Magnetic phases of erbium orthochromite

Brajesh Tiwari, M Krishna Surendra and M S Ramachandra Rao
Nano Functional Materials Technology Centre, Materials Science Research Centre and Department of Physics, Indian Institute of Technology Madras, Chennai-600036, India
E-mail: msrao@iitm.ac.in

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Abstract
Erbium orthochromite, ErCrO$_3$, is a distorted-perovskite which has antiferromagnetic ground state below 10 K and Cr$^{3+}$ magnetic moments order at 133 K. The temperature dependence of magnetization is studied across different magnetic phases for ErCrO$_3$ and different magnetization isotherms are analyzed. In the presence of external magnetic field, polycrystalline ErCrO$_3$ develops weak ferromagnetism from antiferromagnetic ground state. These magnetic phase transitions are observed to be of first order which is justified by thermal hysteresis and Arrott-plots.

Keywords: rare earth orthochromite, antiferromagnetism, first order magnetic phase transitions

1. Introduction

Rare earth orthochromites (RCrO$_3$) and orthoferrites (RFeO$_3$) which contain two magnetic ions (3d$^n$ and 4f$^m$) have attracted research interest for several decades due to complex magnetic phases over temperature, pressure and magnetic field [1–4]. Recently these material systems received considerable attention in connection with magnetoelectric and multiferroic properties and their potential multifunctional applications [3, 5–7]. The strong exchange interaction within the transition metal 3d, Cr$^{3+}$(Fe$^{3+}$)-Cr$^{3+}$(Fe$^{3+}$) subsystems, is predominantly antiferromagnetic and usually orders at higher temperatures (several hundreds of Kelvin) than that of rare earth 4f, R$^{3+}$-R$^{3+}$subsystems, but these are also less anisotropic compared to the rare earth ions. Hence rare earth magnetic ions can control the orientation of transition metal magnetic moments and give rise to complex magnetic structures. Such re-orientation transitions have profound effects on their magnetic, optical and elastic properties. It was shown by Hornreich et al that the

$^{1}$ Present address: Quantum Phenomenon and Application Division, National Physical Laboratory, New Delhi-110012, India.
magnitude of rare earth-transition metal ion, R3+-Cr3+(Fe3+), coupling strength is large for orthochromites (RCrO3) compared to orthoferrites (RFeO3) because Cr3+ does not have fourfold anisotropic terms [1]. This coupling plays a decisive role in determining the different magnetic phases in orthochromites due to spin reorientation transitions. These several important differences make orthochromites, especially erbium orthochromite, ErCrO3, more suitable for the study of magnetic phases depending on temperature, pressure and applied magnetic fields. ErCrO3 belongs to the crystal space group D2h [16] –Pbnm which contains four distorted perovskite units in the crystallographic cell [2, 3]. Since Er3+ ion has an electronic configuration of 4f11, the quantum number of total angular momentum \( J = \frac{15}{2} \) is a half integral number. Therefore, each multiplet can be split into \( J + \frac{1}{2} \) Kramer’s doublet in low symmetric crystals [6, 8, 9]. Due to interaction with Cr3+ spins, this Er3+ multiplet splitting reflects different effective fields in different magnetic phases which are given in table 1.

| Magnetic Symmetry Group | Compatible Spin Configurations (Magnetic Phases) |
|-------------------------|--------------------------------------------------|
| Atom                    | Pbnm setting                                     | Pnma setting                                      |
| mmm (mmm: d3h)          | \( \Gamma_1 \)                                   | \( \Gamma_1 \)                                    |
|                        | \( A_1 G_x C_z \)                                | \( G_x C_z A_2 \)                                |
|                        | \( 0', 0', 0' \)                                 | \( 0', 0', 0' \)                                 |
| mmm (2/m:c2h)           | \( \Gamma_2 \)                                   | \( \Gamma_2 \)                                    |
|                        | \( F_x C_y G_z \)                                | \( C_y F_z G_x \)                                |
|                        | \( F_z', 0', 0' \)                               | \( C_z', 0', F_z' \)                             |
| mmm (222:d2)            | \( \Gamma_3 \)                                   | \( \Gamma_3 \)                                    |
|                        | \( C_z F_x A_y \)                                | \( F_x C_z A_y \)                                |
|                        | \( C_z', 0', 0' \)                               | \( C_z', 0', 0' \)                               |
| mmm (mm2:c2v)           | \( \Gamma_4 \)                                   | \( \Gamma_4 \)                                    |
|                        | \( G_x A_y F_z \)                                | \( F_x G_y A_z \)                                |
|                        | \( 0', 0', 0' \)                                 | \( 0', 0', 0' \)                                 |
| mmm (mm2:c2v)           | \( \Gamma_5 \)                                   | \( \Gamma_5 \)                                    |
|                        | \( G_z', A_x', 0' \)                             | \( A_x', 0', G_z' \)                             |
| mmm (mm2:c2v)           | \( \Gamma_6 \)                                   | \( \Gamma_6 \)                                    |
|                        | \( 0', 0', A_x' \)                               | \( A_x', 0', 0' \)                               |
| mmm (mm2:c2v)           | \( \Gamma_7 \)                                   | \( \Gamma_7 \)                                    |
|                        | \( 0', 0', G_z' \)                               | \( G_z', 0', 0' \)                               |
| mmm (mm2:c2v)           | \( \Gamma_8 \)                                   | \( \Gamma_8 \)                                    |
|                        | \( A_x' G_z', 0' \)                              | \( G_z', 0', A_x' \)                             |

Different magnetic phases of ErCrO3 have been studied using different experimental techniques such as neutron diffraction [3], magnetization measurements [4, 5] and extensively by optical studies [6, 8–11]. Below \( T_N \) the spin structure of Cr3+ ions in ErCrO3 is G\( _x \) and belongs to \( \Gamma_4 \) \( (G_x A_y F_z G_z') \) in Bertaut notations [2]. Spin reorientation transition \( T_{SR} \) takes place abruptly at 10 K in the absence of external magnetic field where Cr3+ spins reorient in G\( _x \) and belongs to \( \Gamma_1 \) \( (A_x G_y C_z') \). This spin reorientation transition from \( \Gamma_4 \) \( (G_x A_y F_z G_z') \) to \( \Gamma_1 \) \( (A_x G_y C_z') \), where the weak ferromagnetic moment disappears, is a first-order phase transition based as symmetry arguments [12]. It is therefore important to understand the magnetic response of ErCrO3 in its different magnetic phases apart from phase transitions. The temperature dependence of magnetization was measured across different magnetic phases for ErCrO3 and analyzed by different magnetization isotherms.
2. Experimental details

The samples were prepared by the conventional solid state reaction route with nominal chemical composition of ErCrO₃ from starting materials of Er₂O₃ (99.9% Alfa Aesar) and Cr₂O₃ (99.9% Alfa Aesar). Before the final heat treatment at 1300 °C for 24 h, stoichiometric powder of Er₂O₃ and Cr₂O₃ was mixed thoroughly in agate mortar and two intermediate calcinations were carried out at 600 °C and 900 °C for 12 h. The resulting dark green powder samples were used for structural and magnetic studies. The powder x-ray diffraction (XRD) data of the powder samples were collected using a PANalytical X’Pert Pro x-ray diffractometer with Cu Kα radiation under ambient conditions. Crystal structure refinements were carried out using the general structure analysis system (GSAS) [10] for D₂h [16]: Pnma (#62) and structural parameter were obtained. Magnetic measurements of ErCrO₃ were performed using a vibrating sample magnetometer (VSM), an attachment in PPMS (Model 6000, Quantum Design, USA) in the temperature range of 5–300 K. Temperature dependent magnetization measurements were done as follows: zero-field cooled (ZFC) data collected while warming, field-cooled cooling (FCC) and field-cooled warming (FCW) procedures at an applied field. Magnetization (M) isotherms were recorded at different temperatures up to an applied magnetic field (H) of 7 kOe in the vicinity of magnetic transitions.

3. Results and discussion

3.1. Structural analysis

The Rietveld refinement of ErCrO₃ x-ray powder diffraction data is shown in figure 1. The refinement was carried out using GSAS software for the orthorhombic crystal structure with space group Pnma (# 62) [13]. The difference-profile (Diff.) between the observed (Obs.) and calculated (Calc.) diffraction patterns is shown at the bottom of the plot. A good fit was obtained with R factors, wR.p = 7.52%, Rp = 5.23%, and χ² = 1.53. The lattice constants and
volume of the unit cell are found to be $a = 5.512(1)$ Å, $b = 7.520(1)$ Å and $c = 5.226(1)$ Å and $V = 216.58(1)$ Å$^3$, respectively.

The inset in figure 1 shows the chemical unit cell of ErCrO$_3$ which has a total of 20 atoms (4 Er, 4 Cr and 12 O) per unit cell. Each chemical unit cell of ErCrO$_3$ has corner-linked octahedra CrO$_6$ with the centers occupied by centrosymmetric Cr ions (pink) with Wyckoff position 4b (0, 0, 1/2) while corner atoms of octahedra are oxygen ions (red) with two nonequivalent positions, the apex oxygen (O1 ion) at 4c ($-0.025$, 0.250, 0.597) and planar oxygen (O2 ion) at 8d (0.714, −0.032, 0.307). Erbium ions (green) occupy the space among the octahedra at 4c (0.064, 0.25, 0.015). The distortion from ideal perovskite structure happens because of geometric tolerance factor of 0.903 as well as antiphase tilt of adjacent octahedra which in turn lead to Cr-O1-Cr bond angle $\sim 144^\circ$.

### 3.2. Magnetization study

The temperature dependence of magnetization was measured across different magnetic phases for ErCrO$_3$ and analyzed by different magnetization isotherms. Figure 2 shows the magnetization curves as a function of temperature for ErCrO$_3$ recorded using an applied magnetic field of 100 Oe for different thermal cycles to understand the magnetic interactions; first, in zero-field the sample is cooled down to 5 K and data recorded while warming (ZFC); second, data is recorded along with cooling in the presence of external field (FCC); and third, field-cooled and data is recorded while warming (FCW). The temperature dependence of reciprocal of magnetic susceptibility $1/\chi$ is fitted to Curie–Weiss equation (red line), presented on the right hand side of y-axis. Inset: Magnetization curves are magnified in the vicinity of antiferromagnetic ordering of Cr$^{3+}$ magnetic moments.

![Figure 2. Magnetization of ErCrO$_3$ recorded under 100 Oe applied magnetic field for different thermal cycles: first, zero-field cooled down to 5 K and data recorded while warming (ZFC); second, field-cooled (100 Oe) and data is recorded along with cooling (FCC); and third, field-cooled (100 Oe) and data is recorded while warming (FCW). The temperature dependence of reciprocal of magnetic susceptibility $1/\chi$ is fitted to Curie–Weiss equation (red line), presented as right of the y-axis. Inset: Magnetization curves are magnified in the vicinity of antiferromagnetic ordering of Cr$^{3+}$ magnetic moments.](image-url)
transitions can be observed; the first at 133 K corresponds to Cr\(^{3+}\) antiferromagnetic ordering and the second at 10 K is related to the spin reorientation transition of ErCrO\(_3\).

Above \(T_N = 133\) K in paramagnetic phase of ErCrO\(_3\), \(\chi\) versus \(T\) curve follows the Curie–Weiss law and is fitted as shown in figure 2. The estimated effective magnetic moment is \(\mu_{eff} = 10.23 \mu_B\) for ErCrO\(_3\) which is close to the theoretical value \(\mu_{eff}(\text{ErCrO}_3) = 10.35 \mu_B\) calculated from the free ion values 9.59\(\mu_B\) for Er\(^{3+}\) and 3.87\(\mu_B\) for Cr\(^{3+}\) (spin only values) moments added assuming their total randomness in paramagnetic phase i.e. \(\mu_{eff}(\text{ErCrO}_3) = \sqrt{\mu_{Er}^2 + \mu_{Cr}^2} \mu_B\). Below chromium ordering, it is also observed that magnetization gradually reaches a maximum at 19 K for ErCrO\(_3\) showing paramagnetic \('Er'\) moments until ordering occurs at \(\sim 10\) K. The asymptotically observed Weiss constant \(\Theta = -29\) K for ErCrO\(_3\) is negative, indicating the predominance of antiferromagnetic interactions. The value of \(|\Theta|/T_N\) for ErCrO\(_3\) is 0.21 (<1) which differs from unity implying that the next-nearest neighbor couplings have considerable strength for the determination of ground state magnetic structure of ErCrO\(_3\) which is effectively antiferromagnetic.

Magnetization curves show a thermal hysteresis in the vicinity of antiferromagnetic ordering of Cr\(^{3+}\) magnetic moments as shown as inset of figure 2 (a magnified view of magnetization curves). The magnetization onset for ZFC and FCW curves is 133.7 K while FCC shows at 131.6 K. A difference of 4.6 K is observed when magnetization is recorded during cooling of ErCrO\(_3\) in the presence of magnetic field (FCC) compared to data recorded during warming (FCW and ZFC), which will be explained later and is significant compared to HoCrO\(_3\) and YCrO\(_3\) [14].

Figure 3(a) shows a clear thermal hysteresis in the magnetization curves for applied magnetic fields 100 Oe (lower panel) and 1000 Oe (upper panel) with a temperature difference of 4.6 K. In La doped GdCrO\(_3\) a similar thermal hysteresis was observed by Sharma et al [15] concluding it to be first-order phase transition between different magnetic phases. This type of thermal hysteresis in magnetization measurements can be explained by considering the possibility that the lattice is deformable and a spontaneous lattice deformation of lattice occurs in the magnetically ordered state [16]. However, there are several other origins of this type of thermal hysteresis; for example, in doped lanthanum manganites systems which show thermal hysteresis due to first-order ferromagnetic to antiferromagnetic in conjugation to metal to insulator transition in orbital and/or charge order systems [17–19]. The exchange interaction that gives rise to magnetically ordered state and also determines the transition temperature is a strong function of interatomic spacing. Figure 3(b) shows the schematic to explain the phenomenon that leads to thermal hysteresis in magnetization. In the high temperature state and above Curie temperature the lattice volume is \(V_o\) and the transition temperature is \(T_C\); if the sample is cooled across the transition temperature then the volume due to lattice distortion is \(V'\) and corresponding transition temperature is \(T_o\). In the cooled state if the sample is warmed then the volume is \(V'\) and the corresponding transition temperature \(T_o\) is seen. This can be understood based on the fact that if the sample is cooled to the lowest temperature in the presence (or absence) of field which can distort the lattice (or free system) at the transition temperature (\(T_C\) or \(T_N\)), and if the sample is warmed from its lowest temperature (in figure 2 down to 5 K and figure 3(a) down to 120 K), then the free energy may be lowered in the direction of increasing transition temperature (\(T_C\) or \(T_N\)) as in the case when magnetization is recorded while warming, i.e. FCW (or ZFC). Now if magnetization data while warming (FCW or ZFC) is compared with the magnetization curve recorded while cooling (FCC) the sample
shows its intrinsic (or clamped system) lattice volume ($V_0$) and a lower magnetic ordering temperature ($T_0$). Further, to understand the different magnetic phases and nature of magnetic transitions of ErCrO$_3$, magnetization isotherms over the temperature range 5 K to 300 K were recorded and are shown in figure 4. Magnetization curves up to applied magnetic fields of 70 kOe, as shown in figure 4(a), indicate a sign of magnetization saturation only at 5 K while others isotherms above the spin reorientation transition of 10 K do not saturate. Magnetization curves for low applied magnetic fields (~2 kOe to 2 kOe) are shown in figure 4(b). Magnetic susceptibilities ($M/H$) over the temperature range 5–300 K are shown in log-log scale in figure 4(c) which was obtained from magnetization isotherms from figure 4(a). At low magnetic fields (0.1 kOe and 1.0 kOe) spin reorientation transition ($T_{SR} = 10$ K) can be observed which is similar to magnetization as a function of temperature (figure 2), but for high applied magnetic fields, this spin reorientation transition gets suppressed as can be seen from figure 4(c), retaining weak ferromagnetic nature of ErCrO$_3$. The applied magnetic field which suppresses the spin reorientation transition can be determined by the first derivative ($dM/dH$) of magnetization isotherms, as shown in figure 4(d) for temperatures close to $T_{SR}$. For temperatures above spin reorientation ($T > T_{SR}$), $dM/dH$ shows two sharp maxima, one in the magnetic fields 5–12 kOe, and the second around 16 kOe, indicating two magnetic behavior/phases change which are weak ferromagnetic phases of ErCrO$_3$, $\Gamma_2(C, G, F; C', F')$ and $\Gamma_4(A, F, G; F', F')$. Also, it is important to note that the magnetic susceptibility $dM/dH$, at 5 K, shows minimum value in the
absence of external field, in contrast to other higher temperatures, which justifies the fact that ground state of ErCrO₃ is antiferromagnetic $\Gamma'_G C A C (\Gamma'_y z y)$. Magnetization curve at 5 K does not show any loop for low field opening indicating perfect antiferromagnetic phase $\Gamma'_G C A A'_y C'_y$ in the absence of strong magnetic fields for ErCrO₃ in Bertaut notation which are given in Table 1. As the applied magnetic fields increase, the magnetization starts increasing and tending towards saturation which corresponds to weak ferromagnetic phases $\Gamma'_C C F F' C F'$ when applied magnetic field is above 1 kOe along crystallographic z-axis and $\Gamma'_A A' C C' F' C$ and when the applied magnetic field is above 10 kOe along crystallographic y-axis. These magnetic phases are well studied using optical absorption by Hasson et al and Toyokawa et al [8, 10]. These field induced transitions are first-order phase transition. Even in the absence of magnetic field along y-axis Cr³⁺, magnetic moments undergo a spin reorientation-type transition around 10 K from weak ferromagnetic $\Gamma'_A A' C C' F' C$ phase to $\Gamma'_C C A A'_y C'_y$ in which the ferromagnetic moments vanish.

Since in the present study, polycrystalline ErCrO₃ is used, apart from 5 K magnetization isotherm at low magnetic field which is perfect antiferromagnetic with $\Gamma'_C C A A'_y C'_y$ as shown...
in figure 5, magnetization isotherms between $T_{\text{SR}}$ and $T_N$ show the magnetic phase of $\Gamma_1(A_x F_x G_z F'_y)$, even in the absence of magnetic field. In $\Gamma_1(G_x C_y A_z' C_y')$, phase below $T_{\text{SR}} \sim 10$ K, if external magnetic field is applied parallel to the crystallographic z-axis above some critical value $H_{\text{c}/z}$, the spin of $\text{Cr}^{3+}$ reorients itself from $G_x$ to $G_y$ and induces weak ferromagnetism $F_z$ in z-direction which is represented as $\Gamma_2(G_y F_x G_z F'_y)$. Similarly, either by increasing temperature above $T_{\text{SR}}$ or by applying external magnetic field parallel to y-axis above a critical value $H_{\text{c}/y}$ results in $\Gamma_3(A_x F_y G_y)$ which has ferromagnetic component $F_y$ in y-direction, see figure 5. These weak ferromagnetic phases of $\text{ErCrO}_3$ up on application of external fields $\Gamma_4(A_x F_y G_z' F'_y)$ and $\Gamma_5(\text{C}_x G_y F_x G'_z)$ along two different directions are observed as two magnetization behaviors in figure 5. Transitions between two magnetic phases of $\text{ErCrO}_3$ either by magnetic field or upon temperature are first-order, which can be justified by Arrott plots, which is based on phenomenological Ginzberg–Landau theory in the vicinity of these magnetic transitions [12, 20, 21].

Ginzburg–Landau formulation which includes the magnetostatic field energy ($MH$), where $M$ is experimentally observed specific magnetization as an order parameter and $H$ is the applied magnetic field; the thermodynamic potential is given by $\Phi = \phi_0 + \frac{1}{2}\alpha M^2 + \frac{1}{4}\beta M^4 - MH$, where $\alpha$, $\beta$ are temperature dependent constants. In equilibrium $\frac{\partial \Phi}{\partial M} = 0$ the expression reduces to $H/M = \beta M^2 + \alpha$. Arrott plots, isotherms of $M^2$ against $H/M$ should be a straight line in high applied magnetic field [21]. For second-order phase transitions, $\beta$ should be positive but negative for first-order magnetic phase transition according to the criteria proposed by Banerjee et al [20]. In order to confirm the two magnetic transitions in $\text{ErCrO}_3$, antiferromagnetic Cr with Néel temperature $T_N = 133$ K and spin reorientation transition at $T_{\text{SR}} = 10$ K, which show the thermal hysteresis (figure 2) is first-order magnetic transitions or not, first quadrant magnetization isotherms in the vicinity of these transitions are recorded.

Magnetization isotherms at different temperatures between 128 K to 138 K are shown in figure 6 for $\text{ErCrO}_3$. A linear increase in the magnetization above 133 K (134, 136 and 138 K) over the magnetic range (0–2 kOe) is a clear signature of paramagnetic phase of material, as shown in figure 6(a). Below $T_N = 133$ K a nonlinear behavior indicates the antiferromagnetic phase of $\text{ErCrO}_3$. Arrott plots as presented in figure 6(b) show the slopes of $M^2$ versus $H/M$ curves negative below the $T_N$ (133 K) means negative $\beta$ which supports the observed thermal
hysteresis (about 4.6 K) in FCC and FCW magnetization measurements, as shown in figure 2 and figure 3. As is observed from magnetization measurements, there is a spin reorientation transition ($T_{SR} = 10$ K) from high temperature $\Gamma (A_{x}F_{y}G_{z};F')$ to low temperature $\Gamma (G_{x}C_{y}A_{z};C')$ in the absence of external magnetic fields. Transition between these two magnetic phases should genuinely show first-order transition though not necessarily. To confirm, first quadrant magnetization isotherms were recorded, as shown in figure 7(a), and the corresponding Arrot plots are shown in figure 7(b). At spin reorientation transition, i.e. $T_{SR} = 10$ K, $M^2$ versus $H/M$ curve is linear indicating the transition, whereas at 5 K ($<T_{SR}$) shows a clear negative slope for low magnetic fields indicating this transition to be first-order.

For ErCrO$_3$ two first-order magnetic transitions can be observed. A canted antiferromagnetic or weak ferromagnetic order of phase $\Gamma (A_{x}F_{y}G_{z};F')$ of Cr$^{3+}$ ions occurs at $T_N = 133$ K, and the presence of second magnetic ion Er$^{3+}$ which has aspherical charge distribution with non-zero net magnetic moment, reorient the Cr$^{3+}$ such that a new magnetic phase $\Gamma (G_{x}C_{y}A_{z};C')$ appears at $T_{SR} = 10$ which makes ErCrO$_3$ perfectly antiferromagnetic (ferrimagnetic). These transitions proved to be of first-order, whose origin lies in the
dependence of exchange energy as a strong function of inter-atomic spacing and bond strength. At absolute zero the distortion of lattice favors increasing transition temperature as we observed for ErCrO$_3$ in which the onset of magnetic ordering has been found to increase by $\sim 4.6$ K in FCW compared to FCC measurement cycle.

4. Conclusion

Erbium orthochromite in its distorted-perovskite structure is synthesized and magnetic properties are studied. We observed a thermal hysteresis of 4.6 K in magnetization and this is independent of applied magnetic field strength (up to 1000 Oe), which indicates transition type is first-order. Below 10 K, the complex magnetic phases indicate the significance of Er–Cr coupling in ErCrO$_3$. At 5 K, with external magnetic field the antiferromagnetic ground state $I'_1(G'_1,C'_1,A'_1;C'_1)$ changes to weak ferromagnetic $I'_2(A'_1,F'_1;G'_2)$ phases.

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