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LETTER TO THE EDITOR

Stoichiometry and electronic properties of LaMnO_3

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Abstract. Treating off-stoichiometric $(\text{LaMn})_{0.95}\text{O}_3$ in hydrogen transforms its electrical and magnetic properties. The untreated material is a ferromagnetic narrow-gap semiconductor ($T_c = 125$ K) whereas the near-stoichiometric reduced material is an antiferromagnetic insulator ($T_N = 110$ K). Although the off-stoichiometric manganite has formally the same mixed manganese valency as compounds such as $(\text{La}_{0.7}\text{Ca}_{0.3})\text{MnO}_3$, there is no resistivity peak at T_c and no giant magnetoresistance. The difference may be due to potential fluctuations associated with cation vacancies.

Interest in mixed-valence manganites based on LaMnO_3 has been revived with the observations of unusual I – V characteristics in trilayer structures with high- T_c superconductors [1] and large negative magnetoresistance effects [2], especially in suitably annealed thin films [3]. The magnetoresistance is greatest in the vicinity of the Curie point of ferromagnetic compositions such as $(\text{La}_{0.7}\text{Ca}_{0.3})\text{MnO}_3$ which exhibit ‘metallic’ (temperature-independent) conductivity at low temperatures [4]. These compositions have a structure which is a variant of the cubic perovskite cell where the Mn–O–Mn bond angles differ from 180° [5]. Their electronic properties are related to electron hopping among the Mn ions in octahedral sites; the formula of the compounds with substitution of a divalent cation M for La may be written $(\text{La}_{1-x}^{3+}\text{M}_x^{2+})(\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+})\text{O}_3$, and the metallic conductivity and ferromagnetism are both attributable to electron hopping in a spin-polarized σ^* conduction band of mainly $3d(e_g^\uparrow)$ character [6]. The Mn^{3+} ion has one e_g electron, whereas the Mn^{4+} ion has none. When $x \approx 0.3$, the occupancy of the σ^* band is 0.7, which appears to correspond to the strongest ferromagnetism and the greatest magnetoresistance. The end member LaMnO_3 is orthorhombic with a marked Jahn–Teller distortion of the oxygen octahedron around the manganese, which splits the e_g band, localizing the electrons and rendering the material insulating and antiferromagnetic [7].

It has long been known that LaMnO_3 can exhibit a range of stoichiometry. The formula was given as $\text{LaMnO}_{3+\delta}$ in the early literature, but it is better written as $(\text{LaMn})_{1-\gamma'}\text{O}_3$, reflecting the presence of cation vacancies rather than oxygen excess [8,9]. Here we compare the structure and properties of near-stoichiometric and cation-deficient LaMnO_3 , showing that some of the changes which can be effected by substitution of a divalent cation for lanthanum can equally be produced by varying the metal/oxygen ratio.

Nonstoichiometric La–Mn–O was produced by reacting lanthanum oxalate and manganese carbonate in air at 1200°C . Several firings of reground material led to a pure phase. The x-ray diffraction pattern was indexed on a cubic cell with $a_0 = 0.781$ nm (space group $Fm\bar{3}m$), which corresponds to the composition $\delta = 0.15$, or $(\text{LaMn})_{0.95}\text{O}_3$ [10]. This is sample A. The powder was then heated in hydrogen in a thermopiezic analyser [11], where it was seen to react at about 400°C when heated at 10 K min^{-1} . The resulting powder, sample B, was found to be orthorhombic with $a = 0.554$ nm, $b = 0.573$ nm and

$c = 0.773$ nm (space group $Pbnm$). These parameters correspond to those reported for stoichiometric LaMnO_3 . A small weight loss is observed in thermogravimetric analysis under hydrogen, indicating that oxygen is likely to be removed during the process, but incorporation of some hydrogen in the lattice as OH^- is not excluded.

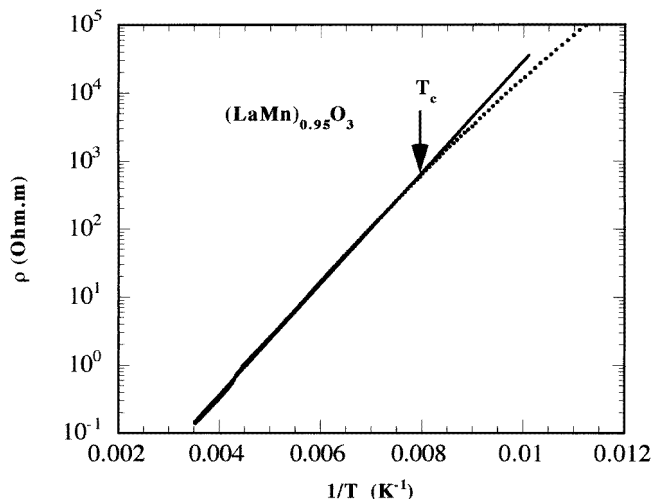


Figure 1. The resistivity of $(\text{LaMn})_{0.95}\text{O}_3$ as a function of temperature. The arrow marks the Curie temperature.

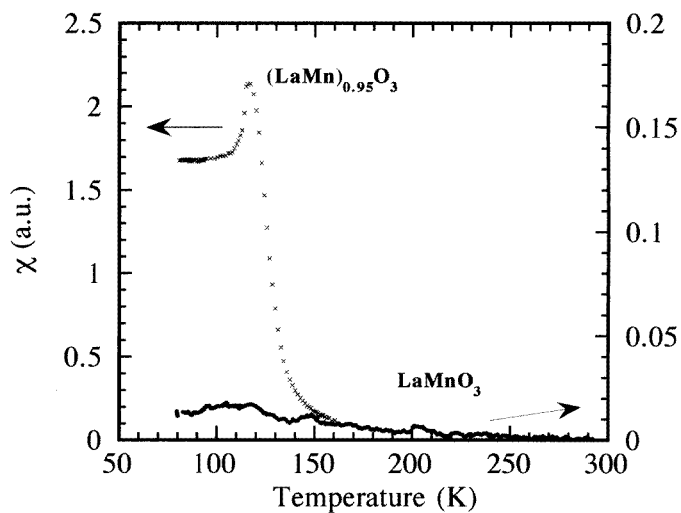


Figure 2. The magnetic susceptibility of $(\text{LaMn})_{0.95}\text{O}_3$ and LaMnO_3 .

The two samples have quite different physical properties. Sample A is a moderately good electrical conductor having $\rho = 10^{-1} \Omega \text{ m}$ at room temperature (figure 1); the conduction above 125 K is thermally activated with an activation energy of 0.15 eV. Sample B shows typically insulating behaviour. Magnetically also the samples are quite different. Measurements of the susceptibility of sample A show that it is ferromagnetic with

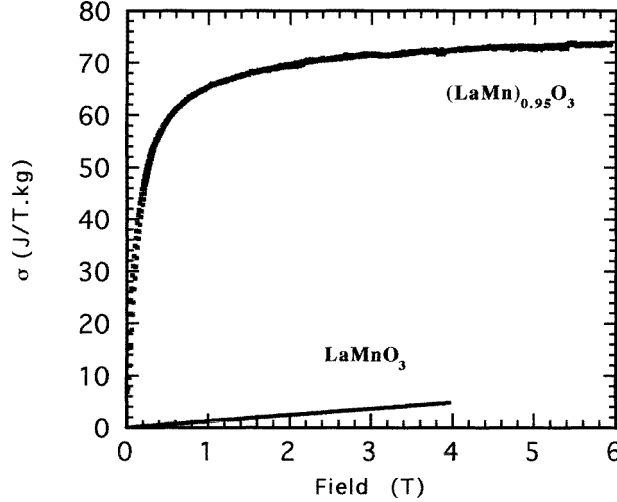


Figure 3. Magnetization curves at 4.2 K for $(\text{LaMn})_{0.95}\text{O}_3$ and LaMnO_3 .

Table 1. Magnetic and electronic properties of La–Mn–O.

	Composition	Structure	Magnetic order	Electrical conductivity
Sample A	$(\text{LaMn})_{0.95}\text{O}_3$	cubic	F $T_C = 125$ K	semicond. $E_a = 0.15$ eV
Sample B	LaMnO_3	orthorhombic	AF $T_N = 120$ K	insulating

a Curie temperature of $T_C = 125$ K (figure 2), whereas stoichiometric LaMnO_3 is a planar antiferromagnet with $T_N \approx 120$ K [12, 13]. Magnetization curves for the two samples at 4.2 K are shown in figure 3. The saturation magnetization of sample A, $\sigma = 75 \text{ J T}^{-1} \text{ kg}^{-1}$, corresponds to an average manganese moment of $3.3 \mu_B$. These results are summarized in table 1.

It appears that the electronic doping in nonstoichiometric $(\text{LaMn})_{1-\delta'}\text{O}_3$ is similar to that of the compounds with divalent substitution. Provided that the oxygen remains divalent, the formula is $\text{La}_{1-\delta'}^{3+}(\text{Mn}_{1-7\delta'}^{3+}\text{Mn}_{6\delta'}^{4+})\text{O}_3^{2-}$. Hence when $\delta' = 1/21$, the $\text{Mn}^{3+}:\text{Mn}^{4+}$ ratio is 7:3, and the e_g band occupancy is similar to that of $(\text{La}_{0.7}\text{Ca}_{0.3})\text{MnO}_3$. However, unlike the latter compound, there is no peak in the resistivity of nonstoichiometric LaMnO_3 near T_C (figure 1) and no large magnetoresistance effect. The low-temperature resistivity is activated, not metallic, although there is a change of activation regime at T_C . A possible explanation is the strong localizing effect of random cation vacancies [4]. The σ^* band is only about 1 eV wide, so the random potential fluctuations due to missing manganese ions may suffice to tip the balance in favour of Anderson localization [14] but the localized wavepackets must nevertheless be large enough for the e_g^\uparrow electrons to extend over several sites to provide the ferromagnetic interaction. A ferromagnetic insulating phase has been reported in the $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ system when $x \approx 0.15$ [13]. We have observed similar behaviour in $(\text{Sm}_{0.7}\text{Bs}_{0.3})\text{MnO}_3$. Furthermore, the band may be narrower in the nonstoichiometric end member on account of its slightly larger unit cell volume. The Mn–O–Mn bond angle is a crucial parameter in these compounds [5] but the effect of cation vacancies on the bond angle [9] has not yet been systematically studied.

In conclusion, the occupancy of the d band in mixed-valence manganites can be varied by changing oxygen stoichiometry or by cation substitution. The change from antiferromagnetic to ferromagnetic LaMnO_3 can be brought about by increasing the oxygen/metal ratio as well as by doping with a divalent ion. The nonstoichiometric $(\text{LaMn})_{0.95}\text{O}_3$ is a ferromagnetic semiconductor. Our results emphasize the need to specify both the cation composition and the cation/oxygen ratio when considering the electronic properties of mixed-valence manganites. Low-temperature reduction with hydrogen is a convenient way to obtain a near-stoichiometric oxide.

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