Lattice strain and heat capacity anomalies at the spin reorientation transitions of ErFeO$_3$ orthoferrite

R. P. Chaudhury$^1$, B. Lorenz$^1$, C. W. Chu$^{1,2,3}$, Ya. B. Bazaliy$^4$ and L. T. Tsymbal$^5$

$^1$ TCSUH and Department of Physics, University of Houston, Houston, TX 77204, USA
$^2$ Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA
$^3$ Hong Kong University of Science and Technology, Hong Kong, China
$^4$ University of South Carolina, Columbia, SC 29208, USA, and Institute of Magnetism, NASU, Kyiv 03142, Ukraine
$^5$ O. Galkin Physics and Technology Institute, NASU, Donetsk 83114, Ukraine

E-mail: blorenz@uh.edu

Abstract. We have investigated the thermal expansivities of an ErFeO$_3$ single crystal along the three crystallographic orientations using a high-resolution capacitance dilatometer and found clear signatures of lattice distortions in the spin rotation region as evidence for strong spin-lattice coupling. The observed lattice strain is consistent with the smooth rotation of the magnetization and it reveals the importance of the magnetoelastic interaction. Heat capacity measurements show a well-defined plateau-like enhancement in the spin re-orientation regime as predicted by the Landau theory of second order phase transitions. The data are used to estimate microscopic anisotropy parameters. Heat capacity is also measured near the low-temperature erbium magnetic ordering transition.

1. Introduction

Rare earth orthoferrites (RFeO$_3$, R= rare earth, Y) have attracted attention because of their complex magnetic structures and phase transitions including canted antiferromagnetism (AFM), spin reorientations, ferromagnetic (FM) compensation temperatures, and rare earth moment orders at low temperatures [1, 2, 3, 4, 5, 6]. The origin in this complex magnetic behavior lies in the existence of two magnetic ions, Fe and rare earth, their mutual interactions, and the peculiarities of the single ion anisotropy. This is also reflected in one particular member of the family, ErFeO$_3$, in a series of subsequent magnetic phase transitions, starting at high temperatures ($T_N=636$ K) with an AFM transition with a small canting (0.5$^\circ$) of iron spins that induces a small ferromagnetic moment along the c-axis. At lower temperatures, between $T_1=97$ K and $T_2=88$ K, the iron spins collectively rotate so that their mainly AFM alignment is still preserved but the FM component is now aligned with the a-axis. This spin rotation occurs over a temperature interval of approximately 10 K so that the magnetic symmetry is lowered within this range. While the primary origin of this transition is magnetic it has been proposed that details of the temperature dependence of the FM magnetization may depend on a possible change of the lattice symmetry in the spin-reorientation regime [7]. However, detailed x-ray scattering measurements have not revealed such a change within the resolution of the experiment [8, 9]. Anomalies of lattice constants were found in Ref. [8], albeit near the
resolution limit. Thermal expansion measurements (see e.g. [10]) provide a resolution which is several orders of magnitude better than the scattering experiments. In order to detect minute structural distortions at the spin rotation transition and to gather evidence for the coupling of the magnetic order and the lattice we employed a high-resolution capacitance dilatometer and report the results in Section 2. The thermodynamic signature of the magnetic phase transition of ErFeO$_3$ between 88 K and 97 K of ErFeO$_3$ has been searched for and the heat capacity $C_p(T)$ of ErFeO$_3$ powder was measured by Saito et al. [11]. Although a small anomaly of $C_p$ near the spin rotation transition was detected, the scattering of the data and the associated error did not warrant any quantitative evaluation and comparison with existing theories. In Section 3 we report the results of our heat capacity experiments measured on high-quality single crystals and compare the data with the mean field theory.

2. Experimental
A single crystal of ErFeO$_3$ was cut from a larger piece grown by the floating zone method. The thermal expansion coefficients of ErFeO$_3$ have been measured along the three main crystallographic orientations employing a high-resolution capacitance dilatometer [12]. The device is capable of detecting length changes of a few Å for a macroscopic sample of the size of 1 mm to 1 cm. This results in a relative resolution of better than $10^{-7}$. The heat capacity was measured by a relaxation method employing the specific heat option of the Physical Property Measurement System.

3. Structural distortions at the spin reorientation transition of ErFeO$_3$
The temperature dependence of the lattice constants $a$, $b$, $c$ and the volume $V$ of ErFeO$_3$ with reference to their values at 110 K is shown in Fig. 1. All three lattice parameters display a distinct change at the spin reorientation transition temperatures, $T_1$ and $T_2$. The $c$-axis shrinks towards lower temperatures whereas the $a$- and $b$-axis expand. It is interesting to note that the volume does not exhibit a clear anomaly within the resolution of the measurement. The change of the lattice constants is smooth between $T_1$ and $T_2$ scaling with the continuous rotation angle of the Fe magnetic moments. While the volume shows the normal decrease due to the thermal
The heat capacity jump at the transition temperatures can be linearized without the loss of accuracy, both models predict the same magnitude of the rotation interval $\Delta T$ in the inclusion of erbium-iron interaction renormalizes the first anisotropy constant $\theta$. For the free energy of the iron system alone, the $\theta$ angle is an immediate expression of the change in magnetic anisotropy parameters. Horner and Varma [17] have proposed a mean field description using the expression of the spin reorientation transition in ErFeO$_3$. Heat capacity anomalies b-, and c-axes are an immediate expression of the change in magnetic anisotropy parameters. Since the lattice strain and the magnetic anisotropy are intimately coupled (the magnetostrictive effect originates from the magnetocrystalline anisotropy) the observed distortions along the a-, b-, and c-axes are an immediate expression of the change in magnetic anisotropy parameters. Accounting for the erbia-iron interactions proved to be essential for a successful mean field theory description of the rotation region ([15, 16]. This field is aligned with the c-axis at 4 K, where the total moment is zero since the moments of the Fe and Er systems are of equal magnitude but of opposite sign. Accounting for the erbium-iron interactions also indirectly inferred from the magnetostriction measurements [4] with comparable results.

While the magnetic orders and the spin rotation are primarily determined by the iron spins, the magnetic moment of the Er ions also has to be considered. A comprehensive discussion of all magnetic structures was given by White [13]. The direct exchange between rare earth moments is weak and their spontaneous magnetic order can only occur at much lower temperature, as observed in ErFeO$_3$ below 4 K, but the Er moments become polarized in the effective field of the iron spin order at higher temperatures [4, 14]. This field is aligned with the c-axis at $T > T_1$ and it lies along the a-axis for $T < T_2$. The resulting total Er moment is opposite to the total Fe moment. The relative magnitude of the FM moments of both magnetic subsystems changes with temperature resulting in a compensation point at 45 K, where the total moment is zero since the moments of the Fe and Er systems are of equal magnitude but of opposite sign. Accounting for the erbium-iron interactions proved to be essential for a successful mean field theory description of the spin rotation transition [15, 16].

The structural distortions shown in Fig. 1 are closely associated with the change of the magnetocristalline anisotropy that drives the spin reorientation phase transition in ErFeO$_3$ [13]. Since the lattice strain and the magnetic anisotropy are intimately coupled (the magnetostrictive effect originates from the magnetocrystalline anisotropy) the observed distortions along the a-, b-, and c-axes are an immediate expression of the change in magnetic anisotropy parameters.

**4. Heat capacity anomalies**

The spin reorientation in ErFeO$_3$ defines two second order phase transitions at $T_1$ and $T_2$, respectively. Horner and Varma [17] have proposed a mean field description using the expression for the free energy of the iron system alone $F = F_0 + K_1 \sin^2 \theta + \frac{2}{3} K_2 \sin^4 \theta$ as a function of rotation angle $\theta$, and calculated the heat capacity $C_p = -T \frac{d^2 F}{dT^2}$. It was later shown [15, 16] that the inclusion of erbium-iron interaction renormalizes the first anisotropy constant $K_1$. However, as long as the rotation interval $\Delta T = T_1 - T_2$ is small, $\Delta T \ll \bar{T} = (T_1 + T_2)/2$, and all parameters can be linearized without the loss of accuracy, both models predict the same magnitude of the heat capacity jump at the transition temperatures $T_1$ and $T_2$: $\Delta C_{1/2} = \pm 2K_2\bar{T}/(\Delta T)^2$.
(accounting for the nonlinear terms introduces corrections that are smaller by a factor $\Delta T/\bar{T}$). This plateau-like enhancement of $C_p(T)$ was observed in YbFeO$_3$ where the spin reorientation occurs at much lower temperature [18].

Our results for the heat capacity of ErFeO$_3$ are shown in Figs. 2 and 3. The strongest anomaly of $C_p(T)$ is detected at low temperatures, $T_{RE} \approx 4$ K, indicating the Er moment ordering [1]. At $T_{RE}$ the heat capacity exhibits a jump characteristic of the second order phase transition. In addition, in the several Kelvin interval above $T_{RE}$ the temperature dependence of $C_p$ shows clear deviations from the general trend at $T > T_{RE}$. In that respect heat capacity behaves similar to magnetic and acoustic characteristics of the material [6].

At higher temperatures a distinct enhancement of $C_p(T)$ in the spin reorientation regime is clearly resolved (Fig. 3). Note that this plateau-like feature could not be resolved in recent measurements on ErFeO$_3$ powder [11]. Our results are in perfect agreement with the expectations from the Landau theory and the above formula can be employed to estimate the magnetic anisotropy constant, $K_2$. With the experimental value (Fig. 3) of $\Delta C_p/T_1 = 0.005$ J/(mol K$^2$) the fourth order magnetic anisotropy constant $K_2$ is determined as $K_2 = 0.2$ J/mol.

5. Conclusion
The thermal expansion anomalies observed in our investigation provide convincing evidence for a sizable lattice strain accompanying the spin reorientation in ErFeO$_3$ and the existence of an appreciable spin lattice coupling. Our current results also show unanimously that the spin reorientation transitions in ErFeO$_3$ are well described by the Landau theory based on the expansion of the free energy with respect to the spin rotation angle. At low temperature, near the erbium ordering transition, the heat capacity behaves similarly to the other material parameters.

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