MAGNETISM
AND FERROELECTRICITY

Colossal Room-Temperature Magnetoresistance
in Thin La_{1-x}Ag_xMnO_3 Epitaxial Films

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Abstract—The first thin La_{1-x}Ag_xMnO_3 epitaxial films (y ≤ x) were grown on SrTiO_3 (110) substrates with silver present in the ionized state (Ag⁺) only. The Curie temperatures T_C of the compositions with x = y = 0.05, x = y = 0.1, and x = 0.3 and y = 0.27 crystallizing in the hexagonal structure R3̅̅̅̅ lie above or close to room temperature. The temperature dependences of electrical resistivity ρ and of magnetoresistance |Δρ/ρ| = (|ρ_H − ρ_0|)/|ρ_H = 0| pass through maxima near T_C, with the magnetoresistance being negative and reaching colossal values of ~7–20% in a magnetic field H = 8.2 kOe not only at T_C but also at room temperature. The magnetic moment per formula unit as derived from the saturation magnetization at T = 5 K is substantially smaller than expected for complete ferromagnetic ordering. The magnetization in fields of up to 6 kOe depends on the actual sample cooling conditions, and the hysteresis loop of a field-cooled sample is displaced along the H axis by ΔH. The above properties can be accounted for by the fact that the films are in a two-phase magnetic (ferromagnetic–antiferromagnetic) state induced by strong s–d exchange. The maximum value of ΔH was used to calculate the energy of exchange coupling between the ferromagnetic and antiferromagnetic parts of a sample. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

The interest in the manganites Re_{1–x}A_xMnO_3 (Re stands here for a rare-earth ion, and A, for a dopant ion) should be assigned to the colossal magnetoresistance (CMR) which some of them exhibit at room temperature. Unfortunately, the magnitude of the CMR observed in the vicinity of the Curie point T_C decreases rapidly with increasing T_C in manganites doped with divalent ions of Ca, Sr, and Pb. Doping LaMnO_3 with univalent ions of Na has revealed, however, that the magnetoresistance also remains colossal at room temperature in compositions whose T_C approaches 300 K [1–4]. The question naturally arises as to whether this effect would be observed in manganites doped by other univalent ions, in particular, by silver. The possibility of doping La_{1–x}MnO_3+δ ceramics with silver, where Ag⁺ ions substitute for the lanthanum vacancies, was demonstrated in [5–7]. CMR has been found to exist in these ceramics at room temperature [8]. However, doping the crystal structure of perovskite manganites with silver was questioned in [9], where doping with silver was found to be similar to the introduction of lanthanum vacancies into La_{1–x}MnO_3+δ. Indeed, the evidence presented thus far for doping manganites with silver has been only indirect, such as, for instance, the absence of metallic silver among the reaction products [8, 10]. However, it should be noted that silver is a highly mobile component.

We forward here compelling evidence for possible silver doping of La_{1–x}MnO_3+δ. It is well known that thin films of such materials would have considerable application potential. We fabricated thin epitaxial La_{1–x}Ag_xMnO_3 films (y ≤ x) on SrTiO_3 (110) substrates, some of which exhibit room-temperature CMR.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Because of the volatile compounds of silver having low thermal stability, the following two-stage technique of synthesis was proposed: (1) preparation of thin lanthanum-deficient La_{1–x}MnO_3 films (through MOCVD) at rates ν(O_2) = ν(Ar) = 7 l/h, a pressure P_tot = 10 mbar, and T = 830°C and (2) saturation of films with silver by annealing lanthanum-deficient compositions in silver vapor in an oxygen environment (at a total pressure of 1 or 20 atm). The changes in film structure were monitored by x-ray diffraction. The chemical composition of the films was established by x-ray microprobe analysis. LaMnO_3 films do not absorb silver at saturation. Silver can be absorbed at positive values of x only. X-ray photoelectron spectroscopy revealed that the silver in the films is only in the...
We studied the magnetization $\sigma$, electrical resistivity $\rho$, and magnetoresistance $\Delta \rho/\rho = (\rho_H - \rho_{H=0})/\rho_{H=0}$ of the thin epitaxial films indicated above. The magnetization was studied with a SQUID magnetometer in the temperature range $5 \leq T \leq 350$ K in magnetic fields of up to 50 kOe. The values of $\rho$ and $\Delta \rho/\rho$ were measured by the standard four-probe method. The electrical resistivity and magnetoresistance were investigated at temperatures ranging from 77 to 350 K. The magnetoresistance was measured in the film plane, with the current through the film being parallel to the applied magnetic field $H$, which did not exceed 8.2 kOe.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 displays in graphical form the temperature dependence of the electrical resistivity $\rho(T)$ of the films studied by us. The $\rho(T)$ curves are seen to exhibit maxima. The temperatures of these maxima, $T_{\text{max}}$, and the values of $\rho$ at the maxima are listed in the table. Figure 2 shows $\{\Delta \rho/\rho\}(T)$ curves for La$_{1-x}$Ag$_x$MnO$_3$ films ($x > y$). The magnetoresistance is negative, and its absolute value reaches a maximum at a temperature $T = T_{\text{max}}$, which is slightly less than $T_C$ (see table). Incidentally, $T_{\text{max}}$ is slightly higher than $T_{(\Delta \rho/\rho)\text{max}}$, a feature typical of magnetic semiconductors [11]. At the maximum, $|\Delta \rho/\rho|$ reaches a colossal value of 25% for a composition with $y = x = 0.05$, 12% for $y = x = 0.1$, and 8% in La$_{0.7}$Ag$_{0.27}$MnO$_3$ at $H = 8.2$ kOe. Note that the room-temperature magnetoresistance of the last two films is high. As seen from Fig. 2, it is ~7% at $H = 8.2$ kOe. Obviously enough, in compositions intermediate between that with $y = x = 0.1$ and La$_{0.7}$Ag$_{0.27}$MnO$_3$, one should expect even higher room-temperature values of $\Delta \rho/\rho$, approaching $|\Delta \rho/\rho|_{\text{max}}$ in the extreme compositions. In contrast to La$_{1-x}$A$_x$MnO$_3$ systems ($A = \text{Sr}^{2+}$, $\text{Ca}^{2+}$; $x \leq 0.3$) and traditional magnetic semiconductors (doped europium monochalcogenides and chalcogenide spinels), in which $|\Delta \rho/\rho|_{\text{max}}$ decreases rapidly as the doping level increases, in La$_{1-x}$Ag$_x$MnO$_3$ films ($y \leq x$) it varies very little with increasing $y$. For instance, in going from $y = 0.05$ to $y = 0.1$, $|\Delta \rho/\rho|_{\text{max}}$ decreases 2.1 times and then, as one goes from the compound...