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Magnetic and Magnetooptical Properties of Polycrystalline Films of $La_{0.7}Sr_{0.3}MnO_3$

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Abstract—Magnetic circular dichroism (MCD) is studied in comparison with the magnetic behavior of polycrystalline films of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) deposited on a single crystal of zirconium oxide stabilized by yttrium (YSZ). It is found that the bands observed in MCD spectra are characterized by different temperature dependences.

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INTRODUCTION

Manganites of the $La_{1-x}A_xMnO_3$ type attract great attention due to their specific magnetic and transport properties, which are of interest from both fundamental and applied viewpoints. Many questions about these materials remain unanswered, since the systems go through a series of phase transitions with various types of magnetic, structural, and electronic ordering when the degree of the bivalent element (A) doping is varied. In the case of thin films, the physical properties of manganites can depend on the nature of the substrate [1]. To obtain the necessary information on the electronic and spin structure of a material along with its magnetic characteristics, attention must be given to magnetooptical effects, of which magnetic circular dichroism (MCD) is the most informative and useful in measuring, since it is observed only on absorption bands. In this work, we study the spectral and temperature dependences of MCD in thin films of $La_{0.7}Sr_{0.3}MnO_3$/YSZ with varying thickness, relative to their magnetic behavior.

Films 20 to 100 nm thick were prepared by magnetron sputtering at a residual chamber pressure of 3×10^{-6} mm Hg prior to film deposition [2, 3]. The substrate temperature during deposition was 750°C. Magnetization (M) was measured on a PPMS-9 unit (Quantum Design) in the temperature range of 5–320 K and magnetic fields of up to 50 kOe, oriented along ($H_\parallel$) and normal ($H_\perp$) to the surface of the film. Absorption spectra were recorded with a Shimadzu UV-3600 instrument at room temperature in the range of 1 to 6 eV. When measuring MCD, the polarization of the light wave is modulated from right circular to left circular. MCD was measured as the difference between signals in two opposite directions of the external magnetic field at temperatures of 90 to 380 K in the energy range of 1–4.5 eV. The field value was 3 or 6 kOe for $H_\parallel$ and $H_\perp$.

The magnetization curves of the samples were symmetrical hysteresis loops with substantially different values of the saturation field (H_s) for two orientations of the external field, indicating predominantly planar magnetic anisotropy in the film. However, the magnetization curve measured in the normal field was different from the classical case of planar anisotropy due to the existence of a hysteresis, albeit with very low coercive force. The magnetization in the saturation field (M_s) was the same for the two directions of the external field. A similar pattern was observed for all the studied samples. At the same time, M_s depended on the film thickness: the greater the thickness, the higher the specific magnetization. This behavior can be explained by the spin disorder at the interfaces, as was suggested in [4, 5].

The typical temperature dependence of film magnetization shown in Fig. 1 generally corresponds to the $M(T)$ curve of bulk samples [6]. From the shape of these curves, we may conclude that the Curie temperature (T_C) for a number of samples varied in the range of ~300 K (T_C for the bulk material, 350–360 K); for others, an overextended tail of magnetization indicates the presence of ferromagnetic regions with different T_C in their volumes.

The absorption spectra measured for all samples at room temperature are similar to one another. A typical curve is characterized by a smooth change in the magnitude absorption upon an increase in the energy of photon with a broad peak in the range of ~ 1.5 eV (Fig. 2, insert). However, the MCD spectral dependences of these samples (except of the thinnest sample) were characterized by the presence of two distinct bands: the band centered at ~1.7 eV is close to the band in the absorption spectrum; the intense MCD

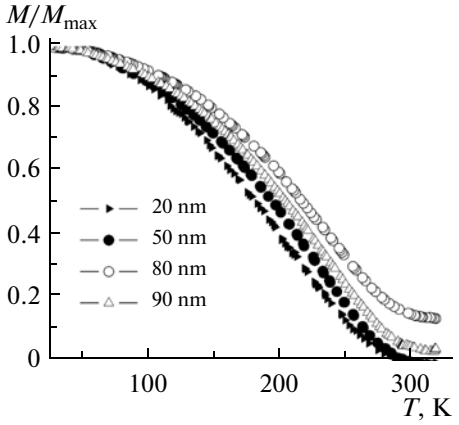

Fig. 1. Temperature dependence of the magnetization of samples with different thicknesses, FC mode at $H_{\parallel}$ = 1 kOe.

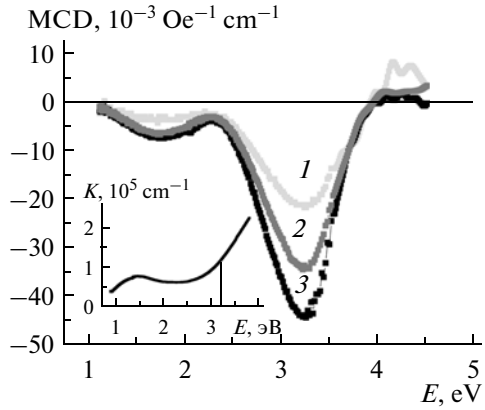

Fig. 2. Spectral dependence of specific MCD for samples with thicknesses of 30, 80, and 100 nm (curves *1–3*, respectively) in field $H_{\perp}$. The insert shows the absorption spectrum of a sample 90 nm thick at room temperature.

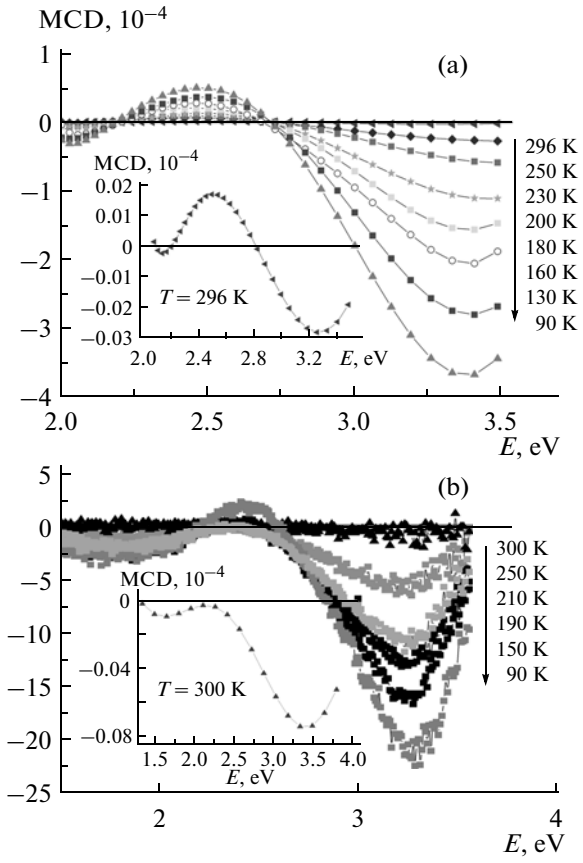

Fig. 3. MCD spectra at different temperatures in field $H_{\parallel}$ = 3 kOe: (a) sample 20 nm thick; (b) sample 90 nm thick. Inserts: MCD spectra of respective samples on the scale at the room temperature.

peak observed at 3.3 eV corresponded to the data of [1]. Like magnetization, the amplitude of the band at 3.3 eV is not proportional to the films thickness. It should be noted that in the MCD spectrum at room temperature for very thin films (20 nm thick), two bands characteristic of all samples are also observed, along with one band of the opposite sign near 2.4 eV (Fig. 3a). This band is most clearly visible in the insert. Interestingly, a relatively weak band of the opposite sign appears near 2.4 eV in the MCD spectral dependence of thicker samples too when the temperature is decreased (Fig. 3b). In order to determine the nature of MCD bands, we fitted the spectra by Gaussian curves whose fitting parameters were the magnitude of the effect (amplitude), the position and the line width. The best agreement between the calculated and experimental spectra was obtained by assuming there were four Gaussian bands with energies of 1.7, 2.4, 3.1, and 3.3 eV. Polynomial regression was used in processing the temperature dependence of these bands' amplitude; this led to the extrapolation of experimental data, i.e., to expanding the temperature interval to 74 K. A typical example is shown in Fig. 4 for a sample thickness of 90 nm. It is clearly seen from these graphs that the temperature variation of the bands amplitude of the same sign at energies of 1.7, 3.1 and 3.3 eV (curves *1*, *2*, and *3*, respectively) is close to the temperature dependence of the sample's magnetization (curve *5*), but the amplitude of the band of opposite sign near 2.4 eV (curve *4*) is fundamentally altered by the different law.

The nature of the bands observed in the $La_{0.7}Sr_{0.3}MnO_3$ magnetooptical spectra has a number of interpretations and still is not clearly defined. A comparison of the band detected in the spectrum of the MCD at 1.7 eV and the data of [7] allows us to relate it to the e_g–e_g transition in the Mn^{3+} ions, since this transition is observed in the structure of $LaMnO_3$, which does not contain Mn^{4+} ions. Based on [8], the band in the range of 3.1 eV must in turn be attributed to the d–d transition of $^4A_{2g}$–$^4T_{1g}$ in Mn^{4+} ions. Note too that more intense band centered at 3.3 eV is

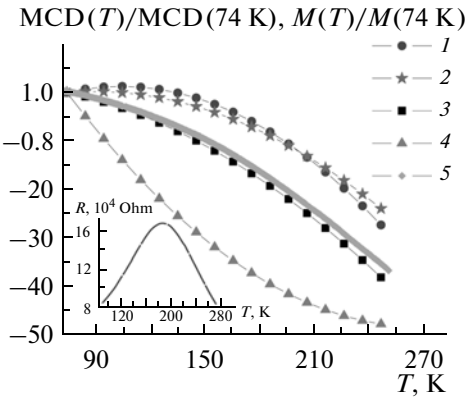

Fig. 4. Temperature dependence of the amplitude of MCD bands (curves *1*–*4*) and magnetization (curve *5*) in field $H_{\parallel} = 3$ kOe for a sample 90 nm thick. The insert shows the temperature dependence of the resistance of the same sample at $H = 5$ kOe.

related to the O2*p*–Mn3*d* transition with charge transfer.

Of particular interest is the band in the region of 2.4 eV, which evidently depends on the film thickness and the shape of its amplitude temperature dependence differs from the magnetization temperature dependence. The difference between the shape of curve *4* and the other shown in Fig. 4 can be attributed to the contribution from conduction electrons, the appearance of which is due to doping. Based on a study of the spectra of optical conductivity, it was shown in [9] that upon increase the concentration of strontium in single crystals of $La_{1-x}Sr_xMnO_3$ to $x = 3$, this contribution becomes dominant. The temperature dependence of the resistance of this sample (see insert in Fig. 4) exhibits in turn that a metal–insulator transition in the film takes place in the region of 190 K. At this temperature, an MCD band of opposite sign appeared for all samples with thicknesses greater than 20 nm. On the other hand, conduction electrons are spin-polarized in the magnetic field of an ion core, as was shown in [10, 11]. In addition, the magnitude of spin polarization is substantially different in the depths and on the surface of the sample. The similarity between curve *4* in Fig. 4 and the form of the temperature dependence of magnetization on an LSMO film's surface (Fig. 4 in [10]) indicates that the band at 2.4 eV could be connected with demonstration of so-called size effects.

CONCLUSIONS

The characteristic shapes of the temperature and field dependences of the films magnetization indicates their magnetic inhomogeneity. The dependence of MCD and specific magnetization on the thickness of our samples is explained by the spin disorder at the film–substrate and film–atmosphere boundaries. The MCD bands of the same sign observed over the range of temperatures below T_C and centered at 1.7, 3.1, and 3.3 eV are comparable to the e_g–e_g transitions in the Mn^{3+} ions, $^4A_{2g}$–$^4T_{1g}$ in the Mn^{4+} ions, and the transition with the charge-transfer O2*p*–Mn3*d*, respectively. For these transitions, the temperature dependence of the band amplitudes corresponds to the temperature dependence of the sample magnetization. It was found that the appearance of the band of opposite sign at 2.4 eV depends on the temperature and thickness of the samples. A distinctive feature of this band is the temperature behavior of its amplitude, which differs from the temperature dependence of film magnetization. This is explained by the contribution from collectivized electrons with different degrees of spin polarization in the depths of the sample and on its surface.

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