JOURNAL OF SOLID STATE CHEMISTRY **130,** 171–175 (1997)
ARTICLE NO. SC967243

Magnetic Study of Orthomanganites $A_{1-x}MnO_{3+y}$ ($A = La, Eu$) with the Perovskite Structure

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Received August 2, 1996; in revised form November 22, 1996; accepted November 25, 1996

The crystal structure and magnetic properties of orthomanganites $A_{1-x}MnO_{3+y}$ ($A = La$, Eu; $x \leq 0.2$; $y \leq 0.13$) were investigated. It was shown that the increase of oxygen content leads to the transformation from the weak ferromagnetic to the ferromagnetic state in these compounds. The Curie temperatures of $La_{1-x}MnO_{3+y}$ and freezing temperatures of magnetic clusters for $Eu_{1-x}MnO_{3+y}$ in the samples with a deficit of A cations are higher than those in parent compounds (with $x = 0$). A mixed magnetic state involving ferro- and antiferromagnetic domains is suggested in the intermediate range of x, y values. Arguments are presented to support the assumption that the magnetic properties in the lightly doped insulating regime are governed by superexchange via anions rather than by exchange via charge carriers.

INTRODUCTION

Orthomanganites of rare-earth elements have interesting magnetic and electric properties for their potential application (1). The effect of the giant magnetoresistance may approach $10^7\%$ in the field 6 T (2). In these systems the ferromagnetic ground state arises by substitution of the alkaline-earth ions for La cations (3). At present it has been shown that nonstoichiometry might arise due to the La-cation deficit (1). The magnetic properties of samples with such a type of nonstoichiometry have not yet been studied.

$EuMnO_3$ has the same perovskite structure as $LaMnO_3$, however its properties as a function of oxygen content are unknown. The ground state of Eu^{3+} is characterized by a total orbital moment $J = 0$ and, hence, magnetic properties of $EuMnO_3$ are governed by magnetic interactions between manganese ions. In order to reach further confirmation about the effect of lanthanoid cation, the present report deals with the magnetic behavior of nonstoichiometric $La_{1-x}MnO_{3+y}$ and $Eu_{1-x}MnO_{3+y}$ with the perovskite structure.

EXPERIMENTAL

The starting samples of $La_{1-x}MnO_{3+y}$ and $Eu_{1-x}MnO_{3+y}$ were synthesized by mixing La_2O_3, Eu_2O_3, and MnO_2 powders, a first solid-state reaction step at 1270 K. Before preparation of the samples La_2O_3 and Eu_2O_3 were fired at 1470 K in air. The pressed powders were fired in air to dense pellets at 1670 K for 3 hr and slowly cooled with a furnace.

In such a way, prepared $LaMnO_{3+y}$ samples were annealed at 1370 K for 48 hr under various oxygen pressure conditions according to the phase diagram composition–oxygen pressure (4).

The specimens with cation deviation from stoichiometry were annealed in air or vacuum, quenched, and slowly cooled with a furnace. Specimens with the lowest oxygen content were received in a quartz tube at 1070 K using metallic tantalum as a getter. Since X-ray diffraction patterns showed the presence of impurity phases for $x < 0.85$, the investigations were carried out on the samples $La_{0.85}MnO_{3+y}$ and $Eu_{0.85}MnO_{3+y}$.

Chemical determination of the oxidative state of the manganese ions was performed by chromatometric titration. ac-magnetic susceptibility was measured by the mutual inductance bridge. Magnetization measurements were performed with a vibrating sample magnetometer.

RESULTS AND DISCUSSION

The X-ray patterns show the O^I-orthorhombic structure of the $LaMnO_{3+y}$ system at $y < 0.05$ ($c/\sqrt{2} < a < b$, orbital ordered phase), the O-orthorhombic structure at $0.07 < y < 0.11$ ($a < c/\sqrt{2} < b$, orbital disordered phase), and the rhombohedral structure at at $y \geq 0.11$ (Table 1).

Figure 1 presents the temperature dependence of the magnetization for $LaMnO_{2.94}$ in the field 40 Oe. The magnetization was measured after cooling in zero field (ZFC) and in the field of 40 Oe (FC). In the first case a maximum

0022-4596/97 $25.00

TABLE 1
Composition, Crystal Structure Type, and Unit Cell Parameters at 293 K of Some Investigated Manganites

Composition	Type	*a* (Å)	*b* (Å)	*c* (Å)	α (deg.)
$\mathrm{LaMnO}_{2.94}$	O^{I}	5.538	5.742	7.720	
$\mathrm{LaMnO}_{2.99}$	O^{I}	5.536	5.733	7.712	
$\mathrm{LaMnO}_{3.07}$	O	5.533	5.574	7.780	
$\mathrm{LaMnO}_{3.13}$	R	5.471			60.7
$\mathrm{La}_{0.85}\mathrm{MnO}_{2.78}$	O^{I}	5.531	5.712	7.715	
$\mathrm{La}_{0.85}\mathrm{MnO}_{2.94}$	R	5.472			60.5
$\mathrm{EuMnO}_{3.02}$	O^{I}	5.331	5.819	7.494	
$\mathrm{Eu}_{0.85}\mathrm{MnO}_{2.91}$	O^{I}	5.335	5.654	7.517	

was found at 147 K, while in the second case no maximum was noted. The temperature dependence of magnetization for $\mathrm{LaMnO}_{2.99}$ is similar to that for $\mathrm{LaMnO}_{2.94}$.

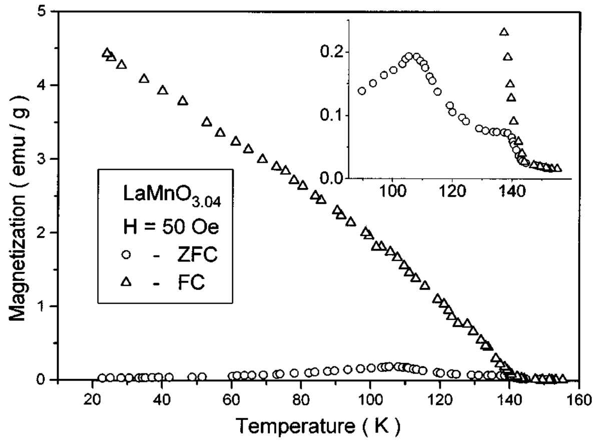

FIG. 2. ZFC and FC magnetization vs temperature at $H = 50$ Oe for $\mathrm{LaMnO}_{3.04}$.

The samples with an oxygen excess demonstrate also a dependence of magnetic properties on the magnetic prehistory (Figs. 2 and 3). The magnetization maximum for $\mathrm{LaMnO}_{3.07}$ arises in $\sigma(T)$ curves for the samples cooled both in magnetic field and without it, however the peak is more pronounced in the latter case (Fig. 3). The temperature behavior of residual magnetization for $y = -0.06$, $y = 0.04$ and $y = 0.07$ samples is shown in Fig. 4. The increasing oxygen content ($y > 0$) leads to broadening of the transition into a paramagnetic state. The residual magnetization for $y = 0.07$ is enhanced with increasing temperature above 110 K. The LaMnO_{3+y} ($-0.06 < y < 0$) samples are characterized with a spontaneous magnetization 2–3 emu/g ($\sim 0.1\ \mu_{\mathrm{B}}$ per formula unit) and high coercive field at 4.2 K. The magnetization is not saturated in the field up to 16 kOe in the temperature range 4.2–115 K (Fig. 5). The magnetization is enhanced with increasing oxygen content. The spontaneous magnetization of $\mathrm{LaMnO}_{3.13}$ reaches the value of 80 emu/g at 4.2 K. This value is close to that calculated for the case of ferromagnetic ordering of Mn^{3+}, Mn^{4+} ions' magnetic moments.

The $\mathrm{LaMnO}_{2.94}$ sample is characterized by very low ac susceptibility in the whole investigated temperature range. A sharp maximum of the susceptibility was revealed for $\mathrm{LaMnO}_{3.04}$ at 115 K (Fig. 6) and the maximum is broadened with increasing oxygen content. The temperature of the peak of susceptibility does not depend on composition in the range $0.04 < y < 0.11$ (Fig. 6). The Curie temperature of $\mathrm{LaMnO}_{3.13}$ is measured to be about 160 K.

The magnetic properties of $\mathrm{La}_{0.85}\mathrm{MnO}_{3+y}$ depend also on the preparation conditions. The onset of the temperature of the magnetic ordering for $\mathrm{La}_{0.85}\mathrm{MnO}_{2.78}$ prepared in the silica tube with getter is 136 K, spontaneous magnetization

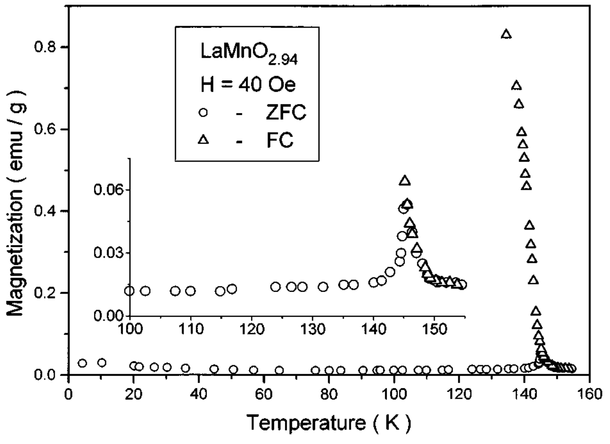

FIG. 1. ZFC and FC magnetization vs temperature at $H = 40$ Oe for $\mathrm{LaMnO}_{2.94}$.

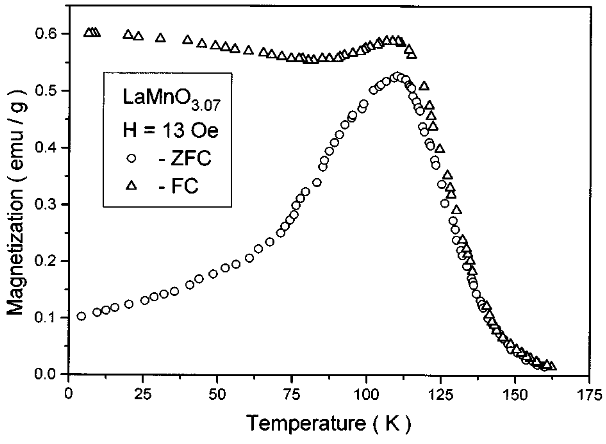

FIG. 3. ZFC and FC magnetization vs temperature at $H = 13$ Oe for $\mathrm{LaMnO}_{3.07}$.

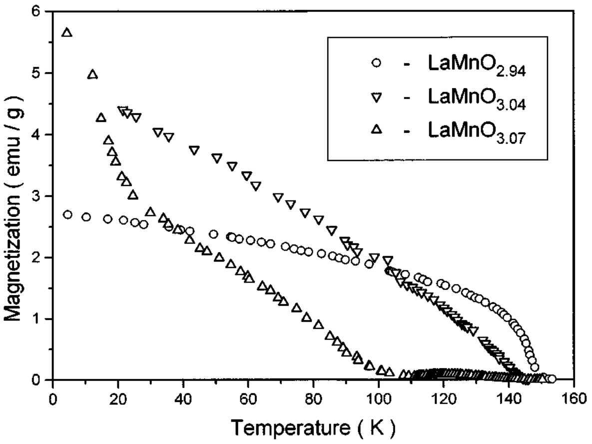

FIG. 4. Residual magnetization vs temperature for $LaMnO_{2.94}$, $LaMnO_{3.04}$, and $LaMnO_{3.07}$.

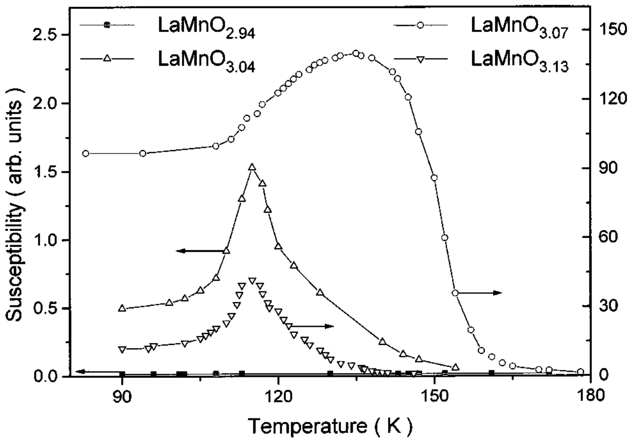

FIG. 6. ac-magnetic susceptibility vs. temperature for $LaMnO_{2.94}$, $LaMnO_{3.04}$, $LaMnO_{3.07}$, and $LaMnO_{3.13}$.

is 2 emu/g, and coercive field is 15 kOe at 4.2 K. A sharp maximum at 115 K was revealed in the $\chi(T)$ curve for the specimen of $La_{0.85}MnO_{2.84}$ annealed in vacuum 10^{-3} Pa at 1070 K for 8 hr (Fig. 7, curve 1). Further annealing at 1070 K in air for 20 min leads to the appreciable enhancement of the susceptibility below 200 K. It has been caused by the appearance of a new magnetic phase. The specimen $La_{0.85}MnO_{2.88}$ quenched from 1400 K had the temperature of the magnetic ordering about 180 K (Fig. 7, curve 2). In all cases anomalous behavior was observed near 115 K. Annealing at 1070 K for 20 hr in air brings about the Curie temperature up to 240 K (Fig. 7, curve 4).

The increasing oxygen content results in the magnetization rise. The spontaneous magnetization of the specimen annealed at 800 C in air is estimated to be about 82 emu/g at 4.2 K.

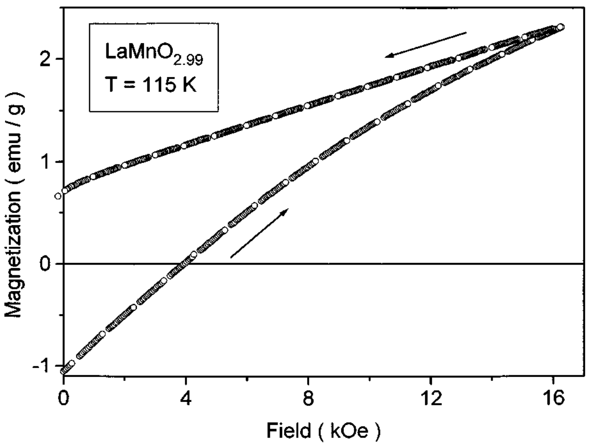

FIG. 5. Magnetization vs field for $LaMnO_{2.99}$ at 115 K.

The samples annealed at 1070 K in air for 20 hr and cooled slowly from 1670 K have a rhombohedrally distorted unit cell in contrast to the specimens reduced in vacuum and characterized by the O^I-orthorhombic structure. All Eu-containing samples have O^I-orthorhombic structure independent of the preparation conditions.

The results of magnetization measurements for $EuMnO_{3.02}$ in field 20 Oe are shown in Fig. 8. Curve ZFC and curve FC do not coincide below 48 K. At 4.2 K the ratio between the FC and ZFC magnetizations is more than three orders of magnitude. A sharp alteration of magnetization near 40 K seems to be due to a magnetic phase transition.

The magnetization of $EuMnO_{3.02}$ depends linearly on the field up to 25 kOe at 4.2 K. The spontaneous magnetization

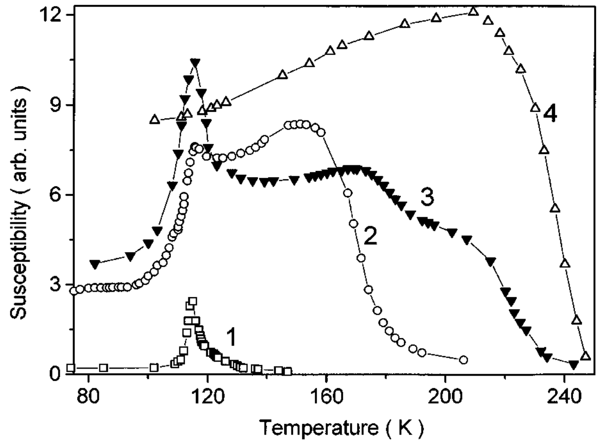

FIG. 7. ac-magnetic susceptibility vs temperature for $La_{0.85}MnO_{3+y}$: 1, sample $La_{0.85}MnO_{2.84}$ annealed in vacuum; 2, sample $La_{0.85}MnO_{2.88}$ quenched from 1400 K; 3, sample $La_{0.85}MnO_{2.90}$ slowly cooled from 1670 K; and 4, sample $La_{0.85}MnO_{2.94}$ annealed at 1070 K for 20 hr.

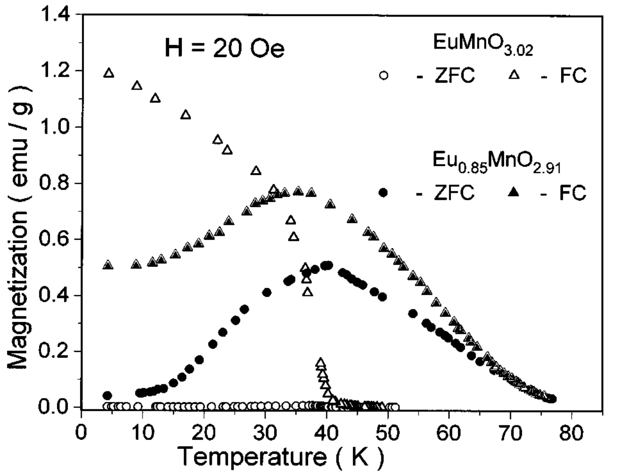

FIG. 8. ZFC and FC magnetization vs temperature at $H = 20$ Oe for $EuMnO_{3.02}$ and $Eu_{0.85}MnO_{2.91}$.

is estimated to be 2.5 emu/g. The magnetic moment reorientation occurs in fields higher than the magnetic anisotropy field (25 kOe at 4.2 K). From these data it follows that the magnetic anisotropy is very large at 4.2 K. However, it changes drastically with increasing temperature. The decrease of the oxygen content in europium manganite leads to an increase of the Neel temperature (Fig. 9).

The decrease in Eu content leads to the abrupt fall of the magnetic anisotropy and increase of both magnetization and freezing temperature of magnetic moments. The ZFC and FC magnetizations of $Eu_{0.85}MnO_{2.91}$ (the specimen was slowly cooled from 1670 K with the furnace) do not coincide below 65 K and have maximum near 40 K (Fig. 8).

The magnetic data (Figs. 1, 4, 9) show the $LaMnO_3$ and $EuMnO_3$ are weak ferromagnets with well-defined Neel temperatures, 147 and 49 K, respectively. It seems that the nonstoichiometric manganites with excess of oxygen content to be inhomogeneous magnetics. Magnetic properties of most of the samples are due to microdomains of ferromagnetic and antiferromagnetic phases. The temperatures of magnetic ordering for the antiferromagnetic phase depend weakly on conditions of the sample preparation (Figs. 2–7). The ratio between ferromagnetic and antiferromagnetic phases depends on the oxygen content. However, the complete disappearance of the antiferromagnetic phase was not observed even after annealing at 1070 K in air for 20 hr. The magnetic moments of the microdomains of both the phases interact through the interphase boundary as seen from the dependence of magnetic properties on the magnetic prehistory and from the considerable decrease of the ac-magnetic susceptibility below 115 K (Figs. 2–7). A mixed two-phase state was confirmed by the X-ray study of $LaMnO_{3+y}$ (4, 5), where the diffraction peaks of both O^{I}- and O-orthorhombic phases were revealed in the concentration ranges $-0.06 < y < 0.01$ and $0.05 < y < 0.07$. However the X-ray study of nonstoichiometric La manganites performed by other authors did not show any phase separation (1). Two series of reflexes belonging to antiferromagnetic and ferromagnetic phases were registered by neutron diffraction for La- and Pr-containing manganites doped with alkaline-earth ions (6, 7). The results of the neutron diffraction under external magnetic field were interpreted on the basis of noncollinear magnetic structure formation (7) and the mixed two-phase model (6).

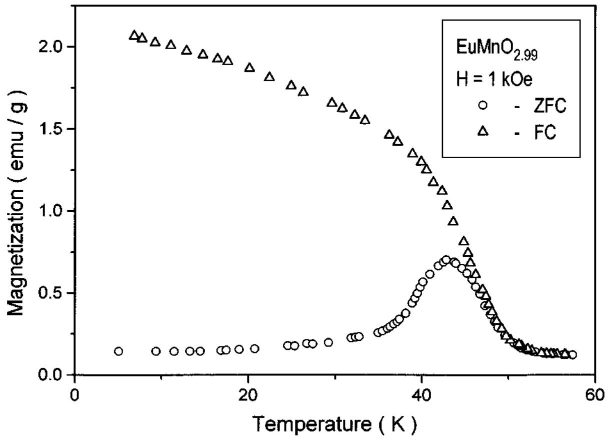

FIG. 9. ZFC and FC magnetization vs. temperature at $H = 1$ kOe for $EuMnO_{2.99}$.

We assume the antiferromagnetism of La manganite to be the result of the orbital ordered phase while the ferromagnetism to be the result of the orbital disordered phase. The magnetic anisotropy of $EuMnO_3$ is higher than that of $LaMnO_3$. The orbital state of Mn^{3+} in $EuMnO_3$ is apparently characterized by a very slow reorientation of the d_z^2 orbitals while such a process for $La_{1-x}MnO_{3+y}$ proceeds faster.

Nonstoichiometry in La and Eu deficit compounds arises probably through the formation of lanthanum or europium, and oxygen vacancies. According to (1) the oxygen nonstoichiometry in $LaMnO_{3+y}$ is caused by the appearance of an equal number of La and Mn vacancies.

It is believed that the double exchange interactions between pairs of Mn^{3+} and Mn^{4+} ions are responsible for the ferromagnetic and transport properties in manganites (6–8). However, for a lightly doped insulating regime at $La_{1-x}MnO_{3+x}$ the double exchange model suggested a canted or spiral antiferromagnetism (8–10). This theory suggests also that the canted state continuously changes to the ferromagnetic state as a function of hole (Mn^{4+}) doping.

It seems that the ferromagnetic ordering in a lightly doped insulating regime can be governed by exchange interactions via oxygen. This assertion is supported by the following facts.

1. The magnetic and neutron diffraction studies of $La_{1-x}Ca_xMnO_3$ indicate that the antiferromagnetic–ferromagnetic transition occurs through a mixed two-phase state (6, 11). The results of the neutron diffraction study of $Pr_{0.9}Ca_{0.1}MnO_3$ and $La_{1-x}Sr_xMnO_3$ (7, 12) can be understood in frames of the two-phase model. The FMR study of the manganites has revealed a large chemical inhomogeneity of samples (13).

2. Giant magnetoresistance has recently been found in $(Tl_{1-x}In_x)Mn_2O_7$ pyrochlores (14). In these $A_2B_2O_7$-type compounds, ferromagnetism arises due to superexchange via oxygen and A cation (15).

3. The transition temperature T_c is approximately the same in the insulators $(La, Ca)_xMn^{3+}O_{3-y}$ (high pressure method preparation) and conducting perovskites $La_{1-x}Ca_xMnO_3$ (16). The ferromagnetism has also been observed in insulating perovskites $La_{1-x}Ba_x(Mn^{3+}_{1-x}Ti^{4+}_x)O_3$ and $BiMnO_3$ (17, 18).

4. The transition to metallic conductivity in $La_{1-x}Ca_xBO_3$ ($B = Cr, V$) is not accompanied by the appearance of ferromagnetism (19).

The superexchange interactions between Mn^{3+}–Mn^{3+} and Mn^{3+}–Mn^{4+} ions via oxygen in octahedral surroundings and with the bond angle of 180° has been discussed earlier by many authors. According to (3, 11, 17), the dominant exchange mechanism is the ferromagnetic. Orbital or charge ordering in the perovskite lattice leads to antiferromagnetism (3). The ferromagnetic part of superexchange interaction decreases abruptly with decreasing Mn–O–Mn angle (11).

CONCLUSION

1. $LaMnO_3$ and $EuMnO_3$ are weak ferromagnets with Neel temperatures of 147 and 49 K, respectively; the spontaneous magnetic moment per formula unit is about 0.1 μ_B. Spontaneous magnetization of $LaMnO_{3+y}$ changes insignificantly with oxygen content decreasing from $y = 0$ to $y = -0.6$. $LaMnO_{3.13}$ is a ferromagnet with a magnetic moment per formula unit of 3.4 μ_B at 4.2 K and a Curie temperature of 150 K.

2. The magnetic properties of $LaMnO_{3+y}$ ($0.02 \leq y \leq 0.10$) are consistent with the mixed two-phase magnetic state. The onsets of magnetic ordering of both phases are weakly dependent on composition in a relatively wide range of oxygen concentration.

3. The deficit of lanthanoid cations leads to the decrease of the Neel temperature of the antiferromagnetic phase (reduced samples) and increase of the Curie temperature of the ferromagnetic phase (oxidized samples). $La_{0.85}MnO_{2.94}$ is a ferromagnet with a well-defined Curie temperature of 240 K while $Eu_{0.85}MnO_3$ is a nonhomogeneous antiferromagnet with ferromagnetic cluster inclusions.

4. The magnetic properties of the nonstoichiometric manganites can be explained in terms of the superexchange interaction via oxygen.

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