Multiple sign reversals of the exchange bias field in polycrystalline $SmCr_{0.9}Fe_{0.1}O_3$*

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We synthesize the perovskite compound $SmCr_{0.9}Fe_{0.1}O_3$ by the sol–gel method and investigate its exchange bias properties through thermomagnetic and isothermal magnetization measurements. The sign reversals of the exchange bias field are observed at the magnetization compensation temperatures 29.6 K and 96.2 K. It is demonstrated that the occurrence of the exchange bias originates from the antiferromagnetic coupling between the Cr-rich and Fe–Cr regions, of which the net magnetization is temperature-dependent. These results imply that there are potential applications in single systems with sign reversals of both magnetization and exchange bias.

Keywords: magnetism, antiferromagnetic, exchange bias

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1. Introduction

Exchange bias, which is characterized by a shift of a magnetic hysteresis loop away from the gravity center, becomes technologically important for applications in ultrahigh-density magnetic recordings, giant magnetoresistance, non-volatile magnetic random access memories, and other spintronic devices.[1–4] This effect is usually observed in a system composed of ferromagnetic and antiferromagnetic substances, in which the Curie temperature (T_C) of the ferromagnetic component is higher than the Néel temperature (T_N) of the antiferromagnetic component.[1–5] When this sample is subjected to a static magnetic field at the temperature above T_N and cooled through T_N down to a low temperature, the ferromagnetic spins adjacent to the antiferromagnetic spins are coupled to the latter ones with uncompensated spins, giving rise to a ferromagnetic unidirectional anisotropy.[6] Since the discovery of the exchange bias effect in the Co/CoO nanostructure by Meiklejohn and Bean in 1956, this peculiar magnetic effect has been well studied in diverse systems containing ferromagnetic, antiferromagnetic, canted antiferromagnetic, ferrimagnetic, spin-glass, and disordered magnetic components, which have been reviewed by different groups.[7–10] Recently, an interesting phenomenon, the sign reversal of the exchange bias field (H_{EB}), was observed in some heterostructures and single-phase materials, such as Co/CuMn, FeF_2/Fe, Fe/Gd multilayers, $La_{1-x}Pr_xCrO_3$ (*xs*Im0.7–0.85) ceramic, $La_{0.2}Ce_{0.8}CrO_3$ nanoparticle, $Co(Cr_{0.95}Fe_{0.05})_2O_4$, etc.[11–16] Under the external stimulation of temperature or a magnetic field, H_{EB} in each of these systems will change from positive to negative or from negative to positive.[11–16] Generally, this effect is realized at the magnetic compensating point (T_{cmp}, the characteristic temperature where the material exhibits a net zero magnetization) and often accompanied by spin reversal, which is meaningful for the technology of thermally assisted magnetic random access memories.[14–18] Due to its promising applications and interesting physical mechanism, further research on the reversal of H_{EB} in many magnetic systems is needed.

Perovskite $SmCrO_3$ is known as a multiferroic perovskite, owing to its special magnetic structure.[19] In this compound, the moments of Cr ions form an antiferromagnetic order at 197 K (T_N) with weak ferromagnetism due to the canted spin structure.[19] With a decrease in temperature, a drop of magnetization is observed around 40 K, which is ascribed to the spin reorientation with the Cr-spin configuration changing from Γ_4 (G_x, A_y, F_z) to Γ_2 (F_x, C_y, G_z).[20] However, with the substitution of Fe^{3+} for Cr^{3+}, the introduction of the exchange interaction between Fe^{3+} and Cr^{3+} modifies the pristine magnetic properties of $SmCrO_3$ and gives rise to an intriguing magnetic behavior in $SmCr_{0.9}Fe_{0.1}O_3$, in which the multiple temperature-induced magnetization reversals are observed.[21] In this paper, we report the exchange bias effect in a single-phase perovskite $SmCr_{0.9}Fe_{0.1}O_3$. Interestingly, due to its complicated spin configuration, H_{EB} of this compound changes from negative to positive and then returns to negative again with an increase in temperature.

2. Experiment

A polycrystalline sample $SmCr_{0.9}Fe_{0.1}O_3$ was prepared by a sol–gel method. Stoichiometric amounts of $Cr(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and Sm_2O_3 (dried at

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1073 K for 12 hours before use) were taken as the starting precursor. First, Sm_2O_3 was converted into nitrate by adding concentrated HNO_3 and evaporated to dryness. Then all three nitrates with citric acid were dissolved together in de-ionized water. The solution was stirred and simultaneously heated at 353 K to evaporate the water until a sol was obtained, and then ethylene glycol was added as fuel. The resulting gel was combusted at 673 K for 2 hours to remove organic residuals. The resultant powders were ground and pressed into circular pellets at 40 MPa followed by sintering in air at 1373 K for 15 hours. Finally, the resulting pellets were reground, repressed into pellets and annealed at 1373 K for 15 hours. The phase purity and crystallinity were checked by X-ray diffraction (XRD) using a Cu Kα radiation. Magnetic measurement was performed with a superconducting quantum interference device (SQUID, Quantum Design).

3. Results and analyses

$SmCr_{0.9}Fe_{0.1}O_3$, in which the transition metal cations of Fe^{3+} and Cr^{3+} randomly occupy the center of BO_6 octahedron and the Sm^{3+} cations are located between two consecutive layers, each of which is made up by tilt octahedrons, has a perovskite (ABO_3) structure.[19] Figure 1 shows a room temperature XRD pattern and Rietveld refinement of the polycrystalline $SmCr_{0.9}Fe_{0.1}O_3$ sample, which suggests that the sample is synthesized in single phase with a space group *Pnma* ($a = 5.383$ Å, $b = 5.523$ Å, $c = 7.669$ Å, $\alpha = \beta = \gamma = 90°$).[19] No impurity phases are detected within the apparatus resolution.

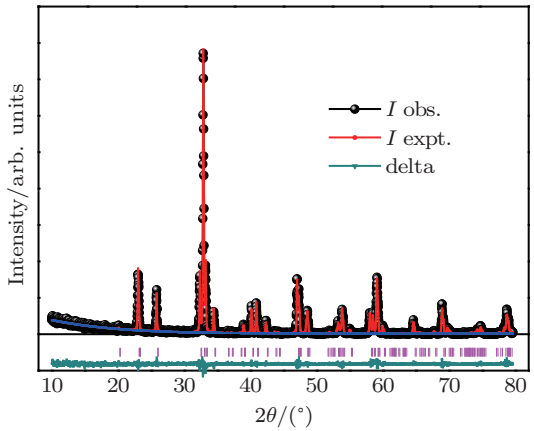


Fig. 1. (color online) Room temperature X-ray powder diffraction pattern and Rietveld refinement of $SmCr_{0.9}Fe_{0.1}O_3$.

The temperature dependence of magnetization (M–T) for the sample under 0.02 T in the field-cooled warming (FCW) mode is shown in Fig. 2. In this measurement, the sample was initially cooled down from 250 K ($> T_N = 185$ K) to 2 K with an external field of 0.02 T, and then the magnetization is recorded in the heating process. The magnetization, in the FCW protocol, decreases with a temperature increase from 2 K, and subsequently goes across zero at the compensation temperature ($T_{cmp1} = 29.6$ K). Above that temperature, the magnetization becomes negative, which suggests that the net moment is opposite to the external magnetic field.[22] With the increase of temperature, the magnetization first increases and then decreases in the absolute value with a maximum around the spin reorientation temperature, T_S, of 40 K.[21] When the temperature is higher than 96.2 K (T_{cmp2}), the magnetization eventually becomes positive in sign again. With a further increase of the temperature, the magnetization increases up to a maximum peak at about 160 K and then decreases to almost zero at T_N of 185 K, suggesting the occurrence of paramagnetism.[21] The interesting temperature dependence of magnetic behavior of $SmCr_{0.9}Fe_{0.1}O_3$ is usually termed 'temperature-induced magnetization reversal', which has been observed in many other systems, such as $La_{1-x}Pr_xCrO_3$ ($x \sim 0.7$–0.85) ceramic, $La_{0.2}Ce_{0.8}CrO_3$ nanoparticles, $SrRuO_3$, and $Nd_{0.75}Ho_{0.25}Al_2$, etc.[14,15,23,24] However, an important feature which should be noticed is that the magnetization reversal takes place twice in $SmCr_{0.9}Fe_{0.1}O_3$, which can be understood in the scenario of the magnetic competition between Cr–Cr and Cr–Fe ordered regions. In our sample, there are two different magnetic ions, Fe^{3+} and Cr^{3+}, which distribute randomly at the same crystallographic site of $SmCr_{0.9}Fe_{0.1}O_3$.[21] According to earlier reports, the super-exchange interaction of Cr–O–Fe is ferromagnetic (Γ_2-type spin configuration) while that of Cr–O–Cr (Γ_4-type spin configuration) is antiferromagnetic, which shows the weak ferromagnetism due to the canted moments of Cr^{3+} ions.[19,25,26] Moreover, the Cr–Cr ordered regions and the Fe–Cr ordered regions are antiferromagnetically coupled in $SmCr_{0.9}Fe_{0.1}O_3$, leading to the anti-parallel alignment of the net moments of these two regions.[21] As the interaction of Cr–Cr and Fe–Cr have different temperature dependences, the multiple temperature-induced magnetization reversals are observed in $SmCr_{0.9}Fe_{0.1}O_3$. In detail, in the temperature region below T_N, the net magnetization of the Cr–Cr regions is parallel to the applied field and larger than that of the Fe–Cr regions, which aligns anti-parallel to the external field. As the temperature decreases below T_{cmp2}, the magnetization of the Fe–Cr regions becomes larger than that of the Cr–Cr regions, leading to the occurrence of the first magnetization reversal. Around the spin reorientation temperature $T_S = 40$ K, the canted moments of the Cr–Cr regions are reoriented to the c axis, which modifies the competition of magnetic moments between the Cr–Cr and Fe–Cr regions, giving rise to the second sign reversal of the magnetization in $SmCr_{0.9}Fe_{0.1}O_3$ at 29.6 K.[21]

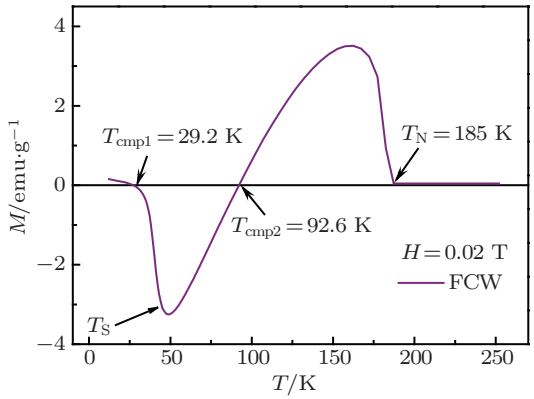


Fig. 2. (color online) Thermomagnetic curve for $SmCr_{0.9}Fe_{0.1}O_3$, measured at 0.02 T under FCW protocol.

The antiferromagnetic coupling between the Cr–Cr and Fe–Cr regions, as well as the multiple temperature-induced magnetization reversals, motivates us to investigate the temperature dependence of the exchange bias effect in $SmCr_{0.9}Fe_{0.1}O_3$. Figure 3 shows the magnetization hysteresis (M–H) for $SmCr_{0.9}Fe_{0.1}O_3$ at various temperatures (T = 10, 29.6, 50, 96.2, 150, 220 K), which are measured in the fields of ±5 T after cooling under an applied field of 1 T. As shown in Fig. 3(a), it is clear that the M–H curve shifts completely to the negative field, exhibiting a considerably large H_{EB} of approximately −0.85 T at 10 K. Here, $H_{EB} = (H_1 + H_2)/2$, where H_1 and H_2 are the left and right coercive fields, respectively.[27] At the temperature of 29.6 K (T_{cmp1}), no obvious shift of the M–H curve is observed as shown in Fig. 3(b), which suggests the disappearance of the exchange bias effect at the compensate point. This phenomenon is also observed in some other systems with sign reversal of H_{EB}.[14–16] When the temperature increases to 50 K, the M–H curve shifts wholly to the positive field as shown in Fig. 3(c), yielding a positive $H_{EB}$of 0.46 T. Figure 3(d) shows the M–H curve measured at the other compensate temperature (T_{cmp2}= 96.2 K) after field-cooling, which also presents no shift along the field-axis. With the further increase of the temperature as shown in Fig. 3(e), a remarkable shift of the M–H curve with $H_{EB} = -0.21$ T is observed at 150 K, where H_{EB} changes its sign again. Finally, when the temperature exceeds T_N, a normal M–H curve is observed at 220 K as shown in Fig. 3(f).

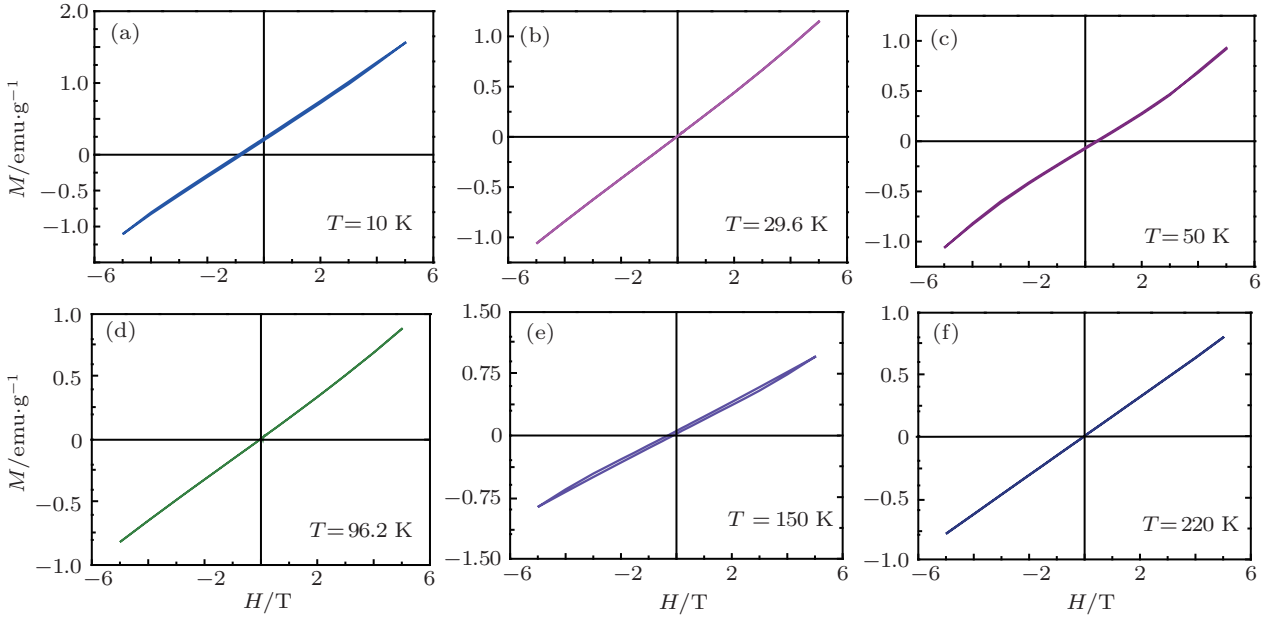


Fig. 3. Magnetic field dependences of magnetization for $SmCr_{0.9}Fe_{0.1}O_3$ at various temperatures (10, 29.6, 50, 96.2, 150, 220 K) after field-cooling at 1 T.

The key parameters of the exchange bias effect for $SmCr_{0.9}Fe_{0.1}O_3$ are presented in Fig. 4, which are obtained from the M–H curves at various temperatures. As shown in Fig. 4(a), the temperature-induced sign reversal of the exchange bias as well as the large exchange bias field is clearly observed. The most noticeable feature is that H_{EB} changes its sign twice at the compensate temperatures, which is rarely reported as far as we know. The temperature dependence of remanence asymmetry ($M_{EB} = (M_1 + M_2/2$, where M_1 and M_2 are the remanent magnetizations, respectively) is shown in Fig. 4(b).[28] Since the magnetic moments of the Fe–Cr and Cr–Cr regions are counteracted with each other, the sign of M_{EB} changes twice at two compensating temperatures, which is different from the behaviors of those materials in which the sign reversal of the remanence asymmetry takes place only once.[14–16,24,29–32] Figure 4(c) shows that the effective coercive field ($H_c^{eff} = (H_2 - H_1)/2$) varies nonmonotonically with temperature.[33] Due to the disappearance of the coercive field

caused by compensated moments, the effective coercive field of $SmCr_{0.9}Fe_{0.1}O_3$ is almost zero at T_{cmp}s.

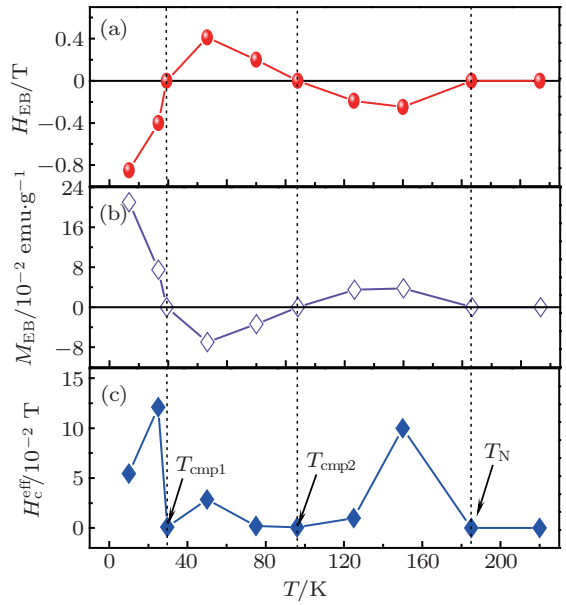


Fig. 4. (color online) Temperature-dependent variations of (a) the exchange bias field; (b) remnant magnetization; and (c) the effective coercive field for $SmCr_{0.9}Fe_{0.1}O_3$ sample, calculated from 1 T-cooled M–H curve as explained in the text. A vertical line intersects all the curves at T_{cmp}s.

The appearance of the exchange bias suggests the existence of pinned spins at the interface between the Cr–Cr and Fe–Cr regions in $SmCr_{0.9}Fe_{0.1}O_3$. As mentioned above, the Cr–Cr and Fe–Cr regions, of which the net moments are oriented in the directions opposite to each other and have different temperature dependences, play a dominant role in determining the magnetization in this system.[21] For this reason, we attribute the sign reversal of H_{EB} to the antiferromagnetic interaction between the Cr–Cr and Fe–Cr regions. The observed sign reversals of the exchange bias can be understood by the configuration as shown schematically in Figs. 5(a)–5(c). In the temperature region $T < T_{cmp1}$, the net moments of Cr–Cr (M_{Cr-Cr}) and Fe–Cr (M_{Fe-Cr}) regions align in the direction along or opposite to the applied field, respectively, as depicted in Fig. 5(a). Meanwhile, M_{Cr-Cr} dominates over M_{Fe-Cr} and the interaction between them gives rise to the net positive magnetization and negative exchange bias, similar to the efficacy of any ferromagnetic/antiferromagnetic interface.[34,35] For $T_{cmp1} < T < T_{cmp2}$, antiferromagnetic interaction also exists between M_{Cr-Cr} and M_{Fe-Cr} but with a difference that M_{Fe-Cr} dominates over M_{Cr-Cr} as shown in Fig. 5(b). Here, the ferromagnetic component of the Fe–Cr region can be visualized as ferromagnetic domains aligned in the direction opposite to the applied field direction, and in such an arrangement, a large positive field is required to bring the magnetization towards zero and positive value.[36] So the entire M–H curve is shifted to the positive field axis, thereby leading to a positive H_{EB}. Finally, when the temperature exceeds T_{cmp2}, the M_{Cr-Cr} dominates over M_{Fe-Cr} again (Fig. 5(c)) and a negative exchange bias field is obtained.

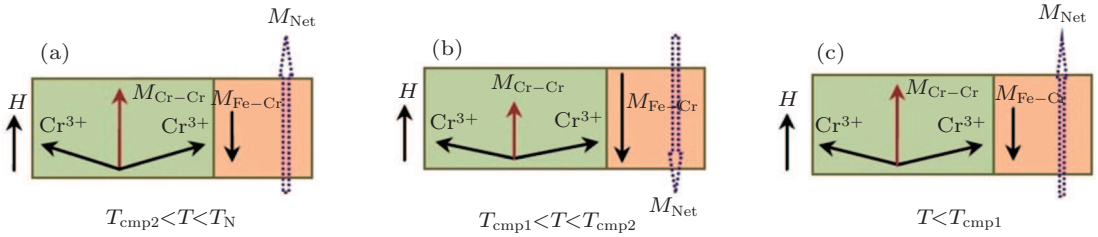


Fig. 5. (color online) Schematic diagrams explaining the sign reversals of the exchange bias field. The darker and lighter parts represent the Cr–Cr and Fe–Cr regions, respectively. Arrows symbolize the directions of the net moments of regions close to the interfaces respectively at (a) $T < T_{cmp1}$, (b) $T_{cmp1} < T < T_{cmp2}$, (c) $T_{cmp2} < T < T_N$.

4. Conclusions

In this paper, an interesting magnetic behavior of multiple temperature-induced reversals of magnetization and H_{EB} are observed in a perovskite compound $SmCr_{0.9}Fe_{0.1}O_3$. Below T_{cmp1}, positive magnetization and negative H_{EB} are obtained in this compound. While in the temperature range, $T_{cmp1} < T < T_{cmp2}$, sign reversals of magnetization and H_{EB} are observed. At $T_{cmp1} < T < T_N$, net magnetization and H_{EB} change their directions again. To the best of our knowledge, this novel magnetic phenomenon of multiple sign reversals of H_{EB} is rarely reported and a simple model is taken to understand this interesting magnetic performance. Our work is expected to be able to arouse the considerable interest in the application of this phenomenon to future spintronic devices.

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