Spin-switching energy gap in a compensated $NdFeO_3$ ferrimagnet

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Spontaneous and field-dependent spin switching (magnetization reversal) has been studied in the compensated ferrimagnet $NdFeO_3$. The spin switching temperature T_{sw} monotonically approaches the compensation temperature T_{comp} with an increase in the applied magnetic field above $T_{comp} \approx 9$ K. However, below T_{comp}, a sharp drop in T_{sw} towards low temperatures and a simultaneous increase in the magnetization jump ΔM at T_{sw} were found. The discontinuity in T_{sw} leads to two different T_{sw}–H phase lines shifted in opposite directions in temperature on the T–H plane. These lines are described by two different spin switching energies. The same splitting in the switching energy of 600 emu g^{-1} Oe follows directly from the magnetization jump data, and also coincides with the difference in unidirectional anisotropy energies for positive and negative exchange bias, both found near T_{comp}. This indicates that the split spin switching energy, responsible for the anomaly in the T–H diagram in $NdFeO_3$, arises from the coexistence of two different exchange biases of opposite signs.

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Orthoferrite $NdFeO_3$ is a compensated ferrimagnet [1–4], which exhibits the exotic phenomenon of negative magnetization and associated magnetization reversal due to fast spin switching between two coexisting states with negative and positive magnetization. Such remarkable properties have potential applications in the development of fast switching and magnetic storage devices. Therefore, an important question is what is the nature of the spin switching, what factors can influence the fast magnetization reversal, and what stimulus can cause it.

The magnetic compensation in $NdFeO_3$ occurs due to antiferromagnetic (AFM) exchange interaction between Nd^{3+} and Fe^{3+} spins, which polarizes the Nd^{3+} spins opposite to the weak ferromagnetic (FM) moment, arising from canted AFM order of Fe spins below $T_N = 690$ K [5] due to the antisymmetric Dzyaloshinskii-Moriya (DM) exchange interaction. The polarized paramagnetic moment of Nd spins increases with decreasing temperature, while the weak FM moment of the canted spins of Fe remains unchanging; therefore, two opposite moments annul each other at the compensation temperature T_{comp} of about 9 K. When an external magnetic field is applied, the metastable states with negative magnetization appear near T_{comp}, and the spontaneous or field-induced spin switching to the equilibrium state occurs as soon as the change in the Zeeman energy upon switching overcomes the anisotropy energy barrier [6]. Similar compensated spin structures and switching between them were found in RMO_3 orthorhombic magnetic perovskites (R = rare earth elements, M = Fe, Cr, Mn) [7–13]. However, in contrast to $NdFeO_3$, where the Nd ions remain in a paramagnetic state up to 1 K [2], in the isostructural ferrimagnet $NdMnO_3$ another type of magnetic compensation is observed, namely, two opposite FM components of the ordered sublattices Mn and Nd compensate each other at the ordering temperature of Nd equal to 15 K, which is accompanied by strong structural distortions due to magnetostructural coupling due to Jahn-Teller nature of Mn ions [14,15].

The anisotropic R-Fe exchange induces in orthoferrites the Fe spin reorientation (SR), leading to the weak FM moment rotation from the c axis to the a axis. Temperature of the reorientation, T_{SR}, varies in a wide range because the R-Fe interaction differs significantly in various compounds. In both Nd and Er orthoferrites, the transition occurs at $T_{SR} \approx 100$ K [16,17], and in $SmFeO_3$ at $T_{SR} \approx 480$ K [7].

It has been found that spin switching in compensated Er, Nd, and Sm orthoferrites can be exchange-biased, as evidenced by the hysteresis loops M vs H [18–21]. The exchange bias (EB) field arises and increases when approaching T_{comp} and changes sign when crossing T_{comp}. The EB sign may be changed as well by varying the field cooling (FC) protocol, depending on whether T_{comp} is reached with a decrease or increase in temperature. Recently, it was found that the EB in $ErFeO_3$ also manifests itself in the temperature shift of the hysteresis loops M vs T [21]. This leads to the remarkable feature that the switching temperature T_{sw} depends on EB, and the T_{sw}–H line, which limits the region of metastable states in T–H phase diagram, shifts to the left or right in temperature, depending on whether EB is positive or negative, respectively. This behavior is explained by the fact that the unidirectional EB anisotropy contributes to the energy barrier for spin switching and, therefore, increases or decreases the switching energy and T_{sw} depending on the sign of the EB.

In the present work, we found that the T_{sw}–H line below T_{comp} in a compensated $NdFeO_3$ ferrimagnet with a low T_{comp} is not continuous and monotonic, as is observed in $ErFeO_3$, but has a discontinuity. There are two different T_{sw}–H phase lines shifted in opposite directions in temperature on the T–H

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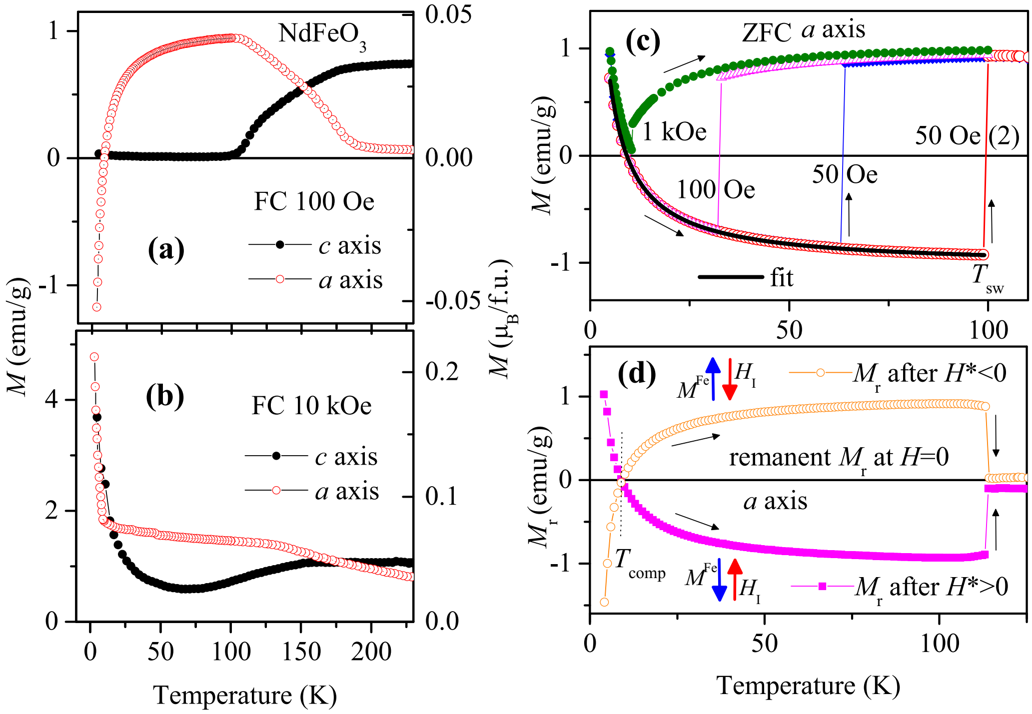

FIG. 1. Temperature dependences of the field-cooled (FC) magnetization of $NdFeO_3$ single crystal measured along the *a* and *c* axes upon cooling in fields of (a) 100 Oe and (b) 10 kOe. *M* vs *T* curves measured upon warming for the *a* axis: (c) in different magnetic fields applied after ZFC; (d) in zero field $H = 0$, which represent two opposite remanent single-domain magnetization M_r, created by a short-term application of a field $H^* = +5$ and -5 kOe at 4 K with two mutually opposite orientations of the FM moment M^{Fe} and internal field H_I. Curve (2) in (c) shows an increase in the switching temperature T_{sw} after a short-term application of a field $H^* > 500$ Oe at 4 K and solid line in (c) represent fit with Eq. (1).

plane, described by two different spin switching energies. This difference of the switching energy turned out to be equal to the difference between the energies of the unidirectional anisotropy for positive and negative EB, both measured near T_{comp}. This proves that the split spin switching energy and the anomalous T_{sw}–H dependence in $NdFeO_3$ arise due to the coexistence of two different exchange biases of opposite signs.

Magnetization measurements were performed on a flux-grown $NdFeO_3$ single crystal with a size of ~2 mm and a mass of 55 mg, which was previously used in the studies of spin switching and exchange bias [3], in the temperature range 3–230 K and in magnetic field up to 15 kOe using a PAR (Model 4500) vibrating sample magnetometer. The *c* axis was identified with x-ray diffraction, and the correct orientation of the *a* and *c* axes along the magnetic field in the magnetometer was established based on the known strong magnetic anisotropy and spontaneous reorientation of the weak FM moment in $NdFeO_3$ [1,4]. Namely, the single crystal was rotated in a small field $H = 100$ Oe and the direction along which the magnetization *M* reached its maximum value at temperatures above the spin reorientation T_{SR} was taken as the direction of the *c* axis, the direction along which *M* showed its maximum value below T_{SR} was established as the *a* axis. A crystal oriented in this way shows rotation of the FM moment from the *c* axis to the *a* axis between temperatures of 185 and 100 K [see Fig. 1(a)]. The magnetization along the *c* axis is 0.74 emu/g at 220 K and along the *a* axis it reaches 0.93 emu/g at 100 K, which agrees well with recent studies [1,4]. Note that each time before starting magnetization measurements in the FC or zero field cooling (ZFC) modes, in order to eliminate or reduce the influence of the previous magnetic history, the sample was demagnetized at 230 K by stepwise reducing the magnetic field to zero with a change in its sign. Curves *M* vs *T* recorded in a weak field, shown in Fig. 1(a), demonstrate that the FM moment directed along the *a* axis below 100 K is completely compensated at $T_{comp} = 9.2$ K, and below T_{comp} a negative FM moment opposite to the applied field arises due to strong magnetic anisotropy. On the contrary, an applied field of 10 kOe strongly suppresses the anisotropy, so both spin reorientation and magnetic compensation are weakly expressed and below 15 K the magnetization along both axes is practically the same [see Fig. 1(b)]. Curves *M* vs *T*, presented in Fig. 1(c), were measured for the *a* axis when heated in various magnetic fields applied at 4 K after ZFC. They show a negative value of *M* and a sharp change in *M* to positive values at temperatures T_{sw}, that are much higher than T_{comp} at a low field, while T_{sw} approaches T_{comp} with increasing field. It was also found that the temperature T_{sw} measured at 50 Oe increases significantly if a field H^* exceeding 500 Oe is applied briefly (for 1 min) at a temperature of 4 K before the measurements. A very similar increase in T_{sw}, which occurs after a short-term application of a strong magnetic field at low temperature, was observed in the $ErFeO_3$ ferrimagnet, and was explained by the field-induced increase in the spin-switching energy barrier [21]. Dependences of the remanent magnetization on temperature, shown in Fig. 1(d), measured at $H = 0$ after a short-term application of a field $H^* = +5$

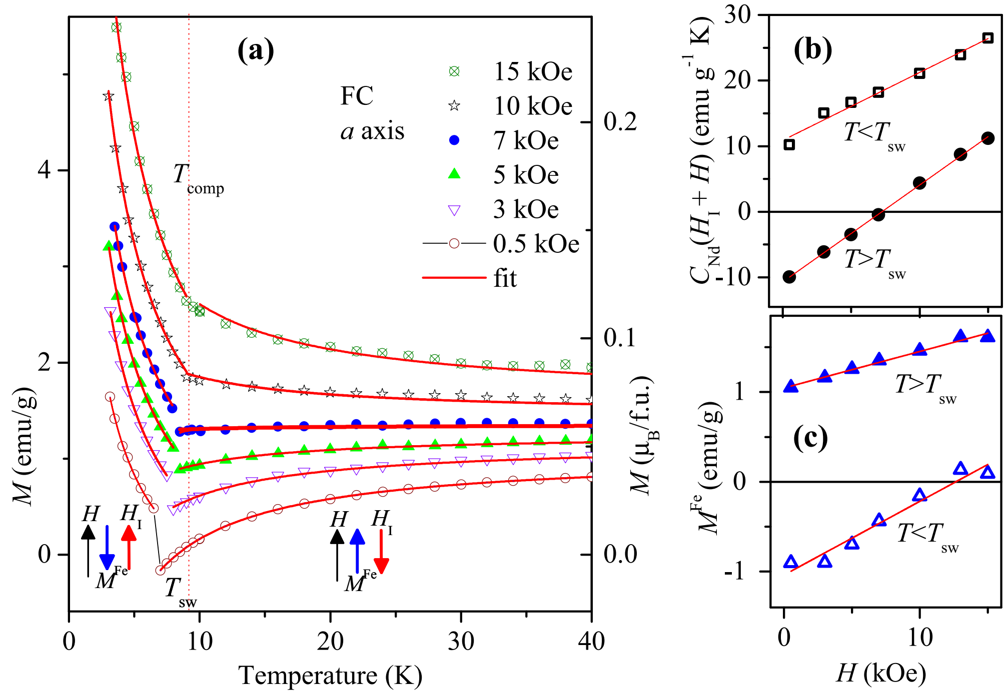

FIG. 2. (a) FC magnetization of $NdFeO_3$ as a function of temperature, measured upon cooling in various magnetic fields applied along the *a* axis. Two opposite orientations of the FM moment M^{Fe} and the internal field H_I are shown above and below the spin switching temperature T_{sw}. Lines in (a) represent fit with Eq. (1) with two fitting parameters, $C_{Nd}(H_I + H)$ and M^{Fe}, shown in (b) and (c) as a function of field *H*, and the lines in (b) and (c) represent the linear fit.

and −5 kOe at 4 K, exhibit two opposite single-domain FM magnetizations with mutually opposite orientations of the FM moment M^{Fe}. Internal field H_I is indicated, which exist up to 114 K and disappear only above 114 K, when spin reorientation already begins (the FM moment deviates from the *a* axis) and, consequently, a multidomain state arises. Both curves intersect at $M = 0$ exactly at $T_{comp} = 9.2$ K and their values of M_r are almost identical in absolute value above T_{comp}, while the unexpected nonzero value of *M* in the multidomain state for the curve with $H^* = +5$ kOe appears due to the nonzero field $H = -2$ Oe instead of the required $H = 0$, which was caused by imperfect stabilization of the magnetic field in this case. Overall, the mirror image of the M_r vs *T* curves well confirms the existence of a strong Fe-Nd AFM interaction, which controls the magnetization in $NdFeO_3$ through the internal field H_I.

The phenomenon of magnetic compensation in $NdFeO_3$ can be satisfactorily described using a simple model, which has been well confirmed for compensated orthoferrites and orthochromites [3,12,21,22]. The model takes into account the weak FM moment M^{Fe} due to the canted AFM ordered spins of Fe and the opposite moment of paramagnetic Nd^{3+} spins induced by the AFM interaction between Fe^{3+} and Nd^{3+} spins, so that the total magnetization in an external field *H* is expressed as

$$M = M^{Fe} + C_{Nd}(H_I + H)/(T - \theta), \quad (1)$$

where $C_{Nd} = Ng^2\mu_B^2 J(J+1)/3k_B$ is the Curie constant, which is equal to 6.5 emu K g^{-1} kOe^{-1} in the case of free Nd^{3+} ions with the ground multiplet $^4I_{9/2}$ $(L = 6, S = 3/2, J = 9/2)$ and $g = 8/11$, H_I is the internal effective exchange field resulting from the Fe-Nd AFM interaction, which induces a paramagnetic moment of Nd spins directed against the M^{Fe} magnetization [it should be noted that the H_I field actually reflects the canted AFM structure of Fe spins and therefore indirectly depends on the antisymmetric DM exchange interaction between Fe spins, so that the H_I is expected to be zero if there is no DM interaction and in consequence no FM moment M^{Fe}], and θ is the Weiss temperature, linked to the AFM interaction between Nd^{3+} spins. It should be noted that M^{Fe} is close to saturation far from the Néel temperature $T_N = 690$ K, since it is considered to follow the Brillouin function $B_{S=5/2}(T)$ for spin $S = 5/2$ and can be considered as independent of temperature below 100 K. Equation (1) was fitted to the dependences of *M* on *T* measured during heating upon warming in a weak field of 50 Oe (see the line in Fig. 1(c) for which the best fitting parameters are: $M^{Fe} = -1.03$ emu/g, $C_{Nd}H_I = 10.8$ emu K/g, and $\theta = -1.2$ K), as well as during cooling in various fields *H* applied along the *a* axis, as shown in Fig. 2(a). These FC curves exhibit the jump in *M* below T_{comp} at T_{sw} at which the mutually opposite magnetization M^{Fe} and the internal field H_I change their direction with respect to the external field *H*, so that the fields H_I and *H* are opposite at $T > T_{sw}$ and parallel at $T < T_{sw}$ [see Fig. 2(a)]. It is clearly seen that above T_{sw}, the magnetization increases with decreasing *T* at high *H* and decreases in low *H*, while for $H = 7$ kOe it remains practically constant [see bold line in Fig. 2(a)]. This means, according to Eq. (1), that the fields *H* and H_I are opposite and compete, and the external field of 7 kOe completely compensates the internal field H_I, therefore, $H_I \approx -7$ kOe. Since for each field *H* there are two opposite spin configurations, the fitting was carried

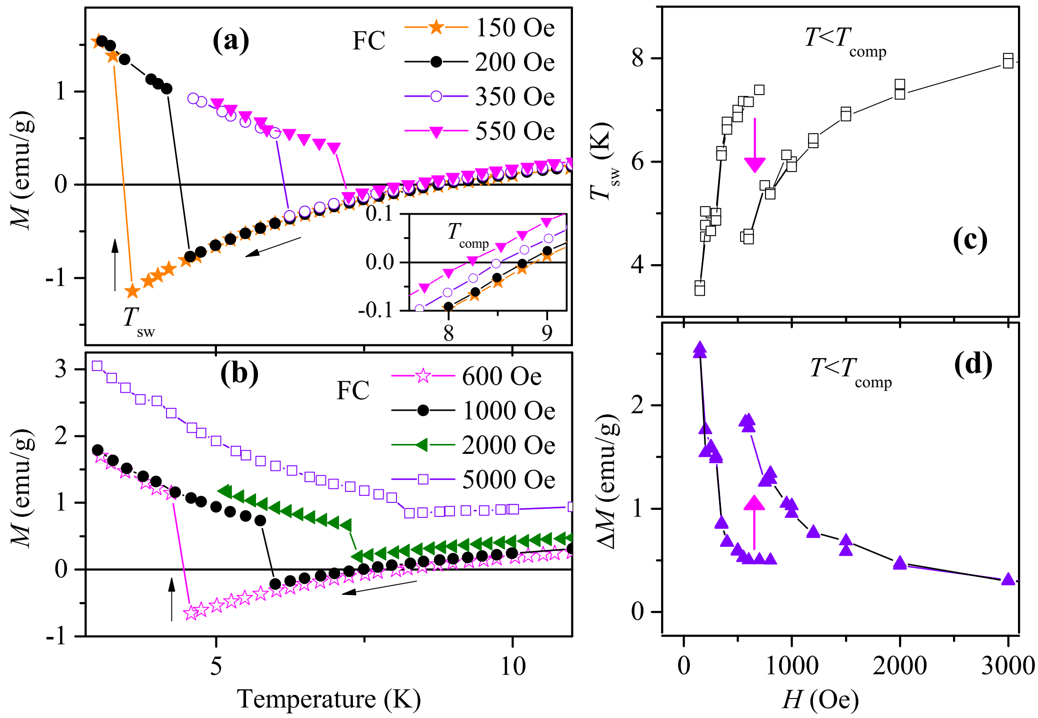

FIG. 3. (a), (b) Field-cooled M vs T curves at several fields H along the a axis show a monotonic increase in the switching temperature T_{sw} with increasing H and an unexpected drop in T_{sw} by 2.5 K as H changes from 550 to 600 Oe. Inset in (a) shows the decrease in temperature T_{comp}, at which $M = 0$, with increasing H. (c), (d) Field dependences of the temperature T_{sw} (c) and the magnetization jump ΔM at T_{sw} (d), demonstrating a sharp drop in T_{sw} and a simultaneous increase in ΔM (marked by arrows) in the range of 600–800 Oe.

out for two temperature intervals above and below T_{sw}. Solid lines in Fig. 2(a) are the best fit with Eq. (1) with two fitting parameters, $C_{Nd}(H_I + H)$ and M^{Fe}, which vary linearly with the field H [see Figs. 2(b) and 2(c)]; the value $\theta = -1.2$ K was fixed at fitting. Fit clearly shows that the magnetization M^{Fe} and the exchange field H_I are always mutually opposite and change sign/direction at the switching temperature T_{sw}. The $C_{Nd}(H_I + H)$ vs H line for $T > T_{sw}$ in Fig. 2(b) crosses zero giving the internal field $H_I = -7.3$ kOe. The line slope corresponds to Curie constant $C_{Nd} = 1.48\,\mathrm{emu\,K\,g^{-1}\,kOe^{-1}}$, which is much smaller than the value of $6.5\,\mathrm{emu\,K\,g^{-1}\,kOe^{-1}}$ calculated for free Nd ions, but practically coincides with the value calculated for a completely isolated ground-state Kramers doublet with effective spin 1/2 and $g = 2$. It was also obtained that at $H = 0$, the canted FM moment $M^{Fe} = 1.04$ emu/g is almost the same in value and has different signs above and below T_{sw}, and the value of M^{Fe} increases linearly with the field H when it is directed along H (the canting angle of Fe spins increases with increasing H) and decreases when it is directed against it [see Fig. 2(c)]. It should be noted that the values $H_I = -7.3$ kOe and $M^{Fe} = 1.04$ emu/g obtained here are in good agreement with the internal effective field $H_{eff} = -7.7$ kOe and the canting angle $\alpha = 8.5$ mrad (which corresponds to $M^{Fe} = gS\mu_B \sin\alpha = 0.96$ emu/g for $S = 5/2$, $g = 2$), determined already by Treves for $NdFeO_3$ [5], so the above fit is a good test of magnetic properties of the studied $NdFeO_3$ sample. We also note that qualitatively the same dependence on magnetic field of the magnetization and fitting parameters shown in Fig. 2 were recently observed in compensated $ErFeO_3$ ferrimagnet [21]. Moreover, as the applied field H increases, the switching temperature T_{sw} approaches T_{comp} and the magnetization jump ΔM at T_{sw} collapses [see Figs. 1(c) and 2(a)], similarly to what was observed in $ErFeO_3$ [21] and $GdCrO_3$ [12]. However, unlike $ErFeO_3$ and $GdCrO_3$ crystals, $NdFeO_3$ surprisingly showed an anomalous discontinuous dependence of T_{sw} on H below T_{comp}, namely: with an increase in the cooling field H, the switching temperature T_{sw} normally increases, approaching T_{comp}, over the entire range of fields, but unexpectedly drops by 2.5 K when changing H from 550 to 600 Oe [see Figs. 3(a) and 3(b)]. Interestingly, when T_{sw} jumps towards a lower temperature, the magnetization jump ΔM, which occurs at T_{sw}, simultaneously sharply increases. This unusual behavior was repeated in several series of measurements, and the values of T_{sw} and ΔM as functions of the field H are shown in Figs. 3(c) and 3(d). They show a sharp drop in T_{sw} and a simultaneous increase in ΔM between 600 and 800 Oe, and also show that in the temperature range from 4.5 to 7.5 K, spin switching with the same temperature T_{sw} can occur with two different applied fields. It should be noted that, despite the discontinuity of T_{sw}, the ΔM value corresponds exactly to the temperature, which may indicate that the observed behavior is inherent in $NdFeO_3$ and is not associated with any parasitic magnetic inclusions. In order to prove this assumption, we further analyzed the ΔM vs T dependence within the model, and we get Eq. (1). When the magnetization direction is reversed, the magnetization jump is $\Delta M = 2M$, therefore, according to Eq. (1), the change in M at T_{sw}, which occurs above T_{comp}, is $\Delta M = 2M^{Fe} - 2C_{Nd}H_I/(T_{sw} - \theta)$, and $\Delta M = -2M^{Fe} + 2C_{Nd}H_I/(T_{sw} - \theta)$ when the spin switching occurs below T_{comp}. Figure 4(a) shows the ΔM vs T_{sw} dependence, where the jump ΔM is determined directly from the M vs T curves, as well as the best fits for parameters $M^{Fe} =$

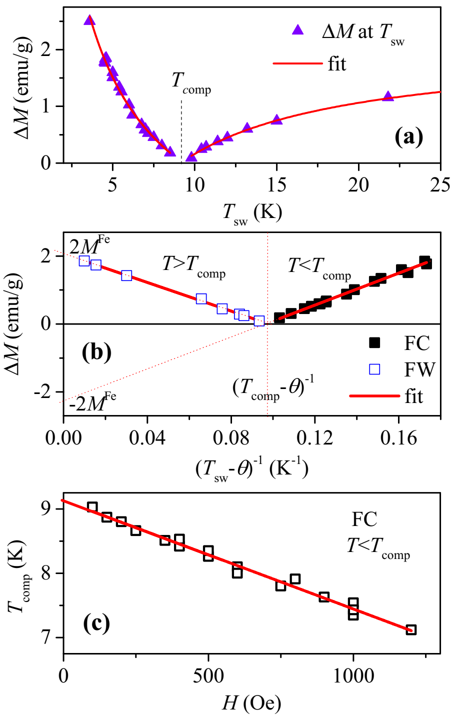

FIG. 4. (a) Dependence of the magnetization jump ΔM on the switching temperature T_{sw}. The lines represent fits by the equation $\Delta M = 2M^{Fe} - 2C_{Nd}H_I/(T_{sw} - \theta)$ for two variable parameters, setting $\theta = -1.2$ K. (b) The jump ΔM at T_{sw}, taken as a function of $(T_{sw} - \theta)^{-1}$ with $\theta = -1.2$ K below and above T_{comp}, and the lines present linear approximation. (c) Decreasing compensation temperature T_{comp} with increasing cooling field H and line is linear fit.

-1.08 emu/g, $C_{Nd}H_I = 11.4\,\mathrm{emu\,g^{-1}}$ K, and $\theta = -1.2$ K, which are close to the values obtained from the above M vs T fit. In Fig. 4(b) the same data ΔM are taken as a function of $(T_{sw} - \theta)^{-1}$, and the lines, which represent linear approximation, intersect at $(T_{comp} - \theta)^{-1} = 0.097\,\mathrm{K^{-1}}$, maintaining $T_{comp} = 9.15$ K and $\theta = -1.2$ K, and $\Delta M = 0$ at T_{comp}. In addition, the compensation temperature calculated with the above parameters as $T_{comp} = -C_{Nd}H_I/M^{Fe} + \theta = 9.35$ K is very close to the measured value. The fact that the magnetization jump ΔM is a smooth function of T_{sw} and is well described by Eq. (1), despite the anomalous discontinuity in T_{sw} and ΔM with a change in the magnetic field, unambiguously indicates that the spin switching is a true reversal of mutually opposite magnetization M^{Fe} and induced paramagnetic moment of Nd^{3+} spins. This conclusion is also supported by the linear decrease in T_{comp} with the FC field H, which is also observed for the region of H where discontinuities T_{sw} and ΔM are pronounced [see Fig. 4(c) and inset of Fig. 3(a)]. Here, a linear fit gives $T_{comp}(H = 0) = 9.13$ K and slope $C_{Nd}/M^{Fe} = -0.00168$ K/Oe, which corresponds to the Curie constant $C_{Nd} = 1.55\,\mathrm{emu\,K\,g^{-1}\,kOe^{-1}}$ in the case $M^{Fe} = -1.08$ emu/g, which agrees well with what was found above from another fit.

Figure 5 shows T–H diagram with the switching temperatures T_{sw} of $NdFeO_3$ at various field H applied along the a axis, determined from the M vs T curves obtained in the FC mode below T_{comp} and in ZFC mode above T_{comp}. The lines

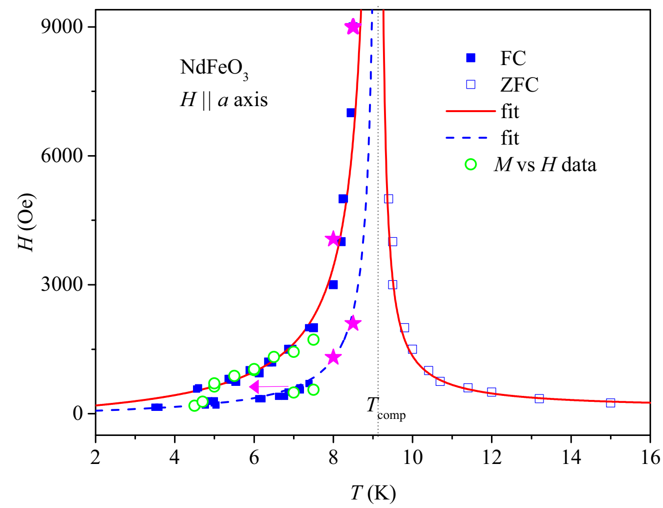

FIG. 5. The spin switching temperature T_{sw} of $NdFeO_3$ as a function of the magnetic field H, determined from the M vs T curves in the FC mode below T_{comp} and in ZFC mode above T_{comp}. The switching fields H_{sw}, determined from the M vs H curves (circles) and from the EB data at $T = 8$ and 8.5 K (asterisks) are also indicated. The lines represent fits with Eq. (2) for the variable parameter $\Delta E_Z/2M^{Fe}$. The arrow shows a sharp drop in T_{sw} as H increases in the range of 600–800 Oe.

T_{sw}–H_{sw} are the boundaries between a metastable state with negative magnetization (at lower H) and an equilibrium magnetic state (at higher H). Near T_{comp}, where the magnetization is very low, the metastable phase propagates into the region of strong magnetic fields. The T_{sw}–H_{sw} line above T_{comp} is very similar to that recently observed for $ErFeO_3$ orthoferrites with $T_{comp} = 45$ K [21]. In contrast to $ErFeO_3$, the anomalous discontinuity in T_{sw}, leading to a double switching field H_{sw} at the same T_{sw}, appears below T_{comp} in $NdFeO_3$. We then analyze the T_{sw} vs H dependence since an understanding of the nature of spin switching will help us to understand the reason for the puzzling jump in T_{sw} below T_{comp}. The spontaneous spin switching is actually a first-order phase transition from a metastable state with the negative magnetization (in this spin configuration the Zeeman energy $E_Z = -MH$ is maximal) to an equilibrium state with positive magnetization and minimum energy E_Z. Consequently, the system must spend the energy required for magnetization reversal by 180° around the a axis in order to overcome the anisotropy energy E_a. This energy is equal to the drop in the Zeeman energy ΔE_Z at T_{sw}. Therefore, spin switching occurs at that temperature at which the modulus of negative magnetization becomes large enough for ΔE_Z to reach the energy barrier E_a. This explains why the temperature T_{sw} is far from T_{comp} at applied small H, and close to T_{comp} at large H. According to Eq. (1), the decrease in the Zeeman energy at spin switching is equal to $\Delta E_Z = \Delta MH = 2[M^{Fe} - C_{Nd}H_I/(T_{sw} - \theta)]H$, and taking into account that $T_{comp} = (C_{Nd}H_I/M^{Fe}) + \theta$, the switching field H_{sw} as a function of temperature can be expressed as follows:

$$H_{sw} = -(\Delta E_Z/2M^{Fe})(T - \theta)/(T - T_{comp}). \qquad (2)$$

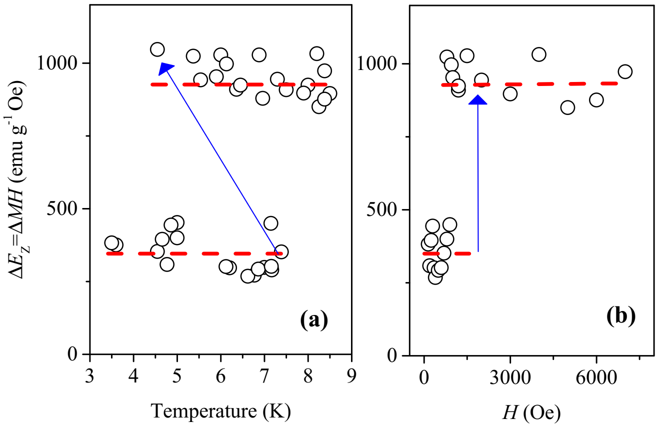

FIG. 6. Spin switching energy ΔE_Z, calculated as ΔMH at T_{sw} directly from the M vs T curves, as a function of (a) temperature and (b) applied magnetic field H. There is a gap in the switching energy at low and high H, and the arrow shows a jump in ΔE_Z as H increases. The dashed lines show the values of $\Delta E_Z = 345$ and $925\,\mathrm{emu\,g^{-1}}$ Oe, obtained as a result of fitting the T_{sw}–H_{sw} line according to Eq. (2), shown in Fig. 5 for low and high fields H, respectively.

This equation was previously successfully used to describe the field dependence of the switching temperature T_{sw} in compensated ferrimagnets $ErFeO_3$ [21] and $GdCrO_3$ [12]. The lines in Fig. 5 represent fits with Eq. (2) for the variable parameter $\Delta E_Z/2M^{Fe}$ while maintaining constant values $T_{comp} = 9.15$ K and $\theta = -1.2$ K. The best fitting value for the line above T_{comp}, $\Delta E_Z/2M^{Fe} = 102$ Oe was obtained, from which we estimate the spin switching energy $\Delta E_Z = 220\,\mathrm{emu\,g^{-1}}$ Oe, taking into account the canted FM moment $M^{Fe} = 1.08\,\mathrm{emu/g}$ as determined above. The data obtained below T_{comp} at temperatures below and above the T_{sw} jump were analyzed separately due to the T_{sw} discontinuity. The solid T_{sw}–H_{sw} line for higher values of H shows the best fitting parameter $\Delta E_Z/2M^{Fe} = 428$ Oe, which corresponds to the switching energy $\Delta E_Z = 925\,\mathrm{emu\,g^{-1}}$ Oe. The dashed line represents the best fit obtained for the low-field switching data, calculated and extrapolated closer to T_{comp} with $\Delta E_Z/2M^{Fe} = 160$ Oe, which corresponds to an energy of $\Delta E_Z = 345\,\mathrm{emu\,g^{-1}}$ Oe. The huge difference in the switching energy ΔE_Z obtained for different regions of fields explains the discontinuity in the T_{sw}–H_{sw} line and its shift away from the T_{comp}. It turns out that an applied field FC above 600–800 Oe causes an increase in the energy barrier for spin switching, and therefore spontaneous magnetization reversal occurs at a lower temperature, when the Zeeman energy $-MH$ is large enough to overcome the increased barrier. On the other hand, the appearance of a gap in ΔE_Z is also clearly seen from the data of the magnetization jump ΔM measured directly at T_{sw}, regardless of the model used. Fig. 6 shows the spin switching energy ΔE_Z, calculated as ΔMH at T_{sw} directly from the M vs T curves, as a function of temperature and applied FC field H. The ΔMH data demonstrate two well-separated energy levels below T_{comp}, which are almost identical to those obtained from the analysis of T_{sw} vs H, see red dashed lines in Fig. 6(a). This fact may indicate that the model used correctly describes the spin switching phenomena. In addition, the dependence of ΔMH on H in Fig. 6(b) clearly shows the field-induced transition from low to high switching energy.

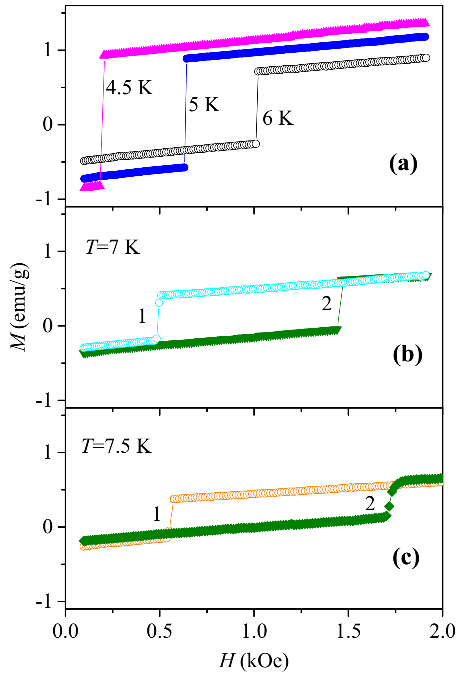

FIG. 7. M vs H curves measured along the a axis at several temperatures below T_{comp} after the same FC procedure in a field of 100 Oe. Two different spin switching fields H_{sw} can be detected in repeated cycles at temperatures of 7 and 7.5 K, see curves 1 and 2 in (b) and (c).

The temperature range between 4.5 and 7.5 K, which exhibits a mysterious splitting of temperature T_{sw} and switching energy ΔE_Z, was further investigated using magnetization curves M vs H measured at different constant temperatures T, presented in Fig. 7. Each magnetization curve began after performing the same FC procedure in a field of 100 Oe from 230 K to a given T. The M vs H curves show a sharp jump in magnetization at spin switching fields H_{sw}, which are shown as open circles in the T–H diagram, see Fig. 5. It appears that the obtained points practically coincide with those determined from the M vs T curves, namely, they are located either on the lower or upper lines T_{sw}–H_{sw}, which are described with different switching energies ΔE_Z. Interestingly, at temperatures of 7 and 7.5 K, spin switching can be detected simultaneously in both the lower and upper H_{sw} fields [see Figs. 7(b) and 7(c)], i.e., a jump in the H_{sw} field is observed, very similar to a temperature jump at fields of about 800 Oe, see Fig. 5. In this case, the gap in switching energy ΔE_Z, calculated as the product $\Delta M \Delta H_{sw}$, also corresponds well to that shown in Fig. 6.

To elucidate the nature of the field-induced transition to states with a high spin-switching energy, which leads to a shift of the T_{sw}–H_{sw} line to low T and high H, we consider possible contributions to the crystal magnetic anisotropy energy E_a, which is actually an energy barrier for spin-switching. Previously, it was shown for a compensated ferrimagnet such as $ErFeO_3$ that, the position of the spin switching line in the T–H plane depends on both the magnitude and the type of

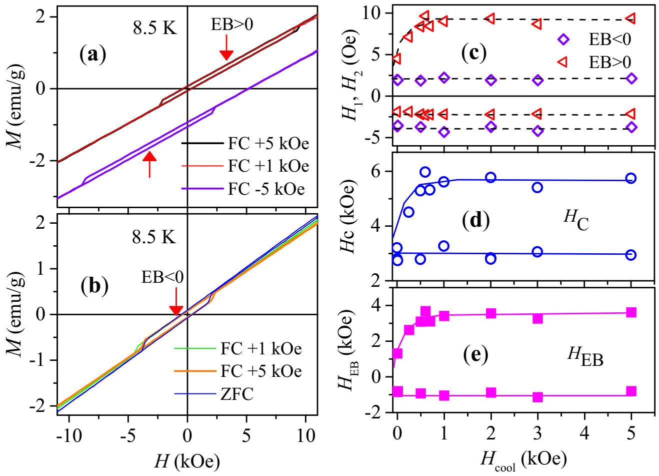

FIG. 8. (a), (b) $NdFeO_3$ magnetization hysteresis loops measured at $T = 8.5$ K, in the field range from 15 kOe to −15 kOe along the *a* axis, and at various cooling fields (the loop for FC −5 kOe is shifted down by 1 emu/g for clarity). Loops randomly show either positive (a) or negative (b) EB field H_{EB}, marked by arrows. (c), (d), (e) For each FC field higher than 800 Oe, two different pairs of switching fields, negative H_1 and positive H_2, are observed, corresponding to two different values of the field H_{EB} and to two average coercive fields H_C (the cases EB > 0 and EB < 0).

magnetic anisotropy [21]. In the case of conventional uniaxial magnetic anisotropy K, which provides the same energy barrier for both spin up and down switching, it turns out that the asteroidlike lines T_{sw}–H_{sw} on the T–H plane limit the region of metastable states (see Fig. 7 in Ref. [21]). This region collapses to the point ($T = T_{comp}, H = 0$) when the anisotropy K decreases to zero. In the case when the unidirectional anisotropy U, which arises due to the exchange bias effect, is added to the uniaxial anisotropy K, the energy barrier for spin switching in one direction of the easy axis increases to a value of $K + U$, and in the opposite direction decreases to $K - U$, since the sign of anisotropy U depends on direction. Consequently, positive anisotropy U shifts the T_{sw}–H_{sw} line further from T_{comp}, and negative anisotropy brings this line closer to T_{comp}. Therefore, it can be assumed that the EB effect, which is known to exist in $NdFeO_3$ near T_{comp} [3], is the cause of the field-induced increase in the spin switching energy and the shift of the T_{sw}–H_{sw} line. Recall that a positive EB (shift of the magnetization hysteresis loop towards field cooling) induced by applied $H_{cool} = 15$ kOe was observed earlier in $NdFeO_3$ below T_{comp} [3]. To elucidate this issue, we studied in detail the EB in $NdFeO_3$ in the vicinity of T_{comp} at various fields FC. Figures 8(a) and 8(b) shows several typical magnetization hysteresis loops between fields of 15 kOe and −15 kOe obtained with different FC modes at $T = 8.5$ K. Surprisingly, the loop measured in the ZFC mode exhibits a negative EB with field $H_{EB} \approx -1000$ Oe, while loops obtained with various H_{cool} from 1 to 5 kOe show randomly either a positive shift $H_{EB} \approx +3500$ Oe, or negative shift $H_{EB} \approx -1000$ Oe. Also, change of the sign of the field H_{cool} symmetrically changes the direction of the loop shift, confirming the occurrence of the positive EB. It turns out that for every FC field greater than 800 Oe, there are two different pairs of switching fields, negative H_1 and positive H_2, [see Fig. 8(c)], corresponding to two different values of the field $H_{EB} = (H_1 + H_2)/2$ [Fig. 8(e)] and to two average coercive fields $H_C = (H_2$–$H_1)/2$ [Fig. 8(d)]. The difference ΔH_{EB} in two different states is 4.5 kOe, and the field H_C is about 5.7 kOe in the case of positive EB and $H_C \approx 3$ kOe in the case of EB < 0. It is noteworthy that the FC field of 800 Oe splits both the exchange bias and the coercive field, and also the same magnitude of the cooling field causes sharp jumps in both T_{sw}, ΔM, and the spin switching energy [see Figs. 3 and 6], which indicates a common origin of these phenomena. The coexistence of positive and negative exchange bias may reflect the existence of two very different spin-switching energies ΔE_Z [see Fig. 6], which are associated with two different magnetic states and describe the lower and upper phase lines T_{sw}–H_{sw} below T_{comp} [see Fig. 5]. This is well confirmed by the coincidence of the positive switching fields H_2, determined from the magnetization hysteresis loops, with the upper line T_{sw}–H_{sw} in the case of a positive EB and with the lower line in the case of a negative EB [see fields H_2 at 8 and 8.5 K marked with asterisks in Fig. 5]. Indeed, if the positive/negative EB is associated to the upper/lower T_{sw}–H_{sw} line shown in Fig. 5, one can distinguish between the two separated levels of spin-switching energies shown in Fig. 6 as follows: $\Delta E_Z1 = K + U_{pos} = 925\,\mathrm{emu\,g^{-1}}$ Oe and $\Delta E_Z2 = K + U_{neg} = 345\,\mathrm{emu\,g^{-1}}$ Oe, where K is the uniaxial anisotropy constant, U_{pos}, and U_{neg} are unidirectional anisotropy energies in the cases of positive and negative EB. It follows that the gap in the spin switching energy is equal to the difference in the anisotropy energies U: ΔE_Z1–$\Delta E_Z2 = U_{pos}$–$U_{neg} = 580\,\mathrm{emu\,g^{-1}}$ Oe. Interestingly, the same result follows directly from the EB hysteresis loops data: considering that $U = \Delta M H_{EB}$ and at $T = 8.5$ K $\Delta M = 0.13$ emu/g, and H_{EB} takes values of 3500 Oe or −1000 Oe (see Fig. 8), we calculate $U_{pos} = 455\,\mathrm{emu\,g^{-1}}$Oe and $U_{neg} = -130\,\mathrm{emu\,g^{-1}}$ Oe, so the difference U_{pos}–$U_{neg} = 585\,\mathrm{emu\,g^{-1}}$ Oe represents the gap in the spin switching energy. In addition, from the relationship $\Delta E_Z1 + \Delta E_Z2 = 2K + U_{pos} + U_{neg} = 1270\,\mathrm{emu\,g^{-1}}$ Oe, we estimate the uniaxial anisotropy constant $K = 472\,\mathrm{emu\,g^{-1}}$ Oe. The above estimates, made on the basis of experimental data obtained by various methods, convincingly indicate that the spin switching energy gap in $NdFeO_3$ arises due to the coexistence of positive and negative EB. However, the nature of the EB field fluctuations between the two opposite values remains unclear. It can be assumed that the magnetization vector of the ferrimagnetic system has two local energy minima, separated from each other by an energy barrier and the studied system can quantum-mechanically tunnel between these metastable magnetic states [23]. A good example for such a phenomenon is tunneling of the magnetic moment of a single-domain ferromagnetic particle between the energy minima created by the magnetic anisotropy [24]. As shown above, $NdFeO_3$ exhibits quantum behavior at low temperatures, which is reflected in the effective spin 1/2 for Nd^{3+} due to the well isolated Kramers doublet in the ground state. It is important to note that the zero-field Zeeman splitting of the ground doublet, caused mainly by the Nd-Fe exchange field, is of about 7 K [2,25]. Therefore, it can be expected that at lower temperatures the upper level of the ground doublet will be less filled, which leads to an increase in the density of states of the lower level. An external magnetic field applied in the FC regime can change the effective Zeeman splitting and, consequently, varies the populations of both levels of the ground doublet. Moreover, the FC field in the temperatures above the switching temperature T_{sw} is opposite to the exchange field, so that the doublet splitting effectively decreases, while below T_{sw} it is directed along the exchange field and the splitting increases. This competition between external and internal fields strongly affects the metastable magnetic state, characterized by negative magnetization and known to be responsible for the positive EB effect in compensated orthoferrites [3,21], while the negative EB is associated with the equilibrium magnetic state. Here, we note that in conventional bilayer FM-AFM systems, the positive EB appears in the case of AFM interaction between layers [26]. The complex interplay of the above effects can push the magnetic system towards one of the two local energy minima through the energy barrier between them during the FC process, resulting in a positive or negative EB effect. However, to elucidate the true reason for the coexistence of opposite EB effects and the appearance of a gap in the spin switching energy in $NdFeO_3$, further studies are required. In particular, one way, expanding the temperature range of magnetic measurements to higher temperatures up to 690 K, in order to be able to start measurements from the paramagnetic state [27], can provide useful information and shed light on the mysterious nature of EB in $NdFeO_3$.

It should also be noted that the observed anomalous discontinuity in the T_{sw}–H phase line may be of interest in connection with very recent discovery of the possibility of toroidal ordering in $NdFeO_3$ obtained in neutron diffraction experiments [28]. It has been suggested [29] that Nd ions possess Dirac multipoles, both magnetic and polar, which are permitted in the monoclinic space group found in $NdFeO_3$ instead of the usual orthorhombic one [28], so this compound is unique, providing strong correlations between anapole and orbital degrees of freedom.

In conclusion, it was found that in the compensated $NdFeO_3$ ferrimagnet, the magnetization M, the spin switching temperature T_{sw}, and the magnetization jump ΔH at T_{sw} are well described within a simple compensation model that includes the competition of the FM moment from the canted spins of Fe and the effective interaction field Nd-Fe, as was found earlier in compensated $ErFeO_3$ and $GdCrO_3$. However, in contrast to these ferrimagnets, below T_{comp} in $NdFeO_3$ there is an anomalous discontinuity in the dependence of T_{sw} on the cooling field H, which actually leads to two different T_{sw}–H phase lines shifted in opposite directions in temperature, which are described by two different spin-switching energies. In an agreement, the same discontinuity of about 600 emu g^{-1} Oe in the switching energy in low and high fields was determined directly from the data on the magnetization jump ΔM at T_{sw}. On the other hand, this switching energy difference turned out to be equal to the difference between the energies of the unidirectional anisotropy for positive and negative EB, both measured near T_{comp}. This convincingly indicates that the split spin switching energy and the anomalous T_{sw}–H dependence in $NdFeO_3$ arise below T_{comp} due to the coexistence of two different exchange biases of opposite signs.

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[1] S. J. Yuan, W. Ren, F. Hong, Y. B. Wang, J. C. Zhang, L. Bellaiche, S. X. Cao, and G. Cao, Spin switching and magnetization reversal in single-crystal $NdFeO_3$, Phys. Rev. B **87**, 184405 (2013).

[2] J. Bartolome, E. Palacios, M. D. Kuz'min, F. Bartolome, I. Sosnowska, R. Przeniosło, R. Sonntag, and M. M. Lukina, Single-crystal neutron diffraction study of Nd magnetic ordering in $NdFeO_3$ at low temperature, Phys. Rev.B **55**, 11432 (1997).

[3] I. Fita, A. Wisniewski, R. Puzniak, E. E. Zubov, V. Markovich, and G. Gorodetsky, Common exchange-biased spin switching mechanism in orthoferrites, Phys. Rev. B **98**, 094421 (2018).

[4] M. H. Mohammed, Zh. Cheng, S. X. Cao, and J. Horvat, Magnetization reversal on different time-scales for $ErFeO_3$ and $NdFeO_3$ single crystals, Phys. Chem. Chem. Phys. **23**, 5415 (2021).

[5] D. Treves, Studies on orthoferrites at the Weizmann Institute of Science, J. Appl. Phys. **36**, 1033 (1965).

[6] A. Kumar and S. M. Yusuf, The phenomenon of negative magnetization and its implications, Phys. Rep. **556**, 1 (2015).

[7] S. Cao, H. Zhao, B. Kang, J. Zhang, and W. Ren, Temperature induced spin switching in $SmFeO_3$ single crystal, Sci. Rep. **4**, 5960 (2014).

[8] J.-H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son, and J. F. Scott, Spin-canting-induced improper ferroelectricity and spontaneous magnetization reversal in $SmFeO_3$, Phys. Rev. Lett. **107**, 117201 (2011).

[9] J. A. de Jong, A. V. Kimel, R. V. Pisarev, A. Kirilyuk, and Th. Rasing, Laser-induced ultrafast spin dynamics in $ErFeO_3$, Phys. Rev. B **84**, 104421 (2011).

[10] J.-S. Jung, A. Iyama, H. Nakamura, M. Mizumaki, N. Kawamura, Y. Wakabayashi, and T. Kimura, Magnetocapacitive effects in the Néel N-type ferrimagnet $SmMnO_3$, Phys Rev. B **82**, 212403 (2010).

[11] R. Huang, S. Cao, W. Ren, S. Zhan, B. Kang, and J. Zhang, Large rotating field entropy change in $ErFeO_3$ single crystal with angular distribution contribution, Appl. Phys. Lett. **103**, 162412 (2013).

[12] I. Fita, R. Puzniak, A. Wisniewski, and V. Markovich, Spin switching and unusual exchange bias in the single-crystalline $GdCrO_3$ compensated ferrimagnet, Phys. Rev. B **100**, 144426 (2019); I. Fita, R. Puzniak, and A. Wisniewski, Pressure-tuned spin switching in compensated $GdCrO_3$ ferrimagnet, *ibid.* **103**, 054423 (2021).

[13] Y. Cao, S. Cao, W. Ren, Z. Feng, S. Yuan, B. Kang, B. Lu, and J. Zhang, Magnetization switching of rare earth orthochromite $CeCrO_3$, Appl. Phys. Lett. **104**, 232405 (2014).

[14] A. Kumar, S. M. Yusuf, and C. Ritter, Nd-ordering-driven Mn spin reorientation and magnetization reversal in the magnetostructurally coupled compound $NdMnO_3$, Phys. Rev. B **96**, 014427 (2017).

[15] Ankita Singh, A. Jain, Avijeet Ray, B. Padmanabhan, Ruchika Yadav, Vivian Nassif, Sajid Husain, S. M. Yusuf, T. Maitra, and V. K. Malik, Spin reorientation in $NdFe_{0.5}Mn_{0.5}O_3$: Neutron scattering and *ab initio* study, Phys. Rev. B **96**, 144420 (2017).

[16] W. Sławiński, R. Przeniosło, I. Sosnowska, and E. Suard, Spin reorientation and structural changes in $NdFeO_3$, J. Phys.: Condens. Matter **17**, 4605 (2005).

[17] Ya. B. Bazaliy, L. T. Tsymbal, G. N. Kakazei, A. I. Izotov, and P. E. Wigen, Spin-reorientation in $ErFeO_3$: Zero-field transitions, three-dimensional phase diagram, and anisotropy of erbium magnetism, Phys. Rev. B **69**, 104429 (2004).

[18] I. Fita, A. Wisniewski, R. Puzniak, V. Markovich, and G. Gorodetsky, Exchange-bias reversal in magnetically compensated $ErFeO_3$ single crystal, Phys. Rev. B **93**, 184432 (2016).

[19] X. Wang, S. Gao, X. Yan, Q. Li, J. Zhang, Y. Long, K. Ruan, and X. Li, Giant spontaneous exchange bias obtained by tuning magnetic compensation in samarium ferrite single crystals, Phys. Chem. Chem. Phys. **20**, 3687 (2018).

[20] S. L. Ding, M. Z. Xue, Z. Y. Liang, Z. Liu, R. B. Li, S. X. Cao, Y. B. Sun, J. J. Zhao, W. Y. Yang, and J. B. Yang, Spin switching temperature modulated by the magnetic field and spontaneous exchange bias effect in single crystal $SmFeO_3$, J. Phys.: Condens. Matter. **31**, 435801 (2019).

[21] I. Fita, R. Puzniak, E. E. Zubov, P. Iwanowski, and A. Wisniewski, Temperature-driven spin switching and exchange bias in the $ErFeO_3$ ferrimagnet, Phys. Rev. B **105**, 094424 (2022).

[22] A. H. Cooke, D. M. Martin, and M. R. Wells, Magnetic interactions in gadolinium orthochromite, $GdCrO_3$, J. Phys. C **7**, 3133 (1974).

[23] E. M. Chudnovsky, Macroscopic quantum tunneling of the magnetic moment (invited), J. Appl. Phys. **73**, 6697 (1993).

[24] E. M. Chudnovsky and L. Gunther, Quantum tunneling of magnetization in small ferromagnetic particles, Phys. Rev. Lett. **60**, 661 (1988).

[25] M. Loewenhaupt, I. Sosnowska, and B. Frick, Spin-reorientation in $NdFeO_3$ and the magnetic excitation spectrum of Nd, J. Phys. Colloques **49**, C8-921 (1988).

[26] J. Nogues, D. Lederman, T. J. Moran, and Ivan K. Schuller, Positive exchange bias in $FeF_2 - Fe$ bilayers, Phys. Rev. Lett **76**, 4624 (1996).

[27] T. Shalini, P. Vijayakumar, and J. Kumar, Studies on structural and magnetic properties of $NdFeO_3$ single crystals grown by optical floating zone technique, Bull. Mater. Sci. **43**, 285 (2020).

[28] P. Fabrykiewicz, R. Przeniosło, and I. Sosnowska, Magnetic, electric and toroidal polarization modes describing the physical properties of crystals. $NdFeO_3$ case, Acta. Crystallogr. A **79** 80 (2023).

[29] S. W. Lovesey, Orthoferrite with a hidden lanthanide magnetic motif: $NdFeO_3$, Phys. Rev. B **107**, 214426 (2023); see also: S. W. Lovesey, T. Chatterji, A. Stunalt, D. D. Khalyavin, and G. van der Laan, Direct observation of anapoles by neutron diffraction, Phys. Rev. Lett. **122**, 047203 (2019).