Exchange bias and glassy behaviors at high magnetic field in low doped La$_{1-x}$Sr$_x$CoO$_3$

Kun Xu$^1$, Shujuan Yuan$^{1,2,3}$, Qianying Yu$^1$, Baojuan Kang$^1$ and Jincang Zhang$^1$

$^1$Department of Physics, Shanghai University, No.99 Shangda Road, Shanghai 200444, China

$^2$Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

Abstract. Exchange bias phenomena and the glassy behavior were investigated in low doped La$_{1-x}$Sr$_x$CoO$_3$ cobaltites. Both vertical and horizontal shifts were observed in the hysteresis loops, and the former one vanishes at a critical magnetic field about 40 kOe, the latter one persists to the end. Combining with $R - H$ loop measurement, which shows asymmetric both in resistivity maximum and its corresponding fields, we ascribe the horizontal shifts to the exchange coupling between the surface spin disorder region and ferromagnetic clusters; and the vertical one to the incompletely reversal of ferromagnetic spins. The dc magnetization at low fields and high fields were systematically investigated, and the spin glass region was approved to exist robustly.

1. Introduction
Exchange bias refers to a unidirectional anisotropy in exchange coupled ferromagnetic (FM) and antiferromagnetic (AFM) systems, which is investigated mostly in artificial FM/AFM bilayers.[1] In addition to FM/AFM systems, exchange bias has been observed in other types of interfaces involving a spin glass (SG) such as FM/SG[2], AFM/SG[3] system etc.

Recently, exchange bias phenomena have been observed in spontaneously phase-separated perovskite oxides (manganites, cobaltites). Several fundamental problems of cobaltite are still not unambiguously settled, e.g., glassy behaviors, spin state of Co ions with different doping, and the influence of spin glass on magnetotransport properties. Tang et al.[4] have reported that exchange bias phenomenon exists in La$_{1-x}$Sr$_x$CoO$_3$ (LSCO) systems, which express shifts in both vertical and horizontal axis in hysteresis loops, and they vanish simultaneously at a high magnetic field ($H = 30$ kOe). It is worth to note that, horizontal shift exists when vertical one disappears at high magnetic fields ($H = 50$ kOe) for La$_{0.88}$Sr$_{0.12}$CoO$_3$[5]. The exchange bias at high applied field should not be thought in terms of canonical spin glass, which is expected to be destroyed in relative low fields (10 ~ 30 kOe). Therefore, the intrinsic origin of exchange bias in cobaltites is still mysterious.

In this work, we present a detailed study of the magnetic and magnetotransport properties of low doped LSCO with emphasis on the $x = 0.12$ sample. The vertical and horizontal shifts in hysteresis

$^3$ Corresponding author: shujuanyuan@shu.edu.cn
loop are found to have different origins: the former one arises from the incomplete reversal of FM clusters due to great freezing effect at low temperature; the latter one is produced by the unidirectional pinning effect of glassy surface spin disorders. The existence of non-zero exchange bias field $H_E$ for an applied field as large as 80 kOe indicates that the SG-like state has its degeneracy not completely lifted.

2. Experiments

Polycrystals of La$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.08, 0.12, 0.5$) were fabricated from La$_2$O$_3$ (99.99%), SrCO$_3$ (99%), and Co$_2$O$_3$ (99%) starting materials by standard solid-state reaction method. The powders were thoroughly ground and calcined twice at 800 and 950 °C for 24 h. The reacted powders were then cold pressed into pellets and sintered at 1100 and 1150 °C for 24 h, respectively. X-ray diffraction (XRD) patterns were obtained at room temperature using a diffractometer with a Cu – $K_\alpha$ radiation, by powder diffraction method. The results show that the samples are stable and of high purity without other cobalt oxides. The dc magnetization and resistivity measurements were performed using a physical property measurement system (PPMS) with applied magnetic fields $H$ up to 90 kOe in the temperature range $1.9 \text{ K} \leq T \leq 400 \text{ K}$.

3. Results and discussion

Hysteresis loops at 3 K were measured with different maximum measuring fields (5, 10, 20, 40, 50, 60, 80 kOe) in a constant cooling field at 10 kOe, as shown in figure 1. Exchange bias phenomena at different extents are observed in all of the loops measured. When the measuring fields are low (< 40 kOe), there exist both horizontal and vertical shifts in hysteresis loop. However, once the measuring fields exceed a critical field ($H = 40 \text{ kOe}$), the vertical shift disappears, whereas horizontal one is still present. Tang et al. have done analogues work on La$_{0.82}$Sr$_{0.18}$CoO$_3$. But diverse from their results, the vertical shift disappears at 40 kOe, while the horizontal shift doesn’t degenerate completely even at 80 kOe. It is ascribed to the smaller size of FM clusters in $x = 0.12$ compared to $x = 0.18$ samples, which is preferable to percolate and coalesce for FM clusters. Smaller FM clusters have larger local anisotropy and are comparatively harder to rotate thoroughly.

Figure 2 shows temperature dependence of dc magnetization with zero-field-cooling (ZFC) and field-cooling (FC) processes for La$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.08, 0.12, 0.5$) samples respectively. The curves in left panel were measured in 20 Oe, while the curves in right panel were measured in 50 kOe.
2(a), 2(b) and 2(c) were measured at a lower magnetic field (20 Oe). The FC curve of \( x = 0.5 \) shows a “Brillouin-like” temperature dependence of the magnetization. The FC and ZFC curves bifurcate and a peak is observed in ZFC curve at irreversible temperature \( (T_{irr}=250 \text{ K}) \). In contrast with \( x = 0.5 \), a sharp cusp in ZFC curve is observed at a temperature significantly below \( T_{irr} \), which is denoted as freezing temperature \( (T_f) \) of SG. The \( T_f \) of \( x = 0.08 \) and 0.12 are 32 K and 63 K, respectively.

\[ \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \] was reported to have cluster-glass properties. However, the cluster glass are destroyed by high magnetic fields as shown in figure 2 (f). The ZFC and FC curves overlap each other, and bifurcation phenomenon is no longer detectable. In contrast, in low doped LSCO, the magnetization of ZFC and FC curves don’t coincide at low temperature, which manifests the surface spin disorder robustly exists even in such a high Zeeman energy. We ascribe this to the “finite size effect” of FM clusters, and the FM clusters can’t coalesce with each other. A transition area (surface spin disorder) is supposed to exist between FM particles and their non-FM matrix LaCoO\(_3\) even though intense magnetic fields are applied. It is reasonable to elucidate that this kind of surface spin disorder is more prominent in smaller FM particle systems.

![Figure 3](image_url)  
**Figure 3.** Measuring field dependence of \( H_E, H_C, M_E, \) and \( M_S \) obtained from figure 1.

![Figure 4](image_url)  
**Figure 4.** \( H \) dependence of \( MR \) for \( \text{La}_{0.88}\text{Sr}_{0.12}\text{CoO}_3 \) at 3 K after field cooling in 10 kOe. In (a), the \( MR \) (\( H \)) loop is measured between \( \pm 30 \) kOe. The \( MR \) (\( H \)) loops in (b) and (c) are measured between \( \pm 50 \) kOe. And loop in (b) is measured for the first time and the one in (c) is the consecutive 8\(^{th} \) loop.

The measuring field dependence of the exchange bias properties is shown in figure 3. Here, the parameters \((H_E, H_C, M_E, \) and \( M_S)\) were deduced from figure 1. \( M_E \) and \( H_E \) is defined as the shift of gravity center of hysteresis loop along the magnetization and field axis. In figure 3, \( M_S \) increases monotonously with increasing measuring fields, which is an evidence of the growth of FM clusters. Non-zero vertical shift \( M_E \) reflects that a part of frozen FM spin aligned in FC direction will not reverse in the field cycling. \( M_E \) decreases monotonously, and approaches to zero when the field reaches to 40 kOe, which means the Zeeman energy overcomes the anisotropy of frozen FM clusters. Therefore, the increase of magnetization can be divided into two regions: below 40 kOe, the growth of FM clusters and the enhancement of alignment degree of FM spins to fields direction dominate; and above 40 kOe, only the growth of FM clusters contributes to the enhancement of magnetization. It can also be seen that \( H_E \) increases first then decreases with increasing measuring fields. The increase of \( H_E \) can be attributed to enlargement of measuring fields, which win over the decrease caused by the growth of FM clusters. The decrease of \( H_E \) is caused by the increasing of FM clusters’ size, thus, the pinning strength exerted on FM clusters weakened. The coercivity \( H_C \) is supposed to decrease due to
the growth of FM clusters’ size, and the increase of interaction between them. The enhancement of $H_C$ can be ascribed to the increase of measuring field and the properties of exchange bias.

The $R - H$ loop exhibits a large negative magnetoresistance, and it’s likely due to spin dependent effects in hopping regime, maybe undergoes a similar process with FM/insulator/FM tunnel magnetoresistance effect[7]. The small FM metal clusters are imbedded in insulated LaCoO$_3$ matrix. The electron transportation depends on the spin-alignment from one FM metal cluster to another through glassy boundary and matrix. Additionally, when magnetic fields are applied, the transportation paths for electron are shortened, and the resistivity decreases. Due to the asymmetry of increasing and decreasing branches of $R - H$ loop, the resistivity in zero fields is hard to define. So we define the magnetoresistance (MR) as $MR = (R (H) – R (50 \text{ kOe}))/ R (50 \text{ kOe})$. The $R - H$ was first measured between ±30 kOe, as shown in figure 4 (a). The current, applied fields and cooling field are parallel to each other. The loops are of hysteresis behavior expressively, furthermore, the ascending and descending branches of the loop are asymmetric, and the maximum resistivity and its corresponding field are unequal. It’s worth to note that the resistivity at ±30 kOe is smaller than that at -30 kOe, reflecting the ferromagnetic clusters don’t reverse entirely. As expected, the asymmetry near coercivity region is still observed as the fields increase to 50 kOe, as shown in figure 4 (b) and (c). The $R - H$ loops are measured consecutively, the first and the eighth loop are present in figure. 4 (b) and (c). In figure 4(b), the resistivity at ±50 kOe are equal, manifesting the thorough rotation of FM clusters, however, the peaks and their positions are withal asymmetry. The asymmetry of resistivity maximum of ascending and descending branches can be explained as follows: firstly, after field cooling, some spins of SG region are preferable aligned along cooling field, and the spin of FM and frozen SG spins are parallel and anti-parallel with each other before reversal, which would cause the asymmetry of $R_{\text{max}}$ in $R - H$ loops. Secondly, the reversal of ascending and descending branches might have different mechanism: one is partially induced by domain nucleation and wall propagation and the other is entirely realized by coherent rotation.[8] The asymmetry in resistivity maximum remarkably weakens when several reversals are implemented.

4. Conclusion
In summary, exchange bias phenomena were investigated in low doped La$_{1-x}$Sr$_x$CoO$_3$ cobaltites. The hysteresis loops and $R - H$ loops both show vertical and horizontal shifts, the former one vanishes at a critical magnetic field about 40 kOe, and the latter one persists to the end. We ascribe the horizontal shifts to the exchange coupling between the glassy surface spin disorder region and ferromagnetic clusters; and the vertical shifts to the incompletely reversal of ferromagnetic spins.

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