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## Positive and negative exchange bias effects in the simple perovskite manganite NdMnO<sub>3</sub>

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## Positive and negative exchange bias effects in the simple perovskite manganite NdMnO<sub>3</sub>

### Abstract

Exchange bias effects were studied in the simple perovskite NdMnO<sub>3</sub>. Nd<sup>3+</sup> ordering is induced by the Mn<sup>3+</sup> ferromagnetic component, and they are antiferromagnetically coupled with each other. At 30 K, both negative and positive exchange bias effects are found, which are dependent on the cooling field. The exchange bias fields are around -2400 Oe and 1800 Oe, respectively. Positive and negative exchange bias effects were also observed at 8 K, but the exchange bias fields are only 130 Oe and -120 Oe. The coupling intensity between Nd<sup>3+</sup> ordering and Mn<sup>3+</sup> ordering, and their initial states determine the polarity of the exchange bias fields. © 2012 American Institute of Physics.

### Keywords

manganite, perovskite, simple, negative, effects, positive, bias, exchange, ndmno3

### Disciplines

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## Positive and negative exchange bias effects in the simple perovskite manganite $\text{NdMnO}_3$

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Exchange bias effects were studied in the simple perovskite  $\text{NdMnO}_3$ .  $\text{Nd}^{3+}$  ordering is induced by the  $\text{Mn}^{3+}$  ferromagnetic component, and they are antiferromagnetically coupled with each other. At 30 K, both negative and positive exchange bias effects are found, which are dependent on the cooling field. The exchange bias fields are around  $-2400$  Oe and  $1800$  Oe, respectively. Positive and negative exchange bias effects were also observed at 8 K, but the exchange bias fields are only  $130$  Oe and  $-120$  Oe. The coupling intensity between  $\text{Nd}^{3+}$  ordering and  $\text{Mn}^{3+}$  ordering, and their initial states determine the polarity of the exchange bias fields. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4751990>]

The exchange bias effect usually occurs in ferromagnetic and antiferromagnetic bilayers or multilayers. In such a system, the two coercive fields of the magnetic hysteresis loop are not symmetric, and the centre of the magnetic hysteresis loop shifts to the left or right. A representative system is Co-CoO,<sup>1,2</sup> where Co is ferromagnetic and CoO is antiferromagnetic. In this system, exchange bias occurs at the interface between these two different magnetic materials, and the maximum exchange bias field in this system is  $9500$  Oe.<sup>3</sup> In a similar system, Fe- $\text{Fe}_3\text{O}_4$ ,<sup>4,5</sup> the exchange bias field is about  $120$  Oe, much smaller than that in Co-CoO. Materials with exchange bias effects are widely used in magnetic recording devices.<sup>3,6</sup> In recent years, the exchange bias effect has been found in heterostructures and artificial interfaces, in which the exchange bias effect can be adjustable. In the  $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{BiFeO}_3$  system, the intensity of the exchange bias interaction is found to be dependent on the properties of the ferroelectric domain walls in the  $\text{BiFeO}_3$  layer,<sup>7</sup> which sheds light on how to control the exchange bias effect by an external electric field.<sup>8</sup> A similar study was also reported on the Co/ $\text{BiFeO}_3$  system<sup>9</sup> and the  $\text{BiFeO}_3/\text{YMnO}_3$  system.<sup>10</sup> Interface interaction may induce unique properties and change the magnetic properties of bulk materials, as in a systematic study of the exchange bias effect that was carried out on  $\text{LaNiO}_3$ - $\text{LaMnO}_3$  superlattices.<sup>11</sup> On the other hand, the exchange bias effect can also exist in compounds or composites which allow the coexistence of both a ferromagnetic component and an antiferromagnetic component. Recently, the exchange bias effect was intensively studied in  $\text{La}_{1-x}\text{Pr}_x\text{CrO}_3$  and  $\text{Sr}_2\text{YbRuO}_6$ , in which both positive and negative exchange bias effects can be observed and are dependent on the cooling field and temperature.<sup>12,13</sup> In these two compounds, the exchange bias effect is different from what appears in bilayer and other interface structures. The coupling between the  $\text{Pr}^{3+}$  magnetic rare earth ions and the  $\text{Cr}^{3+}$  transition metal ions at different atomic sites in the  $\text{ABO}_3$  structure determines the properties of the exchange bias effect in  $\text{La}_{1-x}\text{Pr}_x\text{CrO}_3$ .<sup>12</sup> In  $\text{Sr}_2\text{YbRuO}_6$ , however, the

exchange bias effect originates from the Dzyaloshinsky-Moria interaction induced ferromagnetic component and from the antiferromagnetic coupling between the magnetic rare earth ion  $\text{Yb}^{3+}$  and the transition metal ion  $\text{Ru}^{3+}$ , which are in the same atomic site in the  $\text{ABO}_3$  structure. Therefore, it is likely that the exchange bias effect may be observed in some other similar systems. To explore new materials with exchange bias based on this idea, we have chosen to study the simple perovskite manganite  $\text{NdMnO}_3$ , considering that the  $\text{Nd}^{3+}$  spins enter into ferromagnetic ordering, while  $\text{Mn}^{3+}$  is in the antiferromagnetic state at low temperature. Our results show that both a positive and a negative exchange bias effect can be observed for different magnetic states. The cooling field can affect the exchange bias field and change the polarity of the exchange bias effects. A simple scheme is proposed to explain these unique exchange bias effects.

Polycrystalline samples of  $\text{NdMnO}_3$  were made by the traditional solid state reaction method from  $\text{Nd}_2\text{O}_3$  (99.9%) and  $\text{MnCO}_3$  (99.9%) powders bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets  $15$  mm in diameter at  $20$  MPa. Samples were calcined at  $950$  °C for  $10$  h and sintered at  $1450$  °C for  $48$  h. The crystal structures of the samples were examined by X-ray diffraction at room temperature (XRD, model: GBC MMA), using Cu  $K\alpha$  radiation at  $\lambda = 1.54056$  Å. The Rietveld refinement calculations were conducted via FULLPROF software. The magnetic measurements were carried out using a  $5$  T magnetic property measurement system (MPMS) and a  $14$  T physical property measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), over a wide temperature range from  $5$  to  $300$  K.

The results of structural characterization of the sample by XRD are given in Figure 1. We employed Rietveld analysis to refine the diffraction patterns. The quality of the refinement is expressed by the refinement parameter  $\chi^2 = 2.4$ . All XRD peaks can be assigned to the single phase orthorhombic structure with space group  $Pnma$ , and no detectable impurity phase is present. The lattice parameters are  $a = 5.7524$  Å,  $b = 7.5623$  Å, and  $c = 5.4068$  Å, respectively.

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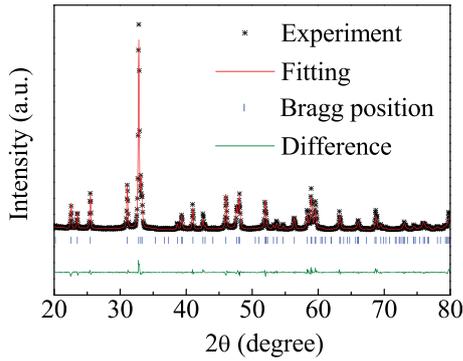


FIG. 1. XRD Rietveld refinement results for NdMnO<sub>3</sub>, with  $\chi^2 = 2.4$  (star symbols, experimental data, and solid red line, fitted pattern from Rietveld structural refinement, respectively). The mismatch between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions.

The temperature dependence of the magnetic moment was measured under both zero field cooling (ZFC) and 5000 Oe field cooling (FC) conditions in warming up mode, and the results are given in Figure 2(a). A clear peak can be identified in the ZFC curve around 13 K, which is assigned to the occurrence of the Nd<sup>3+</sup> long-range ordering. This result is consistent with the neutron diffraction results.<sup>14</sup> When the temperature increases, there is a sudden decrease in the ZFC moment, due to the dropping out of the Nd<sup>3+</sup> long-range ordering. The bump starting at around 79 K (shown by the black arrow) is ascribed to the Mn<sup>3+</sup> magnetic ordering. The Curie-Weiss law fitting over the interval from 150 K to 300 K, as shown in Figure 2(b), gives a positive Curie temperature of about 50 K, indicating that there is relatively strong ferromagnetic interaction in the Mn<sup>3+</sup>

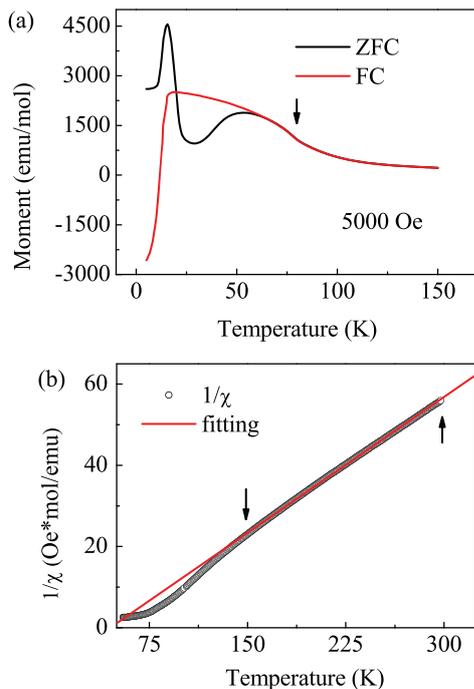


FIG. 2. (a) Zero field cooling and 5000 Oe field cooling temperature dependence of magnetic moment; (b) Curie-Weiss law fitting for spin state calculation.

sublattice. It is also true that we observe an increasing moment below 79 K, which suggests ferromagnetic behaviour. Meanwhile, the Curie-Weiss law fitting also gives a total effective moment of about  $6.0 \mu_B$ . If we calculate the theoretical moment, the high spin state will produce an effective moment of about  $6.09 \mu_B$ , while the low spin state will produce an effective moment of about  $4.59 \mu_B$  (Mn<sup>3+</sup>:  $2.828 \mu_B/\text{atom}$  in the low spin state and  $4.9 \mu_B/\text{atom}$  in the high spin state; Nd<sup>3+</sup>:  $3.62 \mu_B/\text{atom}$ ). The close agreement between the experimental effective moment and the theoretical moment in the high spin state indicates that the Mn<sup>3+</sup> is in the high spin state. This high spin state determines the relatively strong trend towards antiferromagnetic interaction among the Mn<sup>3+</sup> ions, because the Mn<sup>3+</sup> 3d orbital has four electrons. Neutron studies also confirm the antiferromagnetic property of Mn<sup>3+</sup> ordering.<sup>14</sup> Similar to the case of LaMnO<sub>3</sub>, it was reported that the Mn<sup>3+</sup> ordering in NdMnO<sub>3</sub> is also A-type antiferromagnetic ordering.<sup>14</sup> In this case, the ferromagnetic component should originate from the canted A-type antiferromagnetic spin arrangement. The FC moment is negative at low temperature and reaches its maximum value at 13 K. This abnormal phenomenon indicates that the Nd<sup>3+</sup> ordering is antiferromagnetically coupled with the Mn<sup>3+</sup> ferromagnetic component. A higher measuring field, such as 5 T, can force the Nd<sup>3+</sup> spins to flip below 13 K and give a positive total moment (not shown), which follows the trend of a common ZFC and FC temperature dependence of the magnetic moment. Our previous work has claimed that short-range Nd<sup>3+</sup> ordering still exists above 13 K.<sup>15</sup> This means that the Nd<sup>3+</sup> ordering is induced by the strong Mn<sup>3+</sup> ferromagnetic component, which is similar to the case of SmMnO<sub>3</sub>.<sup>16</sup> This phenomenon can also be confirmed by the magnetic hysteresis loops in Figure 3, which will be discussed later. Therefore, in NdMnO<sub>3</sub>, ferromagnetic ordering and antiferromagnetic ordering coexist, and they are coupled with each other. Exchange bias may occur in such a system.

To study the possible exchange bias effect, we measured the magnetic hysteresis loops when the Nd<sup>3+</sup> was in the short-range ordering state at 30 K and in the long-range ordering state at 8 K. The magnetic hysteresis loops at 30 K and 8 K are presented in Figures 3 and 4, respectively. Figure 3 shows the cooling field dependence of the magnetic hysteresis loop at 30 K, after the sample was cooled down from 150 K (which is much higher than the Mn<sup>3+</sup> ordering temperature) to 30 K in various positive cooling fields. The measuring fields range from  $-3$  T to 3 T, in which Nd<sup>3+</sup> spins will remain relatively still, while the Mn<sup>3+</sup> spins will easily follow the external field (as will be discussed later). When the sample is cooled down to 30 K without magnetic field, a nearly symmetric hysteresis loop is obtained, and no obvious exchange bias effect is presented, because of the disordered nature of the ferromagnetic-like initial domain state, as shown in Figure 3(a). However, a significant negative exchange bias effect is observed when the cooling field is 2 T, with the exchange bias field reaching about  $-2400$  Oe, as shown in Figure 3(b). The negative exchange bias effect will become weaker when the cooling field increases to 5 T, at which there is only a shift of about  $-340$  Oe, as shown in Figure 3(c). On the contrary, a significant positive exchange bias effect occurs when the cooling field is 10 T, at which the

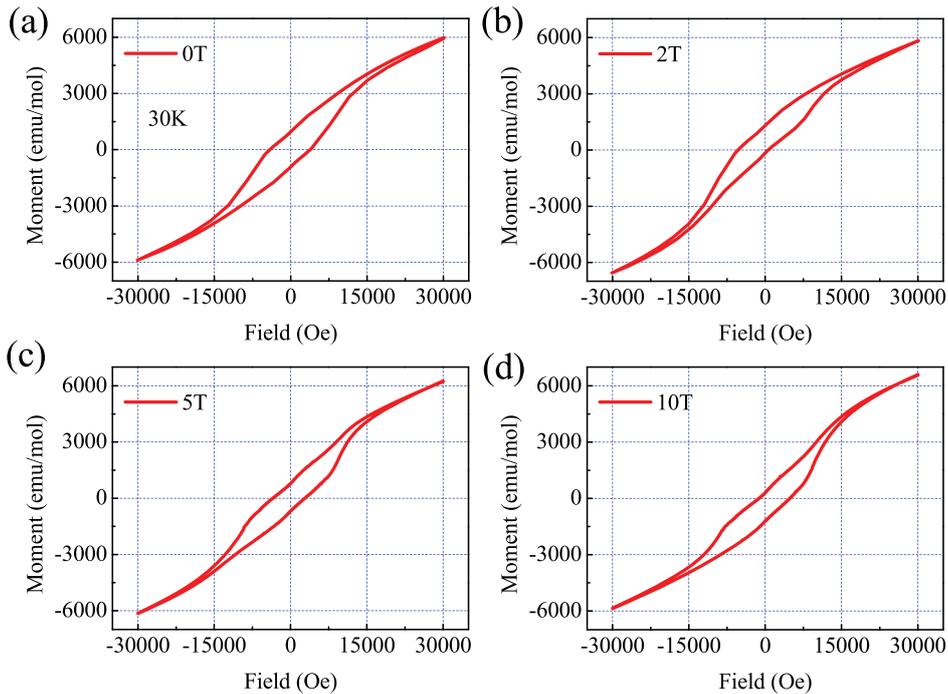


FIG. 3. (a)–(d) Magnetic hysteresis loop measured at 30 K while the  $\text{Nd}^{3+}$  is in the short range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

exchange bias field is about 1800 Oe, as shown Figure 3(d). The cooling field dependence of the exchange bias field at 30 K is presented in Figure 5(a).

On the other hand, Figure 4 presents the cooling field dependence of the magnetic hysteresis loop at 8 K. When the sample is cooled down from 150 K to 8 K in the zero field, below the  $\text{Nd}^{3+}$  ordering temperature, no obvious shift can be observed, as shown in Figure 4(a). However, a positive exchange bias effect can be observed in a 2 T cooling field, and the exchange bias field is about 130 Oe, as shown in Figure 4(b). Because of the strong  $\text{Nd}^{3+}$  ferromagnetic contribution at 8 K, the coercive fields are very strong, and the shift

is not as significant as that measured above the  $\text{Nd}^{3+}$  ordering temperature. When the cooling field increases to 5 T, a negative exchange bias effect occurs with an exchange bias field of about  $-70$  Oe, as shown in Figure 4(c). When the cooling field further increases to 10 T, the exchange bias field reaches  $-120$  Oe, as shown in Figure 4(d). The cooling field dependence of the exchange bias field at 8 K is presented in Figure 5(b). We also measured the exchange bias effect in the vicinity of the  $\text{Nd}^{3+}$  ferromagnetic ordering temperature at 13 K and found that only a very weak exchange bias effect occurs, which can be neglected (not shown). In this case, the exchange bias effect is strongly

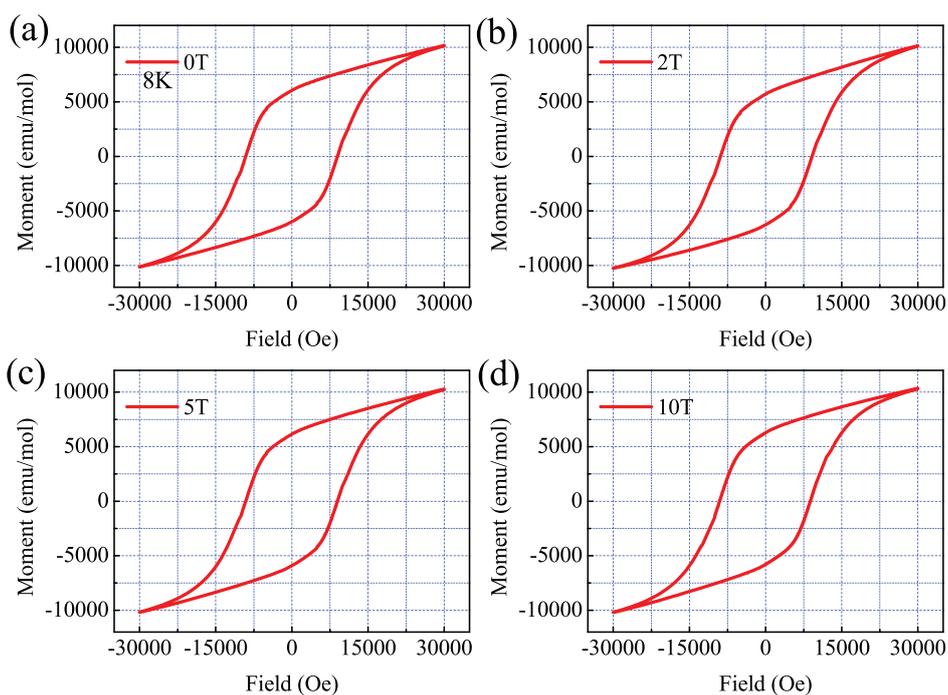


FIG. 4. (a)–(d) Magnetic hysteresis loop measured at 8 K, at which temperature the  $\text{Nd}^{3+}$  is in the long-range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

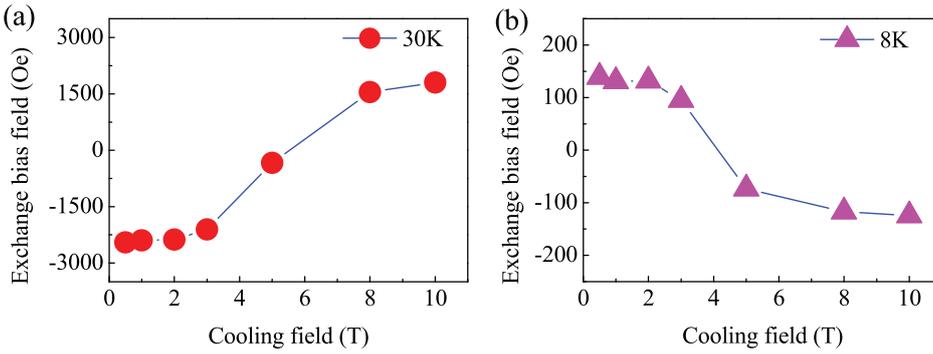


FIG. 5. (a) Cooling field dependence of the exchange bias field at 30K (red solid circles) and (b) cooling field dependence at 8K (pink triangles).

dependent on the coupling intensity between the  $\text{Nd}^{3+}$  ordering and the  $\text{Mn}^{3+}$  ordering, and on the initial states as well.

The positive and negative exchange bias effects take place in different magnetic states, which indicates that their mechanisms may be different. First of all, we discuss the case of the negative exchange bias observed at 30 K. When the  $\text{Nd}^{3+}$  is in the short-range ordering state, local ferromagnetic spin arrangements could form, as shown in Figure 6, which are not strictly antiferromagnetically coupled with the ferromagnetic component of  $\text{Mn}^{3+}$ . When the sample is cooled down in a relatively low cooling field, which does not exceed the exchange field ( $\sim 6$  T, which can be obtained from Figure 5(a)) between  $\text{Mn}^{3+}$  and  $\text{Nd}^{3+}$ , the spin arrangement between  $\text{Mn}^{3+}$  and  $\text{Nd}^{3+}$  spins does not change too much, so that the  $\text{Mn}^{3+}$  spins will be aligned along the cooling field, and the  $\text{Mn}^{3+}$  and  $\text{Nd}^{3+}$  ions still tend to couple with each other antiferromagnetically. A positive measuring field will favour this  $\text{Nd}^{3+}/\text{Mn}^{3+}$  antiferromagnetically coupled state if the maximum field is much smaller than the exchange field. When an opposite measuring field (compared with that of the  $\text{Mn}^{3+}$  ferromagnetic component) is applied, the  $\text{Mn}^{3+}$  ferromagnetic component becomes unstable and begins to break free, which weakens the exchange interaction between  $\text{Mn}^{3+}$  and  $\text{Nd}^{3+}$ . In this case, the antiferromagnetic exchange field is not  $\sim 6$  T any longer, but begins to

decrease, which further favours the switching of  $\text{Mn}^{3+}$  spins. During this process, the  $\text{Nd}^{3+}$  spins remain relatively still and offer a strong pinning force, while the  $\text{Mn}^{3+}$  spins follow the measuring field. Once  $\text{Mn}^{3+}$  spins are aligned along the negative measuring field, the  $\text{Mn}^{3+}$  and  $\text{Nd}^{3+}$  spins are ferromagnetically coupled, which is a metastable state with a ferromagnetic exchange field and could be favoured by the negative measuring field. The  $\text{Nd}^{3+}/\text{Mn}^{3+}$  antiferromagnetically coupled state, however, is more stable in terms of energy than the ferromagnetically coupled state. Therefore, it is much easier for the measuring field to achieve the antiferromagnetically coupled state than to achieve the ferromagnetically coupled state. Consequently, the negative exchange bias effect can be observed. When the cooling field is higher than the exchange field, both  $\text{Nd}^{3+}$  and  $\text{Mn}^{3+}$  ions will be aligned along the external field, and run in the same direction. The positive measuring field favours this metastable  $\text{Nd}^{3+}/\text{Mn}^{3+}$  ferromagnetically coupled state, but it is easy to go back to the more stable antiferromagnetically coupled state once the measuring field changes from positive to negative. A positive exchange bias can then be observed. As illustrated in Figure 6(a), a low positive cooling field could give a negative exchange bias effect because the  $\text{Nd}^{3+}$  spins are always opposite to the direction of the cooling field; when the positive cooling field is very high, high enough to

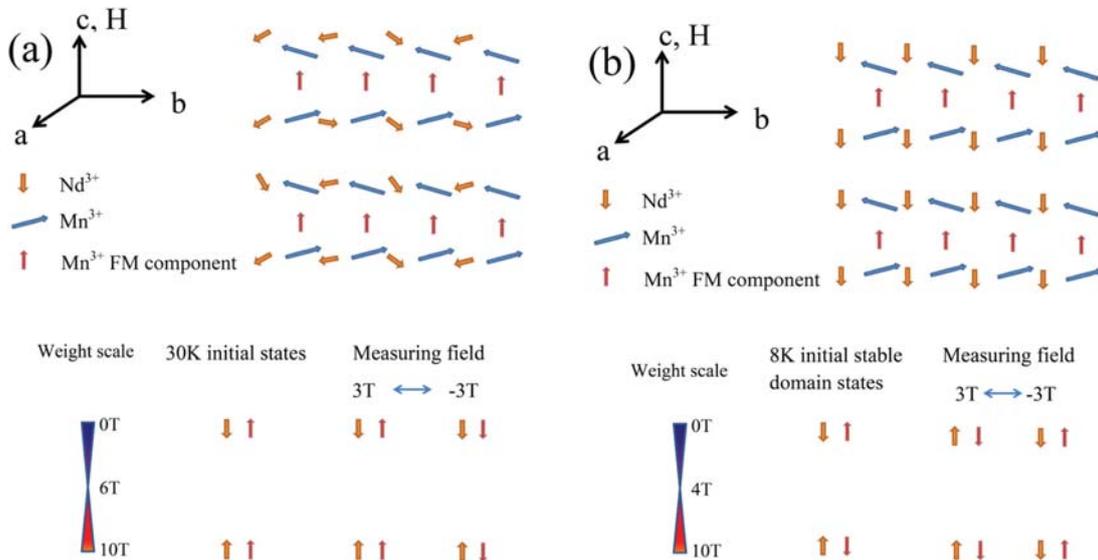


FIG. 6. (a) Scheme of the spin arrangement when  $\text{Nd}^{3+}$  is in the short-range ordering state at 30 K and (b) scheme of the spin arrangement when  $\text{Nd}^{3+}$  is in the long-range ordering state at 8 K.

align both the  $\text{Nd}^{3+}$  spins and the  $\text{Mn}^{3+}$  spins, then a positive exchange bias effect occurs, because the  $\text{Nd}^{3+}$  spins are always along the direction of the cooling field. When the cooling field is moderate, the  $\text{Nd}^{3+}$  spin arrangement will be disturbed, and the ions are unable to order along the same direction any more, but enter into a disorder-like state. In that case, the total pinning force will decrease, and the previous significant negative exchange bias effect will be suppressed.

On the other hand, when  $\text{Nd}^{3+}$  is in the long-range ordering state at 8 K, as shown in Figure 6(b), a strong ferromagnetic spin arrangement is present, which could always antiferromagnetically couple with the ferromagnetic component of the  $\text{Mn}^{3+}$  ordering, considering that the exchange field is about 10 T.<sup>17</sup> Then, the  $\text{Nd}^{3+}$  and  $\text{Mn}^{3+}$  spin system can be simply regarded as a ferromagnetic or ferrimagnetic state at 8 K, and we could also only consider the contribution from  $\text{Nd}^{3+}$  spins because their moments are much larger than those of the  $\text{Mn}^{3+}$  spins. Therefore, when the sample is cooled down from high temperature in an external magnetic field, the ferromagnetic component of the  $\text{Mn}^{3+}$  ordering will be in the direction of the external field above the  $\text{Nd}^{3+}$  ordering temperature. Below the  $\text{Nd}^{3+}$  ordering temperature, the  $\text{Mn}^{3+}$  ions are still aligned along the external cooling field, if it is not high enough to flip all the  $\text{Nd}^{3+}$  spins. Normally, the cooling field should be no more than  $\sim 1$  T, which is the coercive field of  $\text{Nd}^{3+}$  spins, as illustrated in Figure 4. In this case, negative  $\text{Nd}^{3+}$  domains have formed before we measure the hysteresis loop. If the cooling field is higher than  $\sim 1$  T, but lower than the field which could switch all the negative domains, then there are still minority negative domains which could offer a pinning force to prevent the switching of majority domains, as illustrated in Figure 6(b). Consequently, the negative domain state is easier to achieve than the positive domain state, and a positive exchange bias effect occurs. If the cooling field is high enough to flip the  $\text{Nd}^{3+}$  below 13 K or above 13 K, positive domains will form before we measure the hysteresis loop, and then the positive domain state is easier to achieve, and a negative exchange bias effect occurs. Therefore, the exchange bias effects at 8 K stem from domain-domain interaction, which could be suppressed by a very high measuring field.<sup>18,19</sup>

In summary, positive and negative exchange bias effects in the simple perovskite manganite  $\text{NdMnO}_3$  were studied. The temperature dependence of the magnetic moment reveals that  $\text{Mn}^{3+}$  has canted A-type antiferromagnetic ordering below 79 K. On the other hand,  $\text{Nd}^{3+}$  shows long-range ferromagnetic ordering below 13 K and short-range ordering below the  $\text{Mn}^{3+}$  ordering temperature. The ferromagnetic component of the  $\text{Mn}^{3+}$  sublattice is antiferromag-

netically coupled with the ferromagnetic ordering of the  $\text{Nd}^{3+}$  sublattice, which provides the possibility for the exchange bias effect to occur. Systematic magnetic hysteresis loop measurements have confirmed the exchange bias effect. At 30 K,  $\text{Nd}^{3+}$  is in the short-range ordering state, so a significant negative exchange bias effect occurs when the cooling field is relatively small, reaching  $-2500$  Oe when the cooling field is 1 T. Meanwhile, a positive exchange bias can also be achieved by using a big cooling field such as 10 T, in which the exchange bias field reaches 1800 Oe. In addition, a negative cooling field can also switch the negative exchange bias effect to the positive exchange effect, with almost same absolute values of the exchange bias fields. On the other hand, both positive and negative exchange bias effects can also be observed at 8 K. They can reach 130 Oe in 2 T cooling field and  $-120$  Oe in 10 T cooling field, respectively. The polarity of the exchange bias field depends on the coupling intensity between the  $\text{Nd}^{3+}$  ordering and the  $\text{Mn}^{3+}$  ferromagnetic component, and on the initial states as well.

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