Reversals of magnetization and exchange-bias in perovskite chromite TmCrO_3

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Abstract

Reversals of magnetization and exchange bias field were observed in polycrystalline perovskite TmCrO_3 . Interestingly, the sign reversal of exchange bias can be driven by both temperature and cooling field. The temperature dependence of exchange bias reversal takes place around 31 K and the sign reversal of exchange bias driven by cooling field occurs when the system exhibits positive exchange bias. The reversals can be elucidated based on the antiferromagnetic coupling between the canted Cr^{3+} moments and Tm^{3+} moments. This antiferromagnetic coupling will hinder or benefit the reversal of Cr^{3+} moments or Tm^{3+} moments when the system were cooled under different magnetic field.

Keywords: Magnetization reversal; Exchange bias reversal; Magnetism

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1. Introduction

Exchange bias (EB) effect has attracted a great amount of attention owing to its potential applications in spin-valve devices and in magnetic random access memories (MRAM). The EB initially occurs in slightly oxidized cobalt particles by Meiklejohn and Bean in 1956 [1]. It is defined as a shift of the magnetic hysteresis loop along the field axis for a system cooled down in static magnetic field from above the Néel temperature (T_N) of the antiferromagnet. Usually, a negative exchange bias (NEB) is observed, i.e. the hysteresis loop is shifted to the negative direction of H axis. EB with hysteresis loop shifted to positive direction of H axis, on the other hand, is termed as positive exchange bias (PEB). PEB was first observed in FeF₂-Fe bilayers by Nogués et al. [2], and Koon presented calculations of exchange bias in thin films for explaining it [3]. As the sign reversal of the exchange bias field (H_E) between the NEB and PEB has great deal of applications, it arouses intense interest of the researchers. The sign reversal of EB was reported in many heterostructure systems [2-5] and even in structurally single-phase alloys and compounds [6-9].

It is commonly announced that the magnetic coupling is ferromagnetic at the FM-AFM interface when the system exhibits NEB, and a necessary condition for PEB is an antiferromagnetic coupling at the FM-AFM interface [4]. In this paper, we report the EB reversal driven by temperature and cooling field in TmCrO₃. Both of the NEB and PEB were illustrated based on antiferromagnetic coupling between FM component of the canted Cr³⁺ moments (M_{Cr}) and Tm³⁺ moments (M_{Tm}). The antiferromagnetic coupling between Tm³⁺ and Cr³⁺ moments will hinder or benefit the reversal of M_{Cr} or M_{Tm} when the system

were cooled under different field from above T_N to a specific temperature.

Magnetization reversal had been observed in some of perovskite chromite RCrO_3 [10,11]. The widely accepted mechanism model of magnetization reversal is due to the antiferromagnetic coupling between the R^{3+} moments and Cr^{3+} moments. The R sublattice moments is induced by the antiparallel internal field of the canted Cr^{3+} spins. Interestingly, magnetization reversal and EB reversal were observed together frequently [8,9]. In our previous work [12], we have highlighted the intrinsic association of the two reversals, and the explanation model in YbCrO_3 can also be applicable to TmCrO_3 .

2. Experimental

Polycrystalline sample of perovskite chromite TmCrO_3 were prepared with the conventional solid state reaction method. High purity Tm_2O_3 (99.99%), and Cr_2O_3 (99.9%) powders were mixed according to atomic ratio of Tm: Cr = 1:1. And then, the mixed powder was pressed into pellets and sintered at 1400 °C for 48 hours in the air. The sintering process might be repeated until the sample was identified as single phase by X-ray powder diffraction (XRD). Room temperature XRD measurement was carried out on a PANalytical X-ray diffractometer with Cu $K\alpha_1$ radiation ($\lambda=1.54056$ Å). Magnetic measurements were performed on a physical properties measurement system (PPMS 9 T, Quantum Design).

3. Results and discussion

Figure 1 shows the XRD pattern and the Rietveld refinement results of the crystal structure of polycrystalline TmCrO_3 with the goodness-of-fitting $\chi^2=2.64$. All peaks can be indexed by an orthorhombic structure with Pbnm space group with the lattice parameters of

$a = 5.19672(6)$ Å, $b = 5.49182(6)$ Å, and $c = 7.48290(4)$ Å, respectively. The details of structural parameters of TmCrO_3 were presented in Table 1, indicating a reasonable structural model.

Figure 2 shows the magnetization-temperature curve ($M \sim T$) of polycrystalline perovskite chromite TmCrO_3 . The sample was pre-cooled from 300 K to 5 K in zero-field (ZFC) or in an applied field of 100 Oe (FC), and then measured from 5 K to 200 K under 100 Oe. The inset (a) of Figure 2 shows the reciprocal of the dc magnetic susceptibility vs temperature ($\chi^{-1} \sim T$). The reciprocal of the dc magnetic susceptibility varies linearly with temperature from 135 K ($> T_N \approx 125$ K) to 200 K, obeying the Curie-Weiss law. The effective magnetic moment calculated based on Curie constant is $8.95 \mu_B/\text{f.u.}$ and the Curie-Weiss temperature is about -45 K. The calculated effective magnetic moment is close to the theoretical one ($8.50 \mu_B/\text{f.u.}$). The inset (b) of Figure 2 shows the $M \sim T$ curve measured under an applied field of 10 kOe, which indicates that the magnetization reversal disappears when the cooling field increases to 10 kOe. Previous studies on TmCrO_3 indicate that the Cr^{3+} moments ordered in a canted antiferromagnetic structure with a weak ferromagnetic moment below $T_N = 125$ K and the magnetic structure of the compound is Γ_2 ($F_x \ C_y \ G_z; F_x^R \ C_y^R$) [13,14]. During FC measurement, The sample exhibits negative magnetization at low temperature, and the magnetization gradually changes to positive as temperature increases. The compensation temperature (T_{comp}) is around 28 K. The negative magnetization of TmCrO_3 should be due to the AFM coupling between Tm^{3+} and Cr^{3+} sublattices, as illustrated by Shukla [10] and Cao [11], Cr sublattice moments order at T_N and impose a negative internal field over the R^{3+} moments. Therefore, Tm sublattice

experiences a composite field, which is the sum of the internal field due to Cr sublattice and the external field, and the total magnetization is a superposition of the magnetizations from Cr sublattice and Tm sublattice. Figure 3(a) manifests the coupling scheme of the Cr^{3+} moments (M_{Cr}) and Tm^{3+} moments (M_{Tm}) at different temperature regions, where H is the applied magnetic field and H_{I} is the internal field due to the canted AFM ordered Cr^{3+} spins, respectively. When the temperature is higher than T_{comp} ($T > T_{\text{comp}}$), the M_{Cr} dominates over M_{Tm} ($M_{\text{Cr}} > M_{\text{Tm}}$) and this leads to a positive magnetization. Below the T_{max} , M_{Cr} varies slightly with temperature, while M_{Tm} keeps increase with decreasing temperature, leading to the decrease of total magnetization. M_{Tm} is equal but antiparallel to the M_{Cr} at $T_{\text{comp}} = 28$ K. When the temperature is lower than T_{comp} ($T < T_{\text{comp}}$), the M_{Tm} exceeds the M_{Cr} ($M_{\text{Tm}} > M_{\text{Cr}}$), giving rise to a negative magnetization. In contrast, during ZFC measurement (data collected in warming process), M_{Tm} dominates over M_{Cr} at low temperature, and M_{Tm} aligns to the measuring field. Therefore, the antiferromagnetically coupling M_{Tm} and M_{Cr} were just in the opposite directions compared to those in FC mode [11]. The disappeared magnetization reversal in Figure 2 (b) indicates that when the cooling field increases to 10 kOe (exceeds the negative internal field), the Tm^{3+} moment will flip to the direction of the external field[11,12]. As reported earlier, the minimum value of magnetization (at ~ 10 K) should be brought about by the spin reorientation of Tm^{3+} [14].

The magnetization reversal driven by temperature triggers an interest in magnetic field response of the magnetization of TmCrO_3 in different temperature regions. Interestingly, the EB effect was observed in this system. In order to investigate details about exchange bias field (H_E) in the compound, the $M \sim H$ loops at different temperature were measured

(the range of measuring field is ± 40 kOe) and the sample was cooled down from 200 K to the specific temperature under 10 kOe before each measurement. Figure 4(a) shows the temperature dependence of H_E . The H_E is defined as $H_E = (H_1 + H_2)/2$, where H_1 and H_2 are the right and left coercivity fields in the $M \sim H$ curve [5]. NEB and PEB are observed at high temperature and at low temperature, respectively. The EB reversal occurs around 31 K (T_0) and there are two blocking temperatures ($T_B \approx 10$ K and $T_B' \approx 88$ K) in H_E (T). Figure 4(b) shows the temperature dependence of coercivity field (H_C). The H_C is defined as $H_C = (H_1 - H_2)/2$. There are two peaks and one valley in H_C (T) which are perfectly coincident with the two blocking temperature (T_B and T_B') and the T_0 as shown in H_E (T), respectively.

The temperature-driven EB reversal could be attributed to the coupling between the M_{Cr} and the antiparallel M_{Tm} . As we discussed for the magnetization reversal, the dominant M_{Cr} or M_{Tm} determines the major properties of the system. The AFM coupling between the M_{Cr} and M_{Tm} will hinder the reversal of the greater one of M_{Cr} or M_{Tm} . When the temperature $T > 31$ K, M_{Cr} dominates over M_{Tm} and Tm^{3+}/Cr^{3+} coupled antiferromagnetically. It can be visualized that, during demagnetization process, the AFM coupling between the M_{Cr} and M_{Tm} will hinder the reversal of M_{Cr} and an additional antiparallel applied field (H_E) is required to bring the magnetization towards zero, so the hysteresis loops shift to negative direction of H axis. When the temperature $T < 31$ K, M_{Tm} dominates over M_{Cr} , the antiparallel M_{Tm} will flip to the direction of the applied field and become parallel to M_{Cr} with the increase of measuring field. During demagnetization process, the AFM character of coupling between Tm sublattice and Cr sublattice benefits the reversal of M_{Tm} , leading to a smaller applied field along the negative direction to

achieve zero magnetization. Therefore, the hysteresis loops shift to positive direction of H axis.

The collapse in the width of the $M \sim H$ loop at T_{comp} of H_E (T) had been observed in single crystal of $\text{Nd}_{0.75}\text{Ho}_{0.25}\text{Al}_2$ [8], polycrystalline $\text{LaCr}_{0.85}\text{Mn}_{0.15}\text{O}_3$ [9], etc. Webb et al. [15] had argued that in ferrimagnets the drop in coercive field should commence when temperature is close to T_{comp} . Therefore, the valley in H_C (T) of TmCrO_3 should be attributed to the competition between the M_{Cr} and antiparallel polarized M_{Tm} . As we discussed above, the M_{Cr} varies slightly when the temperature is below T_{max} , while M_{Tm} keeps increase with decreasing temperature till the spin reorientation temperature (T_{SR}). Thus, one may expect that the EB effect can set in at T_B (~ 88 K), when the pinning by the AFM coupled interfacial Tm^{3+} moment becomes strong enough. The EB effect blocked at T_B' (~ 10 K) could be attributed to the spin reorientation of the Tm^{3+} moments. The spin configuration gradually changes from $F_x^R C_y^R$ to F_z^R [13] while the temperature decreases from ~ 21 K to ~ 10 K. This change rotates the direction of the Tm^{3+} moments by 90 degrees which makes the M_{Cr} and M_{Tm} away from collinear. Corresponding to the inset of Fig. 4(b), the dM/dT changed sharply around 21 K. This feature could be identically due to the spin reorientation of Tm^{3+} spins. Since the coupling between the M_{Cr} and M_{Tm} weakened at the blocking temperature, each of them is allowed to order independently. In other words, one component would not strongly affected by the molecular field of the other, leading to the two peaks in H_C (T).

For a further understanding of the EB effect in perovskite chromite TmCrO_3 , we studied the cooling field dependence of the EB at different temperatures. The $M \sim H$

hysteresis loops were measured between ± 40 KOe after the sample of TmCrO_3 was cooled under different field from 200 K to the specific temperatures. As shown in Figure 5, there is no significant change of H_E at 10 K, 40 K and 50 K. The EB reversal driven by cooling field takes place when the system is PEB (20 K, 22 K, 25 K and 30 K,) but there is only irregularly fluctuation when the system is NEB (40 K and 50 K). It is similar to the observations in FeF_2 -Fe and MnF_2 -Fe bilayers [4] and polycrystalline $\text{La}_{1-x}\text{Pr}_x\text{CrO}_3$ [6]. Figure 3(b) manifests the coupling scheme of the Cr^{3+} moments and the Tm^{3+} moments after cooling under low and high field. As we discussed above, when the system was cooled under low field, the AFM character of the coupling between Tm^{3+} and Cr^{3+} benefits the reversal of M_{Tm} during the demagnetization process, leading to a PEB. In contrast, when the compound was cooled under high field, the M_{Cr} and M_{Tm} were forced to align parallel with each other. Therefore, this parallel coupling status will hinder the reversal of M_{Tm} during the demagnetization process, leading to a NEB. However, this parallel statue is unstable and is compelled by the high cooling field due to the fact that the AFM exchange coupling energy became lower than Zeeman energy[2, 11].

4. Conclusions

In summary, the sign reversal of EB driven by both temperature and cooling field in the polycrystalline TmCrO_3 were observed. The elucidation of the observed negative EB and positive EB is given based on the AFM coupling between the M_{Cr} and M_{Tm} which makes TmCrO_3 distinguished from other exchange bias systems. The sign reversal of the H_E driven by temperature is the main principle to design a thermally assisted magnetic random access memory (TAMRAM) [16] and the switching between NEB and PEB driven

by cooling field could be used to design spin-valve devices, magnetic tunnel junctions, etc. [17]. Since both temperature and cooling field can drive the EB reversal, our work is expected to generate a considerable interest among researchers working on films or multilayers to realize a sign reversal of EB and to have more choices for implementing this physical effect in future spintronic devices.

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	x	y	z	$B_{iso}(\text{\AA}^2)$	Occ
Tm(4c)	0.98199 (7)	0.06801 (6)	0.25	0.792 (7)	0.5
Cr (4b)	0	0.5	0	0.827 (17)	0.5
O1(4c)	0.1120 (6)	0.4592 (7)	0.25	0.52 (4)	0.5
O2(8d)	0.6924 (5)	0.3023 (5)	0.0557 (3)	0.49 (4)	1
lattice parameters ($\text{\AA}$): a= 5.19672 (6) b= 5.49182 (6) c= 7.48290 (4)					
Bragg R-factor= 4.41, Rf- factor=4 .36					
Rp= 15.8, Rwp= 17.9					
$\chi^2 = 2.64$					

Table 1. Structural parameters obtained from the Rietveld refinement of XRD pattern of TmCrO₃ with the space group Pbnm.

Figure 1. Rietveld refinement results of the XRD pattern of TmCrO_3

Figure 2. Magnetization-temperature ($M \sim T$) curve of TmCrO_3 measured in ZFC and FC processes under the applied field (H) of 100 Oe, the inset (a) shows the reciprocal of dc magnetic susceptibility vs temperature, the inset (b) shows the $M \sim T$ curve measured under an applied field of 10 kOe.

Figure 3. The scheme diagrams of the Cr^{3+} moments (M_{Cr}) and the Tm^{3+} moments (M_{Tm}) at different temperature regions (a) and at low/high cooling field (b).

Figure 4. The temperature dependence of H_E (a) and H_C (b) measured with a cooling field of 10 kOe; the inset shows the first derivative of magnetic susceptibility vs temperature.

Figure 5. The cooling field dependence of H_E at different temperature.