Anisotropic magnetoresistive and magnetic properties of La$_{0.5}$Sr$_{0.5}$CoO$_3$–δ film

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The magnetic and transport properties of La$_{0.5}$Sr$_{0.5}$CoO$_3$–δ film grown on a LaAlO$_3$ substrate by pulsed-laser deposition are studied. The properties are found to be influenced by the magnetic anisotropy and inhomogeneity. Magnetoresistance anisotropy is determined by the shape anisotropy of the magnetization and the strain-induced magnetic anisotropy due to the film-substrate lattice interaction. Indications of the temperature-driven spin reorientation transition from an out-of-plane ordered state at low temperatures to an in-plane ordered state at high temperatures as a result of competition between the mentioned sources of magnetic anisotropy are found.

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I. INTRODUCTION

Mixed-valence lanthanum cobaltites of the type La$_{1-x}$Sr$_x$CoO$_3$ have attracted much attention in recent years due to their unique magnetic and transport properties [1,2]. Study of this system is also important for understanding the nature of colossal magnetoresistance in the related oxides, mixed-valence manganites [3,4]. For technical application, the epitaxial films of these compounds are mainly implied to be used. In that case the shape anisotropy (due to the demagnetization effect) and the film-substrate lattice interaction can induce magnetization anisotropy and, therefore, magnetoresistance (MR) anisotropy (bulk samples of these compounds show no marked magnetic or MR anisotropy). This point was studied rather intensively in manganite films (see [5] and references therein). Studies of this type can hardly be found in literature for cobaltites. In addition, the properties of mixed-valence cobaltites are influenced by their unavoidable magnetic inhomogeneity, which is caused by different extrinsic and intrinsic reasons. The extrinsic ones are determined by various technological factors in the sample preparation. They can cause inhomogeneity in chemical composition (for example in oxygen concentration) or in crystal structure (polycrystalline or granular samples). The intrinsic sources of inhomogeneity are believed to arise for thermodynamical reasons and can lead to phase separation into two phases with different concentration of the charge carriers and, therefore, to significant magnetic inhomogeneity [1,2]. In this article we present a study of La$_{0.5}$Sr$_{0.5}$CoO$_3$–δ film which demonstrates a combined influence of the magnetic anisotropy and inhomogeneity on its transport, magnetoresistive and magnetic properties. Indications of the temperature-driven spin reorientation transition from an out-of-plane ordered state at low temperatures to an in-plane ordered state at high temperatures as a result of competition between the mentioned anisotropy sources are found.

II. EXPERIMENTAL

The La$_{0.5}$Sr$_{0.5}$CoO$_3$–δ film (about 220 nm thick) was grown by pulsed-laser deposition (PLD) on a (001) oriented LaAlO$_3$ substrate. The ceramic target used was prepared by a standard solid-state reaction technique. A PLD system with an Nd-YAG laser operating at 1.06 µm was used to ablate the target. The pulse energy was about 0.39 J with a repetition rate of 12 Hz and pulse duration of 10 ns. The film was deposited with a substrate temperature of 880 ± 5°C in oxygen atmosphere at a pressure of about 8 Pa. The film was cooled down to room temperature after deposition at an oxygen pressure about 10$^5$ Pa. The target and film were characterized by X-ray diffraction (XRD) study.

The film resistance, as a function of temperature and magnetic field $H$ (up to 20 kOe), was measured using a standard four-point technique. The field was applied parallel or perpendicular to the film plane. In both cases it was perpendicular to the transport current. The magnetization, $M$, was measured in a Faraday-type magnetometer. A rotating electromagnet makes it possible to measure the magnetization with different directions of $H$ relative to the plane of the film.

III. RESULTS AND DISCUSSION

We have found a strong anisotropy in magnetic and magnetoresistive properties of the film studied. The anisotropy manifests itself as dramatic differences in those properties for magnetic fields applied parallel and perpendicular to the film plane. Consider at first the anisotropy of magnetic properties. Magnetization curves for the fields parallel ($H_\parallel$) and perpendicular ($H_\perp$) to the film plane demonstrate a strong anisotropy (Fig. I). At the maximum field applied (7 kOe), the magnetization...
seems to be rather close to saturation for the in-plane field orientation, but it is far from it for the out-of-plane one. It is reasonable to suppose that this is determined mainly by the shape anisotropy.

Temperature dependences of the film magnetization for the field directions parallel \([M_\parallel]\) and perpendicular \([M_\perp]\) to the film plane are shown in Fig. 2. The Curie temperature, \(T_c\), is found to be about 250 K. The \(M_\parallel(T)\) behaviour is quite common for ferromagnetic (FM) metals: it saturates with temperature decreasing. The behaviour of \(M_\perp(T)\) is quite different from that of \(M_\parallel(T)\). At fairly high field used, 2 kOe, the \(M_\perp(T)\) curve is found to be well below the \(M_\parallel(T)\) curve. Besides, in low temperature range the \(M_\perp(T)\) curve is non-monotonic (Fig. 2).

Figure 2 presents actually the \(M(T)\) behavior only for two values of the angle, \(\theta\), between the field and the film plane: \(\theta = 0^\circ\) and \(\theta = 90^\circ\). It is helpful to consider the whole angle dependences of the magnetization which are presented in Fig. 3(a). Here, the curves \(M_{\text{up}}(\theta)\) and \(M_{\text{down}}(\theta)\) were recorded with step rotating of the field from 0° to 360° and back to 0°, respectively. It can be seen that the magnetization takes maximum values at \(\theta \approx 0^\circ, 180^\circ\) and 360°, that is for the in-plane field orientations. The magnetization magnitude at \(\theta \approx 180^\circ\) is less than these at \(\theta \approx 0^\circ\) and 360°. This is determined by the shape of a magnetization loop and thermomagnetic prehistory of the sample. The minimum magnetization values are found, as expected, at \(\theta \approx 90^\circ\) and 270°, that is for the out-of-plane field orientations.

It is seen a considerable hysteresis effect in the \(M(\theta)\) curves [Fig. 3(a)]. To present the effect more clearly, an angular dependence of the difference between the \(M_{\text{up}}(\theta)\) and \(M_{\text{down}}(\theta)\) is shown in Fig. 3(b). The function \(d(\theta) = M_{\text{up}}(\theta) - M_{\text{down}}(\theta)\) can be taken as some measure of the angular hysteresis effect. It is seen that the \(d(\theta)\) dependence is close to a periodic one with a period equal to 180°. It takes zero value at the angles multiple of 90°, corresponding to both the in-plane and out-of-plane directions of magnetic field [Fig. 3(b)]. The extreme values of \(d(\theta)\) are situated at some intermediate angles, which are, however, more close to the out-of-plane directions than to the in-plane ones.

As indicated above, the magnetization anisotropy in the film studied should be determined mainly by the shape anisotropy. Closer inspection shows, however, that \(M_\perp(T)\) behavior cannot be attributed solely to the shape-anisotropy effect: \(M_\perp(T)\) and \(M_\parallel(T)\) are practically equal in rather broad temperature range just below \(T_c\), then (going to lower temperature) the \(M_\perp(T)\) curve goes rather abruptly well below the \(M_\parallel(T)\) curve and becomes non-monotonic with a pronounced increase in \(M_\perp(T)\) at low temperatures (Fig. 2). These \(M_\perp(T)\) features can be caused by the strain-induced magnetic anisotropy due to lattice mismatch between the film and the substrate. This guess is supported by our XRD study which has revealed that the film has an out-of-plane tensile strain. For materials with the positive magnetostriction this must favor an out-of-plane easy magnetization. An additional corroborations of this suggestion have been
found in the MR properties of the film, described below.

![Graph](image)

FIG. 3: Panel (a) presents dependences of the magnetization on the angle $\theta$ between the magnetic field and the film plane (at $H = 2$ kOe and $T = 77.3$ K). The thermomagnetic pre-history is described in capture for Fig. 2. The curves $M_{\text{up}}(\theta)$ and $M_{\text{down}}(\theta)$ were recorded with step rotating of the field from 0° to 360° and back to 0°, respectively. It can be seen a considerable hysteresis effect. The angular dependence of the difference between the $M_{\text{up}}(\theta)$ and $M_{\text{down}}(\theta)$ in panel (b) enables to present this effect more clearly.

Now turn to transport properties of the film. The temperature dependence of the resistivity, $\rho(T)$, is found to be non-monotonic (Fig. 4) with a maximum at $T \approx 250$ K and a minimum at $T \approx 107$ K. $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta$ samples with fairly perfect crystalline structure and $\delta$ close to zero are known to be metallic ($d\rho/dT > 0$) in the whole range below and above $T_\text{c}$ [2]. The $\rho(T)$ behavior in Fig. 4 reflects inhomogeneous structure of the film and some oxygen deficiency. Due to the last factor, the hole concentration is less than a nominal one (at $\delta = 0$). This is responsible for a resistance peak at $T = 250$ K which is common for low-doped $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with $0.2 \leq x \leq 0.3$ [2]. The low temperature resistance minimum is typical for systems of FM regions (grains or clusters) with rather weak interconnections. For example, it has been frequently seen in polycrystalline manganites [8]. The inhomogeneous structure can be determined by technological factors of sample preparation (causing the polycrystalline structure with rather high tunneling barriers between the grains) or by the phase separation into the hole-rich and hole-poor phase [1, 2]. The conductivity of inhomogeneous systems of this type is determined by the intragrain conductivity and the tunneling of charge carriers through the boundaries between the grains. A competition between these two contributions can lead to a resistance minimum [8]. For an extended discussion of the most obvious reasons for the appearance of the resistance minimum in polycrystalline cobaltites see Ref. [2].

![Graph](image)

FIG. 4: Temperature dependence of the film resistivity.

The MR in the film studied is found to be anisotropic. The absolute values of negative MR in fields parallel to the film plane are considerably above those in perpendicular fields (Fig. 5). The temperature behavior of the ratio between the in-plane and out-of-plane MRs is shown in Fig. 6. It is seen from Figs. 5 and 6 that this MR anisotropy takes place only in FM state and disappears for $T > T_c$. Since the conductivity of mixed-valence cobaltites increases with enhancement of the magnetic (spin) order, this behavior just reflects the point that the magnetization increases more easily in a magnetic field parallel to the film plane, as it has been indeed found in this study (Figs. 1, 2 and 3).

In polycrystalline samples (beside an intrinsic MR, which depends on magnetic order inside the grains) a significant contribution to the MR comes from grain boundaries, and this contribution increases with decreasing temperature. Discussion of the possible mechanisms for this extrinsic type of MR can be found in Refs. [10, 11, 12, 13]. The film studied shows indeed a con-
FIG. 5: Temperature dependence of the magnetoresistance at $H = 20$ kOe for fields parallel ($H_\parallel$) and perpendicular ($H_\perp$) to the film plane. In both cases the fields were perpendicular to the transport current. The solid lines present a B-spline fitting.

continuous increase in MR for decreasing temperature (for the temperatures well below $T_c$) (Fig. 5). This behavior is expected for polycrystalline FM samples with poor enough intergrain conductivity [10, 11]. In contrast, for cobaltite and manganite samples with fairly good crystalline perfection and even for polycrystalline samples of these materials but with a good intergrain connectivity, the MR goes nearly to zero with decreasing temperature [10, 11]. It should be mentioned that grain boundaries in FM oxides are regions of perturbation of structural and magnetic orders, and, therefore, induce a magnetic inhomogeneity as well. These boundaries (and, maybe, other sources of inhomogeneity, i.e., the phase separation) can cause the significant angular hysteresis effect found in this study (Fig. 4) since they hinder the motion of FM domains at a rotation of magnetic field. It is noteworthy, however, that hysteresis effect is minimal at the angles corresponding to both the in-plane and out-of-plane directions of magnetic field. In summary, the behavior of resistivity, MR and magnetization of the film corresponds to that of a system of weakly connected grains.

The data presented in Fig. 5 are pertaining to negative MR for fairly high fields. In general, the MR curves are hysteretic and have specific features in low-field range (Fig. 4). Symmetric hysteresis curves, like that in Fig. 7, were obtained for the film studied after some number of repeated sweeps between the chosen maximum (positive and negative) field magnitudes. For the first sweeps, the hysteresis curves were somewhat asymmetric. Actually, their behavior correlates with that of magnetization loops [13]. In particular, the field $H = H_p$, at which resistance peaks (Fig. 4), corresponds to value of the coercive force ($H_c$). The value of $H = H_p$ decreases with increasing temperature and goes to zero with approaching $T_c$. The magnitude of positive MR in the low-field

FIG. 6: Temperature dependence of the ratio of magnetoresistances for fields parallel ($H_\parallel$) and perpendicular ($H_\perp$) to the film plane. The fields were equal to 20 kOe.

FIG. 7: Magnetoresistive hysteresis at $T = 78$ K for fields parallel to the film plane and perpendicular to the transport current.
H force (R range, ∆ anisotropy. The temperature dependences of direction and reflect in this way the magnetization of the remanent magnetization.

FIG. 8: Temperature dependence of characteristic field, \( H_p \), at which resistance peaks in the magnetoresistive hysteresis curves (Fig. 4) for fields parallel (\( H_\parallel \)) and perpendicular (\( H_\perp \)) to the film plane. The field \( H_p \) corresponds to coercive force (\( H_c \)) in magnetization loops.

range, \( \Delta R(H_p) = |R(H_p) - R(0)|/R(0) \), is some measure of the remanent magnetization.

We found that \( H_p \) and \( \Delta R(H_p) \) depend on the field direction and reflect in this way the magnetization anisotropy. The temperature dependences of \( H_p \) for the in-plane and out-of-plane directions of magnetic field are shown in Fig. 8. It is seen that at \( T \approx 4.2 \) K the value of \( H_p \) in the out-of-plane field is less than that in the in-plane field, but at \( T \approx 78 \) K and higher temperatures the opposite relation is true. For high enough temperature \( (T > T_c) \) the \( H_p \) values go to zero for both field directions. The \( \Delta R(H_p) \) values are found to be higher for the out-of-plane field direction as compared with the in-plane one at \( T \approx 4.2 \) K. At \( T \approx 78 \) K and \( T = 200 \) K, the opposite relation holds true. All this implies that at low temperatures the out-of-plane magnetization is favored, whereas for higher temperatures the in-plane magnetization becomes dominant. The pronounced increase in \( M_\perp(T) \) at low temperatures (Fig. 2) and decrease in the ratio between the in-plane and out-of-plane MRs below \( T \approx 80 \) K (Fig. 4) support additionally this suggestion. All these are indications of the temperature-driven spin reorientation transition which can be determined by competition between the shape anisotropy and the strain-induced anisotropy. This transition has been studied rather intensively (theoretically and experimentally) for films of common FM metals [15, 16], but has never been mentioned for cobaltite films. It should be noted, however, that theoretical models, like [15, 16], are applicable only for ultrathin magnetic films (up to 10 monolayers), whereas the film studied is much thicker and rather disordered. Consequently, a spin-reorientation transition in the film studied can have a different nature than those proposed for ultrathin films.

In conclusion, we have revealed and investigated the magnetic and magnetoresistance anisotropy in \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta \) film. Among other things, we found indications of the temperature-driven spin reorientation transition in the film studied: at low temperature, the magnetization vector is prone to be perpendicular to the film plane, but by increasing the temperature the magnetization vector goes entirely to the in-plane direction.

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