# Structural properties of $ErFeO_3$ in the spin-reorientation region

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In spin-reorientation transition in orthoferrites the temperature dependence of the magnetization differs from that predicted by conventional mean-field theory. One of the explanations of this discrepancy is based on the assumption that structural changes accompany magnetic transitions. Recently we proposed an explanation of this phenomena based on purely magnetic grounds. In this x-ray study a possible structural change in an $ErFeO_3$ single crystal is probed. Our measurements find no lattice distortions in the spin-reorientation region, thus supporting the purely magnetic nature of spin rotation.

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## I. INTRODUCTION

Rare-earth orthoferrites exhibit characteristic orientation phase transitions, most often of the type

$$\Gamma_4(G_x,F_z) \rightarrow \Gamma_{24}(G_{xz},F_{xz}) \rightarrow \Gamma_2(G_z,F_x).$$

Upon cooling below the Néel temperature $T_N$, the subsystem of iron ions initially orders into the same symmetry configuration $\Gamma_4(G_x,F_z)$ in all orthoferrites. The corresponding spin arrangement is a canted antiferromagnetic structure with a small total ferromagnetic moment **F** directed along the **c**(**c**$\|$**z**) crystal axis, and an antiferromagnetic vector **G** directed along the **a**(**a**$\|$**x**) crystal axis. The rare-earth ions remain paramagnetic but develop a magnetic moment **m** in the molecular field of the iron ions subsystem. Thus the total magnetization is given by **M**=**F**+**m**.

Spin-reorientation transition is a continuous rotation of vector **F** with temperature, happening in the temperature interval $[T_2,T_1]$ with $T_2<T_1<T_N$. In this interval vector **F** rotates from the **c** axis (above $T_1$) towards the **a** axis staying in the (**ac**) plane. At $T_2$ the system reaches another symmetry configuration $\Gamma_2(G_z,F_x)$ with **F**$\|$**a**. Temperatures $T_1$ and $T_2$ mark two second-order phase transitions. The symmetry of the spin configuration in the $[T_2,T_1]$ interval is lower than outside of it and corresponds to the $\Gamma_{24}(G_{x,z},F_{x,z})$ irreducible representation. Recently, spin-reorientation transition in orthoferrites attracted attention due to the observations of picosecond spin rotation times in antiferromagnets,[1,2] a discovery associated with potential technical applications.

It was suggested in the literature that spin-reorientation transition is accompanied by a structural change, which lowers the lattice symmetry from rhombic to monoclinic. This conjecture is based in part on the results of NMR experiments in crystals of $ErFeO_3$ (Ref. 3) and $TmFeO_3$.[4] It was found in Refs. 3 and 4 that (1) outside of the reorientation region, for $T>T_1$ or $T<T_2$, single NMR lines are observed on $Fe^{57}$ nuclei; (2) inside the reorientation region the lowered magnetic symmetry of the material leads to the symmetric splitting of the NMR frequencies of the $Fe^{57}$ nuclei into pairs; and (3) the temperature dependence of the NMR frequencies splitting is continuous and has a dome-shaped form, symmetric with respect to the center of the spin-reorientation interval. These are very reliable results because experimental measurements of the NMR frequencies were made with high accuracy. Based on the data on intensity of the split NMR lines, the authors of Refs. 3 and 4 also calculated the temperature dependence of the rotation angle $\theta(T)$ of the magnetization vector **M**. According to their calculation this dependence is markedly asymmetric. The angle $\theta(T)$ changes abruptly near one of the edges and then stays at a small constant value for most of the temperature interval $[T_2,T_1]$. To explain the calculated asymmetric behavior of the rotation angle, the authors of Refs. 3 and 4 assumed that magnetic transitions at temperatures $T_1$ and $T_2$ are accompanied by lattice distortions. Subsequent theoretical analysis[5] of the results obtained in Ref. 3 seemed to confirm the assumption of NMR line splitting being caused by a change not only in the magnetic environment of the iron nuclei, but also in the crystallographic positions of the nuclei.

However, the following should be noted. First, in NMR experiment the accuracy of intensity measurements is much lower than the accuracy of frequency measurement. In particular, according to Refs. 3 and 4 such accuracy is no better than 30%. Second, and this may be more essential, the authors assumed the constancy of $|\mathbf{M}|$ in their calculation, while this assumption is not supported by experiment, as discussed below. Third, the assumption of Refs. 3 and 5 contradicts the earlier paper,[6] where the results of Mossbauer spectroscopy of single-crystal $ErFeO_3$ showed no evidence of nonequivalent positions of $Fe^{3+}$ ions in the reorientation region. Last, according to Ref. 5, dipole-dipole interaction between nuclear magnetic moments and iron spins is sufficient to produce the observed splitting of NMR frequencies. It is only the asymmetric shape of the temperature dependence of the rotation angle (inferred from the intensity measurements) that forces one to resort to the assumption of structural transformation lowering the symmetry of the crystal and producing nonequivalent positions of iron nuclei.

Recently, more experimental studies of the rotation angle temperature dependence were performed. This time a much

 

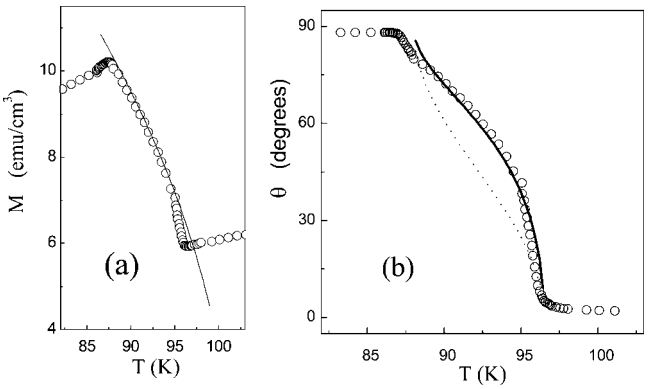


FIG. 1. Left panel: temperature dependence of the absolute value of the magnetization $|\mathbf{M}|$. Right panel: temperature dependence of the rotation angle $\theta(T)$ of the magnetization $\mathbf{M}$ in the spin rotation interval of the $ErFeO_3$ crystal. The empty symbols represent experimental results, while the full line is given by the modified mean field theory. (Refs. 8 and 9). The dashed line on the right panel is given by conventional mean field theory. (Refs. 11–13).

more accurate technique of SQUID magnetometer measurements was used[7–10] and both the absolute value $|\mathbf{M}|(T)$ of the magnetic moment and the angle $\theta(T)$ between magnetization and **c** axis were obtained for an $ErFeO_3$ crystal. This was achieved in Refs. 7–10 by measuring both $M_a$ and $M_c$ components of vector $\mathbf{M}$ and using the formulas

$$|\mathbf{M}| = \sqrt{M_a^2 + M_c^2}, \quad \theta = \arctan\left(\frac{M_a}{M_c}\right).$$

The results of a more accurate measurements in the $[T_2, T_1]$ interval are presented on Fig. 1. In contrast to Ref. 3, they produced a smooth and practically symmetric dependence $\theta(T)$ in the reorientation region, which still did not follow the standard mean field theory prediction.[11–13] Moreover, the absolute value of the magnetization, assumed to be constant in Refs. 11–13 and in calculations of Refs. 3 and 4, changed almost by a factor of 2 in the $[T_2, T_1]$ region (Fig. 1).

To explain these findings, the authors of Refs. 7–10 put forward a modified mean field theory based on the proper account of the rare-earth ions paramagnetism. The key point of the theory is the anisotropy of the paramagnetic susceptibility of the rare-earth subsystem to the molecular field of the ordered iron subsystem. It is assumed, that the iron magnetic moment $\mathbf{F}$ is indeed constant as long as the inequality $T_1, T_2 \ll T_N$ holds. However, due to the crystallographic anisotropy of susceptibility, rotation of $\mathbf{F}$ leads to the change of the magnitude of the rare-earth moment $\mathbf{m}$. The large difference between susceptibilities along the **a** and **c** axes, and a substantial magnitude of $\mathbf{m}$ result in anomalous change of the total magnetization $\mathbf{M}$ within a narrow temperature interval $[T_2, T_1]$. This modified mean field model does not invoke the assumption of lattice distortion to account for the behavior of the $\theta(T)$ dependence and explains experimental data very well without invoking any fitting parameters.

As the crystal structure changes of rare-earth orthoferrites inside the spin-reorientation temperature interval is still not studied experimentally, the present work was aimed at performing a detailed x-ray study which would detect a possible lattice distortion or prove its absence. A single crystal of $ErFeO_3$ was chosen for the study to compare with the results of Refs. 3, 5, and 10.

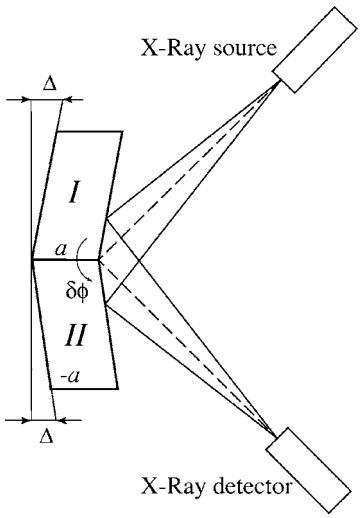


FIG. 2. Schematic view of the x-ray setup for $\phi$-scanning of $ErFeO_3$ crystals.

## II. EXPERIMENTAL RESULTS

Measurements were performed on a single-crystal $ErFeO_3$ disk-shaped sample with phase transitions happening at $T_1 = 97$ K and $T_2 = 88$ K.

According to Ref. 5, monoclinic distortions are expected to emerge upon cooling below $T_1 = 97$ K and then disappear upon further cooling below $T_2 = 88$ K. Both structural transitions are predicted to be of the second order. In a narrow reorientation temperature interval the lattice distortions, associated with the structural change, cannot reach the magnitude large enough to affect the interplane distances and thus may not be observed in x-ray studies on powders or polycrystalline samples. For this reason the assumption of Refs. 3 and 5 can be only checked on single-crystal samples.

We searched for possible changes in the crystal structures of an $ErFeO_3$ sample that could indicate a transition to a distorted phase. If the symmetry of the crystal is lowered, a multi-domain polycrystal state is usually formed. The structure of such polycrystals will reflect all possible orientations of the lattice distortion. The orthorhombic lattice can be distorted into either a monoclinic or a triclinic system. However, it is known[14] that the triclcinic system does not support canted antiferromagnetism which is certainly present in the reorientation region of the orthoferrites. The conclustion of Ref. 14 is that distortions, if present, would happen in the (**ac**) plane, i.e., the **c** axis would tilt with respect to the **a** axis by an angle $\Delta$. Two possible distortions of this type have tilting angles $+\Delta$ (type-I domains) and $-\Delta$ (type-II domains). The resulting domain structure with minimal elastic energy of distortion is shown on Fig. 2. Domain structure formation would be a clear signature of a transition from an orthorhombic single-domain structure to a monoclinic multi-domain

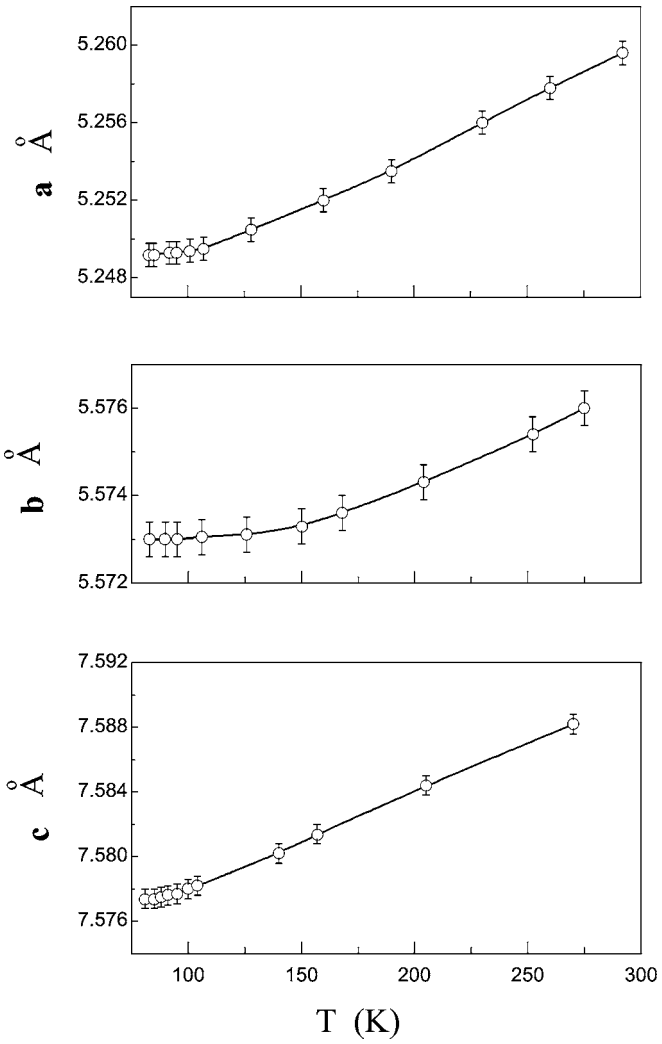


FIG. 3. The temperatue dependence of the lattice parameters of $ErFeO_3$ determined from x-ray measurement on a single-crystal sample. Open symbols with error bars are the experimental results, while the solid lines are a guide to the eye. The accuracy of the temperature determination is less than the symbol size.

state and could be easily observed in an x-ray experiment. Additionally, temperature dependencies of the lattice constants should be checked for possible anomalies in thermal expansion.

Temperature dependencies of lattice constants $a$, $b$, $c$ in orthorhombic setting (space group $P_{bnm}$) were measured using reflexes from (400), (040), and (006) planes. The orientation of the crystal was set in advance and it was mounted in the low-temperature chamber of the x-ray diffractometer DRON-3. The chamber was cooled by evaporating nitrogen. The lattice parameters were determined using a Debye-Scherer procedure with experimental error less than $\pm 5 \times 10^{-4}$ Å. The temperature was measured with an accuracy of ±0.3 K.

The experimental arrangement is shown on Fig. 2 and represents a standard setup for detecting the structural texture in a sample. The single crystal of $ErFeO_3$ was mounted in the low-temperature chamber so that its (**ac**) plane corresponded to the diffraction plane. The x-ray detector was positioned at

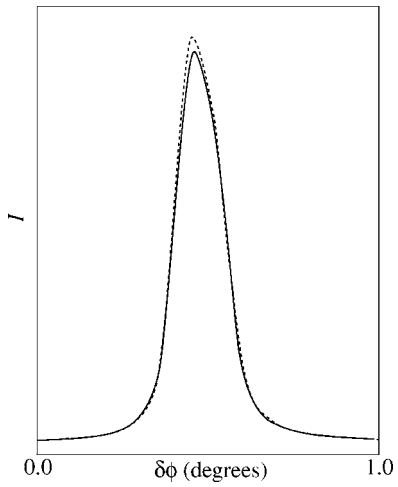


FIG. 4. Intensity measurement in $\phi$ scanning experiments on single-crystal $ErFeO_3$ at different temperatures: solid line—300 K, dashed line—92 K.

a diffraction angle $2\theta_{(400)}$ with respect to the (400) crystal planes. At each temperature the signal was scanned as the sample was rocked in the (**ac**) plane around the **b** axis by an angle $\delta\phi$ ($\phi$ scanning), so that the reflection angle from the (400) plane was inside the scanning interval. The intensity of the diffraction signal $I$ was measured as a function of the rocking angle $\delta\phi$.

Temperature dependencies of the $a$, $b$, and $c$ lattice parameters of $ErFeO_3$ are shown in Fig. 3. No anomaly of thermal expansion is observed within the experimental error. In fact, the lattice parameters are practically temperature independent below 105 K. This is interpreted as reaching the well-known harmonic limit, as the amplitude of atomic oscillations decreases with temperature. It should be underscored that the diffraction maxima intensities do not change in the spin-reorientation region.

Figure 4 shows the results of the $\phi$ scanning at room temperature and at 92 K. The latter temperature is in the middle of the reorientation region. The x-ray spot of the diffractometer was larger than the size of the sample and captured the signal from all possible crystalline domains. The same crystal was used to obtain magnetic data shown on Fig. 1 and x-ray data shown on Fig. 4. The x-ray intensity was recorded by a plotter, scanned, and digitized. Both curves represent the angle of mosaic spread in our specimen near the **a** axis. They follow each other with the angular accuracy of 2% everywhere, except near the maximum, where in the 0.05° interval of $\delta\phi$ the intensities differ by 4%. From the width of the curves we conclude that the angle of the mosaic block misorientation does not exceed 0.4°. Thus the sample may be considered a practically perfect single crystal at both temperatures. Had the symmetry of the lattice decreased in the reorientation region as assumed in Ref. 5, the $\phi$ scanning curve would split into two peaks shifted by $2\Delta$. This would be observed as a splitting of the peak, or at least its widening in the case of $\Delta$ being comparable to the resolution of the device. The minimal value of $\Delta$ that can be reliably observed in our experimental setup is about 0.06°. We conclude that neither the shape nor the width of the $I(\delta\phi)$

curve changes, thus the crystal structure of the sample must be unchanged inside the reorientation interval. The same measurement was performed by scanning rotations around the **a** axis of the sample. Again, there was no evidence of a change of the crystal structure.

## III. CONCLUSIONS

Systematic x-ray measurements on a $ErFeO_3$ single-crystal sample show the absence of any evidence of a lattice distortion in the spin-reorientation region up to the accuracy of our apparatus. The lattice parameters $a$, $b$, and $c$ change smoothly in the region and do not exhibit anomalies near the second-order phase transitions $T_1$ and $T_2$. No domain structure is formed inside the region, contrary to the conjectured[3–5] lowering of the lattice symmetry over the transition range. This result proves that there is no distortion of the sample that lowers the symmetry from orthorhombic to monoclinic.

We conclude that $\Gamma_4(G_x,F_z)\rightarrow\Gamma_{24}(G_{xz},F_{xz})\rightarrow\Gamma_2(G_z,F_x)$ orientation phase transitions in orthoferrites are purely magnetic. This conclusion perfectly correlates with results of Ref. 6 and the fact that spin rotation is well described by the modified mean field theory proposed in Refs. 7–10.

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