Relation between crystal and magnetic structures of the layered manganites
La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($0.30 \leq x \leq 0.50$)

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Comprehensive neutron-powder diffraction and Rietveld analyses were carried out to clarify the
relation between the crystal and magnetic structures of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($0.30 \leq x \leq 0.50$).
The Jahn-Teller (JT) distortion of Mn-O$_6$ octahedra, i.e., the ratio of the averaged apical Mn-O
bond length to the equatorial Mn-O bond length, is $\Delta_{JT} = 1.042(5)$ at $x = 0.30$, where the magnetic
easy-axis at low temperature is parallel to the $c$ axis. As the JT distortion becomes suppressed with
increasing $x$, a planar ferromagnetic structure appears at $x \geq 0.32$, which is followed by a canted
antiferromagnetic (AFM) structure at $x \geq 0.39$. The canting angle between neighboring planes
continuously increases from $0^\circ$ (planar ferromagnet: $0.32 \leq x < 0.39$) to $180^\circ$ (A-type AFM:
$x = 0.48$ where $\Delta_{JT} = 1.013(5)$). Dominance of the A-type AF structure with decrease of JT
distortion can be ascribed to the change in the $e_g$ orbital state from $d_{x^2-y^2}$ to $d_{z^2}$.

It is now the received wisdom that the colossal magnetoresistance (CMR) discovered in Perovskite Mn
oxides R$_{1-x}$A$_x$MnO$_3$ (R: Rare-earth ion, A: Alkaline-earth ion) is originated from a complicated interplay of spin-charge-
lattice degrees of freedom. We can control the hole concentration $x$ and the effective band-width through
the tolerance factor. This controllability makes this system an ideal platform to study various phenomena
related to CMR. Recently, the dimensionality of the crystal structure has been focused upon. In general,
layered Mn oxides are written as the Ruddelesden-Popper type system such as (La,Sr)$_{n+1}$Mn$_n$O$_{3n+1}$. By
changing the number of MnO$_2$ sheets, $n$, blocked with (La,Sr)$_2$O$_2$ layers, the effective dimensionality
can be adjusted. As for La$_{1-x}$Sr$_x$MnO$_3$ ($n = \infty$) and single-layered La$_{1-x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($n = 1$), the magnetic phase
diagrams in a wide $x$ range were reported.

Recently, Moritomo $et$ $al.$ have synthesized a single crystal of La$_{1+3}$Sr$_{1+8}$Mn$_2$O$_7$ ($n = 2$) and found
an extremely large magnetoresistance. This discovery has clarified the importance of effective dimensionality
in CMR, and was followed by intensive studies of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ abbreviated to LSMO327 in
the present Communication. Hirota $et$ $al.$ studied the magnetic structure LSMO327 for $x = 0.40, 0.45$ and 0.48
by neutron diffraction using single crystals. They have found that the magnetic structure is not simple ferromagnetic
(FM) but planar canted antiferromagnetic (AFM) and that the canting angle increases from $6.3^\circ$ ($x = 0.40$)
to $180^\circ$ ($x = 0.48$) while $T_C$ decreases with increasing $x$. They also pointed out the existence of A-type AFM
ordering in the intermediate temperature range above $T_C$. Fujioka $et$ $al.$ measured the spin wave dispersion
of a large single-grain single crystal of LSMO327 with $x = 0.40$ and found that the intra-plane coupling between
a bilayer is about 30% of the in-plane coupling ($D \sim 151$ meV) though the Mn-O bond lengths are similar, which
they ascribed to the dominance of $d_{x^2-y^2}$ orbital.

The importance of the $e_g$ orbital degree of freedom has been pointed out theoretically as to the change of the magnetic
structure in manganites. Note that the $e_g$ orbital state is governed by the Jahn-Teller (JT) type
distortion of the MnO$_6$ octahedron. Since LSMO327 ($0.30 \leq x \leq 0.50$) has neither buckling nor structural
phase transition unlike the three dimensional (3d) Mn
Perovskite such as La$_{1-x}$Sr$_x$MnO$_3$, we can study more directly how the change of the $e_g$ orbital state affects the magnetic structure. In this Communication, we have established by neutron diffraction experiment close interrelation between the orbital state and the magnetic structure in the layered manganites LSMO$_{327}$. The prescribed amount of dried La$_2$O$_3$, SrCO$_3$, and Mn$_3$O$_4$ are thoroughly mixed and calcined in the air at 1200–1450°C for total 4 days with frequent grinding. Sample rods were melt-grown in a floating-zone optical image furnace, then powderized again. No detectable impurities were found in these samples at room temperature (R.T.) by x-ray diffraction. As for $x = 0.30$, inductively coupled plasma (ICP) analysis shows that the ratio of La, Sr, and Mn is 28.6 : 32.2 : 39.2, which is in good agreement with the ideal ratio 28.0 : 32.0 : 40.0. We also checked an $x = 0.40$ single crystal with electron probe microanalysis (EPMA), which indicates no particular spatial inhomogeneity within the instrumental error. These analyses indicate that our samples are sufficiently stoichiometric and homogeneous. The crystal structures were studied as a function of $x$ as well as temperature using the powder neutron diffractometer HERMES, which is equipped with multi-detectors with the Ge (3 3 1) monochromator ($\lambda = 1.819$ Å), located in the JRR-3M reactor in JAERI. We have taken powder diffraction patterns at R.T. and low temperature ($\sim 10$ K). As described in Ref. [5], the peak profiles as well as the magnetic order parameters indicate that none of our samples show biphasic properties as previously reported for $x = 0.50$ by Battle et al. [1].

The powder diffraction patterns were analyzed with the Rietveld method for $x = 0.30$, 0.35, 0.40, 0.45, 0.48, and 0.50 at R.T. and at 10 K. We used melt-grown samples except $x = 0.35$. We confirmed that $T_C$ and the results of Rietveld analyses of the calcined $x = 0.40$ sample are consistent with those of the melted $x = 0.40$ sample. Therefore using the calcined $x = 0.35$ sample should have no fundamental problems in terms of a systematic study of a relation between the structural and magnetic structures. We found that LSMO$_{327}$ belongs to the space group $I4/mmm$ ($z = 2$) over the whole hole concentration range ($0.30 \leq x \leq 0.50$). The results of Rietveld analyses are summarized in Tables I and II.

Let us first mention the magnetic phase diagram of LSMO$_{327}$ shown in Figs. 1(a) and (b). We have found that the low-temperature magnetic structure for $0.32 \leq x \leq 0.48$ is essentially classified into a single magnetic phase which consists of FM (FM-I: planar FM) and AFM (AFM-I: intra-bilayer AFM and inter-layer FM) components as previously reported for $x = 0.40, 0.45, 0.48$ single crystals. Note that the AFM-I component exists only above $x = 0.39$. The intermediate AFM-I phase was observed for $0.39 \leq x \leq 0.48$. For $x = 0.30$, a different planar AFM structure appears in the intermediate temperature range, which we denote AFM-II (intra-bilayer AFM and inter-layer FM). At low temperature, a new FM phase with the magnetic easy-axis parallel to $c$ appears. We define this phase as FM-II. At the other end, $x = 0.50$, the magnetic structure shows fairly complicated temperature dependence because of charge ordering. Neutron-diffraction study on an $x = 0.50$ single crystal revealed that the CE-type phase and A-type AFM ordering occurs below 210 K and that the CE-type AFM coexists the A-type AFM below 145 K, though the CE-type AFM and charge ordering become unstable at low temperature. Present powder diffraction study is consistent with Ref. [5]. Detailed powder patterns are published elsewhere.

Figure 1(c) show the $x$ dependence of magnetic moments. Only the FM component exists for $x = 0.30–0.38$ at 10 K. However the FM component starts decreasing on the appearance of the AFM component at $x = 0.39$. This makes a sharp contrast with the case of the 3$d$ Mn Perovskites La$_{1-x}$Sr$_x$MnO$_3$, in which FM structure exists over $0.17 < x < 0.50$. As the AFM component increases as $x$ increases, the FM component diminishes and finally disappears at $x = 0.48$. These results are consistent with neutron diffraction studies using single crystals. Figure 1(d) describes the JT distortion $\Delta_{JT}$ defined as the ratio of the averaged apical bond length $a_{JT}$ and the equatorial Mn-O bond lengths at 10 K and R.T. At R.T., the lattice constant $c$ greatly decreases with increasing $x$, while the lattice constant $a$ stays almost constant (See Table I): $a(x = 0.50) = a(x = 0.30)$, while $\frac{a(x = 0.50)}{a(x = 0.30)}$ is $1.46 \%$, while $\frac{a(x = 0.50)}{a(x = 0.30)}$ is only 0.38 %. At 10 K, the former value is $1.61 \%$ and the latter is $0.45 \%$ (See Table II). Thus the lattice shrinks along $c$ as $x$ increases. On the other hand, the out-of-plane Mn-O-Mn angle $\Theta_o$ is found almost $180^\circ$ independent of $x$, indicating no buckling. The angle along $c$, $\Theta_c$, is $180^\circ$ because of the $I4/mmm$ ($z = 2$) tetragonal symmetry. As expected from the $x$ dependence of the lattice constants $a$ and $c$, the bond length Mn-O$_{equatorial}$ in MnO$_6$ octahedra stays almost constant and the bond length Mn-O$_{apical}$ largely decreases with increasing $x$. Thus $\Delta_{JT}$ changes from 1.042(5) ($x = 0.30$) to 1.010(6) ($x = 0.50$) at R.T. At 10 K, the former value is 1.034(6) and the latter is 1.010(5). In the high dope region ($0.45 \leq x \leq 0.50$), the JT distortion is so small that MnO$_6$ octahedron is almost regular ($\Delta_{JT} = 1$).

In manganites, FM double-exchange (DE) interaction, mediated by carrier hopping, and AFM superexchange (SE) interaction compete with each other. The change of the $e_g$ orbital state through the structural parameters should modify the anisotropic transfer integral, and affect the above competition. The $d_{z^2} - y^2$ orbital, which are theoretically more stable than $d_{3z^2} - r^2$ orbitals in LSMO$_{327}$, reflecting the two-dimensional character, facilitates the FM DE interactions within the plane, while interactions along $c$ are dominated by the AFM SE coupling between $t_{2g}$ spins. Consequently the layered A-type AFM structure prevails over 3$d$ FM structure, making a sharp contrast with cubic Perovskites like La$_{1-x}$Sr$_x$MnO$_3$. As shown in Figs. 1(c) and (d), we have found a clear correlation between the decrease of
\[ \Delta_{JT} \text{ and the crossover from FM to AFM component for } 0.32 \leq x \leq 0.48. \] Here, the contraction of \[ \Delta_{JT} \text{ with increasing } x \text{ stabilizes the energy level of the } d_{x^2-y^2} \text{ orbital.} \] This observation indicates that the increase of \[ d_{x^2-y^2} \text{ orbital polarization enhances the A-type AFM component.} \] We should also point out a compositional phase boundary between \( x = 0.30 \) and 0.32, which is clearly indicated by an abrupt change in the direction of the easy axis through the structural parameters change continuously. Note that different magnetic structures have been reported for \( x = 0.30 \). Perring et al. reported a low-temperature AFM structure, which is intra-bilayer FM and inter-bilayer AFM coupling with the easy axis parallel to \( c \) (AFM-III in Fig. 1(b)). Argyriou et al. reported that their \( x = 0.30 \) phase is biphasic and that the majority phase (hole poor) is a canted AFM structure and the minority phase (hole rich) is a tilted FM structure with inter-bilayer FM coupling. The tilt angle approaches 0°, i.e., parallel to \( c \), as temperature decreases for the both phases. Thus the majority phase becomes AFM-III as suggested by Perring et al. and the minority phases becomes FM-II consistent with the present study. These results indicate that there exist at least two low-temperature magnetic phases (FM-II and AFM-III) around \( x = 0.30 \). As Moritomo et al. concluded in their study of chemical pressure effects on the magnetotransport properties of Nd-doped LSMO327, the complicated magnetic phases around \( x = 0.30 \) as above result from a subtle balance between inter-bilayer FM and AFM coupling, thus is sensitive to the hole concentration controlling the magnetic interactions through structural parameters.

In summary, we have determined the crystal and magnetic structure of layered manganites \( \text{La}_{2-x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7 \), and established the close relation between the JT distortion and the magnetic structure. Continuous variation from FM to canted AFM structure with increasing \( x (0.32-0.48) \) is interpreted in terms of increase of the \( d_{x^2-y^2} \text{ orbital polarization associated with decrease of the JT distortion.} \)

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FIG. 1. (a) Magnetic phase diagram of \(\text{La}_{2-x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7\) \((0.30 \leq x \leq 0.50)\). (b) Several different magnetic structures appearing in the phase diagram are schematically drawn. AFM-III is reported in Ref. 9. (c) Hole concentration dependence of FM and AFM magnetic moments at 10 K. (d) Hole concentration dependence of JT distortion defined as the ratio of the averaged apical and the equatorial Mn-O bond lengths at room temperature and 10 K.
TABLE I. Structural parameters for La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ at room temperature. In the space group $I4/mmm$, the Mn is placed at (0, 0, z), La,Sr(1) at (0, 0, 0.5), La,Sr(2) at (0, 0, z), O(1) at (0, 0, 0), O(2) at (0, 0, z), O(3) at (0, 0.5, z), respectively. $\Theta_a$ and $\Delta_{JT}$ denote the out-of-plane angle between Mn and O(3) and the Jahn-Teller distortion, respectively. $R_{wp}$ is a weighted pattern R-factor and $R_e$ is an expected R-factor. Non-melted samples were used for $x = 0.35^\circ$ and 0.40$^\circ$.

| Parameter | $x = 0.30$ | $x = 0.35^\circ$ | $x = 0.40$ | $x = 0.40^\circ$ | $x = 0.45$ | $x = 0.48$ | $x = 0.50$ |
|-----------|------------|----------------|-------------|----------------|-------------|-------------|-------------|
| $a$ (Å)   | 3.8600(1)  | 3.8652(3)     | 3.8711(1)   | 3.8703(2)     | 3.8729(2)   | 3.8765(2)   | 3.8748(3)   |
| $c$ (Å)   | 20.324(1)  | 20.177(2)     | 20.126(1)   | 20.110(1)     | 20.056(1)   | 20.049(1)   | 20.032(1)   |
| Mn        | 0.097(1)   | 0.097(1)      | 0.097(1)    | 0.097(1)      | 0.097(1)    | 0.097(1)    | 0.098(1)    |
| La,Sr(2)  | 0.3172(7)  | 0.3174(8)     | 0.3174(6)   | 0.3170(7)     | 0.3171(6)   | 0.3168(6)   | 0.3161(7)   |
| O(2)      | 0.1980(9)  | 0.197(1)      | 0.1965(8)   | 0.196(1)      | 0.1956(8)   | 0.1960(9)   | 0.195(1)    |
| O(3)      | 0.0958(6)  | 0.0946(7)     | 0.0955(5)   | 0.0955(6)     | 0.0949(5)   | 0.0948(5)   | 0.0944(6)   |
| $\Theta_a$ (deg) | 177.7(4) | 176.7(5)     | 178.0(4)    | 178.3(4)      | 177.1(3)    | 176.7(4)    | 175.3(4)    |
| $\Delta_{JT}$ | 1.042(5) | 1.029(8)     | 1.021(4)    | 1.019(5)      | 1.013(4)    | 1.013(5)    | 1.010(6)    |
| $R_{wp}$  | 10.23      | 11.69         | 9.41        | 12.82         | 9.28        | 10.14       | 11.13       |
| $R_e$     | 3.92       | 4.50          | 4.85        | 6.02          | 4.62        | 4.94        | 4.51        |

TABLE II. Structural parameters for La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ at 10 K. $\mu_F$ and $\mu_{AF}$ indicate ferromagnetic moment and antiferromagnetic moment per Mn site. Non-melted samples were used for $x = 0.35^\circ$.

| Parameter | $x = 0.30$ | $x = 0.35^\circ$ | $x = 0.40$ | $x = 0.45$ | $x = 0.48$ | $x = 0.50$ |
|-----------|------------|----------------|-------------|-------------|-------------|-------------|
| $a$ (Å)   | 3.8566(4)  | 3.8587(2)     | 3.8645(1)   | 3.8713(2)   | 3.8782(1)   | 3.873(3)    |
| $c$ (Å)   | 20.239(2)  | 20.096(2)     | 20.065(1)   | 19.963(1)   | 19.952(1)   | 19.918(2)   |
| Mn        | 0.097(1)   | 0.096(1)      | 0.096(1)    | 0.097(1)    | 0.097(1)    | 0.097(1)    |
| La,Sr(2)  | 0.3182(8)  | 0.3173(7)     | 0.3178(6)   | 0.3165(6)   | 0.3174(8)   | 0.3174(7)   |
| O(2)      | 0.197(1)   | 0.196(1)      | 0.1966(8)   | 0.1954(8)   | 0.195(1)    | 0.1965(9)   |
| O(3)      | 0.0955(7)  | 0.0949(7)     | 0.0957(5)   | 0.0951(5)   | 0.0949(7)   | 0.0949(6)   |
| $\Theta_a$ (deg) | 177.9(5) | 177.9(5)     | 178.9(3)    | 177.7(3)    | 178.5(5)    | 177.0(4)    |
| $\mu_F$   | 2.9(2)     | 3.2(2)        | 3.1(1)      | 2.3(2)      | --          | --          |
| $\mu_{AF}$ | --         | --            | 1.7(2)      | 1.4(1)      | 3.1(3)      | 2.8(1)      |
| $\Delta_{JT}$ | 1.034(6) | 1.025(6)     | 1.021(4)    | 1.008(4)    | 1.006(5)    | 1.010(5)    |
| $R_{wp}$  | 13.07      | 12.21         | 11.94       | 12.21       | 13.35       | 13.16       |
| $R_e$     | 5.12       | 4.80          | 5.26        | 4.81        | 5.38        | 5.01        |
La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$

(a) $T_C$, $T_N$, $T_{CO}$, $T_{CE}$

(b) AFM-III, FM-II, AFM-II, FM-I, AFM-I

(c) FM, AFM

(d) RT, LT

$\Delta_{JT}$ vs hole concentration $x$