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Intrinsic exchange bias effect in phase-separated $La_{0.82}Sr_{0.18}CoO_3$ single crystal

Wan-Guo Huang, Xiang-Qun Zhang, Hai-Feng Du, Ren-Fu Yang, Yan-Kun Tang, Young Sun and Zhao-Hua Cheng[1]

State Key Laboratory of Magnetism and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

E-mail: zhcheng@aphy.iphy.ac.cn

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Abstract

We report a study of the exchange bias of a high quality perovskite cobaltite $La_{0.82}Sr_{0.18}CoO_3$ single crystal with spin glass (SG) like nature. According to the dependence of exchange bias field on the cooling field, an antiferromagnetic (AFM) interfacial exchange coupling constant at the spin-glass region $J_i \approx -0.68$ meV was found. The size of the FM regions $t_{FM} \approx 9$ nm was estimated in the spin-glass system from the inverse proportion of exchange bias field H_{EB} to the size of the FM regions.

(Some figures in this article are in colour only in the electronic version)

Since its discovery fifty years ago [1], the exchange bias phenomenon has been found in different types of systems: nanoparticles where the cores couple to the shells [1–3], thin films consisting of FM/AFM systems [4, 5], as well as inhomogeneous spin glasses [6]. Nowadays materials with large exchange bias field H_{EB} have attracted much attention because of their potential application in spin valves and magnetic recording and reading heads [7–9]. In addition to the FM/AFM heterostructure, the exchange bias effect has also been observed in single phase perovskite manganites and cobaltites with intrinsic phase separation [10–12]. Intrinsic magnetic phase separation plays a crucial role in unusual magnetoelectronic properties. The investigation of the exchange bias effect in perovskite manganites and cobaltites with intrinsic phase separation can yield information regarding the exchange anisotropy coupling between FM and AFM clusters, and consequently can help us to understand the colossal magnetoresistive effect. The doped perovskite cobaltites $La_{1-x}Sr_xCoO_3$, which are an appropriate system to investigate magnetic phase separation, possess a quite different magnetic phase diagram from that of the doped perovskite manganites $La_{1-x}Sr_xMnO_3$ [13, 14]. Recent experiments including electron microscopy [15, 16], nuclear magnetic resonance [17, 18], and small-angle neutron scattering [19] have revealed that the hole-doped cobaltites $La_{1-x}Sr_xCoO_3$ exhibit a particularly clear form of phase separation with FM, spin-glass (SG), and paramagnetic(PM) regions coexisting for a broad range of doping level x. In our previous work, the exchange bias effect associated with phase separation was observed in the perovskite cobaltites $La_{1-x}Sr_xCoO_3$ polycrystalline materials, where there are no AFM clusters coexisting with FM clusters [11]. The unique spin-glass region in the perovskite cobaltites $La_{1-x}Sr_xCoO_3$ opens an opportunity to investigate the interfacial exchange coupling in the spin-glass region. So far, the research in the exchange bias effect in bulk perovskite oxides is mainly focused on polycrystalline materials [10–12]. Since the magnitude of H_{EB} results from both intrinsic factors, e.g. spin orientation or anisotropy, and extrinsic factors, e.g. roughness or crystallinity, high quality single crystals with uniform chemical composition, which can eliminate the effect of grain sizes, grain boundaries and crystallographic orientation, can reveal the intrinsic exchange bias effect in the bulk perovskite oxides. In this paper, the exchange bias effect in a high quality $La_{0.82}Sr_{0.18}CoO_3$ single crystal was systematically investigated by changing the cooling field and measuring field and the interfacial exchange coupling was obtained.

[1] Author to whom any correspondence should be addressed.

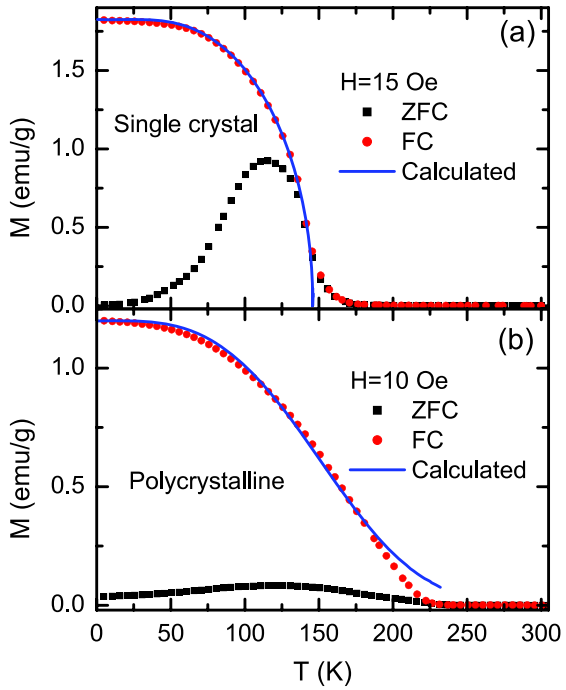

Figure 1. Temperature dependence of DC magnetization with ZFC and FC processes for the $La_{0.82}Sr_{0.18}CoO_3$ single crystal (a) and polycrystalline (b) in measuring fields of 15 Oe and 10 Oe, respectively.

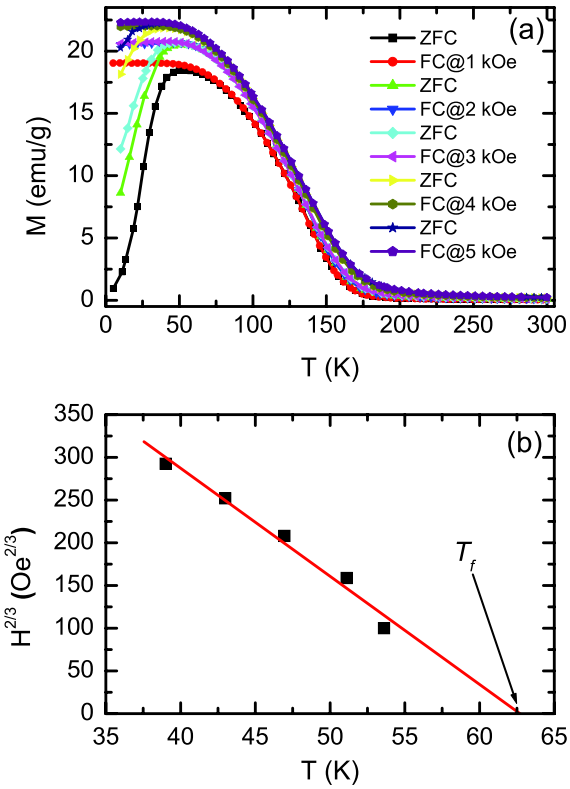

Figure 2. Temperature dependence of DC magnetization with ZFC and FC processes for the $La_{0.82}Sr_{0.18}CoO_3$ single crystal in different measuring fields (a), and field dependence of the spin-glass transition temperature showing the AT line (b).

A floating-zone technique was employed to grow the single crystal of $La_{0.82}Sr_{0.18}CoO_3$. Polycrystalline samples with nominal composition $La_{0.82}Sr_{0.18}CoO_3$ were prepared by the conventional solid-state reaction method [11]. The as-grown single phase powders were then hydrostatically pressed into feed and seed rods with a diameter of 6 mm and a length of about 90 mm. The rods were sintered at 1450 °C for 48 h. In an optical floating-zone furnace equipped with four halogen lamps, a single crystal was grown under 6 atm oxygen pressure at a growth rate of 3 mm h^{-1}. The composition of the single crystal was determined by inductively coupled plasma atomic emission spectroscopy. A back-reflection Laue x-ray diffraction experiment was carried out to determine the crystallographic directions. A rectangular piece of crystal was cut and measured using a commercial Superconducting Quantum Interference Device (SQUID) magnetometer in magnetic fields up to 50 kOe over the temperature range from 5 to 300 K. To restore the sample to the same demagnetized initial state, the sample was warmed up to 300 K after each measurement of the hysteresis loop.

In order to explore the glassy magnetic behavior of the $La_{0.82}Sr_{0.18}CoO_3$ single crystal, the temperature dependence of zero field cooled (ZFC) and field cooled (FC) magnetization with an external field of 15 Oe was recorded and is shown in figure 1(a). For comparison, the ZFC and FC thermomagnetization curves for corresponding polycrystalline materials is also illustrated in figure 1(b). The field cooling magnetization increases rapidly to form a plateau with lowering temperature, which suggests FM correlation of the spins. It can be observed that the FC curve of the single crystal shows a 'Brillouin-like' temperature dependence of the magnetization. The exchange coupling constant $J_{FM} = 2.39$ meV can be obtained by fitting the FC magnetization versus temperature (M–T) curve for single crystal with Brillouin function. In contrast to the single crystal sample, the FC curve of the polycrystalline sample no longer shows a simple 'Brillouin-like' FM behavior, implying a more inhomogeneous exchange interaction of Co ions in ferromagnetic clusters than that in the single crystal. The FC M–T curve for the polycrystalline sample can be fitted by an exchange coupling constant with a broad distribution. Above T_C, the M–T curve for the single crystal can be fitted exactly with the Curie–Weiss law $\chi = \frac{N\mu_0\mu_{eff}^2}{3k_B(T-\theta)}$, where $\mu_{eff} = 0.59\mu_B$, which is far smaller than the average magnetic moment of Co^{3+} and Co^{4+} ions ($2.19\mu_B$) and $\theta \approx -161$ K, indicating the existence of AFM interaction in this compound. The competition of the FM and AFM interactions results in an obvious bifurcation between the ZFC and FC curves, implying the spin-glass-like magnetic behavior in the single crystal.

In order to further characterize the spin-glass-like behavior in the single crystal, the temperature dependence of DC magnetization with ZFC and FC processes for the $La_{0.82}Sr_{0.18}CoO_3$ single crystal were measured under different applied fields and illustrated in figure 2(a). From figure 2(a), one can see that the peak of the ZFC curve significantly broadens and the freezing temperature T_f shifts towards lower temperatures with increasing applied field. As is illustrated

in figure 2(b), the spin-glass magnetic nature is proved in the $La_{0.82}Sr_{0.18}CoO_3$ single crystal by the field dependence of T_f following the de Almeida–Thouless (AT) line, $\delta T_f \propto H^{2/3}$. The extrapolation of the AT line back to $H = 0$ gives the spin-glass transition temperature, $T_f = 62.7$ K. Compared with that of the polycrystalline samples [11], both the more obvious peak in the ZFC curve and the sharper FM-PM transition in the FC curve indicate the uniformity of the composition and the crystal grains in the single crystal, and that the SG behavior is due to the intrinsic phase separation in this compound.

In the FM/AFM system, the exchange bias effect results from a unidirectional anisotropy of exchange interaction between FM materials and AFM materials at their interface. In the case of $La_{0.82}Sr_{0.18}CoO_3$, the SG regions have an exchange coupling with FM clusters as the AFM layers do with FM layers in multilayers [11]. Competing exchange interactions in the spin-glass system determine the spin configuration in the frozen state. In order to investigate the effect of exchange coupling at the interface of FM clusters and the spin-glass region, the FC magnetic hysteresis loops below the freezing temperature were measured.

In contrast to the conventional exchange bias phenomenon, a strong influence of the cooling field on the exchange bias effect may be expected in the case of the multiple equivalent spin configurations of the SG phase. Figures 3(a)–(c) illustrate H_{EB}, H_C and M_{EB}/M_{sat} as a function of cooling field H_{FC} in the phase-separated $La_{0.82}Sr_{0.18}CoO_3$ single crystal measured at 5 K, respectively. The maximal measuring field is ±10 kOe. $H_{EB} = (H_+ + H_-)/2$, and $M_{EB} = (M_+ + M_-)/2$, where H_+, H_-, M_+, and M_- stand for the positive and negative intercepts with the magnetic field axis and the magnetization axis, respectively. The coercivity field H_C and M_{sat} are defined as $H_C = (H_+ - H_-)/2$, $M_{sat} = (M_+ - M_-)/2$, respectively. H_{EB} increases initially with increasing cooling field H_{FC}, and achieves a maximum value of 90 Oe when the cooling field $H_{FC} = 2$ kOe. With a further increase in cooling field H_{FC}, the exchange bias field decreases. The exchange bias in the SG system also gives rise to an enhanced coercivity as well as an asymmetric reversal of the magnetization, M_{EB}. From figures 3(b) and (c), one finds that the increase in H_C and M_{EB} with H_{FC} is consistent with the increase in H_{EB}.

The exchange bias field is usually thought of as the balance between the Zeeman energy of the FM particles and the surface energy due to the exchange interaction at the interface. The cooling field of $H_{FC} = 2$ kOe can be considered as an effective depinning threshold field at which the magnetic interaction is overcome by the Zeeman coupling. Below $H_{FC} = 2$ kOe, the Zeeman coupling should be not strong enough to compete with the exchange interaction and produces a negative H_{EB}. The spins in the SG regions partly frozen collinearly with the field direction serve as the uncompensated spins and the exchange bias effect appears. The increase of cooling field converts more and more SG regions into such frozen regions, and consequently the exchange bias field increases with increasing cooling field. Above this field, due to the Zeeman coupling, the SG region exerts a weaker pinning on the FM cluster moment, resulting in a decrease of exchange bias field and coercivity. When the field is large enough to destroy the SG regions frozen collinearly with the external field, the exchange bias effect diminishes again.

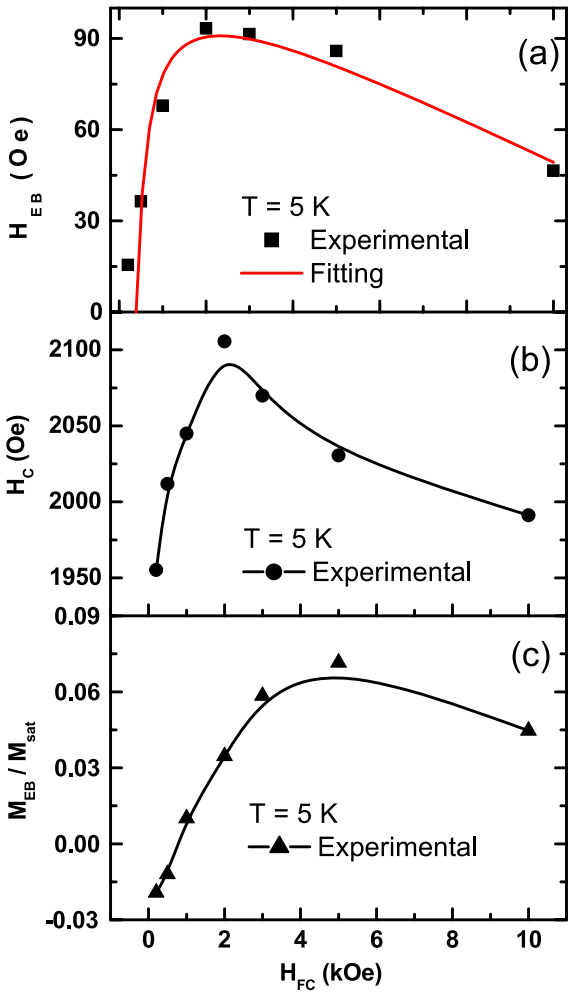

Figure 3. Cooling field dependence of H_{EB} (a), H_C (b), and M_{EB}/M_{sat} (c) measured at 5 K.

In the case of $\mu_0 H_{FC} < k_B T_f$, the effect of cooling field on exchange bias field was discussed in the charge-ordered $Pr_{1/3}Ca_{2/3}MnO_3$ manganite by Niebieskikwiat and Salamon [10]. The H_{EB} can be expressed by the following relation:

$$-H_{EB} \propto J_i \left[\frac{J_i \mu_0}{(g\mu_B)^2} L\left(\frac{\mu H_{FC}}{k_B T_f}\right) + H_{FC} \right] \qquad (1)$$

where J_i is the interface exchange coupling constant, g is the gyromagnetic factor, $L(x)$ is the Langevin function, $x = \mu H_{FC}/k_B T_f k_B$ is the Boltzmann constant, μ_B is the Bohr magneton and μ is the magnetic moment of the FM particles. From figure 2(a), it can be seen that the experimental data can be best fitted by adjusting the interfacial exchange constant, $J_i \approx -0.68$ meV. The negative interface exchange constant, obtained from the best fit to the experimental data, for the present sample indicated that AFM coupling existed between the FM domain and spin-glass region. This coupling constant is in excellent agreement with the estimated value $T_f \approx 63$ K from mean field theory. Compared with the interfacial

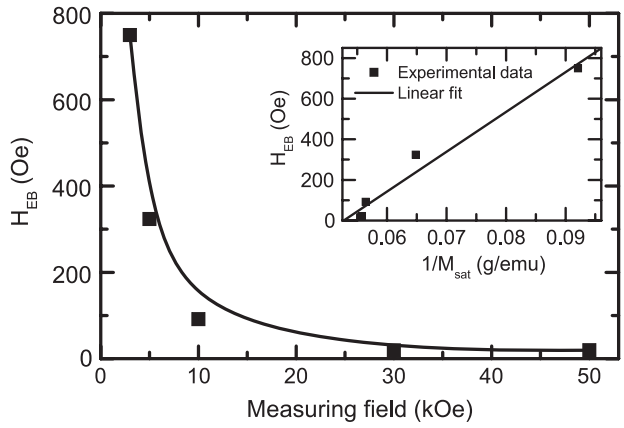

Figure 4. H_{EB} of the single crystal after cooling in a field of 3 kOe at 5 K as a function of maximal measuring field. Inset: linear relationship between H_{EB} and $1/M_{sat}$.

exchange coupling constant between the FM domains and AFM host in the $Pr_{1/3}Ca_{2/3}MnO_3$ charge-ordered manganite, $J_i \approx -1.7$ meV [10], our results indicated the interfacial exchange coupling is relatively weaker in the spin-glass region of $La_{0.82}Sr_{0.18}CoO_3$, and consequently, results in a significant field cooling effect of the exchange bias. A similar dependence of cooling field on the exchange bias field was also observed in spin-glass-like disordered $L_{0.5}Sr_{0.5}MnO_3$ manganites (L = Y, $Y_{0.5}Sm_{0.5}$, and $Y_{0.5}La_{0.5}$) [20].

In addition to the cooling field, the magnetic glassy behavior is significantly dependent upon the applied field as illustrated in figure 2(a). Therefore, the exchange bias effect can be also tuned by an applied magnetic field. Figure 4 illustrates the exchange bias field as a function of measuring field. It is worth noting that the H_{EB} of the single crystal reaches about 750 Oe when the measuring field is 3 kOe, nearly three times larger than that of the corresponding polycrystalline sample (250 Oe) [11]. The enhancement of exchange bias field in the single crystal is possibly related to the flat interface and the perfect orientation of crystallites. The rapid decrease of H_{EB} with increasing maximal measuring field after FC in 3 kOe is clearly seen from figure 4. To avoid the training effect, the demagnetization of the sample was carried out before measuring each hysteresis loop by warming the sample to 300 K and then field cooling to 5 K again. Thus, the dependence of the exchange bias field on the applied field plotted in figure 4 is reversible. There should be two factors which contribute to this peculiar feature of exchange bias in the $La_{0.82}Sr_{0.18}CoO_3$ single crystal. On the one hand, as the measuring field increases, the effective Zeeman energy also increases. The increase in measuring field can make more and more FM spins align until all spins are parallel to the external field, resulting in 'unfreezing' the SG regions and consequently a decrease of the exchange coupling between AFM and FM. Accordingly, H_{EB} decreases due to the reduction of the proportion of the FM spins staying 'frozen.' On the other hand, in phase-separated cobaltites, the FM clusters grow with increasing applied magnetic field, and the SG regions are somehow destroyed by applied magnetic field. With the reduction of the SG regions and the increment of the size of the FM clusters, the relative proportion of the SG layers to the FM clusters significantly decreases. Once the measuring field exceeds 30 kOe and is high enough, the small portion of the SG spins cannot pin the huge moments of the FM region, resulting in the disappearance of exchange anisotropy.

According to the M–H measurement, the magnetization of the FM regions almost saturates under an applied field of 3 kOe. Therefore, the saturation magnetization of $La_{0.82}Sr_{0.18}CoO_3$, M_{sat}, can be regarded as being proportional to the volume fraction of the FM region, whose increase with H originates from the increasing size of the ferromagnetic region, t_{FM} i.e. $M_{sat} \propto M_{FM}t_{FM}$. After cooling in a magnetic field of 3 kOe from 300 to 5 K, H_{EB} and M_{sat} were obtained with the variation of maximal measuring fields as illustrated in the inset of figure 4. There is a linear relationship between H_{EB} and $1/M_{sat}$, and the intersections between the linear fitted line and the coordinate axes are very close to the zero point. One can deduce that H_{EB} is roughly inversely proportional to t_{FM}, which is a common feature in various exchange bias systems.

High resolution electron microscopy micrographs demonstrate that the periodicity of the bright fringes changes with the spatial position inside the $La_{1-x}Sr_xCoO_3$ samples, indicating hole-rich region (FM clusters) embedded in a hole-poor (spin-glass) matrix [15]. Since the interface exchange coupling between FM clusters and the spin-glass (SG) region is negative, the exchange bias effect in our FM/SG system is qualitatively analogous to an FM/AFM thin film. Therefore, the phenomenological formula of the exchange bias field H_{EB} can be expressed by the following relation, on the basis of the assumption that domain wall forms in the antiferromagnet [21],

$$H_{EB} = \frac{2\sqrt{A_{AF}K_{AF}}}{M_{FM}t_{FM}}, \tag{2}$$

where K_{AF} and A_{AF} are the uniaxial anisotropy energy and the exchange stiffness of the AFM, and M_{FM} and t_{FM} are the magnetic moment and the size of FM regions. Identifying the FM with the FM layers and the AFM with the spin-glass layer, the magnitude of t_{FM} can be approximately estimated from equation (2). Our results show that the $H_{EB} \approx$ 100 Oe (figure 2(a)), $A_{AF} \approx 1.12 \times 10^{-8}$ erg cm^{-1} estimated from freezing temperature of spin-glass system, $M_{FM} \approx$ 51.4 emu g^{-1} assuming Co^{3+} and Co^{4+} are intermediate spin states. If we use $K_{AF} \approx 2.26 \times 10^6$ erg cm^{-3} obtained from the M–H curve (not shown) of the $La_{0.82}Sr_{0.18}CoO_3$ single crystal on the basis of approach to saturation, as discussed in [22], the size of the FM regions is estimated as $t_{FM} \approx 9$ nm according to equation (2). The estimated size of FM region is in good agreement with high resolution TEM image, which indicates that the phase separation occurs on length scales of the order of 10 nm [15].

In summary, the spin-glass magnetic characteristics in the $La_{0.82}Sr_{0.18}CoO_3$ single crystal offers a possibility to investigate the intrinsic exchange bias effect excluding the effects of grain sizes and grain boundaries which exist in the corresponding polycrystalline samples. An antiferromagnetically (AFM) interfacial exchange coupling constant at the spin-glass region $J_i \approx -0.68$ meV was found on the basis of the dependence of exchange bias field on

the cooling field. The size of the ferromagnetic regions was estimated as $t_{FM} \approx 9$ nm in the spin-glass system from the inverse proportionality of exchange bias field H_{EB} to the size of ferromagnetic regions.

Acknowledgments

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