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Origin of the magnetic moments in $La_{0.65}Pb_{0.35}MnO_3$ epitaxial thin films

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Crystalline films of $La_{0.65}Pb_{0.35}MnO_3$ grown on (100) $LaAlO_3$ substrates by rf sputtering have been investigated using magnetic circular dichroism and inverse photoemission spectroscopy. We find evidence for strong hybridization between unoccupied levels associated with Mn *3d* and O *2p* states. The oxygen atoms ''pick-up'' a small magnetic moment through hybridization with Mn. © *2000 American Institute of Physics.* [S0021-8979(00)41908-0]

I. INTRODUCTION

The observation of colossal magnetoresistance (CMR) in manganese oxides crystallizing in the perovskite structure has generated considerable interest in the physical properties of the class of compound, particularly the interplay of structure, magnetism, and electronic transport. The $La_{0.65}Pb_{0.35}MnO_3$ system has been given scant attention and few studies of the epitaxial thin films exist.[1] Recent results[2] have shown that the magnetoresistance (MR) in this system can be optimized so that the magnitude of the MR is more than 40% at 300 K. As with all CMR manganese perovskites, one issue of considerable interest is the origin of the coupling and medium of exchange as well as the origin of the moment. The present article reports on the magnetic properties obtained from magnetic circular dichroism (MCD) and inverse photoemission spectroscopy performed on single-crystal thin films of $La_{0.65}Pb_{0.35}MnO_3$.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The $La_{0.65}Pb_{0.35}MnO_3$ films, with a nominal thickness of 1000 Å, were grown on (100) $LaAlO_3$ substrates by rf sputtering in a 4:1 argon/oxygen atmosphere maintained at 15 mTorr. The samples were subsequently annealed in two steps in order to prevent Pb evaporation: at a temperature of 650 °C for 10 h and at 850 °C for 2 h in an oxygen pressure of 1 atm. The bulk chemical composition was determined from energy dispersive analysis of the x-ray emission. The orientation (100) and the epitaxial characteristics were determined by x-ray diffraction[2] and low electron energy diffraction.

The x-ray absorption spectroscopy (XAS) and MCD spectra were recorded by monitoring the sample current, which corresponds to the total electron yield. For magnetizing the sample, a 400 Oe pulse field was applied along the in-plane easy axis. The spectra for two different helicities were recorded by alternating the magnetization at every photon energy. In the total electron yield mode, the SAX spectra probes approximately 100 Å in depth, which is an intermediate length scale between the bulk and the surface boundary.

The inverse photoemission data were obtained on a home made system by using variable energy electrons and an ultraviolet detector (Geiger–Muller). In our scheme, 9.8 eV photons were detected with the Geiger–Muller tube with ~400 meV bandwidth. The overall energy resolution in inverse photoemission was ~450 meV.

Neutron powder diffraction patterns show that the $La_{0.65}Pb_{0.35}MnO_3$ is single-phase polycrystalline with a rhombohedral $R3c$ structure. The lattice parameters are $a = b = 5.51$ Å and $c = 13.38$ Å, and the angles $\alpha = \beta = 90°, \gamma = 120°$ at room temperature. The same crystallographic group symmetry was reported in Refs. 3–5.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The XAS and MCD spectra for the MN L-edge at different temperatures is shown in Figs. 1(a) and 1(b), respectively. As can be seen in panel (a) of Fig. 1, the $L_{2,3}$ edges are very well defined and exhibit sharp peaks. These spectra are comparable with the Mn $2p$ core levels obtained using x-ray photoemission spectroscopy,[6] which can only probe 5–15 Å from the surface. The conclusion here is that the sample is relatively free of defects and homogenous, except in the surface region, which is compositionally different from the bulk. The surface region, discussed in detail elsewhere,[6] exhibits Mn $2p$ binding energies for $La_{0.65}Pb_{0.35}MnO_3$ consistent with a Mn^{3+} state rather than a Mn^{4+} state. The MCD spectra presented in panel (b) of Fig. 1 is given by the difference between the absorption signals having the photon helicity parallel and respectively, antiparallel to the saturation magnetization. The MCD anisotropy, the difference divided by the sum of the two absorption signals, is proportional to the Mn magnetic moment. The tem-

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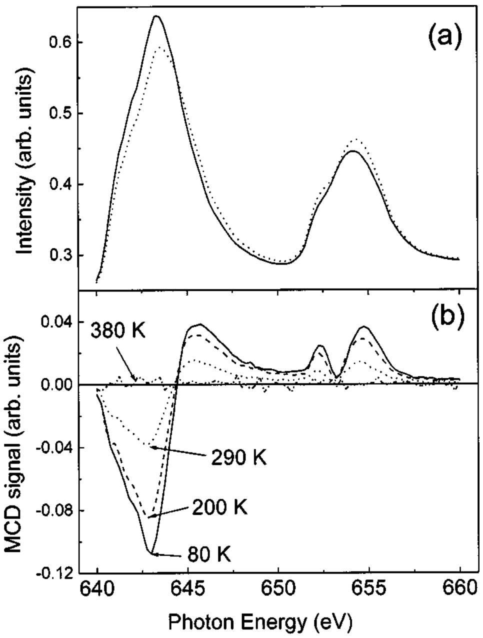

FIG. 1. X-ray absorption (a) and the magnetic circular dichroism (MCD) spectra (b) at Mn *L*-edge. In panel (a) the absorption spectra, at 80 K, are presented for the photon helicity parallel (continuous line) and antiparallel (dotted line) with the magnetization direction. The photon incident angle and the degree of circular polarization were taken into account for the spectra.

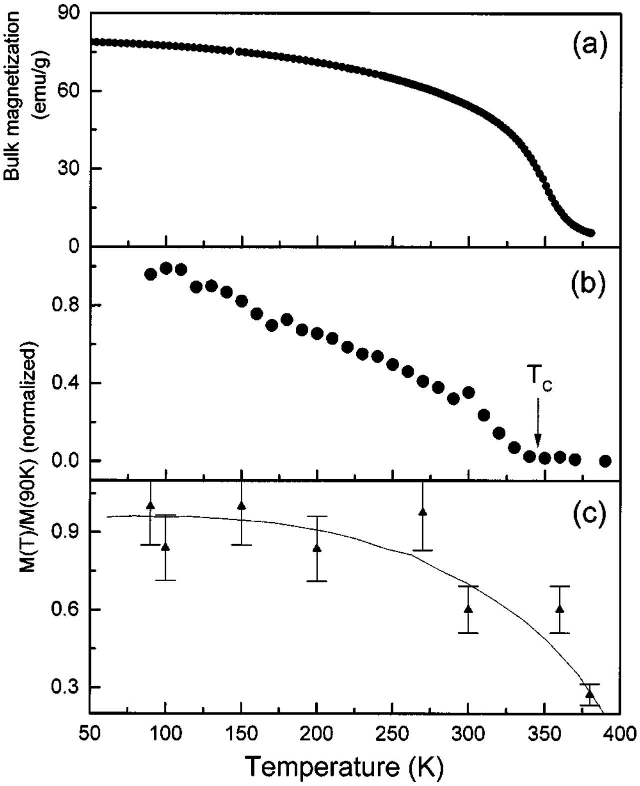

FIG. 2. (a) Temperature dependence of the $La_{0.65}Pb_{0.35}MnO_3$ bulk magnetization measured by SQUID. (b) Temperature dependence of the MCD anisotropy of Mn *L*-absorption edge, which is proportional to the MN magnetic moment in the surface region. (c) Temperature dependence of the MCD signal of oxygen 1*s* edge from the film surface region.

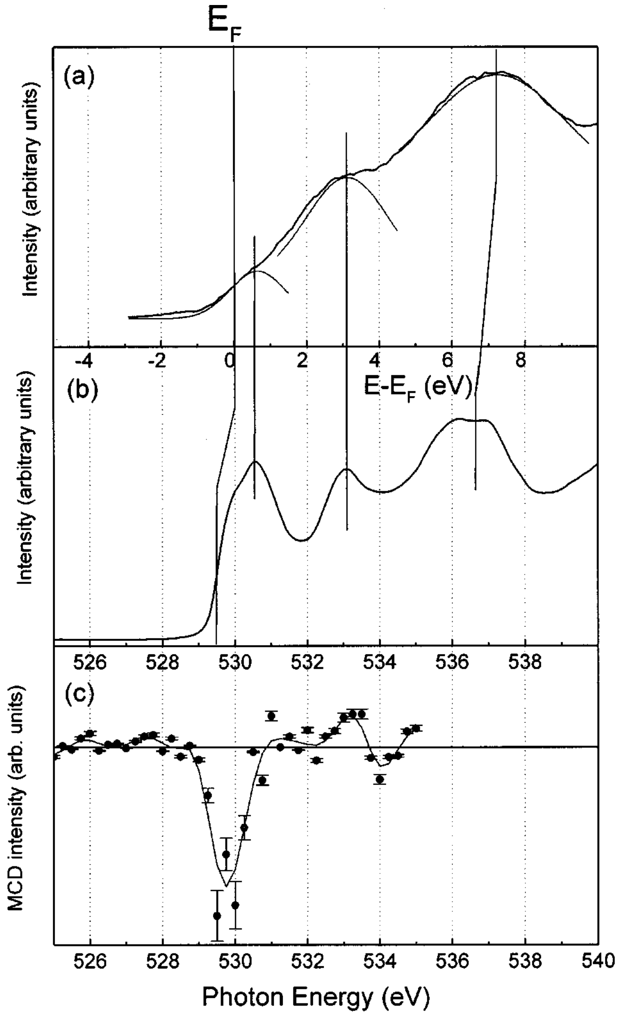

FIG. 3. Normalized inverse photoemission spectrum taken at 300 K (a) oxygen 1*s* XAS (b) and MCD (c) spectra at 90 K. The data in (b) and (c) are normalized with respect to the photon incident angle and the degree of circular polarization.

perature dependence of the MCD anisotropy is presented in Fig. 2(b). The magnetic moment decreases smoothly with increasing temperature without any change in the MCD line shape.

The magnetization of the bulk measured with a superconducting quantum interference device (SQUID) is shown in Fig. 2(a). By comparison, the magnetization dependence obtained by MCD deviates from the bulk, and the Curie temperature determined from the Mn MCD signal is lower than the bulk T_C. This deviation can be attributed to compositional differences at the surface boundary layer.[6]

In Fig. 3(b) we show the temperature dependence of the O 1*s* XAS spectra of $La_{0.65}Pb_{0.35}MnO_3$ single-crystal thin film. The two features in the spectrum represent the hybridization band between O 2*p* and Mn 3*d*/4*s* unoccupied levels. Panel (c) in Fig. 3 shows the MCD signal at 90 K. It is clear that the O atoms become ferromagnetically aligned with a small, but not negligible, magnetic moment. The temperature dependence of the normalized O moment is presented in Fig. 2(c).

The electronic valence band structure of the manganese transition metal oxides, $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Sr, and

Ba), is mostly dominated with the extensively hybridized Mn $3d$–O $2p$states.[7–20] Nonetheless, the inverse photoemission spectra for the conduction band structure are dominated by two clear features, as shown in Fig. 3(a). There are two main features at 3 and 7 eV above the Fermi level and a satellite about 0.7 eV above E_F.The first two features (at 0.7 and 3 eV above the Fermi level) are generally considered to correspond to the nonbonding or antibonding-like states with Mn $3d$– O $2p$ hybridized character.[20] The higher energy feature at 7 eV above the Fermi level corresponds to the La $4f$ states.[20,21] The major intensity from the antibonding-like states of the Mn $3d$–O $2p$ are positioned at approximately 2 eV above the Fermi level for both $La_{0.65}Ca_{0.35}MnO_3$ and $La_{0.65}Ba_{0.35}MnO_3$ while the antibonding-like states of the Mn $3d$–O $2p$ hybridization states for the $La_{0.65}Sr_{0.35}MnO_3$ is at about 4 eV above the Fermi level.[22] The $La_{0.65}Pb_{0.35}MnO_3$ system is very similar in character with $La_{0.65}Ca_{0.35}MnO_3$ and $La_{0.65}Ba_{0.35}MnO_3$ as seen in Fig. 3(a). The feature at 7 eV in the conduction band inverse photoemission spectra, corresponding to the La $4f$ states,[20–22] is clearly observed in the conduction band of $La_{0.65}A_{0.35}MnO_3$ (A=Ca, Ba, and Sr) and is also observed for $La_{0.65}Pb_{0.35}MnO_3$ both in the inverse photoemission and XAS O ($1s$) spectra (Fig. 3).

The unoccupied electronic structure of $La_{0.65}Pb_{0.35}MnO_3$ films dominates the XAS spectra shown in Fig. 3(b). From the comparison of the inverse photoemission with the XAS spectra we can use the above assignments of the unoccupied electronic structure to postulate the origin of the oxygen MCD signal. It is clear that most of the oxygen moment arises in the unoccupied levels associated with the Mn $3d$–O $2p$ hybridization states. There is far less signal associated with the La–O states. This is consistent with the fact that we obtained no MCD signal from the La or Pb cores.

IV. CONCLUSIONS

We have found that one can obtain a large MCD signal in Pb-doped $LaMnO_3$ films. From x-ray MCD we find that most of the magnetic moment resides in the Mn atoms. The oxygen atoms have a small moment that is ferromagnetically aligned with the Mn atoms, and it has its origin in the Mn–O hybridized states, not in the Pb/La–O plane.

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