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# High temperature negative magnetization, spin reorientation and their suppression with magnetic field in $ErFe_{0.55}Mn_{0.45}O_3$ single crystal

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ABSTRACT

$ErFe_{0.55}Mn_{0.45}O_3$ single crystal shows canted antiferromagnetic ordering below 365 K with weak ferromagnetic moment along c axis. On cooling, the magnetic moment is completely suppressed at a certain temperature due to Er and Fe/Mn sublattice compensation, below which negative magnetization is observed. The compensation and negative magnetization temperatures are much higher than those in other orthoferrite systems. There is a spin reorientation transition from $\Gamma_4(G_x, A_y, F_z)$ to $\Gamma_1(A_x, G_y, C_z)$ structure at 255 K along c axis which is not seen along a and b axes. The spin reorientation is tunable with applied magnetic field and is completely suppressed at sufficiently high magnetic field. The behavior is explained by spin configuration and net magnetization orientation of individual Er and Fe/Mn sublattices. The proposed model is further validated by measurements using 'training' protocol.

## 1. Introduction

Rare earth orthoferrites with general formula $RFeO_3$ (R = rare earth ion) were first identified and magnetic properties studied in late 1940s [1]. Since then, they became subjects of fundamental interest and technological importance. Their rich and versatile magnetic properties such as spin reorientation, spin switching, compensation temperature, magnetization reversal and multiferroicity due to R ion ordering ($DyFeO_3$) enable them find potential applications in ultrafast photomagnetic recording, laser induced ultrafast spin reorientation [2], excitation of precession [3], non-thermal spin dynamics [4], inertia driven spin switching [5] and as ambient multiferroics [6]. $RFeO_3$ inherits the orthorhombic crystal structure with space group Pbnm and comprises of two magnetic sublattices associated to 4f electrons of R cation and 3d electrons of Fe ion with each unit cell containing four R and four Fe ions. There are three possible magnetic interactions within $RFeO_3$ which are, R-R, Fe-Fe and R-Fe type. The most striking magnetic features such as spin reorientation, spin switching, magnetization reversal are consequence of interaction between those magnetic sublattices. The strongest one is Fe-Fe interaction which causes G type antiferromagnetic (AFM) ordering of Fe sublattice at relatively high temperature (T~*N* 650–760 K). However, this is not a collinear AFM ordering. Due to Dzyaloshinskii-Moriya (DM) interaction, magnetic moments of G-AFM ordering become canted. Conjoint to the assumption that magnetic and crystallographic unit cell are the same, the compatible magnetic spin configurations of $RFeO_3$ systems can be expressed with eight irreducible representations following Wollan and Bertaut notation ($\Gamma_1$ to $\Gamma_8$) [1]. $\Gamma_5$ to $\Gamma_8$ are not possible since they do not have net moment on iron site which is not consistent with the system. Moreover, $\Gamma_3$ is also not compatible to the observed strong AFM coupling of Fe ions with nearest neighbors. Finally, three configurations are possible for $RFeO_3$ systems which are $\Gamma_1(A_x, G_y, C_z)$, $\Gamma_2(F_x, C_y, G_z)$ and $\Gamma_4(G_x, A_y, F_z)$ and they are seen to occur in different situations.

Just below $T_N$, spin configuration of Fe sublattice in $RFeO_3$ can be represented with $\Gamma_4(G_x, A_y, F_z)$. This forms the basic G-antiferromagnetic (G-AFM) arrangement of $Fe^{3+}$ spins along a(x)-axis, a ferromagnetic moment F along c(z)-axis and an A-AFM arrangement along b(y)-axis. The ferromagnetic moment is usually very small but plays an important role to bring forth interesting phenomena in orthoferrite systems. Although R subsystem orders at low temperature, molecular field of Fe-subsystem partially magnetizes R-subsystem at much higher temperature than the actual R magnetic ordering temperature. If the induced magnetic moment of R subsystem is m (due to the weak ferromagnetic moment (WFM) $F_z$ of Fe sublattice), then the net magnetic moment of the system is $\mathbf{M} = \mathbf{F} + \mathbf{m}$. $\mathbf{F}$ and $\mathbf{m}$ are seen to have opposite sign such

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that they are oppositely coupled to each other and also they have different temperature dependence. Consequently, $\mathbf{M} = \mathbf{0}$ at temperature 'Tcomp' where $|\mathbf{F}| = |\mathbf{m}|$. Magnetization reversal happens above $T_{comp}$ where one of these two terms dominates the other.

An interesting and prominent feature of $RFeO_3$ is spin reorientation. Here, the direction of magnetization of easy axis changes from one crystallographic direction to the other while varying temperature and/or magnetic field. It is generally considered that competition among R-R, R-Fe and Fe-Fe interactions is the cause of spin reorientation, but an explicit picture is still not forthcoming. It seems obvious that R-4f electrons have a major role in the process. As temperature decreases, this R-Fe interaction becomes relevant. Magnetic moment of Fe sublattice induces moment **m** in R-sublattice which is antiparallel to Fe-sublattice. This R-Fe interaction leads to the spin reorientation and determines the magnetic phase based on the type of R cation [7]. $RFeO_3$ systems are classified in four categories.

I. $\Gamma_4(G_x, A_y, F_z)$ (below $T_N$ spin configuration): As temperature is lowered, these systems undergo continuous spin reorientation to $\Gamma_2(F_x, C_y, G_z)$ in a temperature window. This occurs for most R cations (R = Nd, Sm, Tb, Ho, Er, Tm, Yb [1,6,8–10,10–15]).
II. $\Gamma_4(G_x, A_y, F_z)$ (below $T_N$ spin configuration): Similar to previous case, when temperature is lowered, spin reorientation occurs from $\Gamma_4(G_x, A_y, F_z)$ to $\Gamma_1(A_x, G_y, C_z)$ at a specific temperature. Unlike earlier, $\Gamma_4$ to $\Gamma_1$ reorientation is sharp and happens within a very short temperature window. This is seen for $DyFeO_3$ and $CeFeO_3$ [16,17].
III. $\Gamma_4(G_x, A_y, F_z)$ for $RFeO_3$ with non magnetic R ion (La, Eu, Lu and Y): Spin configuration. However, no spin reorientation occurs and $\Gamma_4$ configuration remains unchanged till the lowest temperature [1,17,18].
IV. Similar to Category III, for $PrFeO_3$ and $GdFeO_3$, spin reorientation does not occur and spin configuration $\Gamma_4$ remains below $T_N$ at the lowest temperature although Pr and Gd have magnetic moment [1,19,20].

Assuming the magnetic and crystallographic unit cells of $RFeO_3$ systems are same, there can be four $Fe^{3+}$ spins which are represented as $S_1, S_2, S_3$ and $S_4$ and located at site: (4b) (0, 1/2, 0), (0, 1/2, 1/2), (1/2, 0, 1/2), (1/2, 0, 0). Possible spin configurations and spin canting of this sublattice are schematically shown in Fig. 1.

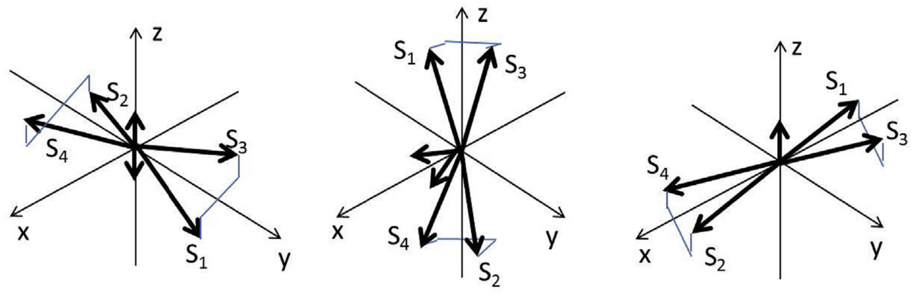
$RMnO_3$ possesses an entirely different magnetic structure. $Mn^{3+}$ in oxygen octahedra is Jahn-Teller active whereas, $Fe^{3+}$ is not. This leaves competition between ferromagnetic and antiferromagnetic super exchange interactions on *ab* plane. A-type antiferromagnetic ordering is observed in systems with large R ion (R = La to Gd). For those with small radii (Ho to Lu), E-type antiferromagnetic configuration results. In between, for Gd and Tb there is no classic ordering [21,22]. A mixed system with both Fe and Mn in B site is therefore always interesting. Studies on B-site doped $RFeO_3$ with Mn were recently reported [23–25]. They found that the spin reorientation temperature increases while $T_N$ decreases with increasing Mn concentration however, beyond a threshold content of Mn, spin reorientation disappears. Many of the studies were hampered due to lack of single crystalline sample. B site doped perovskites (or double perovskites) grow by incongruent melting. Comparatively, crystalline phase is easily obtained in doped systems with small R ion. There are few recent reports on single crystals of Mn doped $TbFeO_3$ and $HoFeO_3$ in which, by varying the Mn content, spin reorientation transition could be enhanced to room temperature [26,27]. Moreover, an interesting feature of reentrant spin reorientation of type $\Gamma_4$ to $\Gamma_1$ to $\Gamma_4$ is reported in $TbFe_{0.75}Mn_{0.25}O_3$. Here, we report the magnetic properties of $ErFe_{0.55}Mn_{0.45}O_3$ single crystals grown by optical floating zone technique. The parent compound $ErFeO_3$ orders with G-AFM spin configuration below $T_N = 636$ K and undergoes spin reorientation from $\Gamma_4$ to $\Gamma_2$ configuration within the temperature range 88–97 K [28]. On the other end, $ErMnO_3$ in orthorhombic structure orders E-type antiferromagnetically below $T_N = 42$ K [29]. Fe concentration is maintained slightly high to retain spin reorientation.

## 2. Experimental

Polycrystalline samples are first prepared by solid state synthesis route. Stoichiometric amounts of highly pure $Er_2O_3$ (4N), $Fe_2O_3$ (4N) and $MnO_2$ (4N) are mixed and sintered in furnace with intermediate grinding at 1000, 1100 and 1300 °C for 48, 60 and 70 h respectively. Phase purity is checked by powder X-ray diffraction using Cu-K$\alpha$ radiation. Single crystals are grown from polycrystalline sample in an optical floating zone furnace. Feed and seed rods are counter rotated at 35 rpm. A growth rate of 3.3 mm/h is maintained in atmospheric air flow of 3 L/min. Crystal orientation is performed using Orient Express software on Laue back reflection patterns. Oriented pieces along crystallographic a, b and c planes are cut with diamond cutter for magnetic measurements in a commercial Magnetic Property Measurement System from Quantum Design Inc. The composition of the grown crystals are determined with EPMA and EDS.

## 3. Results and discussion

Room temperature powder X-ray diffraction pattern of $ErFe_{0.55}Mn_{0.45}O_3$ refined using orthorhombic space group Pbnm is shown in Fig. 2. The sample is in pure phase and no impurity is observed. Although Fe and Mn were initially taken in the 0.55 to 0.45 (Fe/Mn = 1.2) stoichiometry, composition analysis of the as



$\Gamma_1$ (0) $\Gamma_2$ ($F_x$) $\Gamma_4$ ($F_z$)

Fig. 1. Schematic picture of three possible spin configurations in orthoferrite systems. Weak ferromagnetic component and its orientation should be noted in various configurations (Adopted from Refs. [1,11]).