Magnetic field induced discontinuous spin reorientation in ErFeO3 single crystal

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Abstract
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Magnetic field induced discontinuous spin reorientation in ErFeO₃ single crystal

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The spin reorientation of ErFeO₃ that spontaneously occurs at low temperature has been previously determined to be a process involving the continuous rotation of Fe³⁺ spins. In this work, the dynamic process of spin reorientation in ErFeO₃ single crystal has been investigated by AC susceptibility measurements at various frequencies and static magnetic fields. Interestingly, two completely discontinuous steps are induced by a relatively large static magnetic field due to the variation in the magnetic anisotropy during this process. It provides deeper insights into the intriguing magnetic exchange interactions which dominate the sophisticated magnetic phase transitions in the orthoferrite systems. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4829468]

In recent years, orthoferrites (RFeO₃, R = rare earths) with the Pbnm structure have gained renewed interest, thanks to their unique physical properties and some potential applications, such as in multiferroics, ultra-fast photomagnetic excitation, and ultra-fast spin switching.1–5 Some of them surprisingly display magnetic ordering induced ferroelectric polarization. In GdFeO₃ single crystal, ferroelectric polarization and magnetization have been successfully controlled by magnetic and electric fields, respectively, which is attributed to the unique feature of composite domain wall clamping of the respective domain walls for the electric and magnetic fields.1

In GdFeO₃ single crystal, ferroelectric polarization is induced by the exchange striction mechanism.6,7 and ultra-fast spin switching.1–5 Some of them are believed to be driven by the exchange striction mechanism.6,7

Room temperature ferroelectricity is observed in SmFeO₃, and the canted antiferromagnetic ordering is responsible for this extraordinary polarization.8 This system is also the subject of considerable research aimed at better understanding of the complex and competing magnetic interactions, which can be modified by many parameters, such as the doping level, temperature, field, and pressure. For example, substitution of Mn in non-multiferroic YFeO₃ (YFe₀.₆Mn₀.₄O₃) effectively induces large magnetocapacitance (18% at 50 kOe) at 320 K and ferroelectricity with a relatively high ferroelectric transition temperature (~115 K).9

The electronic structure of ErFeO₃ has been studied by spectroscopic ellipsometry, showing the charge transfer transitions in octahedral FeO₆ centers.10

Spin reorientation is another attractive characteristic of orthoferrites, in which the direction of the easy axis of magnetization changes from one crystal axis to another.11,12

The following three types of G-type antiferromagnetic (AFM) configurations can be observed for orthoferrites: Γ₁(Aₓ, Gᵧ, Cｚ), Γ₂(Fₓ, Cᵧ, Gｚ), and Γ₄(Gₓ, Aᵧ, Fｚ), following the Bertaut notation.13 Γ₄ is the basal magnetic structure of Fe³⁺ just below the Néel temperature, Tₑl, which is a canted AFM structure with a total ferromagnetic (FM) vector F directed along the c (c/|/z) crystal axis, and an AFM vector G directed along the a (a/|/x) crystal axis.14 For non-magnetic R⁺³⁺ orthoferrites (YFeO₃, LaFeO₃, and LuFeO₃) and some magnetic R⁺³⁺ orthoferrites (GdFeO₃, EuFeO₃, and PrFeO₃), Γ₄ is retained down to the lowest temperature. DyFeO₃ is the only orthoferrite to show a Morin transition, where the Fe³⁺ system spins are reoriented from Γ₄ to Γ₂ around 35 K, at which the AFM spins rotate from the a-axis to the b-axis.15 For all other orthoferrites, such as ErFeO₃, it is commonly believed that the FM vector F continuously rotates from the a-axis (Γ₄) towards the b-axis (Γ₂) while staying in the ac-plane through the intermediate phase (Γ₂₄(Gₓz, Fₓz)),16,17 upon cooling below its Néel temperature, as seen in Fig. 1.

At present, interest in the spin reorientation of orthoferrites is being greatly revived because this transition is closely related to the magnetically driven ferroelectricity. Moreover, laser induced ultra-fast control of this transition has been reported in several orthoferrites, including DyFeO₃, TbFeO₃, and also ErFeO₃.18,19 In order to uncover the mechanism of this process, the spin dynamics have been investigated by several kinds of technological methods, including terahertz time

![FIG. 1. Simplified magnetic configuration of ErFeO₃ upon cooling below Tₑl, the black arrow at the bottom indicates the decreasing temperature; S₁ and S₂ are the two pairs of spins for Fe³⁺ in the G-type AFM; M₀ is the net FM moment of Fe³⁺ for ErFeO₃, and M₀ is the moment of Er³⁺.](http://dx.doi.org/10.1063/1.4829468)
domain spectroscopy, ultrafast laser pulses, neutron diffraction, etc.15–21 In AC measurements, an oscillating component is added to the static magnetic field, causing a time-dependent moment in the sample, which is a very sensitive probe for detecting a magnetic phase transition initiated by a change in the magnetocrystalline anisotropy energy.22 The spin reorientation process in ErFeO$_3$ that spontaneously occurs at low temperature has been previously determined to be a continuous and coherent rotation of Fe$^{3+}$.23 In the present work, an interesting phenomenon, the discontinuous rotation of Fe$^{3+}$ spins in ErFeO$_3$, has been observed in AC magnetic susceptibility measurements. The possible mechanism for this dynamic process is also proposed.

The material studied in this work is ErFeO$_3$ single crystal. The starting materials for the preparation of feed and seed rods for the floating zone crystal growth were powders of Er$_2$O$_3$ (99.99%) and Fe$_2$O$_3$ (99.99%). The raw materials were manually mixed in stoichiometric amounts and calcined at 1200°C for 24 h in air. After cooling down to room temperature, these samples were thoroughly reground and pressed into a rod with a diameter of 8 mm and a length of 10 cm. Then, the rod was sintered at 1400°C for 24 h in air in order to obtain high quality polycrystalline rods. Single crystals were grown by the floating zone method using an image furnace (Crystal System Inc.). The magnetic measurements were carried out using a 9 T physical properties measurement system (PPMS; Quantum Design). In zero-field cooled (ZFC) measurements of magnetization, the sample was cooled down to 5 K without magnetic field, and the measurements were performed in the warming up process in applied magnetic field. For the field cooled (FC) conditions, the samples were first cooled down to 5 K in cooling fields, and then the measurements were performed in warming-up mode. The AC susceptibility was measured in frequencies ranging from 100 Hz to 5000 Hz while the sample was heated from 83 K to 105 K with ac excitation amplitude ($H_{ac}$) of 1 Oe and static magnetic field ($H_d$) of 0 Oe to 1000 Oe.

Figs. 2(a) and 2(b) display the temperature dependence of the ZFC and FC magnetization for ErFeO$_3$ single crystal at different magnetic fields ($H$) of 200 Oe and 1000 Oe. Below its Néel temperature ($T_N \approx 640$ K) temperature, the Fe$^{3+}$ sublattice is in a canted G-type AFM ordering, resulting in a weak FM.$^{24}$ This can be proved by the hysteresis loop measured at 300 K, as shown in Fig. 2(c). A characteristic feature of R$_m$FeO$_3$ (R$_m$ $^{3+}$, magnetic rare earth ion) is the presence of two magnetic sublattices of Fe$^{3+}$ and R$_m$$^{3+}$, in which Fe$^{3+}$–Fe$^{3+}$, R$_m$$^{3+}$–Fe$^{3+}$, and R$_m$$^{3+}$–R$_m$$^{3+}$ exchange interactions coexist. The competition between these interactions gives rise to interesting and complex magnetic properties. Among these interactions, the Fe$^{3+}$–O–Fe$^{3+}$ superexchange interaction in ErFeO$_3$ is the dominant one, with Fe$^{3+}$–O–Fe$^{3+}$ bond angle close to 144°,25 which contributes to the AFM ordering with a weak FM component. The weak FM is attributed to the antisymmetric Dzyaloshinskii–Moriya (DM) exchange interaction ($D_iS_i \times S_i$) (where $D_i$ is the exchange interaction intensity, and $S_i$ and $S_j$ are the two nearest spins) between neighbouring spins induced by the spin-orbit interaction, which reflects the local crystal anisotropy.$^{11}$

In Figs. 2(a) and 2(b), sudden changes of magnetic moment were observed around 87 K and 97 K, which is in good agreement with the temperature interval of the spin reorientation of ErFeO$_3$.16,26 With decreasing temperature below $T_N$, Er$^{3+}$ is expected to be increasingly polarized, and its effective anisotropy increases, leading to the reorientation of the magnetization of Fe$^{3+}$. With further decreasing temperature, the magnetic moment decreases sharply and approaches zero around 50 K for $H = 200$ Oe and around 75 K for $H = 1000$ Oe. This indicates that the net moments of Fe$^{3+}$ and Er$^{3+}$ are antiparallel to each other due to the superexchange interaction, which is also shown in Fig. 1. The Er$^{3+}$ ions only order below 4.4 K.$^{19}$ This interaction is relatively weak, and the Er$^{3+}$ magnetization can be negligible.
above 100 K. As the temperature decreases, however, the magnetization of Er$^{3+}$ increases, and the total moments of the Fe$^{3+}$ and Er$^{3+}$ sublattices are cancelled at a point called the compensation point.$^{27}$ Thereafter, the paramagnetic characteristics of the curve mainly originate from the larger magnetic moment of Er$^{3+}$ ($9.59 \mu_B/\text{Er}^{3+}$, $5.9 \mu_B/\text{Fe}^{3+}$), which is gradually enhanced with decreasing temperature. As shown in Fig. 2(c), linear behaviour of the magnetic hysteresis loop was observed at 45 K, confirming the characteristics of the paramagnetic state below the compensation point. In Figs. 2(a) and 2(b), neither a divergence between the FC and ZFC curves nor a cusp in the ZFC curve are observed, which rules out spin-glass-like behaviour in ErFeO$_3$.

The dynamic process of spin reorientation in ErFeO$_3$ single crystal was systematically investigated by AC susceptibility measurements with varied $H_{dc}$ and at various frequencies. Figs. 3(a) and 3(b) show the real part ($\chi'$) and imaginary part ($\chi''$) of the AC susceptibility of ErFeO$_3$ as a function of temperature at $H_{ac} = 1$ Oe and $H_{dc} = 0$ Oe, for various frequencies from 100 Hz to 5000 Hz. The real part $\chi'$ is the initial susceptibility, which is related to the variation in the sample magnetization, and $\chi''$ is non-zero if the magnetic energy is absorbed by the sample.$^{28}$ With zero static magnetic field, a clear peak is observed around 96 K where the starting of the spin reorientation occurs. With decreasing temperature, both $\chi'$ ($T$) and $\chi''$ ($T$) change slightly to form plateau-like peaks. Thereafter, they decrease steeply at the end of this transition, showing another peak at about 87 K. The position of the platform shows almost no dependence on the frequency of the oscillating field. It is noticeable, however, that there is a two-step process during the rotation of the FM vector $\mathbf{F}$ from the $c$-axis towards $a$-axis. The AC susceptibility of TmFeO$_3$ single crystal also changes irregularly with temperature, with a step-like shape.$^{29}$ This suggests a well-developed and rich magnetic structure in that particular temperature region.

The static magnetic field has especially strong effects on the dynamic susceptibility of ErFeO$_3$ in the spin reorientation temperature region (87 K–97 K). When $H_{dc}$ increases to 100 Oe, the two-step process becomes more distinctive, as seen in Figs. 3(c) and 3(d). With increasing frequency, the peak at low temperature shifts to lower temperature while the peak at high temperature moves to higher temperature, resulting in greater separation of the two peaks. Similar
behaviour was also observed in TbFeO$_3$ at 2.8 K $\leq$ T $\leq$ 10 K. The slope change in the $\chi'$(T) and the relatively large maximum of $\chi''$(T) around 3.6 K are believed to be originated from the ordering of Tb$^{3+}$. Long-range ordering of Er$^{3+}$, however, does not occur in the temperature range for the spin reorientation of ErFeO$_3$. The spin reorientation of ErFeO$_3$ is mainly related to the rotation of the ferromagnetic vector $\mathbf{F}$ of Fe$^{3+}$. When $H_{dc}$ continues to increase to 500 Oe and 1000 Oe, two completely distinctive peaks are formed at 87 K and 97 K, as shown in Figs. 4(a) and 4(b). This indicates that at higher static magnetic field, discontinuous rotations of the FM vector occur at the beginning and end of the spin reorientation.

The spin reorientation in ErFeO$_3$ reflects the exchange anisotropy evolution with temperature, which emerges from the strong competition between the two magnetic sublattices (Fe$^{3+}$ and Er$^{3+}$). According to the $M$-$H$ hysteresis loops shown in Fig. 2(c), the coercive field at 300 K (above the spin reorientation temperature) is much larger than that at 83 K (below the spin reorientation temperature), which indicates that the magnetic anisotropy of $\Gamma_4$ is larger than that of $\Gamma_2$. Both $\Gamma_4$ and $\Gamma_2$ are stable magnetic states for ErFeO$_3$, with FM vector $\mathbf{F}$ along the $c$ and $a$ crystal axes, respectively. In the temperature region of 87 K–97 K, the intermediate state is metastable, and its anisotropy is expected to be determined by the competition between $\Gamma_4$ and $\Gamma_2$ during the rotation of the FM vector $\mathbf{F}$. With decreasing temperature below $T_N$, due to the large anisotropy and strong pinning force, it is difficult to rotate the FM vector of Fe$^{3+}$ from the $c$-axis at the beginning of the transition. So, a clear peak was observed at 97 K. At the end of the transition (87 K), the ErFeO$_3$ changes from the metastable state to the stable state for the lower temperature ($\Gamma_2$), causing another steep decrease in the moment. When the static magnetic field increases to 100 Oe, the steps in the two-step process become more separated.

With further increase of the static magnetic field to 500 Oe and 1000 Oe, two completely discontinuous steps were observed at the beginning and end of the transition. When the static magnetic field is applied, especially for a higher field, it may couple with vector $\mathbf{F}$ and pull the sublattice magnetization towards the field direction, eventually inducing a spin-flip transition. During the spin reorientation, for ErFeO$_3$, with smaller anisotropy of the metastable state, the FM vector $\mathbf{F}$ is possibly driven towards the field direction by the larger static magnetic field, resulting in deviation from the $ac$-plane. The initial and the final magnetic states, $\Gamma_4$ and $\Gamma_2$, remain unchanged, however, with larger anisotropy and a stronger pinning force. Therefore, the FM vector $\mathbf{F}$ rotates discontinuously, inducing two completely discontinuous steps at the beginning and end of this transition. This result suggests that the spin reorientation process could be manipulated by an external magnetic field and that a magnetic switching device could be designed based on effective control of the spin reorientation process.

The complex dynamic susceptibility of ErFeO$_3$ single crystal has been investigated in order to discover the possible mechanism of its spin reorientation. The static magnetic field shows especially strong effects on the dynamic susceptibility of ErFeO$_3$ during the spin reorientation process. When zero magnetic field is applied, a plateau-like peak is observed in the spin reorientation region. A high static magnetic field drives the transition into two completely discontinuous steps, showing discontinuous rotation of the FM vector at the beginning and end of the transition. Changes in the magnetic anisotropy or the interaction between the external magnetic field and the FM vector in ErFeO$_3$ during the transition account for this intriguing behaviour. Novel magnetic switching devices could be designed based on this work.

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