nd_{1/2})_{1/2}Sr_{1/2}\text{MnO}_3$, $Pr_{1/2}Sr_{1/2}\text{MnO}_3$, and $Nd_{1/2}Sr_{1/2}\text{MnO}_3$, and $Pbnm, Z=4$ for other samples]. The atomic sites are $R/A, 4e[x,0,\frac{x}{2}]$, Mn, $4b[\frac{3}{4},0,0]$, O(1), $4c[x,\frac{1}{2},\frac{x}{2}]$, O(2), $8g[\frac{1}{2},\frac{1}{2},z]$ for Ibmm symmetry and $R/A, 4c[x,\frac{1}{2},\frac{1}{2}]$, Mn, $4b[\frac{1}{4},0,0]$, O(1), $4c[x,y,\frac{1}{2}]$, O(2), $8d[x,y,z]$ for Pbnm symmetry. $T_C$ and $T_{CO}$ are the Curie and charge-ordering temperatures, respectively.

<table>
<thead>
<tr>
<th>$a$ ($\text{Å}$)</th>
<th>$b$ ($\text{Å}$)</th>
<th>$c$ ($\text{Å}$)</th>
<th>$R_{\text{mp}}$ (%)</th>
<th>$T_C$ (K)</th>
<th>$T_{CO}$ (K)</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{1/2}Sr_{1/2}\text{MnO}_3$</td>
<td>5.4412(5)</td>
<td>5.4418(5)</td>
<td>7.7643(2)</td>
<td>7.97</td>
<td>360</td>
<td>1.021(5)</td>
</tr>
<tr>
<td>($La_{1/2}Nd_{1/2})<em>{1/2}Sr</em>{1/2}\text{MnO}_3$</td>
<td>5.4783(3)</td>
<td>5.4512(3)</td>
<td>7.6654(3)</td>
<td>7.36</td>
<td>305$^b$</td>
<td>0.991(5)</td>
</tr>
<tr>
<td>$Pr_{1/2}Sr_{1/2}\text{MnO}_3$</td>
<td>5.413(1)</td>
<td>5.408(1)</td>
<td>7.7541(6)</td>
<td>3.16</td>
<td>265$^b$</td>
<td>0.981(7)</td>
</tr>
<tr>
<td>$Nd_{1/2}Sr_{1/2}\text{MnO}_3$</td>
<td>5.4405(2)</td>
<td>5.3986(2)</td>
<td>7.5832(3)</td>
<td>6.36</td>
<td>265</td>
<td>0.999(5)</td>
</tr>
<tr>
<td>($Nd_{1/2}Tb_{1/2})<em>{1/2}Sr</em>{1/2}\text{MnO}_3$</td>
<td>5.4104(8)</td>
<td>5.3990(8)</td>
<td>7.6052(6)</td>
<td>5.98</td>
<td>280$^b$</td>
<td>0.944(6)</td>
</tr>
<tr>
<td>$Tb_{1/2}Sr_{1/2}\text{MnO}_3$</td>
<td>5.4051(7)</td>
<td>5.4078(7)</td>
<td>7.6159(4)</td>
<td>3.58</td>
<td>300</td>
<td>0.999(3)</td>
</tr>
<tr>
<td>$La_{1/2}Ca_{1/2}\text{MnO}_3$</td>
<td>5.4243(3)</td>
<td>5.4156(3)</td>
<td>7.6334(2)</td>
<td>6.19</td>
<td>240</td>
<td>1.017(4)</td>
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<td>$Nd_{1/2}Ca_{1/2}\text{MnO}_3$</td>
<td>5.3815(2)</td>
<td>5.4026(2)</td>
<td>7.5974(2)</td>
<td>5.24</td>
<td>223</td>
<td>1.006(4)</td>
</tr>
<tr>
<td>($Nd_{1/2}Tb_{1/2})<em>{1/2}Ca</em>{1/2}\text{MnO}_3$</td>
<td>5.3565(3)</td>
<td>5.4156(3)</td>
<td>7.5505(4)</td>
<td>5.38</td>
<td>240</td>
<td>1.001(5)</td>
</tr>
<tr>
<td>$Tb_{1/2}Ca_{1/2}\text{MnO}_3$</td>
<td>5.3206(2)</td>
<td>5.4449(2)</td>
<td>7.4477(3)</td>
<td>5.63</td>
<td>289</td>
<td>1.000(5)</td>
</tr>
</tbody>
</table>

$A$-type antiferromagnetic metallic phase appears at low temperature. (Ref. 19).

$B$ The magnetization at low temperature ($\sim 1\mu_B$ under 0.5 T) is much smaller than the ideal value ($\sim 3.5\mu_B$).

Figure 1 shows temperature dependence of (a) activation energy $E_{\text{ac}}=d(ln\rho)/d(1/T)$, where $\rho$ is resistivity and (b) susceptibility $x$ for $R_{1/2}A_{1/2}\text{MnO}_3$. For four-probe resistivity measurements, the sample was cut into a rectangular shape, typically of $3 \times 2 \times 1$ mm$^3$, and electrical contacts were made with a heat-treatment-type silver paint. The $E_{\text{ac}}$-T curve of $Tb_{1/2}Ca_{1/2}\text{MnO}_3$ has a peak at $\approx 289$ K due to the charge-ordering transition. The transition temperature $T_{CO}$ was defined as the maximal point (downward arrow) of the $E_{\text{ac}}$-T curve. In the case of Ca compounds (solid curves), $T_{CO}$ decreases with increase of $\langle r_A \rangle$: $T_{CO}=289$ K (Ref. 14) for $Tb_{1/2}Ca_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.270$ Å), $\approx 223$ K for $Nd_{1/2}Ca_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.305$ Å), and $\approx 140$ K for $La_{1/2}Ca_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.350$ Å). This trend is consistent with the recent work done by Fontcuberta et al. The charge-ordering transition accompanies the CE-type spin-ordering, which causes the reduction of the $\chi$-T curve. Figure 1(b) shows the $\chi$-T curves for $R_{1/2}A_{1/2}\text{MnO}_3$. $\chi$ was measured under a field of $\mu_B H=0.5$ T after cooling down to 5 K in the zero field (ZFC), using a superconducting quantum interference device magnetometer.

Curiously enough, there is no trace of the charge-ordering transition in the $E_{\text{ac}}$-T curve of $Tb_{1/2}Sr_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.320$ Å; broken curve of Fig. 1(a)). and the curve monotonously decreases with decrease of temperature. In addition, the $\chi$-T curve of $Tb_{1/2}Sr_{1/2}\text{MnO}_3$ shows Curie-Weiss behavior down to $\sim 40$ K [broken curve of Fig. 1(b)]. Similarly, there is no trace of the charge-ordering transition in $(Nd_{1/2}Tb_{1/2})_{1/2}Sr_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.338$ Å; not shown). Sundaresan et al. and Kasper et al. have investigated magnetic properties of $R_{1/2}Sr_{1/2}\text{MnO}_3$ ($R=Eu$, Gd, Tb, Dy and Y) at $x=0.5$, and have observed spin-glass behavior at low temperature. We think that the low-temperature spin state of $Tb_{1/2}Sr_{1/2}\text{MnO}_3$ and $(Nd_{1/2}Tb_{1/2})_{1/2}Sr_{1/2}\text{MnO}_3$ is also spin-glass-like. Looking at Table I, $T_{CO}$ is $\approx 223$ K for $Nd_{1/2}Ca_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.305$ Å) and $\approx 140$ K for $La_{1/2}Ca_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.350$ Å). So, we could expect the charge-ordering transition at $\sim 200$ K for $Tb_{1/2}Sr_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.320$ Å) and $(Nd_{1/2}Tb_{1/2})_{1/2}Sr_{1/2}\text{MnO}_3$ ($\langle r_A \rangle=1.338$ Å), if the transition were governed by the $\langle r_A \rangle$ value.

Now, let us proceed to the overall structural feature of $R_{1/2}A_{1/2}\text{MnO}_3$. We have used the RIETAN-97β program, and have analyzed the neutron powder patterns at room temperature. The obtained lattice parameters, as well as oxygen occupancy, at room temperature are listed in Table I. We also
FIG. 1. Temperature dependence of (a) activation energy $E_{ac}$ [$=d(\ln \rho)/d(1/T)$; $\rho$ is resistivity] and (b) susceptibility $\chi$ for $R_{1/2}A_{1/2}MnO_3$. $\chi$ was measured after cooling down to 5 K in the zero field (ZFC). Downward arrows indicate the critical temperatures $T_{CO}$ for the charge-ordering transition, determined from the maximal point of the $E_{ac}$-$T$ curve.

listed $T_{CO}$ and $T_C$, which were determined from temperature dependence of $E_{ac}$ and magnetization $M$, respectively. Figure 2 shows thus obtained structural parameters against (a) lattice constants, (b) Mn-O-Mn angles $Q$, and (c) Mn-O bond lengths $d$. Open and closed symbols stand for the Ca and Sr compounds, respectively. Variation of the lattice constants $a$, $b$, and $c/\sqrt{2}$ [Fig. 2(a)], as well as of the $Q$ values [Fig. 2(b)] is nearly scaled to $\langle r_A \rangle$ irrespective of the alkaline-earth species. Note that there are two Mn-O-Mn angles, i.e., out-of-plane ($Q_c$, square) and in-plane ($Q_{ab}$, circle) angles, in the $Pbnm$ setting. The averaged $Q$ value increases almost linearly with $\langle r_A \rangle$: $\langle Q \rangle = -34 + 148\langle r_A \rangle$. A similar interrelation between $\langle Q \rangle$ and $\langle r_A \rangle$ has been reported by Radaelli et al.\textsuperscript{1} at $x = 0.3$: $\langle Q \rangle = -7 + 124\langle r_A \rangle$.

Here, $La_{1/2}Sr_{1/2}MnO_3$, $Pr_{1/2}Sr_{1/2}MnO_3$, and $(La_{1/2}Nd_{1/2})_{1/2}Sr_{1/2}MnO_3$ are known to be metallic\textsuperscript{19} down to the lowest temperature, due to the large $\Theta$ value, or the large one-electron bandwidth $W$.

Now, let us proceed to the distortion of the MnO$_6$ octahedra of the insulating manganites. In the $Pbnm$ setting, there are three kinds of Mn-O bonds, i.e., out-of-plane ($d_c$, square) and in-plane ($d_{ab}$, circle and triangle) bonds. In the four Ca compounds, i.e., $La_{1/2}Ca_{1/2}MnO_3$, $Nd_{1/2}Ca_{1/2}MnO_3$, $(Nd_{1/2}Tb_{1/2})_{1/2}Ca_{1/2}MnO_3$, and $Tb_{1/2}Ca_{1/2}MnO_3$, $d_c$ is the shortest among the three bond lengths. With this structure, the $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbitals are stable as compared with the $d_{3x^2-r^2}$ orbital. Then, the $e_g$ electrons tend to occupy the $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals, and hence, are easy to form the $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbital alternation at low temperatures to cause the charge-ordering transition. By contrast, in $(Nd_{1/2}Tb_{1/2})_{1/2}Sr_{1/2}MnO_3$ and $Tb_{1/2}Sr_{1/2}MnO_3$, one of the $d_{ab}$ is the longest. Such a Jahn-Teller-type distortion of the MnO$_6$ octahedra fairly destabilizes the orbital alternation, which is indispensable to the charge-ordering transition of the half-doped manganites.

To quantitatively estimate the stability of the respective $e_g$ orbital, we have calculated the Madelung potential $V$ for each orbital\textsuperscript{20} based on the structural data. The Madelung potential acting on a hole in the $d_{3x^2-r^2}$, $d_{3y^2-r^2}$, and $d_{3z^2-r^2}$ orbitals is given by

$$V(d_{3z^2-r^2}) = [V(r_0 + r_d) + V(r_0 - r_d)]/2.$$ (1)
FIG. 3. Critical temperature $T_{CO}$ for the charge-ordering transition for $R_{1/2}A_{1/2}$MnO$_3$ against the difference of the Madelung energies $\Delta V = [V(d_{3z^2-r^2}) + V(d_{3z^2-r^2})]/2 - \langle V \rangle$. $\langle V \rangle$ is the averaged value for the three orbitals: $d_{3z^2-r^2}$, $d_{3y^2-r^2}$, and $d_{3x^2-r^2}$. Hatching is a guide to the eye.

$V(d_{3z^2-r^2}) = [V(\vec{r}_0 + r_d \hat{y}) + V(\vec{r}_0 - r_d \hat{y})]/2,$

and

$V(d_{3y^2-r^2}) = [V(\vec{r}_0 + r_d \hat{x}) + V(\vec{r}_0 - r_d \hat{x})]/2,$

respectively. Here, $\vec{r}_0$ indicates the position of the Mn ion and $r_d$ (≈ 0.42 Å) is the radius where the radial charge density of the Mn $3d$ orbital becomes maximum. $\hat{x}, \hat{y},$ and $\hat{z}$ are the unit vectors along the respective Mn-O bond directions. The magnitudes of the charge at $A$, Mn, and oxygen sites are assumed to be $+2.5, +3.5$, and $-2$, respectively, and the conventional Ewald method is used. The larger $V$ is, the more stable the corresponding orbital becomes. The stability of the $d_{3z^2-r^2}/d_{3y^2-r^2}$ orbital alternation can be estimated by the difference of the Madelung potential $\Delta V$:

$$\Delta V = [V(d_{3z^2-r^2}) + V(d_{3y^2-r^2})]/2 - \langle V \rangle.$$ (4)

Here, $\langle V \rangle = [V(d_{3z^2-r^2}) + V(d_{3y^2-r^2}) + V(d_{3x^2-r^2})]/3$ is the averaged value. We plotted in Fig. 3 the charge-ordering temperature $T_{CO}$ against $\Delta V$. If one sees the phase diagram from left to right (the stability of the $d_{3z^2-r^2}/d_{3y^2-r^2}$ orbital alternation increases), the CO state appears and $T_{CO}$ increases. Thus, the orbital stability is an important factor for the charge-ordering transition in the structure-controlled half-doped manganites.

Finally, let us compare the lattice effects of the present cubic system with those of the layered manganites. In the layered manganites, chemical substitution scarcely alters the in-plane Mn-O bond length $d_{in}$ or the in-plane Mn-O-Mn angle $\Theta_{in}$, and hence does not alter the in-plane $t$ value for example, $\Theta_{in}(d_{in})$ is 178.9º (1.934 Å) for La$_3$Sr$_2$Mn$_2$O$_7$ and 176.7º (1.929 Å) for (La$_{0.6}$Nd$_{0.4}$)$_3$Sr$_1$Mn$_2$O$_7$. The chemical pressure, on the other hand, changes the position of the apical oxygen, and modifies the orbital stability via deformation of the MnO$_6$ octahedra. In fact, a lattice effect observed in several layered systems, e.g., (La,Nd)$_{0.5}$Sr$_{1.5}$MnO$_4$ (Ref. 2) and (La,Nd)$_{1.2}$(Sr,Ca)$_{1.8}$Mn$_2$O$_7$ (Ref. 3) has been ascribed to the variation of the orbital stability. Even in the cubic system, orbital stability plays an important role on the charge/orbital-ordered state of the half-doped manganites.

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18B. Gracia-Landa et al. [J. Appl. Phys. 83, 7664 (1998)] have observed anomalies in magnetic behavior of Gd$_2$Sr$_2$MnO$_4$, and ascribed it to charge-ordering transition. Judging from $(r_A)$ dependence of $T_{CO}$ in the Sr-based compounds, however, the anomalies are considered to be ascribed to the spin-glass transition.