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Giant magnetoresistance in bulk samples of $LaMnO_3$ with varying Mn^{4+} content

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Abstract. Magnetoresistance (MR) in bulk samples of $LaMnO_3$ has been investigated by varying the Mn^{4+} content from 10 to 33 per cent by chemical means, without aliovalent doping. With the increase in Mn^{4+} content, the structure of $LaMnO_3$ changes first from orthorhombic to rhombohedral and then to cubic and the material becomes increasingly ferromagnetic, exhibiting a resistivity maximum akin to an insulator-metal transition at T_{Peak}, just below the ferromagnetic T_c. The magnitude of MR is highest in the cubic sample (with 33% Mn^{4+}) around the T_{Peak}, and negligible in the non-magnetic orthorhombic sample (12% Mn^{4+}).

Keywords. Metal-nonmetal transition; perovskite oxides; mixed valency; giant magnetoresistance.

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The observation of giant magnetoresistance (GMR) in films of the perovskite oxides, $La_{1-x}A_xMnO_3$(A = Ca or Ba) has caused considerable sensation in recent months ([1]–[3]). GMR in these oxide films is found in the range 77–300 K where the material is ferromagnetic and nearly metallic. The magnitude of magnetoresistance, as defined by,

$$GMR = \Delta\rho/\rho(0) = [\rho(H) - \rho(0)]/\rho(0),$$

where $\rho(H)$ and $\rho(0)$ are respectively the resistivities at magnetic field H and zero field at the same temperature, has been found to be very high in some of the films. The $La_{1-x}A_xMnO_3$ (A = Ca, Ba) perovskites are itinerant electron ferromagnets wherein the ferromagnetism is caused by Mn^{3+}-O-Mn^{4+} interaction of the Zener-type ([4]–[6]). Because of fast electron hopping between Mn^{3+} and Mn^{4+}, the material shows metal-like resistivity behaviour as it becomes ferromagnetic, exhibiting a resistivity maximum signifying an insulator-metal (I-M) type transition, just below the ferromagnetic Curie temperature. We have explored the occurrence of GMR in bulk samples of $LaMnO_3$ without substituting La partly by an alkaline earth, but by varying the proportion of Mn^{4+} by chemical means.

$LaMnO_3$ samples were prepared by decomposing a gel, obtained by treating citric acid and ethylene diamine with the nitrate solution of La and Mn ions, at various temperatures [7]. The sample sintered at 1470 K in air for 12 hr was orthorhombic (figure 1) with **a** = 5·543 Å, **b** = 5·494 Å and **c** = 7·805 Å, containing 12% Mn^{4+} as determined by redox titrations and thermogravimetry and was a paramagnetic insulator. Progressive oxidation of the orthorhombic sample in a stream of oxygen

around 1200 K transformed it to a rhombohedral ($\mathbf{a} = 5{\cdot}478$ Å, $\alpha = 60{\cdot}55°$) and then to a cubic structure ($\mathbf{a} = 7{\cdot}788$ Å) containing 24% and 33% Mn^{4+} respectively [7] as shown in figure 1. We could also prepare rhombohedral and cubic samples of $LaMnO_3$ by electrochemical oxidation ([8]–[9]). The resistivity of $LaMnO_3$ decreases with increase in Mn^{4+} content. Furthermore, the ferromagnetism as well as the resistivity maxima associated with the I-M type transition manifest themselves in $LaMnO_3$ with increasing percentage of Mn^{4+}, the magnitudes of T_c and T_{Peak} increasing with % Mn^{4+}. Accordingly, the rhombohedral and cubic samples were ferromagnetic ($T_c \sim 180$ and 220 K) and showed the resistivity maxima around 170 and 200 K (T_{Peak}) respectively (figure 2).

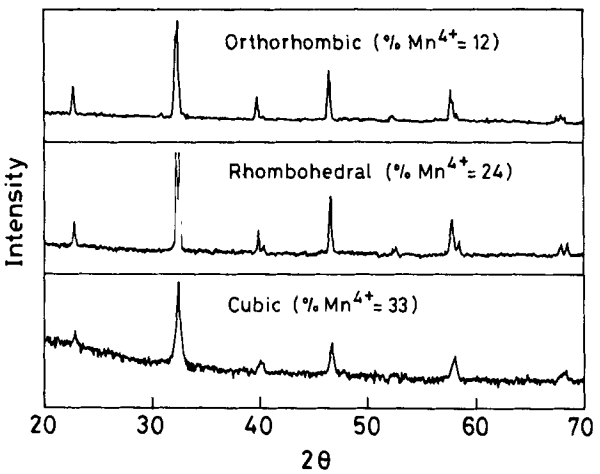

Figure 1. X-ray diffraction patterns of $LaMnO_3$ containing different percentages of Mn^{4+} showing orthorhombic, rhombohedral and cubic structures. The width of the X-ray diffraction profiles is slightly broader, specially in the cubic phase, due to the small particle size.

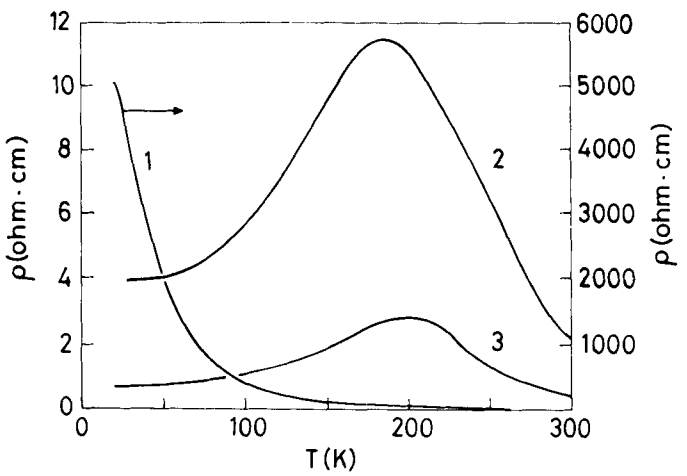

Figure 2. Temperature variation of resistivity of $LaMnO_3$ samples at zero field: 1, orthorhombic; 2, rhombohedral and 3, cubic.

We have determined the extent of oxidation of $LaMnO_3$ in different samples in terms of % Mn^{4+}. This is justified because of the defect structure of this perovskite. Although traditionally considered to be anion excess, detailed investigations by employing high-resolution electron microscopy and other cognate techniques, besides density measurements, has established that the defect structure does not involve oxygen excess to produce Mn^{4+} as there is no room for the excess oxygen in the close-packed structure ([10]–[11]). In fact, all the samples have three oxygens as given by the formula. We do not observe any defect ordering, extended defects or cation displacements. Instead, there is a random distribution of cation vacancies on both the La and Mn sites. Accordingly, $LaMnO_3$ with 12% Mn^{4+} is to be written on $La_{0.98}Mn_{0.98}O_3$ or $La_{0.98}Mn^{3+}_{0.86}Mn^{4+}_{0.12}O_3$. With 24% and 33% Mn^{4+}, the compositions are $La_{0.96}Mn_{0.96}O_3$ and $La_{0.945}Mn_{0.945}O_3$ respectively.

Magnetoresistance measurements on the $LaMnO_3$ samples were carried out with bar-shaped samples (0·5 mm × 1 mm × 10 mm) of $LaMnO_3$ up to an applied field of 6 T using a superconducting solenoid. The field was applied perpendicular to the direction of the current and the resistance was measured by the 4-probe technique by the low-frequency (20 Hz) a.c. method as well as by the d.c. method.

In figure 3 we have shown the temperature variation of the per cent magnetoresistance, $100 \times \Delta\rho/\rho(0)$, for the three samples of $LaMnO_3$ (figure 1) containing different percentages of Mn^{4+}. The orthorhombic sample with ~ 12% Mn^{4+} does not show magnetoresistance above 100 K. The rhombohedral sample with 24% Mn^{4+}, on the other hand, shows 52% MR at $H = 6$ T with the MR peaking around 165 K. The cubic sample with 33% Mn^{4+} shows 69% MR at 6 T, the MR peaking around 170 K. In figure 4, we show the variation of $\Delta\rho/\rho(0)$ with the applied magnetic field for the three samples of $LaMnO_3$ at 4·2 K. Cubic and rhombohedral $LaMnO_3$ show MR of 49% and 43% respectively at 6 T whereas the orthorhombic phase shows hardly 17% MR. Figure 4 also suggests that there are two types of contributions to MR.

The present study demonstrates that magnetoresistance in $LaMnO_3$ becomes maximum around a temperature just around the temperature corresponding to the

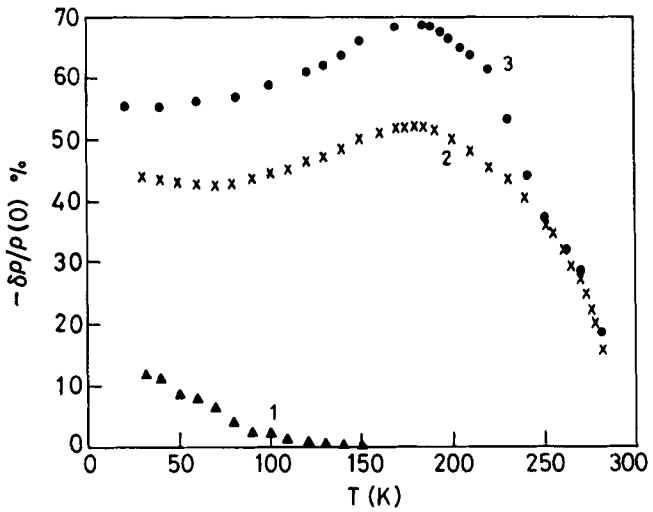

Figure 3. Temperature variation of per cent magnetoresistance, $100 \times \Delta\rho/\rho(0)$, of $LaMnO_3$ samples at $H = 6$ T: 1, orthorhombic; 2, rhombohedral and 3, cubic.

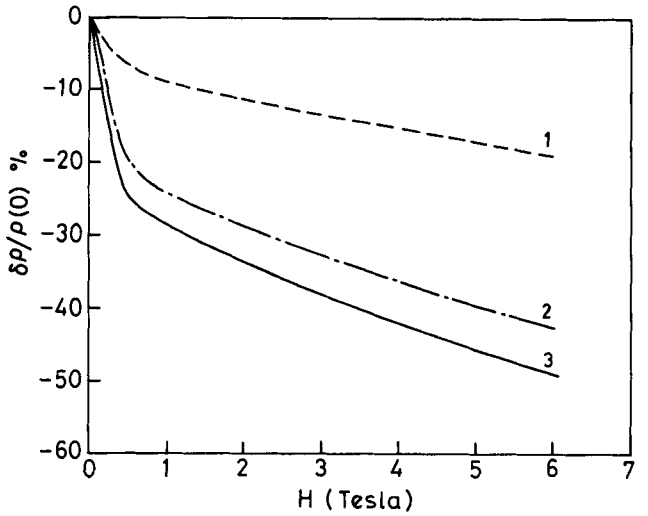

Figure 4. Variation of per cent magnetoresistance of $LaMnO_3$ samples with magnetic field at 4·2 K: 1, orthorhombic; 2, rhombohedral and 3, cubic.

resistivity maximum, T_{peak}, or the ferromagnetic T_c, both of which are related to the Mn^{4+} content. It is noteworthy that in the ferromagnetic regime, when the resistivity decreases with decreasing temperature, the material is really not a metal in the conventional sense. While the electrons become itinerant because of fast hopping between Mn^{3+} and Mn^{4+} ions below T_c, it is likely that scattering of conducting electrons by ferromagnetic clusters is the important factor.

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