

Exchange bias phenomenon in $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) perovskites

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Exchange bias phenomenon, evident of antiferromagnetic–ferromagnetic phase segregation state, has been observed in $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) compounds at low temperatures. A contribution to the total magnetization of the compounds due to the ferromagnetic phase has been evaluated. It has been found that yttrium doping leads to the growth of the ferromagnetic phase fraction. The ferromagnetic phase in the doped compound has a lower coercivity H_c and more rectangular form of the hysteresis loop. The values of the exchange bias field H_{EB} and coercivity are found to be strongly dependent on the cooling magnetic field H_{cool} . In sufficiently high magnetic fields, $H_{cool} > 5$ kOe, H_{EB} in the doped compound is about twice as low as in the parent compound. This difference is attributed to a lower exchange interaction and higher saturation magnetization of the ferromagnetic phase in $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936671>]

1. Introduction

Exchange coupling at the interface between antiferromagnetic (AFM) and ferromagnetic (FM) layers in composite materials results in an additional unidirectional anisotropy of magnetization, the consequence of which is the exchange bias (EB) phenomenon.^{1–3} This effect is manifested as a shift of magnetic hysteresis loops along the

magnetic field axis on the graph, occurring when the material is cooled in an external magnetic field below the magnetic ordering temperature. Nowadays the EB phenomenon is actively studied in view of possible application in recording devices, electronics and spintronics. The main focal point is on artificial systems such as core-shell nanoparticles with the shell exchange-coupled to the core^{1,4} and thin films

composed of exchange-coupled FM and AFM layers.^{2,5–7} In the materials which are single-phase at high temperatures but exhibit spontaneous phase separation at low temperatures due to first-order phase transitions, the exchange bias phenomenon has been found relatively recently. Among these compounds, perovskite manganites^{8–13} and cobaltites^{14–17} should be mentioned. For instance, it was shown that the compound $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ with spontaneous phase separation consists of an antiferromagnetic matrix with embedded ferromagnetic clusters.⁸ The exchange coupling between the FM regions and the surrounding AFM matrix results in unidirectional anisotropy and leads to the exchange bias phenomenon.

As a general theoretical approach to the description of the phenomenon, theoretical models of the EB in AFM single crystals with the perfect^{18–20} and imperfect^{21,22} boundaries have been developed. Later, more sophisticated theoretical models, applicable to the description of the EB in polycrystalline AFM–FM samples with spontaneous phase separation have also been proposed.²³

Manganites $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) of a perovskite structure, which exhibit giant magnetoresistive effect, like $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, are the compounds where spontaneous phase separation in many ways determines their properties.^{24,25} Thus, the compound $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, which is single-phase and paramagnetic at high temperatures, becomes a mixture of AFM and FM phases at low temperature. The martensitic nature of charge ordering in the vicinity of $T_{co} \sim 212$ K leads to phase separation into charge-ordered and charge-disordered phases. This electronic phase separation forms a basis for the magnetic one. Below room temperature, the compound undergoes several successive magnetic phase transitions, two of which are antiferromagnetic at $T_{N1} \sim 130$ K and $T_{N2} \sim 80$ K and one is ferromagnetic at $T_C \sim 70$ K. This is what leads to the ground state, consisting of an AFM charge-ordered matrix with FM charge-disordered inclusions (Fig. 1). According to neutron diffraction data, the total amount of the AFM phase is about 82% and the fraction of the FM phase is about 18% at 4 K.²⁶ This low-temperature AFM–FM state with phase separation has been confirmed in studies using scanning SQUID-microscope.²⁷

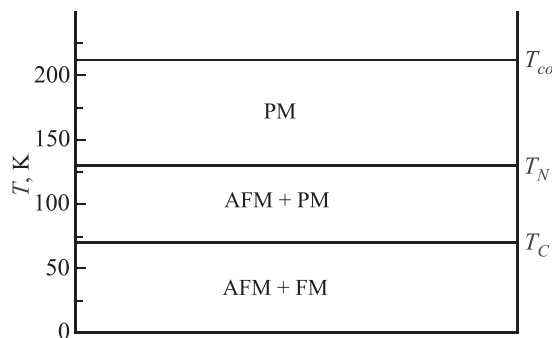


FIG. 1. Magnetic phase diagram of $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. The horizontal lines correspond to the transition temperatures between different magnetic states: PM stands for the paramagnetic phase, AFM + PM and AFM + FM denote the regions of coexistence of antiferromagnetic and paramagnetic phases and antiferromagnetic and ferromagnetic phases, respectively.

Our previous studies have revealed the EB phenomenon in the compound $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$,¹³ which is closely related to spontaneous phase separation. The EB phenomenon depends non-monotonically on temperature and the cooling magnetic field, completely disappearing with the disappearance of the FM phase upon heating. In this paper, we continued to study the EB phenomenon in $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) manganites.

2. Experimental

Polycrystalline $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) samples were obtained by the standard technique of solid-state sintering of the mixture of Nd_2O_3 , Y_2O_3 , CaCO_3 and Mn_2O_3 powders, taken in the desired proportions. After pre-annealing at 900 °C, the powder mixture was pressed into a pellet and baked at 1500 °C for 10 h. The pellets were then cooled slowly in an oven at a rate of 80 °C per hour. The conducted X-ray analysis confirmed that single-phase samples were obtained.

Neutron diffraction studies showed that at room temperature, the crystal structure of both compounds is orthorhombic (space group $Pnma$),²⁸ in agreement with the data of Ref. 29.

Investigation of the magnetic characteristics was performed using a Quantum Design Magnetic Properties Measurement System (MPMS), as well as a custom-made SQUID-magnetometer.³⁰ Magnetic hysteresis was measured at 10 K for the parent $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and the doped $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ compounds in the cases of zero field cooling (ZFC) and field cooling (FC) with $H_{cool} = 0.5, 0.8, 1, 2, 5, 10$ and 20 kOe. In contrast to our earlier studies,¹³ where the magnetic hysteresis loops $M(H)$ were measured between $\pm H_{cool}$, the data in the present study were obtained for ± 20 kOe. After each hysteresis measurement, the sample was heated to 320 K and kept at this temperature for 0.5 h.

3. Results and Discussion

Given the magnetic phase-separation state of the compounds $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$) at low temperatures, consisting of an antiferromagnetic matrix with ferromagnetic inclusions, we should expect the exchange coupling at the interfaces between the coexisting AFM and FM phases, which manifests itself as the EB effect. It was found that all the hysteresis loops $M(H)$ for both compounds studied are symmetrical with respect to the origin when measured after cooling in a zero magnetic field (ZFC). However the loops measured after the samples were cooled in a magnetic field (FC) were shifted towards negative magnetic fields (Figs. 2 and 3).

In the fields above $H \sim 7$ kOe, the hysteresis loops for both compounds collapsed and the total magnetic moment M was almost a linear function of the magnetic field, which is consistent with the data of Ref. 31. This indicates that in the fields above 7 kOe, the magnetization of the ferromagnetic phase has reached the saturation, while the magnetization of the antiferromagnetic phase continues to increase. Since the magnetic moment of the antiferromagnetic phase M_{AFM} depends linearly on the field, we can separate the magnetic

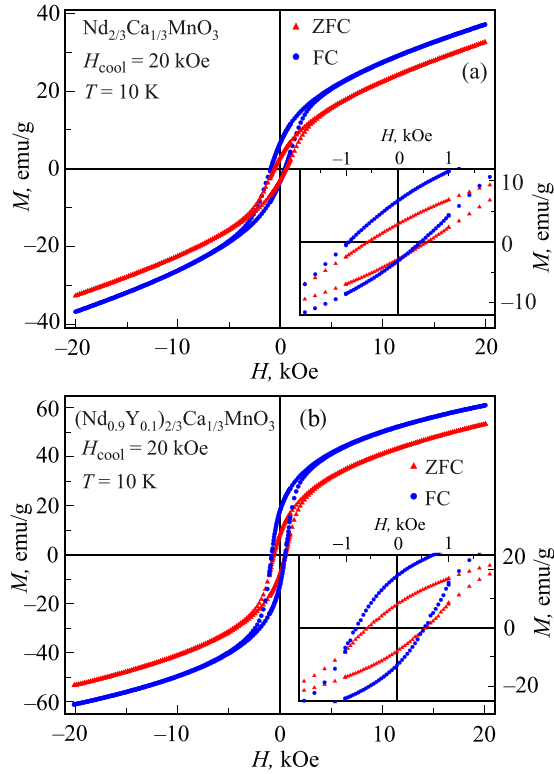


FIG. 2. Magnetic hysteresis loops for $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (a) and $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (b) obtained at 10 K after cooling in zero magnetic field (ZFC) and in a magnetic field $H_{\text{cool}} = 20$ kOe (FC). The insets show enlarged view of the central regions of the hysteresis loops.

contribution of the FM phase M_{AFM} to the total magnetization, by subtracting the AFM contribution from it

$$M_{\text{FM}} = M - M_{\text{AFM}} = M - (dM/dH)H, \quad (1)$$

where the derivative dM/dH is calculated in the linear region of $M(H)$, i.e., for high magnetic fields.

Fig. 4(a) shows the hysteresis loops characterizing the ferromagnetic phases in both compounds studied (AFM contribution is subtracted). The saturation magnetization of the ferromagnetic phase $M_{s-\text{FM}}$ in the doped compound $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ was about two times higher than

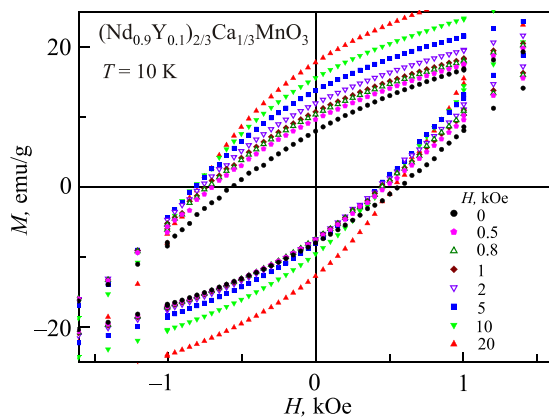


FIG. 3. Magnetic hysteresis loops for $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ obtained at 10 K after cooling in a magnetic field $H_{\text{cool}} = 0.5, 0.8, 1, 2, 5, 10$, and 20 kOe.

that of the parent compound $\text{Nd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, 42 and 19 emu/g, respectively. Doping with yttrium led to a sharp increase in the amount of the ferromagnetic phase. At the same time, the ferromagnetic phase in the doped compound is magnetically softer, as evidenced by a lower value of the coercive force H_c (see inset in Figs. 4(a) and 5(b)) and rectangular shape of the hysteresis loop (Fig. 4(b)).

Cooling in a magnetic field (FC) induces a shift of the magnetic hysteresis loops. The exchange bias field H_{EB} and the coercive force H_c were determined as

$$H_{\text{EB}} = (H_1 + H_2)/2, \quad (2)$$

$$H_c = (H_2 - H_1)/2, \quad (3)$$

where H_1 and H_2 are the values of the magnetic field at which the magnetization becomes zero (Fig. 4(a), inset). For example, in the sample $(\text{Nd}_{0.9}\text{Y}_{0.1})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, cooled to 10 K in an external magnetic field $H_{\text{cool}} = 5$ kOe, the magnetic moment of the FM phase changes sign at $H_1 \sim -0.853$ kOe. For the ascending branch of the hysteresis loop, the magnetic moment of the FM phase changes sign at $H_2 \sim 0.448$ kOe. Substituting these data in Eqs. (2) and (3), we obtain the exchange bias field $H_{\text{EB}} \sim -0.202$ kOe and the coercive force $H_c \sim 0.650$ kOe. The exchange bias indicates the presence of unidirectional anisotropic exchange interactions, which rotate the magnetic moments of the FM clusters to their original direction when the magnetic field is turned off.

Fig. 5 shows the evolution of the exchange bias depending on the cooling magnetic field. Both the exchange bias field H_{EB} and the coercive force H_c depend

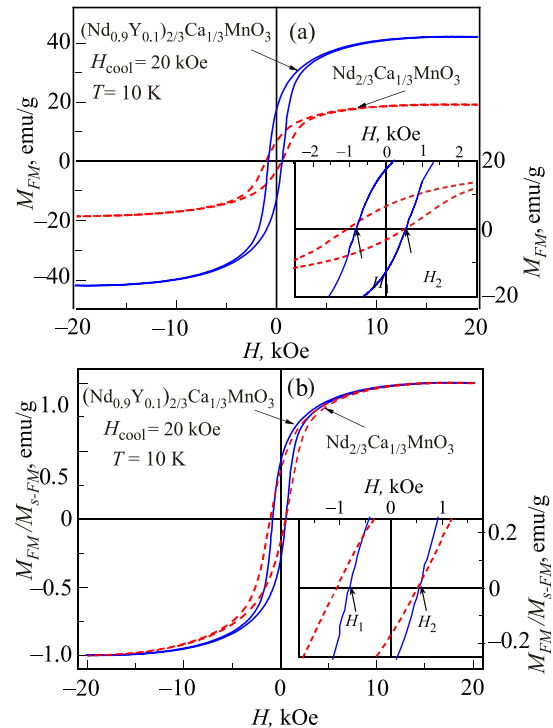


FIG. 4. Contribution of the ferromagnetic phase to the total magnetization of the compounds $(\text{Nd}_{1-x}\text{Y}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ ($x = 0, 0.1$), cooled in a magnetic field $H_{\text{cool}} = 20$ kOe at 10 K (a). Ferromagnetic contributions normalized to the saturation magnetization $M_{s-\text{FM}}$ of the ferromagnetic phase (b). The insets show enlarged central regions of the respective hysteresis loops.

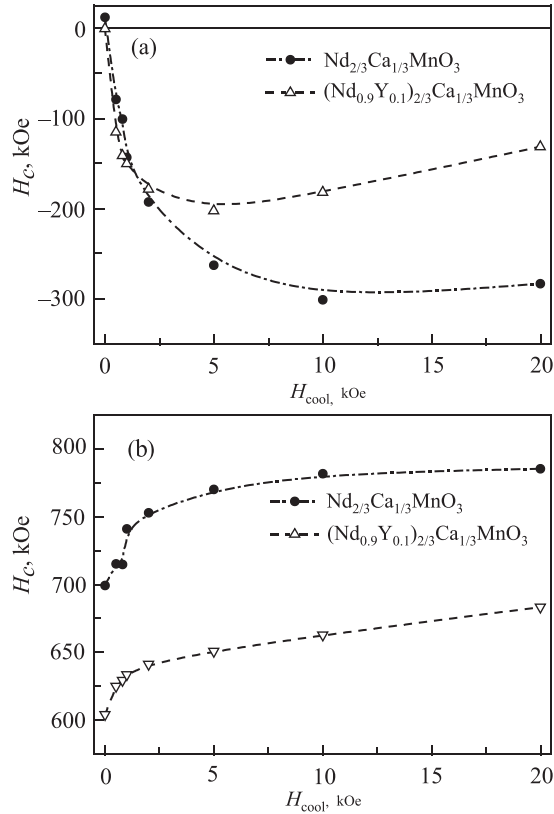


FIG. 5. Dependence of exchange bias field H_{EB} (a) and coercive force H_c (b) on the cooling magnetic field H_{cool} for the compounds $(Nd_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x = 0, 0.1$) at 10 K.

non-monotonically on the cooling magnetic field H_{cool} . The resulting values of the coercive force were significantly higher for the parent compound $Nd_{2/3}Ca_{1/3}MnO_3$ (about 15%), indicating a higher magnetic hardness in this direction. In low magnetic fields, $H_{cool} < 2$ kOe, the effect of the exchange bias increases sharply with an increase in the cooling field, which is characteristic for both compounds studied (Fig. 5). This is due to the fact that at low magnetic fields, not all the FM clusters are involved in the formation of the EB phenomenon, since the anisotropy field of some ferromagnetic particles is greater than the external magnetic field, which tries to rotate the particles. With increasing the magnetic field, an increasing number of FM clusters is involved in the formation of the EB effect, leading to its sharp increase. In a sufficiently high magnetic fields, $H_{cool} > 5$ kOe, the dependence $H_{EB}(H_{cool})$ reaches “quasi” saturation, where the EB field H_{EB} for the doped compound $(Nd_{0.9}Y_{0.1})_{2/3}Ca_{1/3}MnO_3$ is roughly twice as high as that for the parent compound $Nd_{2/3}Ca_{1/3}MnO_3$.

It is known that the magnitude of the exchange bias effect is proportional to the exchange integral J_{ex} and inversely proportional to the saturation magnetization M_s of the ferromagnetic phase M_{s-FM} ¹⁸

$$H_{EB} \sim J_{ex}/M_{s-FM}. \quad (4)$$

Therefore, the observed differences in the exchange bias magnitude for the studied compounds can be associated with a weaker exchange coupling and higher magnetization of the

FM phase in doped $(Nd_{0.9}Y_{0.1})_{2/3}Ca_{1/3}MnO_3$. This agrees well with the fact that the temperatures of all the magnetic phase transitions are shifted toward lower temperatures by 20–30 K in doped yttrium compound, as compared to the parent compound,³² indicating a lower exchange coupling J_{ex} in doped compounds. As was shown above, the saturation magnetization of the FM phase M_{s-FM} is also significantly higher. Therefore, H_{EB} should be lower in the doped compound, which is in agreement with the experimental data (Fig. 5(a)).

Besides that, we also cannot exclude the effect of different area of the AFM-FM interface on the exchange bias, arising due to various sizes and shapes of the FM inclusions in these compounds. Increasing the size of the inclusions with the same content of the ferromagnetic phase should lead to a reduction in the area of the interface and a corresponding decrease of the EB. However, the studied compounds have a different content of the ferromagnetic phase, while evaluation of the form and dispersion of the ferromagnetic clusters is beyond the scope of this paper. Nevertheless, given a lower H_{EB} in the doped compound, it can be concluded that the combined effect of geometric factors is smaller than that of J_{ex} and M_{s-FM} .

4. Conclusions

Exchange bias phenomenon was observed in $(Nd_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ ($x = 0, 0.1$) compounds. It arises upon cooling in a magnetic field below the magnetic ordering temperature and is evident of magnetic AFM-FM phase separation in these compounds at low temperatures. The dependence of the exchange bias field on the cooling magnetic field for these compounds in the AFM-FM phase separation state was studied in a magnetic field up to 20 kOe. The contribution of the FM phase to the total magnetization of the samples was revealed. It was found that the saturation magnetization of the ferromagnetic phase in the doped compound $(Nd_{0.9}Y_{0.1})_{2/3}Ca_{1/3}MnO_3$ is about twice as high as in the parent $Nd_{2/3}Ca_{1/3}MnO_3$, indicating a higher amount of the FM phase in the former. At the same time the ferromagnetic phase of $(Nd_{0.9}Y_{0.1})_{2/3}Ca_{1/3}MnO_3$ is magnetically softer, as evidenced by a lower magnitude of the coercive force H_c and more rectangular shape of the hysteresis loop. It was also found that the value of the exchange bias H_{EB} for the doped compound, which depends non-monotonically on the cooling magnetic field H_{cool} , is about twice as small as in the parent compound for sufficiently large cooling fields $H_{cool} > 5$ kOe. This difference is due to a lower exchange coupling and higher saturation magnetization in the ferromagnetic phase $(Nd_{0.9}Y_{0.1})_{2/3}Ca_{1/3}MnO_3$.

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