Twofold spin reorientation and field-induced incomplete phase transition in single-crystal Dy$_{0.5}$Pr$_{0.5}$FeO$_3$

Hailong Wu, Shixun Cao,* Ming Liu, Yiming Cao, Baojuan Kang, Jincang Zhang, and Wei Ren†

Department of Physics, and International Center of Quantum and Molecular Structures, Shanghai University, Shanghai 200444, China

(Received 9 June 2014; revised manuscript received 18 September 2014; published 13 October 2014)

We report an intriguing twofold spin reorientation transition of type $\Gamma_4(G_x, A_y, F_z) \rightarrow \Gamma_1(A_x, G_y, C_z) \rightarrow \Gamma_3(F_x, C_y, G_z)$ for the Fe$^{3+}$ magnetic sublattice near spin reorientation temperatures $T_{SR1} \sim 77$ K and $T_{SR2} \sim 45$ K in a rare-earth orthoferrite Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal. Magnetic-field-induced incomplete spin-configuration transitions ($\Gamma_4 \rightarrow \Gamma_{41} \rightarrow \Gamma_{42}$ for $H = 20$ kOe and $\Gamma_4 \rightarrow \Gamma_{42}$ for $H = 40$ kOe) were observed by measurement of magnetization as a function of temperature. The spin reorientation temperature of a Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal can be controlled by changing the magnitude of the applied magnetic field. We also show that spin reorientation of the $\Gamma_1 \rightarrow \Gamma_4$ type between $T_{SR2}$ and $T_{SR1}$ can be induced by an applied magnetic field along the $c$ axis. The origin of the intriguing magnetic behavior is ascribed to the anisotropic effective field whose strength is determined by the interactions with $R^{3+}(R = $ Dy, Pr) spins and can be modified by the external applied magnetic field. It provides deeper insight into the Fe$^{3+}$-$R^{3+}$ magnetic interaction which dominates the sophisticated magnetic phase transitions in the rare-earth orthoferrites.

DOI: 10.1103/PhysRevB.90.144415 PACS number(s): 75.30.Gw, 75.30.Sg, 75.40.--s, 75.85.+t

I. INTRODUCTION

Emerging technologies are increasingly predicated upon the discovery of novel functional materials that exhibit striking physical properties, such as phase transition and field-induced spin reorientation (SR) transition [1–10]. Materials, such as the rare-earth orthoferrites $R$FeO$_3$ ($R =$ rare-earth ion) with a $Pbnm$ structure, are of fundamental interest and technological importance for potential applications, such as inertia-driven spin switching [11], ultrafast photomagnetic recording, laser-induced ultrafast SR [12], ultrafast manipulation of spins through thermally induced SR transition [13], ambient multiferroics [14], and magnetic biasing on $P-E$ hysteresis loops [15]. Remarkably, some of them surprisingly display magnetic ordering induced ferroelectric polarization.

The Dy$_{0.7}$Tb$_{0.3}$FeO$_3$ single crystal even shows a gigantic effect of magnetic-field biasing on $P-E$ hysteresis loops under a rapid $E$ sweep. The bias $E$ field can be controlled, and its sign can be reversed by changing the sign of $H$ or the relative direction between $P$ and $M$ [15]. Certainly, many future device applications are possible in such a class of materials [16–20]. However, before this is vigorously pursued, better knowledge of their properties needs to be established.

$R$FeO$_3$ compounds have a distorted perovskite structure. Their low symmetry combined with spin-orbital coupling gives rise to an antisymmetric exchange interaction as described by Dzyaloshinskii [21], Moriya [22], and Treves [23] in addition to the antiferromagnetic exchange interaction [24]. The weak ferromagnetic moment of the Fe$^{3+}$ sublattices is approximately 0.04μ$_B$/f.u. (where f.u. represents formula units) at room temperature. Except for nonmagnetic-$R^{3+}$ orthoferrites (YFeO$_3$, LaFeO$_3$, and LuFeO$_3$) and some particular orthoferrites (GdFeO$_3$ and EuFeO$_3$), the antiferromagnetic vector rotates by 90° as the temperature is varied across characteristic SR temperatures; within this temperature range, the equilibrium magnetization could be found in any direction on the (010) plane. This SR phenomenon has been studied in different orthoferrites [2,16,25,26] and is being revived because such a transition might be closely related to the magnetically driven ferroelectricity. In order to uncover the mechanism of this process, the spin dynamics have been investigated by several techniques including terahertz time-domain spectroscopy, ultrafast laser pulses, etc. [12,27,28]. In particular, the SR transition induced by an applied field has attracted increasing interest over the past years. The field-induced SR was studied by neutron diffraction [29], ac magnetic susceptibility measurements [30,31], and spectroscopic study [32–35], etc. Here, we focus our investigations on the twofold SR magnetic transition [36] ($\Gamma_4 \rightarrow \Gamma_{1} \rightarrow \Gamma_{2}$) of Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ from the temperature dependence of the magnetization ($M$-$T$) under external applied fields and hysteresis loops ($M$-$H$) between the two SR transition temperatures. By comparing with the hysteresis loops at different temperatures, we monitor the relative change magnitude of critical fields ($H_{c2}$) for the Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal. Then we compare our observations to the effective-field model and evaluate the temperature dependence of the critical magnetic field.

II. EXPERIMENTAL DETAILS

A single crystal of Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ was grown in a four-mirror optical floating-zone furnace (FZ-T-10000-H-VI-P-SH, Crystal System Corp.) by using four 1-kW halogen lamps as the infrared radiation source with flowing air. Temperature of the molten zone was precisely controlled by adjusting the power of the lamps. During the growth process, the molten zone moved upwards at a rate of 2 mm/h, with the seed rod (lower shaft) and the feed rod (upper shaft) counter-rotating at 15 rpm in an air flow of 3 liter/min. The compositional homogeneity and crystal morphology were analyzed by x-ray diffraction and scanning electron microscopy with energy-dispersive x-ray spectroscopy. Laue backreflection was used to check the crystal’s quality and orientation. All results confirmed the high homogeneity of the studied crystals.

*Corresponding author: sxcao@shu.edu.cn
†renwei@shu.edu.cn
Measurements of magnetization as functions of temperature and magnetic field were carried out using physical property measurement system PPMS-9, Quantum Design, Inc. In zero-field-cooling (ZFC) measurements of magnetization, the sample was cooled down to 3 K without a magnetic field, and measurements were performed in the warming up process in the magnetic field. Field-cooled-cooling (FCC) measurement was also performed during the cooling process under an applied magnetic field. All the $M-H$ curves were recorded after the sample was cooled down to the measurement temperature under a zero-field condition from room temperature.

III. RESULTS AND DISCUSSION

Figure 1 presents the temperature dependence of ZFC magnetizations measured under $H = 0.1$ kOe for a Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal along the $a$ and $c$ axes, respectively. One of the major characteristics of Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ is the strong magnetic anisotropy that leads to different temperature dependences of $M_a(T)$ and $M_c(T)$. The sharp transition starting from $T_{SR1} = 77$ K is the onset of the SR of the Fe$^{3+}$ sublattice and is completed at 76 K as seen in the right inset of Fig. 1. The SR where the Fe$^{3+}$ spins reorient from a configuration of canted antiferromagnetism along the $a$ axis with weak ferromagnetism along the $c$ axis to a configuration of antiferromagnetism along the $b$ axis with no effective moment vector below $T_{SR1}$ suggests the transition configuration of type $\Gamma_4 \rightarrow \Gamma_1$, and similar behavior was also observed in DyFeO$_3$ [37,38] and ErCrO$_3$ [39]. In the high-temperature (HT) phase, the Fe$^{3+}$ anisotropy favors the $\Gamma_4$ configuration (see the colored zone marked $\Gamma_4$ in Fig. 1). Once the temperature is slightly below 77 K, the Fe$^{3+}$ spins abruptly change to the $\Gamma_1$ configuration (see the colored zone marked $\Gamma_1$ in Fig. 1). This abrupt SR transition implies that the Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal may find potential use for temperature-induced magnetic-switching devices for a liquid-nitrogen temperature gauge.

Another unique feature of $M-T$ is that below ~45 K, the Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ crystal undergoes a second SR transition to a low-temperature phase which flips the antiferromagnetic vector to the $c$ axis and recovers the weak ferromagnetic moment along the $a$ axis. Such a spin transition can be explained as follows. Below ~45 K, the rare-earth ions are increasingly polarized, and the effective anisotropy field further increases. Then, the free energy $F(\Gamma_2)$ is lower than $F(\Gamma_1)$, and the Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ single crystal undergoes a spin-configuration transition of type $\Gamma_1 \rightarrow \Gamma_2$, (see the $M_a-T$ curve in Fig. 1 from 45 to 25 K, although there is no change observed in the $M_c-T$ curve). Therefore, Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ experiences the spin-configuration transitions of type $\Gamma_4 \rightarrow \Gamma_1 \rightarrow \Gamma_2$, and we name it the twofold SR transition. It should be noticed that DyFeO$_3$ and PrFeO$_3$ possess spin configurations of types $\Gamma_1$ and $\Gamma_2$, respectively. Such an unusual SR transition of type $\Gamma_4 \rightarrow \Gamma_1 \rightarrow \Gamma_2$ results from the interactions between Dy-4$f$ and Pr-4$f$ electrons and their coupling between $R^{3+}$ (Dy, Pr) and Fe$^{3+}$-sublattices. The antiferromagnetic ordering of rare earth $R^{3+}$ spins occurs at $T_N(R) \sim 3.6$ K (as shown in the left inset of Fig. 1) where a divergence of ZFC and FCC $M-T$ curves is clearly seen for a magnetic moment along the $a$ axis. Decreasing the external magnetic field from 100 to 50 Oe can lead to the appearance of a possible antiferromagnetic transition of $R$ moments as well (see the blue curve in the left inset of Fig. 1). It will be interesting to further investigate the reason for such an anomaly in magnetization, whether it is simply due to the change in the coercive magnetic field or the magnetic transition of rare-earth moments.

In order to explore the impact of applied magnetic fields on the magnetizations, we investigated the $M_c-T$ curve measured under the $c$-axis field of different magnitudes. As shown in Fig. 2, SR transition tends to take place at lower temperatures with higher applied fields. This means that the applications of higher magnetic fields modify an addition to field-independent anisotropy and favor the HT phase at lower temperatures. The temperature dependence of magnetization measured in 20 kOe shows two apparent incomplete SR phase transitions of type $\Gamma_4 \rightarrow \Gamma_{41}$ near 45 K and $\Gamma_{41} \rightarrow \Gamma_{42}$ near 28 K, respectively. With further increasing in the applied magnetic

![FIG. 1. (Color online) Temperature dependence of the magnetization of Dy$_{0.5}$Pr$_{0.5}$FeO$_3$ along the $a$ and $c$ axes measured in the external field $H = 0.1$ kOe. The left inset, zoom in for the magnetization (ZFC and FCC) as a function of temperature along the $a$ axis below 9 K; the right inset, zoom in for the magnetization as a function of temperature along the $c$ axis from 72 to 80 K (for highlighting the SR transition).](144415-2)

![FIG. 2. (Color online) Magnetization along the $c$ axis as a function of the temperature measured under different magnetic fields $H = 0.1$, 20, and 40 kOe.](144415-2)
field to \( H = 40 \text{ kOe} \), the SR transition of type \( \Gamma_4 \rightarrow \Gamma_{41} \) is suppressed, and the magnetic configuration of \( \Gamma_1 \) below \( T_{SR1} \) is passively changed to the configuration of \( \Gamma_4 \) for the wide intermediate-temperature (IT) region of 45–77 K. Consequently, only an incomplete SR transition of type \( \Gamma_4 \rightarrow \Gamma_{42} \) is observed in the \( M_c-T \) curve. We can understand this peculiar magnetic behavior by considering that an applied magnetic field \( H \) along the \( c \) axis makes SR towards other axes suppressed or become incomplete. Especially, the \( \Gamma_4 \rightarrow \Gamma_1 \) transition never occurs under a sufficiently strong magnetic field because the free energy of the antiferromagnetic vector towards the \( b \) axis is higher than that towards the \( c \) axis in the temperature range of 45–77 K. Furthermore, it is expected that a magnetic-field-induced SR transition between \( \Gamma_1 \) and \( \Gamma_4 \) should also be observed by measuring \( M-H \) hysteresis curves, which allows us to get further insight into the field-induced SR transition in the rare-earth orthoferrite system.

Now we clarify how the magnetic field induces the \( \Gamma_1 \rightarrow \Gamma_4 \) SR in a \( \text{Dy}_{0.5}\text{Pr}_{0.5}\text{Fe}_3\text{O}_5 \) single crystal and its spin-configuration evolution by showing the magnetization isotherms (\( M-H \) curves) under an applied magnetic field along the \( c \) axis at some selected temperatures as shown in Fig. 3. For temperatures below \( T_{SR1} \), upon applying a magnetic field to a critical value, it triggers a phase transition starting at field \( H_{crL} \) and changes to another stable configuration at a higher field \( H_{crH} \), that is, hence a field-induced SR transition from \( \Gamma_1 \rightarrow \Gamma_4 \) occurs. Note that, for a given applied magnetic field, if the anisotropic effective field is not strong enough, this temperature-induced SR transition may be an incomplete phase transition at lower temperatures (as seen in Fig. 2 \( M-T \) curves under different fields). As mentioned above, the spin configuration of a \( \text{Dy}_{0.5}\text{Pr}_{0.5}\text{Fe}_3\text{O}_5 \) single crystal is \( \Gamma_1 \) below \( T_{SR1} = 77 \text{ K} \), and this configuration remains the same down to \( T_{SR2} = 45 \text{ K} \), followed by a rotation of the antiferromagnetic axis from \( b \) to \( c \) (\( \Gamma_1 \rightarrow \Gamma_2 \)). When a higher magnetic field is applied along the \( c \) axis at temperatures between \( T_{SR2} \) and \( T_{SR1} \), the HT configuration of \( \Gamma_4 \) can be induced or recovered, similar to the report in \( \text{ErCrO}_3 \) [7]. Figure 4 presents the temperature dependence of the applied critical field \( H_{cr} \) as a function of temperature. By comparing the difference \( \Delta H \) between \( H_{crH} \) and \( H_{crL} \) at different temperatures, it is believed that the transition energy is almost a constant.

Finally, based on the effective-field model [40], let us discuss the mechanism of the observed intriguing magnetic behavior of the field-induced SR from \( \Gamma_1 \) to \( \Gamma_2 \). Suppose that the \( \text{Fe}^{3+} \) spin system is rotated by \( \theta \) in the \( a-b \) plane, and the magnetic interactions with \( \text{R}^{3+} \) spins produce two sets of anisotropic effective fields on the \( \text{Fe}^{3+} \) spins along the crystal axes. One set of effective fields has, as illustrated in Fig. 5(a), the same symmetry as the initial \( \Gamma_4 \) spin configuration and is given by

\[
g_{\mu B}H_{13}^{SR}(\Gamma_4) = -g_{\mu B}H_{24}^{SR}(\Gamma_4) = -2(S_R)(\tilde{D}_c + \tilde{D}_a)F_z^R, \tag{1}
g_{\mu B}H_{12}^{SR}(\Gamma_4) = -g_{\mu B}H_{23}^{SR}(\Gamma_4) = 2(S_R)(\tilde{D}_c + \tilde{D}_a)F_z^R, \tag{2}
g_{\mu B}H_{1324}^{SR}(\Gamma_4) = 2(S_R)(J + J')F_z^R. \tag{3}
\]

Here \( g \) is the Lande factor and \( \mu_B \) is the Bohr magneton; \( H_1^z = -H_{24}^y, H_2^z = -H_{24}^y, \) and \( H_{1234}^z \) are the effective fields acting along the \( a, b, \) and \( c \) axes, respectively; \( \tilde{D}_c, \tilde{D}_a, \) and \( \tilde{D}_b \) are antisymmetric exchange interaction constants between \( \text{Fe}^{3+} \) and \( \text{R}^{3+} \) spins; \( J \) and \( J' \) are isotropic exchange interaction constants, and \( F_z^R \) is the net \( \text{R}^{3+} \) exchange interaction

\[
\begin{align*}
\text{FIG. 3. (Color online) Hysteresis loops of a } \text{Dy}_{0.5}\text{Pr}_{0.5}\text{Fe}_3\text{O}_5 \text{ single crystal along the } c \text{ axis at temperatures of } 45, 50, 60, 65, 70, 75, \text{ and } 80 \text{ K. The field was ramped from } 30 \text{ to } -30 \text{ kOe} \text{ and then to } 30 \text{ kOe. } H_{crL} \text{ and } H_{crH} \text{ correspond to the magnetic fields in between the field-induced SR that occurs from } \Gamma_1 \text{ to } \Gamma_4. \\
\end{align*}
\]

\[
\begin{align*}
\text{FIG. 4. (Color online) Critical fields in the field-induced SR at different temperatures.} \\
\end{align*}
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\[
\begin{align*}
\text{FIG. 5. (Color online) Effective field acting on } \text{Fe}^{3+} \text{ spins for the SR of type } \Gamma_4 \rightarrow \Gamma_1, \text{ which is projected on the } a-b \text{ plane for simplicity. (a) Anisotropic effective fields of type } \Gamma_4. \text{ (b) Anisotropic effective fields of type } \Gamma_1. \\
\end{align*}
\]
moment. These effective fields act on the Fe$^{3+}$ spin system of antiferromagnetic and weak-ferromagnetic configurations, respectively. Then, they obviously favor the $\Gamma_4$ configuration. The other set of effective fields has the symmetry of the final $\Gamma_4$ configuration as shown in Fig. 5(b). These similarly defined effective fields,
\begin{align*}
g \mu_B H^{\Gamma_4}_{12}(\Gamma_1) &= -g \mu_B H^{\Gamma_4}_{12}(\Gamma_1) = 2g \mu_B(\tilde{D}_x - \tilde{D}_y)C^R_z, \quad (4) \\
g \mu_B H^{\Gamma_4}_{13}(\Gamma_1) &= -g \mu_B H^{\Gamma_4}_{13}(\Gamma_1) = 2g \mu_B(\tilde{D}_x - \tilde{D}_y)C^R_z, \quad (5) \\
g \mu_B H^{\Gamma_4}_{12}(\Gamma_1) &= -g \mu_B H^{\Gamma_4}_{12}(\Gamma_1) = 2g \mu_B(\tilde{D}_y - \tilde{D}_x)C^R_z. \quad (6)
\end{align*}
act on Fe$^{3+}$ spins and favor the $\Gamma_4$ configurations, where $C^R_z$ is the antiferromagnetic configuration of $R^{3+}$ spins along the $c$ axis. Now, in the IT phase, as the interaction energy with the applied field increases to a critical value $H_c$, the equilibrium between $\Gamma_4$ and $\Gamma_4$ will break down, and thereby the applied field-induced SR occurs. Especially, as the temperature is lowered, the anisotropic effective field increases due to the increase in the $R^{3+}$ moment. Thus, $H_{c1}$ that triggers the SR transition increases with the decrease in temperature. It can be seen that $H_{c1}$ shifts from 0.6 kOe at $T = 75$ K to 20.2 kOe at $T = 45$ K (Fig. 4).

The free energy of an antiferromagnetic system $G_4$ under a higher magnetic field along the $c$ axis is lower than when the antiferromagnetic vectors are parallel to the $b$ axis ($G_5$) since the applied magnetic field changes the anisotropic effective field and favors the $\Gamma_4$ configuration. Thus, a magnetic field parallel to the $c$ axis causes antiferromagnetic vectors to reorient from the $b$ to the $a$ axis ($\Gamma_4 \rightarrow \Gamma_4$). It is the competition between the external magnetic field and the internal anisotropic effective field that determines the field-induced SR in the orthoferrites.

IV. CONCLUSIONS

To summarize, we report the twofold SR transition of type $\Gamma_4 \rightarrow \Gamma_2$ in a single crystal Dy$_{10.5}$Pr$_{0.5}$Fe$_3$O$_7$ and the incomplete field-induced SR phase transition. SR shifts to a lower temperature as the applied magnetic field along the $c$ axis increases, accompanying an incomplete phase transition at lower temperatures. We attribute this to the competition effect between the application of the magnetic field and the internal anisotropic effective field. For the field-induced SR from $\Gamma_1$ to $\Gamma_4$ in the temperature range between $T_{SR2}$ and $T_{SR1}$, the critical field $H_{c1}$ is approximately inversely proportional to $T$. All the results indicate that it is this instability competition that generates the intriguing magnetic phenomena, such as incomplete SR and magnetic-field-induced SR, which constitute the central findings of this study.

ACKNOWLEDGMENTS

This work was supported by the National Key Basic Research Program of China (Grant No. 2015CB921600), the National Natural Science Foundation of China (NSFC, Grants No. 51372149, No. 50932003, and No. 11274222), the QiMingXing Project (Project No. 14QA1402000) of the Shanghai Municipal Science and Technology Commission, the Eastern Scholar Program, and the Shuguang Program (Grant No. 12SG34) from the Shanghai Municipal Education Commission.