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Exchange bias with Fe substitution in $LaMnO_3$

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Abstract. We observe the negative shift of the magnetic hysteresis loop at 5 K, while the sample is cooled in external magnetic field in case of 30% of Fe substitution in $LaMnO_3$. The negative shift and training effect of the hysteresis loops indicate the phenomenon of exchange bias. The cooling field dependence of the negative shift increases with the cooling field below 7.0 kOe and then, decreases with further increase of cooling field. The temperature dependence of the negative shift of the hysteresis loops exhibits that the negative shift decreases sharply with increasing temperature and vanishes above 20 K. Temperature dependence of dc magnetization and ac susceptibility measurements show a sharp peak (T_p) at 51 K and a shoulder (T_f) around 20 K. The relaxation of magnetization shows the ferromagnetic and glassy magnetic components in the relaxation process, which is in consistent with the cluster-glass compound.

PACS. 75.47.Lx Manganites – 75.50.Lk Spin glasses and other random magnets – 75.30.Gw Magnetic anisotropy

Introduction

Recently, the observation of exchange bias (EB) in the phase separated (PS) charge ordered (CO) manganites opens up a new prospective of technological applications in addition to the colossal magnetoresistance (CMR) properties [1,2]. Exchange bias is a phenomenon, which is ascribed to the induced exchange anisotropy at the interface between ferromagnetic (FM) and antiferromagnetic (AFM) phases in a heterogeneous system [3,4]. The induced exchange anisotropy is unidirectional in character and increases the effective anisotropy of the heterogeneous system, which has the technological applications for storage and spin-electron devices. The evidence of EB was first discovered by Meiklejohn and Bean in 1956 for FM Co core and AFM CoO shell structure [5], which has also been observed at the FM/spin-glass (SG) interface [6–11].

In addition to the technological importance, the evidence of EB further provides the microscopic views of the inhomogeneous phase separation in manganites. The first evidence of EB was observed in CO manganite $Pr_{1/3}Ca_{2/3}MnO_3$, where ferromagnetic (FM) droplets are naturally embedded in the AFM background [1]. The EB have recently been reported for another CO manganite, where the strong cooling field dependence of EB is ascribed to the thickness of the FM layer in a spontaneous lamellar ferromagnetic/antiferromagnetic phase separated $Y_{0.2}Ca_{0.8}MnO_3$ [2]. In this article, we also report the EB in case of 30% of Fe substitution in $LaMnO_3$, where the compound is recognised as a cluster-glass compound [12,13].

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Experimental procedure

The polycrystalline sample of $LaMn_{0.7}Fe_{0.3}O_3$ was prepared by a chemical route [13]. The single rhombohedral phase ($R\bar{3}c$) of the compound was characterized by powder X-ray diffraction pattern. The average size of the particle was observed using Transmission Electron Microscope. The average sizes are 70 and 320 nm, while the as-synthesized sample was heated at 800° and 1200 °C, respectively. The ac and dc magnetizations were measured by a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS, XL). In case of zero-field cooled measurements the sample was cooled down to the desired temperature from well above the transition temperature in zero magnetic field and measurements were performed in the heating cycle with magnetic field, while for field-cooled case the sample was cooled in presence of magnetic field and measured during heating the sample like zero-field cooled case.

Experimental results and discussions

The temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) magnetizations are shown in the top panel of Figure 1, where the ZFC magnetization exhibits a sharp peak (T_p) at 51 K for the measurement in

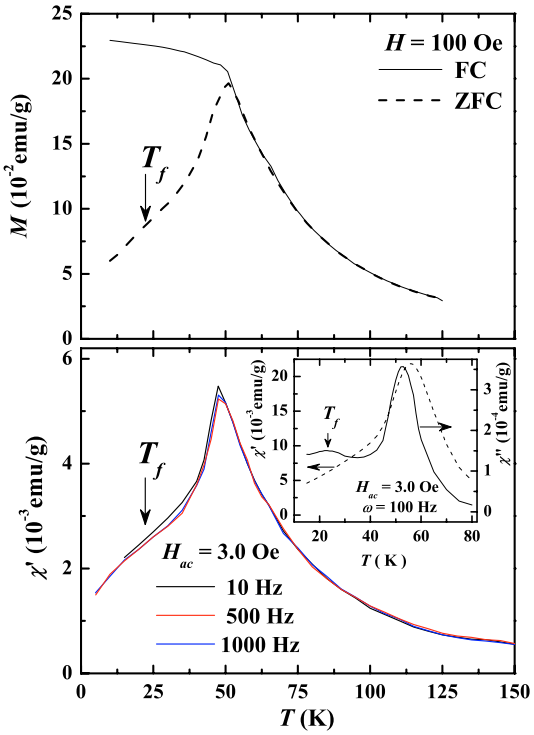

Fig. 1. (Colour online) Temperature dependence of ZFC-FC magnetization (top panel) and χ' with temperature at different frequencies for the sample with average diameter 70 nm (bottom panel). The inset of the bottom panel exhibits the temperature dependence of and χ' and χ'' for the sample with average diameter 320 nm, where spin freezing temperature is indicated by the broad maximum in χ'' at T_f.

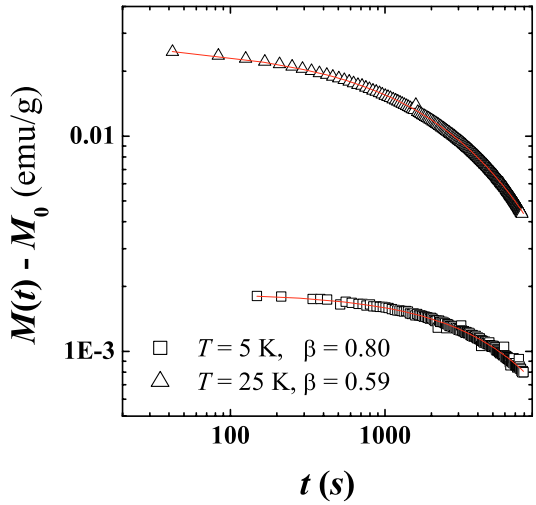

Fig. 2. (Colour online) Relaxation of remanent magnetization with t at 5 K and 25 K .The solid lines exhibit the fit of the experimental data using stretched exponential.

100 Oe [13,12]. In consistent with the dc results, the real part (χ') of ac susceptibility (χ_{ac}) also shows a peak as seen in the bottom panel of Figure 1, where a small frequency dependence of χ' is noticed in between ∼50 and ∼15 K. In addition, a shoulder (T_f) in the low temperature region is observed around 20 K for dc and ac measurements, which is shown by the arrows in Figure 1. The similar characteristic features in the χ' was also reported by Liu et al. [12], where temperature dependence of χ'' was additionally demonstrated with a sharp peak at 52 K and a broad maximum around ∼18 K. The broad maximum was characterized as spin freezing temperature. In the present observation, we could not detect the systematic values of χ'' because of the limitation of the instrumental resolution. Note that the magnitude of dc and ac measurements in the present observation is less than that of results reported by Liu et al., which is ascribed to the effect of particle size dependence. We also observe that the magnitude is increased considerably by the increase of particle size as seen in the inset of the bottom panel of Figure 1, where the magnitude of both χ' and χ'' is increased and signature of spin freezing temperature at T_f is clearly observed by the broad maximum in χ'' for the sample with 320 nm.

In order to understand the origin of weak frequency dependence of χ', we measured dc magnetization with time (t). The sample was cooled down to 5 K and 25 K from 150 K ($\gg T_p$) with 100 Oe and then, remanent magnetization was recorded with t as seen in Figure 2. We considered the stretched exponential, $M(t) = M_0 - M_g \exp(-t/\tau)^\beta$ to fit the relaxation of remanent magnetization, where M_0 and M_g are involved with the FM and glassy components, respectively. For typical SG compounds, the second term in the above expression is sufficient to fit the relaxation, where the values of β are in the range of $0 < \beta < 1$. The term M_0 is required to fit the relaxation of reentrant SG compounds [14]. Here, M_0 was also required to fit the relaxation, while the values of β are 0.80 and 0.59 for 5 and 25 K, respectively. The values of β and non-zero values of M_0 clearly indicate the signature of coexistence of FM and glassy magnetic components in the relaxation process in consistent with the cluster-glass system.

We observe the negative shift of the magnetic hysteresis loop, while the sample was cooled down to 5 K from 150 K ($\gg T_p$) under FC condition with 7.0 kOe and then, the hysteresis was measured in between ±20.0 kOe at 5 K after stabilizing the temperature. The shift is absent while cooling under ZFC condition as seen by the continuous curve in Figure 3. The negative shift of the hysteresis loop in association with the increase of coercivity of the hysteresis loop are in accordance with the features of the exchange bias. The exchange bias field (H_E), coercive field (H_C), EB magnetization (M_E), and remanent magnetization (M_R) are measured to be 332.0 Oe, 2.6 kOe, 0.0160 emu/g, and 3.79 emu/g, respectively from the gravity center of the shifted loop along field and magnetization axes as described in Figure 3. We found that the values of H_E and M_E are increased to H_E = 800 Oe

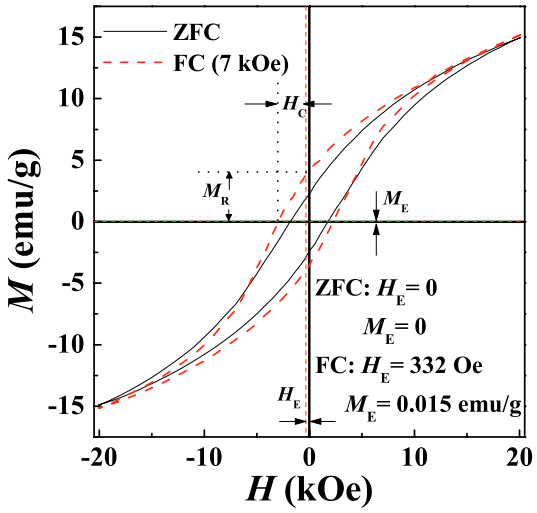

Fig. 3. (Colour online) Magnetic hysteresis loops measured at 5 K after field cooling with 7.0 kOe and zero field cooling. The details of the estimate of H_E, M_E, H_C, and M_R are shown in the figure.

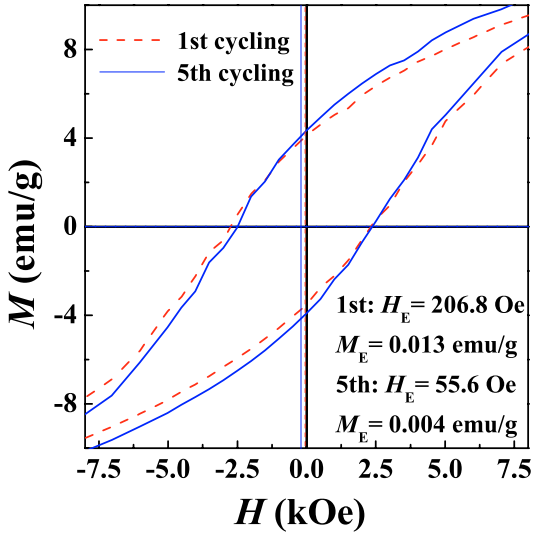

Fig. 4. (Colour online) Magnetic hysteresis loops after first and fifth field-cooled cycling with 10.0 kOe. The values of H_E and M_E after first and fifth cycling are given in the figure.

and M_E = 0.22 emu/g for the measurement of hysteresis loop between ±10.0 kOe. The values of H_E and M_E are small, which are still comparable to the reported values for different systems [2,6,8,9,11]. Recently, the EB is reported for few cluster-glass compounds with perovskite structure, where short range FM and SG states coexist. In case of $La_{0.82}Sr_{0.18}CoO_3$, the EB was reported with maximum values of H_E ≈125 Oe and M_E ≈ 1.2 emu/g at 5 K, while the sample was cooled in 1.0 kOe field and hysteresis loop was measured in between ±10.0 kOe [8]. The maximum values of H_E ≈ 500 Oe and M_E ≈ 0 at 5 K were reported for $La_{0.88}Sr_{0.12}CoO_3$, while the sample was cooled in 10.0 kOe field and hysteresis loop was measured in between ±50.0 kOe [9]. The EB is also reported for another cluster-glass compound $La_{0.80}Ba_{0.20}CoO_3$ with H_E ≈ 500 Oe and M_E ≈ 6.8 emu/g at 5 K, while the sample was cooled in 3.0 kOe field and hysteresis loop was measured in between ±3.0 kOe. The EB was not observed while the hysteresis loop was measured in between ±10.0 kOe, indicating the minor effect of EB [10]. In order to understand the origin of the negative shift of the hysteresis loops, we further study the training effect, which describes the decrease of H_E while hysteresis loops are measured after several times of thermal cycling [3,4]. Here, the sample was cooled down to 5 K in 10.0 kOe and hysteresis loops are measured in between ±20.0 kOe. The hysteresis loops after first and fifth cycling are shown in Figure 4, where the decrease of the negative shift after five successive thermal cycling is noticed as seen in the figure. The values of H_E are 207 and 56 Oe, while for M_E the values are 0.013 and 0.004 emu/g for first and fifth cycling, respectively. The negative shift of the hysteresis loop in the positive cooling field and training effect of the shift of the hysteresis loops indicate the phenomenon of exchange bias in the cluster-glass compound $LaMn_{0.7}Fe_{0.3}O_3$.

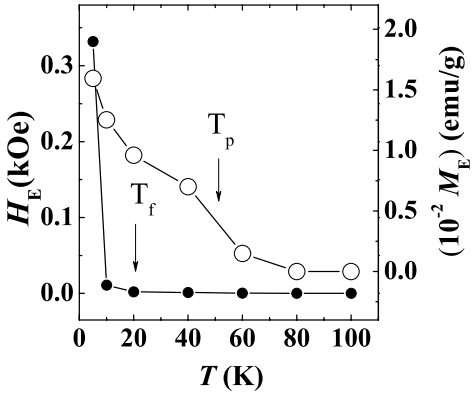

Fig. 5. Temperature dependence of H_E and M_E. The arrows indicate T_p and T_f.

The temperature dependence of EB was studied, while the sample was cooled down to the desired temperatures from 150 K in 7.0 kOe field and the hysteresis loops were measured in between ±20.0 kOe. The values of H_E and M_E as a function of temperature are shown in Figure 5. The values of M_E decrease with increasing temperature, while the sharp decreasing trend is noticed below ∼50 K, which is close to T_p. On the other hand, H_E decreases sharply with increasing temperature and vanishes above 20 K, where a shoulder (T_f) in the dc and ac magnetization is observed. In case of cluster-glass system exhibiting EB, similar temperature dependence of H_E is typical, where the SG phase induces the *frozen* FM spins at the FM/SG interface resulting non-zero values of H_E below spin freezing temperature [7,8,11]. The SG phase can not induce the *frozen* FM spins above spin freezing temperature, resulting $H_E = 0$.

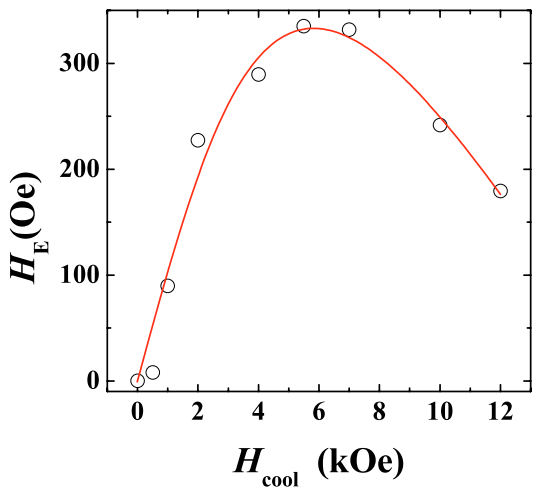

Fig. 6. (Colour online) The plot of H_E as a function of H_{cool}. The continuous curve indicates the fit using equation described in the text.

The EB was further studied at the different cooling field (H_{cool}), while the sample was cooled down to 5 K from 150 K in different H_{cool} and hysteresis was measured in between ±20.0 kOe. The plot of H_E as a function of H_{cool} is shown in Figure 6, which increases with H_{cool} and then, decreases above ∼7.0 kOe with the further increase of H_{cool}. Similar dependence of H_E has been reported for different cases such as, $La_{1-x}Sr_xCoO_3$ [8,9] and Fe nanoparticles in the iron oxide matrix [11], where the following qualitative explanation have been proposed. In case of low cooling field, H_{cool} is not strong enough to magnetize all the spins of the FM clusters toward saturation. Therefore, the degree of alignment of the moment of the FM clusters is enhanced along a preferential direction with the increase of the H_{cool}, which in fact reduces the effect of averaging of the anisotropy due to randomness. Accordingly, the *frozen* FM spins at the FM/SG interface also align along the direction of H_{cool}, resulting the increase of H_E with H_{cool}. When the cooling field is high enough, the FM moments tend toward saturation and the *frozen* FM spins vary a little along the field with the increase of the H_{cool}. Thus, the increase of H_{cool} does not take part in the increase of H_E. In addition, the magnetic coupling (Zeeman coupling) between the field and the glassy magnetic moments increases as well, tending to orient them along the field direction, where magnetic coupling dominates over exchange coupling, resulting the decrease of H_E with the further increase of H_{cool}. Recently, the alternative interpretation of the H_{cool} dependence of H_E was proposed by Niebieskikwiat and Salamon in terms of the simple exchange interaction model for $Pr_{1/3}Ca_{2/3}MnO_3$, where small FM clusters are assumed to be embedded in a SG-like or AFM host material [1]. Despite the small values EB field is observed in the present observation compared to the EB in $Pr_{1/3}Ca_{2/3}MnO_3$, a trial is made to fit the H_{cool} dependence of H_E with the model proposed by Niebieskikwiat and Salamon using the following expression as [1], $H_E \propto J_i[\frac{J_i\mu_0}{(g\mu_B)^2}L(\frac{\mu H_{cool}}{k_BT_f}) + H_{cool}]$ with approximation for $\mu H_E < k_BT_f$, where J_i is the interface exchange constant. We assume the magnetic moment of FM cluster, $\mu = N_v\mu_0$ with $\mu_0 \approx 3\mu_B$ for FM Mn core spin, where N_v is number of spins per FM cluster. The first term in the expression dominates for small H_{cool} ($\propto J_i^2$), while for large H_{cool} the second term ($\propto J_i$) dominates. The solid line in Figure 6 exhibits the satisfactory fit of the experimental data using the above expression with J_i and μ as adjustable parameters. The values of J_i and μ are ≈ -0.143 meV and $141\mu_B$, respectively. Using the values of μ, N_v is ≈47 and the number density of FM clusters (n) can be estimated from the saturation magnetization as $M_s = n\mu$, which gives $n \approx 11.25 \times 10^{-5}$ Å^{-3}. The value of n further gives us the rough estimate of the size of FM cluster ≈25 Å. The value of magnetic anisotropy constant K is estimated $\sim 0.3 \times 10^7$ erg/cm^3 at 5 K from the following expression as $M_E/M_S \sim -2\nu_0\tau \exp(-KV/k_BT)$ $\sinh(\mu H_E/k_BT)$, where V is the volume of the FM cluster [1]. The values of typical measurement time (τ) and the switching frequency of magnetization (ν_0) are typically taken 10^3 s and 10^9 s^{-1}, respectively. Note that the value of K is two order higher than bulk FM manganites [15,16].

Recently, the features of cluster-glass state has been reported for $LaMn_{0.7}Fe_{0.3}O_3$ by Liu et al. based on the ac susceptibility and EPR results, where FM clusters coexist with the glassy magnetic phase [12]. In the present observation, the relaxation of magnetization also indicates the coexistence of FM and glassy magnetic components in the relaxation process in consistent with the cluster-glass state. Here, the negative shift of the hysteresis, training effect, and systematic shift of the hysteresis loops with cooling field and temperature are in good accordance with the phenomenon of exchange bias. Note that the exchange bias involved with the glassy magnetic behaviour has been reported in those systems, where FM clusters or FM nanoparticles or FM layers coexist with the SG or glassy magnetic phase [8–11]. In case of intrinsically phase separated cluster-glass compounds $La_{1-x}(Sr,Ba)_xCoO_3$, exchange bias phenomenon was described by induced *frozen* FM spins at the FM/SG interface. In the present observation, the experimental results may also provide an indication of exchange bias at the FM/glassy magnetic interface in the cluster-glass compound $LaMn_{0.7}Fe_{0.3}O_3$. The adequate experimental results and theories are required more to understand the origin of exchange bias in the intrinsically phase separated cluster-glass compounds.

Conclusion

In conclusion, we observe the coexistence of FM and glassy magnetic components in the relaxation of magnetization in consistent with the cluster-glass state. The negative shift of the hysteresis loops, training effect, and cooling field and temperature dependence of shift of the hysteresis loops indicate the phenomenon of exchange bias in $LaMn_{0.7}Fe_{0.3}O_3$, which is in accordance with the signature of exchange bias in the cluster-glass compounds $La_{1-x}(Sr,Ba)_xCoO_3$ with perovskite structure.

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