SCIENTIFIC REPORTS

Received: 08 January 2016 Accepted: 21 April 2016 Published: 11 May 2016

OPEN Positive to negative zerofield cooled exchange bias in La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics

Cui Shang¹, Shaopu Guo², Ruilong Wang^{1,2}, Zhigang Sun³, Haibo Xiao², Lingfang Xu², Changping Yang² & Zhengcai Xia¹

Exchange bias effect obtained after zero-field cooling from unmagnetized state usually exhibits a shift of hysteresis loop negative to the direction of the initial magnetic field, known as negative zero-field cooled exchange bias. Here, positive zero-field cooled exchange bias is reported in La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics. In addition, a transition from positive to negative exchange bias has been observed with increasing initial magnetization field and measurement temperature. Based on a simple spin bidomain model with variable interface, two type of interfacial spin configuration formed during the initial magnetization process are proposed to interpret the observed phenomenon.

Since first reported in Co/CoO system by Meikle John and Bean¹, exchange bias (EB) effect has received considerable attention due to its importance in fundamental research and memory devices applications like random access magnetic storage units and spin valves²⁻⁵. It manifests itself by a shift of the hysteresis loop away from the magnetic field axis, and the magnitude of this shift is referred to as EB field, $H_{\rm EB}$. Although the origin of EB is still not fully understood, it is generally accepted that it is related to the interfacial ferromagnetic (FM)-antiferomagetic (AFM) exchange coupling interaction across the interface and the AFM unidirectional anisotropy hold a key role to decide the magnitude and sign of the shift⁶⁻⁹. Conventionally, AFM unidirectional anisotropy is induced from an imprint of the FM unidirectional anisotropy during a field-cooling (FC) process through the Néel temperature (T_N) of AFM subsystem, and the FM coupling results in a shift of the hysteresis loop in the opposite ('negative') direction to the cooling field, defined as negative EB. Positive EB effect can be observed upon strong cooling field in some cases, in which the interfacial exchange interaction is believed to be AFM^{10,11}. In the measurement process of obtaining both negative and positive EB effect, the FM-AFM interface is supposed to be fixed due to sufficiently large AFM anisotropy energy. Hence, it is high unexpected to observe zero-field cooled EB (ZFC-EB) effect, in another word, a shift of the magnetic hysteresis loop center away from zero field after zero-field cooling from unmagnetized state due to the formation of two oppositely oriented AFM domains.

Though ZFC-EB effect with small $H_{\rm EB}$ was reported in bilayer systems early¹², it receives wide acceptance until the observation of large ZFC-EB effect with $H_{\rm EB}$ up to 1300 Oe in Ni₅₀Mn₃₇In₁₃ alloy by wang *et al.*¹³, in which the magnitude of the shift can be tuned by the strength of initial magnetization field. From then on, the ZFC-EB effect has been observed in different systems, such as Mn₂PtGa alloy¹⁴, BiFeO₃-Bi₂Fe₄O₉ nanocomposite¹⁵, YMnO₃ nanoparticles¹⁶, Ni₂Mn_{1.4}Ga_{0.6} alloy¹⁷, La_{1.5}Sr_{0.5}CoMnO₆ polycrystalline ceramics¹⁸, Pr_{1-x}Ca_xMnO₃ nanosheet¹⁹, Ni₅₀Mn₃₆Co₄Sn₁₀ alloy²⁰, antiperovskite compound PdNCr₃²¹, Co_{0.8}Cu_{0.2}Cr₂O₄²² and Y_{0.9}Pr_{0.1}CrO₃ ceramics²³. In most cases, the appearance of such ZFC-EB effect is related to newly established interface with AFM unidirectional anisotropy, and the formation or growth of FM (or superferromagnet, SFM) domains at the expense of pinning subsystem (AFM matrix or spin glass) has been proposed as a possible way^{13,16-21}. However, almost all these studies show only the negative ZFC-EB effect, in another word, shift of the hysteresis loop in the opposite direction to the initial magnetization field. It is highly desired of obtaining tunable positive and negative ZFC-EB systematically for an intensively understanding of the EB origination. In present work, we report a transition from positive to negative ZFC-EB effect by increasing initial magnetization field and measurement temperature

¹Wuhan National High Magnetic Field Center & School of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China. ²Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Laboratory of Ferro & Piezoelectric Materials and Devices, Faculty of Physics and Electronic Science, Hubei University, Wuhan 430062, People's Republic of China. ³State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China. Correspondence and requests for materials should be addressed to R.L.W. (email: wangrlnju@gmail.com) or Z.C.X. (email: xia9020@hust.edu.cn)



Figure 1. Room temperature XRD and refinement result of sample $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$. The observed and calculated patterns are denoted by circle and solid line, respectively. The blue solid line at the bottom of the panel shows the difference of the observed and calculated patterns. Green bars correspond to Bragg positions.



Figure 2. (a) Temperature dependence of magnetization M(T) measured at 50 Oe after FC and ZFC procedures. The inset shows the enlarge scale of ZFC curve. (b) Temperature dependence of the real part $\chi'(T)$ of ac susceptibility measured at different frequencies with an ac magnetic field of 5 Oe. The inset shows the fit using the power law.

in $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$ ceramics, which can be ascribed to the evolution of the interfacial spin configuration during the initial magnetization process.

Results

Figure 1 shows the room temperature XRD patterns of $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$, in which no trace of any impurity phases is discernible. The refined data obtained with the Rietveld refinement program FULLPROF are also shown in Fig. 1. The best fitting of the observed diffraction peaks indicates the sample with tetragonal structure and the space group *I4/mcm*. The refined lattice parameters (*a*, *b* and *c*) and unit volume (*V*) of $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$ are a = b = 5.4475 (5) Å, c = 7.7208 (9) Å, and V = 229.12 (4) Å³.

Figure 2(a) shows the temperature dependence of magnetization M(T) measured at 50 Oe with FC and ZFC procedures. The ZFC and FC magnetization curves start to separate from each other at an irreversibility temperature around $T_{ir} \sim 280$ K, and they begin to diverge strongly at low temperatures, which is a strongly pronounced typical feature of both classical spin glasses (SG) and phase-separated manganite systems with coexisting FM clusters and an AFM matrix. Two successive peaks at 133 K and 106 K, recognized as T_N and freezing temperature T_f respectively, can be observed in the ZFC curve (see inset). As reported before, in canonical SG systems T_{ir} is very close to T_f typically²⁴. However, T_{ir} is far above T_f in present case, indicating the possibility of a cluster glass (CG) state at low temperatures^{25,26}. Therefore, the rapid rise of magnetization around the temperature T_G (137 K for FC and 140 K for ZFC, determined from the minimum of dM/dT vs T curve) could be associated with the occurrence of a short range FM ordering, forming FM clusters. Additionally, T_f could be considered as the freezing temperature of the FM clusters.



Figure 3. M(H) loops at 4.2 K within full scale of magnetic field with $H_m^{\text{max}} = 50 \text{ kOe}$ (**a**) and 110 kOe (**b**). The insets are the enlarge scale at low field; (**c**) H_{EB} and H_{C} as a function of H_m^{max} at 4.2 K after ZFC.

In order to get further insight into the magnetic properties of this system, ac susceptibility under different frequencies was measured. Figure 2(b) shows the temperature dependence of the real part $\chi'(T)$ of ac susceptibility measured at different frequencies with an ac magnetic field of 5 Oe. Two pronounced peaks, being close to T_N and T_f respectively, can be observed. It is remarkable that the position of T_f is frequency dependent and obviously shifts toward a higher temperature with increasing frequency. Such behavior indicates a glassy character of the sample. The critical slowing-down power law, which assumes a true equilibrium phase transition with a divergence of relaxation time near the freezing point, was employed to analyze spin dynamics of the glass-like state. According to the power law, the temperature dependence of τ could be described by $\tau/\tau_0 = (T_f/T_g - 1)^{-z_0 27,28}$, where T_f is the peak temperature measured at frequency f, T_g is the critical temperature for SG ordering which is equivalent to T_f as $f \rightarrow 0$, $z\nu$ is a constant exponent, and τ_0 is the characteristic time scale for spin dynamics (the shortest relaxation time of the system). The best fit shown in the inset of Fig. 2(b) gives the value of $T_g = 106.5$ K (nearly equal to the dc value found from dc magnetization), $z\nu = 4.11$, $\tau_0 = 7.92 \times 10^{-10}$ s. The long spin flipping time τ_0 (~ $10^{-12} - 10^{-14}$ for classical SG compounds) and relative small critical exponent $z\nu$ suggests a CG state nature at low temperature magnetism in the La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics^{27,28}, in another word, the state of FM clusters embodied in AFM matrix.

The M(H) loops of La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics measured at 4.2 K with various magnitudes of the initial magnetization field, i.e. maximum measurement field (different H_m^{max}) at 4.2 K after ZFC from 300 K. The unmagnetized initial state at low temperatures can be ensured as 300 K is above the T_G . As representatives, the M(H) loops with $H_m^{max} = 50$ and 110 kOe are shown in Fig. 3(a,b) respectively. Magnetization at the starting point of the initial magnetization curve (open circles) is close to zero, indicating that the initial state at 4.2 K is an unmagnetized state. Obvious positive and negative shift of the hysteresis loop along the magnetic field axis, recognized as positive and negative ZFC-EB effect, can be observed for 50 and 110 kOe, respectively. Figure 3(c) shows H_{EB} and coercivity (H_C) as a function of H_m^{max} . The H_{EB} and H_C were calculated using $H_{EB} = (H_1 + H_2)/2$ and $H_C = |H_1 - H_2|/2$, where H_1 and H_2 are the left and right fields at which the magnetization becomes zero. We can find that H_{EB} exhibits positive value at low field, and first increases with the increase of H_m^{max} , reaching a maximum value of 220 Oe at $H_m^{max} = 65$ kOe and then decreases. Further increasing H_m^{max} , H_{EB} would change to negative value, reaching a minimum value of -520 Oe at $H_m^{max} = 110$ kOe and then increases slowly. The phenomenon of positive ZFC-EB effect and its transition to negative ZFC-EB at high initial magnetization field.

To explore the origin of the ZFC-EB effect, the evolution of the FM/AFM spin interface based on the simple spin bidomain model was proposed, and the schematic diagram of the spin configuration at different stages is shown in Fig. 4. According to the bidomain model, The FM unmagnetized initial state can be seen as two FM



Figure 4. Schematic diagrams of the spin configuration at different stages and corresponding hysteresis loops.

domains with opposite magnetization direction along the direction of the magnetic field and the net magnetization is zero. The FM domain configuration would be imprinted in the AFM during cooling, resulting in the two types of AFM domains with opposite oriented directions at the interface, and both of them align parallel to their neighboring FM domain respectively, as shown in Fig. 4(a). Applying the initial magnetization field will result in FM anisotropy being parallel to the direction of the magnetic field as well as a new fixed interface though the domains growth of FM domains at the expense of AFM domain. It is generally acknowledged that if the interfacial AFM spins are parallel (antiparallel) to the FM spins, the FM (AFM) coupling between them will result in negative (positive) shift of the magnetic hysteresis loop along the magnetic field axis. Hence, two types of interfacial spin configurations after applying the initial magnetization field, corresponding to positive and negative ZFC-EB effect, can be proposed. As shown in Fig. 4(b), under low initial magnetization field, the interfacial AFM spins paralleling to the direction of the magnetic field will merge into FM domains directly, showing AFM coupling and positive shift of the hysteresis loop. While in case of the high initial magnetization field, the high initial magnetization field is large enough to overcome the interfacial AFM anisotropy energy and drives the AFM spins in the new interface formed under low initial magnetization field to rotate from negative direction to the positive direction, and then merge into FM domains, leading to the negative ZFC-EB effect as shown in Fig. 4(c). In another word, low high initial magnetization field is in favor of the positive EB effect while high initial magnetization field is in favor of the negative EB effect. The shift direction of the hysteresis loop can be associated with the competition of the two kind of FM/AFM interfacial spin structure.

Hence, the results in the La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics can be associated with the competition of the two ways of forming the AFM unidirectional anisotropy, highlighting the importance of the AFM spins anisotropy on the sign of ZFC-EB effect. Increasing the initial magnetization field firstly would increase the AFM unidirectional anisotropy that parallels to the direction of initial magnetization field, resulting in the strengthening of the AFM coupling at the interface and larger positive shift and $H_{\rm EB}$. Further increasing the field, the rotation of the AFM spins from negative direction to the positive direction would reduce the AFM anisotropy as well as $H_{\rm EB}$. With the increase of the interface with the AFM anisotropy antiparallel to the direction of initial magnetization field, the enhancement of the negative ZFC-EB effect with the increase of initial magnetization field can be expected. The slight increase of $H_{\rm EB}$ (the decrease of $|H_{\rm EB}|$) at higher $H_m^{\rm max}$ (>110 kOe) may be attributed to the change of bulk AFM spin structure under large applied magnetic field.

Usually in the negative FC and ZFC-EB effects, the absolute value of $H_{\rm EB}$ ($H_{\rm EB} < 0$) approximately linearly decreases with increasing temperature and gradually disappears around the blocking temperature $T_{\rm B}$, which can be attributed to the decrease of the AFM anisotropy paralleling to the direction of positive magnetic field with the increase of temperature^{13,16–21,29}. However, if there is AFM bidomain in the initial state, the decrease of the anisotropy of the right AFM domain would decrease the $H_m^{\rm max}$ needed to generate the rotation of the interfacial AFM spins from negative to positive direction. Thus, the enhancement of the AFM anisotropy paralleling to the direction of positive magnetic field would be beneficial to the positive ZFC-EB effect at low temperature. The M(H) loops at different temperatures with $H_m^{\rm max} = 50$ and 110 kOe were measured after ZFC from 300 K, and the temperature. It is worth noting that $H_{\rm EB}$ for 50 kOe decreases firstly with the increase of temperature, then changes to negative, reaching a negative peak before approaching to zero at 40 K. The temperature of 40 K can be referred as exchange blocking temperature, T_B . A negative peak can also be observed for 110 kOe, indicating the AFM anisotropy parallel to the direction of positive magnetic field at low temperature. All these results are consistent with the discussions above, confirming the reasonable of the model shown in Fig. 4.

Discussion

Magnetic properties of La_{0.5}Sr_{0.5}Mn_{1-x}Co_xO₃ ($0 \le x \le 1$) series of samples were studied systematically, and only La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ exhibits ZFC-EB. As reported before, the formation of new stable FM–SG interface with unidirectional anisotropy is usually though the percolation of isolated FM domains in the initial magnetization process^{17,21}. Hence, the ZEC-EB effect only occurs in system with appropriate magnetic structure, and the size of initial FM clusters (domains) play a critical role^{13,16,17,21}. If the size of initial FM domains is too small, it is hard for



Figure 5. Temperature dependence of $H_{\rm EB}$ and $H_{\rm C}$ with $H_m^{\rm max} = 50$ kOe (**a**) and 110 kOe (**b**) after ZFC.

the FM clusters to be merged with neighboring FM domains, then no EB effect can be observed. The magnetic state of the parent compound $La_{0.5}Sr_{0.5}MnO_3$ exhibits FM ground state with AFM clusters in low-temperature region^{30,31}. Upon Co doping, the double exchange interaction between Mn^{3+} and Mn^{4+} would be partially destroyed and some of the FM ground state would be transformed to a robust AFM state^{32,33}. Then the magnetic state evolves into a coexistence of FM clusters and AFM matrix for x = 0.2 sample, leading to the ZFC-EB effect. However, further increasing the doping level would weaken FM interaction to a higher degree, and the FM clusters in the samples are too small to obtain ZFC-EB effect. Hence, our results are in accordance with the discussions according to the model shown in Fig. 4.

In summary, we have observed positive ZFC-EB effect in $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$ ceramics, and it can transfer into negative ZFC-EB effect with the increase of magnetic field and measuring temperature. Such phenomenon can be attributed to different orientation of interfacial AFM anisotropy formed in the process of initial magnetization. The results here will enrich the type of EB effect, improve the spin bidomain model with variable interface, and benefit the deep understanding of the physical mechanism of exchange bias.

Methods

The La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O₃ ceramics was prepared by sintering corresponding powders derived from sol–gel precursors. A stoichiometric amount of La(NO₃)₃·6H₂O, SrCO₃, Mn(NO₃)₂·4H₂O and Co(NO₃)₂·6H₂O, and appropriate citric acid and nitric acid were used as starting materials. At the end of the process, the gel was first dried at 120 °C and then decomposed at 400 °C to result in dark brown powders, which were ground, then pressed into strip and sintered at 1300 °C for 10 h to produce the finished sample. The good crystallinity of an orthorhombic phase structure without any impurity phases was confirmed by X-ray diffraction (XRD). The magnetic properties were measured by superconducting quantum interference device (SQUID-VSM, Quantum Design) magnetometer and physical property measurement system (PPMS, Quantum Design).

References

- 1. Meiklejohn, W. H. & Bean, C. P. New magnetic anisotropy. Phys. Rev. 102, 1413-1414 (1956).
- 2. Dieny, B. et al. Giant magnetoresistive in soft ferromagnetic multilayers. Phys. Rev. B 43, 1297 (1991).
- 3. Kools, J. C. S. Exchange-biased spin-valves for magnetic storage. IEEE Trans. Magn. 32, 3165-3184 (1996).
- 4. Skumryev, V. et al. Beating the superparamagnetic limit with exchange bias. Nature 423, 850-853 (2003).
- Gider, S., Runge, B. U., Marley, A. C. & Parkin, S. S. P. The magnetic stability of spin-dependent tunneling devices. Science 281, 797–799 (1998).
- 6. Nogues, J. & Schuller, I. K. Exchange bias. J. Magn. Magn. Mater. 192, 203-232 (1999).
- Takano, K., Kodama, R. H., Berkowitz, A. E., Cao, W. & Thomas, G. Interfacial ncompensated antiferromagnetic spins: Role in unidirectional anisotropy in polycrystalline Ni₈₁Fe₁₉/CoO bilayers. *Phys. Rev. Lett.* **79**, 1130–1133 (1997).
- Kodama, R. H., Makhlouf, S. A. & Berkowitz, A. E. Finite size effects in antiferromagnetic NiO nanoparticles. *Phys. Rev. Lett.* 79, 1393–1396 (1997).
- Zhao, H. W., Wang, W. N., Wang, Y. J., Zhan, W. S. & Xiao, J. Q. Investigation of exchange bias in FeMnC/FeMn bilayers. J. Appl. Phys. 91, 6893–6895 (2002).
- Nogues, J., Lederman, D., Moran, T. J. & Schuller, I. K. Positive exchange bias in FeF₂-Fe bilayers. *Phys. Rev. Lett.* 76, 4624–4627 (1996).
- 11. Petracic, O. et al. Bidomain state in exchange biased FeF₂/Ni. Appl. Phys. Lett. 87, 222509 (2005).
- 12. Saha, J. & Victora, R. H. Spontaneous exchange bias: Unidirectional anisotropy in an otherwise isotropic system. *Phys. Rev. B* 76, 100405(R) (2007).
- 13. Wang, B. M. et al. Large exchange bias after zero-field cooling from an unmagnetized state. Phys. Rev. Lett. 106, 077203 (2011).
- 14. Nayak, A. K. *et al.* Large zero-field cooled exchange-bias in bulk Mn₂PtGa. *Phys. Rev. Lett.* **110**, 127204 (2013).
- Maity, T., Goswami, S., Bhattacharya, D. & Roy, S. Superspin glass mediated giant spontaneousexchange bias in a nanocomposite of BiFeO₃-Bi₂Fe₄O₉. *Phys. Rev. Lett.* **110**, 107201 (2013).
- Chauhan, S., Srivastava, S. K. & Chandra, R. Zero-field cooled exchange bias in hexagonal YMnO₃ nanoparticles. *Appl. Phys. Lett.* 103, 042416 (2013).
- 17. Han, Z. D. et al. Magnetic phase separation and exchange bias in off-stoichiometric Ni-Mn-Ga alloys. Appl. Phys. Lett. 103, 172403 (2013).
- Murthy, J. K. & Venimadhav, A. Giant zero field cooled spontaneous exchange bias effect in phase separated La_{1.5}Sr_{0.5}CoMnO₆. Appl. Phys. Lett. 103, 252410 (2013).
- Sadhu, A. & Bhattacharyya, S. Stacked nanosheets of Pr_{1-x}Ca_xMnO₃ (x = 0.3 and 0.49): a ferromagnetic two-dimensional material with spontaneous exchange bias. *J. Phys. Chem. C* 117, 26351 (2013).

- Liao, P. et al. Strongly enhanced antiferromagnetism and giant spontaneous exchange bias in Ni₅₀Mn₃₆Co₄Sn₁₀ Heusler alloy. Appl. Phys. Lett. 104, 092410 (2014).
- 21. Lin, S. *et al.* Spin-glass behavior and zero-field-cooled exchange bias in a Cr-based antiperovskite compound PdNCr₃. *J. Mater. Chem. C* **3**, 5683 (2015).
- Wang, L. G. et al. Negative magnetization and zero-field cooled exchange bias effect in Co_{0.8}Cu_{0.2}Cr₂O₄ Ceramics. Appl. Phys. Lett. 107, 152406 (2015).
- Deng, D. M. et al. Cooling field tuned magnetic phase transition and exchange bias-like effect in Y_{0.9}Pr_{0.1}CrO₃. Appl. Phys. Lett. 107, 102404 (2015).
- Bitoh, T., Ohba, K., Takamatsu, M., Shirane, T. & Chikazawa, S. Field-cooled and zero-field-cooled magnetization of superparamagnetic fine particles in Cu₉₇Co₃ alloy: comparison with spin-glass Au₉₆Fe₄ alloy. J. Phys. Soc. Jpn. 64, 1305–1310 (1995).
- Freitas, R. S. & Ghivelder, L. Magnetic relaxation phenomena and cluster glass properties of La_{0.7-x}Y_xCa_{0.3}MnO₃ manganites. *Phys. Rev. B* 64, 144404 (2001).
- 26. Huang, X. H. et al. Size-dependent exchange bias in La_{0.25}Ca_{0.75}MnO₃ nanoparticles. Phys. Rev. B 78, 224408 (2008).
- 27. Hanasaki, N. *et al.* Nature of the transition between a ferromagnetic metal and a spin-glass insulator in pyrochlore molybdates. *Phys. Rev. Lett.* **99**, 086401 (2007).
- Patra, M., Majumdar, S. & Giri, S. Grain size effect on the magnetic cluster-glass properties of La_{0.88}Sr_{0.12}CoO₃. J. Phys.: Condens. Matter 22, 116001 (2010).
- Soeya, S., Hoshiya, H., Meguro, K. & Fukui, H. Enhanced unidirectional anisotropy of the Co₉₀Fe₁₀/CrMnPt system by the NiO capping layer. *Appl. Phys. Lett.* 71, 3424 (1997).
- Chmaissem, O., Dabrowski, B., Kolesnik, S., Mais, J., Jorgensen, J. D. & Short, S. Effect of Ru doping in La_{0.5}Sr_{0.5}MnO₃ and La_{0.45}Sr_{0.5}MnO₃. *Phys. Rev. B* 74, 144433 (2006).
- 31. Shang, C. et al. Al^{3+} doping effects and high-field phase diagram of $La_{0.5}Sr_{0.5}Mn_{1-x}Al_xO_3$. J. Phys. D: Appl. Phys. **49**, 035001 (2016).
- Shi, J. B., Wu, F. C. & Lin, C. T. Electrical transport, magnetism, and magnetoresistance in La_{0.7}Sr_{0.3}(Mn_{1-x}Co_x)O₃. Appl. Phys. A 68, 577–581 (1999).
- 33. Chen, X. G. et al. Magnetic and transport properties of cobalt doped La_{0.7}Sr_{0.3}MnO₃. J. Appl. Phys. 116, 103907 (2014).

Acknowledgements

The authors thank the Natural Science Foundation of China (Grant Nos 11104065, 11547191, 11174231 and 51402094), Postdoctoral Science Foundation of China (Grant No. 2013M542008), Hubei Provincial Department of Education (Grant Nos Q20120108 and Q20141004), and Hubei Provincial Department of Science & Technology (Grant Nos 2015CFB549 and 2015CFB397) for their financial supports.

Author Contributions

R.L.W. proposed the model and predicted the existence of positive exchange bias. Z.C.X. designed the experiments. C.S. prepared the sample and carried out the measurements with S.P.G., Z.G.S., H.B.X., L.F.X. and C.P.Y. analysed the data. R.L.W. and Z.C.X. wrote the paper. All the authors discussed the results and commented on the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Shang, C. *et al.* Positive to negative zero-field cooled exchange bias in $La_{0.5}Sr_{0.5}Mn_{0.8}Co_{0.2}O_3$ ceramics. *Sci. Rep.* **6**, 25703; doi: 10.1038/srep25703 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/