# Low-temperature spin configuration of iron ions in erbium orthoferrite

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The magnetic structure of $ErFeO_3$ is investigated in the region of rare-earth ion ordering by the NMR technique. Resonance line splitting observed in the NMR spectra indicates reorientation of the $Fe^{3+}$ spin system in the *bc* plane of the crystal. Expressions for the resonance frequencies as functions of the $Fe^{3+}$ spin direction and magnitude of the $Er^{3+}$ magnetic moment are obtained. A noncomplanar magnetic structure in the $Fe^{3+}$ spin system is observed experimentally.

## 1. INTRODUCTION

Rare-earth (RE) orthoferrites, which are a group of substances with chemical formula $RFeO_3$ (R is the rare earth), have an orthorhombic distorted perovskite structure[1], which belongs to the space group $P_{bnm}$. The unit cell of the $RFeO_3$ crystals is shown in Fig. 1.

Magnetic configurations compatible with the group $P_{bnm}$ were first determined by Wollan and Koehler[2] and classified by the type of the magnetic symmetry by Turov and Naĭsh[3], and also by Bertaut[4]. Below the ordering temperature of the spin system of the $Fe^{3+}$ ions, the orthoferrite $ErFeO_3$ is a weak ferromagnet of the Dzyaloshinskiĭ type[5,6] with a weak moment along the c axis and with spins approximately along the a axis (configuration $G_xF_z$). The rare-earth ions are in this case in a paramagnetic state. When the temperature drops below 100°K, the orthoferrite $ErFeO_3$ undergoes a spin-reorientation transition[7,8], in which, in a temperature interval $\approx 10°$, the weak moment and the spins are rotated respectively to the axis a and c (the configuration $G_zF_x$). In the spin-reorientation region, the magnetic space group is an intersection of the groups $P_{b'n'm}$ and $P_{bn'm'}$, which determine the symmetry of the magnetic structure of $ErFEO_3$ outside this region[9]. With further lowering of the temperature as a result of the enhanced influence of the paramagnetic RE ions, a compensation effect takes place at $T \approx 45°K$[10]. However, the configuration $G_zF_x$ is conserved down to the RE-ion ordering temperatures below 4°K.

The magnetic structure of $ErFeO_3$ at still lower temperatures was first investigated by a neutron-diffraction method by Koehler, Wollan, and Wilkinson[11]. It was established that at $T \approx 1.5°K$ the spins of the rare-earth ions are ordered along the c axis, forming the configuration $C_z$, and the spins of the iron ions lie in the ab plane, forming the configuration $G_{xy}F_x$. This conclusion was supported also by the researches of Potand and Sivardiere[12]. However, a detailed analysis of the neutron-diffraction data, with allowance for the results of magnetic measurements, recently performed by Gorodetsky and co-workers[13], has shown that the spins of the iron ions should lie not in the ab plane but in the bc plane, forming the configuration $G_{yz}F_x$ shown in Fig. 2a.

The symmetry of the rare-earth orthoferrites and orthochromites at temperatures below the second Néel temperature $T_{N2}$, where the ordering of the RE ions develops, was considered recently by Yamaguchi and Tsushima[14]. They have indicated that the ordering of the IE ions is usually accompanied by a lowering of the symmetry of the magnetic structure such that the number of symmetry elements is decreased by one half. The latter can be due to the doubling of the magnetic cell, as is assumed for $TbCrO_3$[15]. For most $RMO_3$ compounds (M = Fe or Cr), however, this doubling is not required. It suffices simply to mix two permissible configurations. From this point of view, the "permissible" configuration of $ErFeO_3$ at $T < T_{N2}$ is $\Gamma_{12}(F_x, C_y, G_z, A_x, G_y, C_z; F_x^R, C_y^R, C_z^R)$. If we ignore the possible admixture of the modes $F_x$, $A_x$, $F_x^R$ and $C_y^R$, this configuration takes the form shown in Fig. 2b.

The configuration $\Gamma_{12}$ is symmetrical with respect to inversion and the second-order screw axis $\tilde{C}_{2x}$. The latter symmetry operation transforms the positions of the iron ions in accordance with the scheme $1 \longleftrightarrow 4$ and $2 \longleftrightarrow 3$, i.e., we have two pairs of equivalent ions. We note that the spins of the equivalent ions are almost opposite (Fig. 2b), since $\tilde{C}_{2x}$ is an ordinary and not an inversion symmetry axis. Therefore we should observe in the NMR spectrum two resonant lines, which are

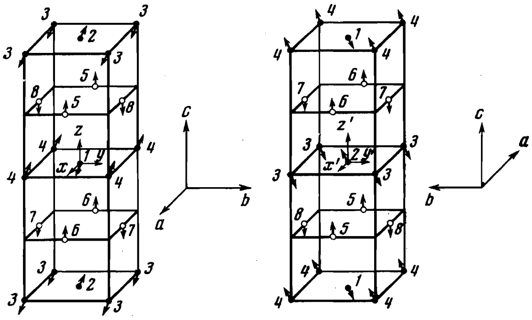

FIG. 1. Crystalline and magnetic structures of $ErFeO_3$ at low temperatures, shown in two reference frames: left—in the system K with center at the ion 1, right—in the system K′ with center at the ion 2 (1–4—Fe ions, 5–8—Er ions).

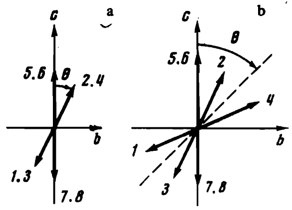

FIG. 2. Spin configuration in $ErFeO_3$ at $T < T_{N2}$: a—from the data of Gorodetsky et al. [13], b—from the data of the present paper (1 to 4—spins of $Fe^{3+}$ ions, 5 to 8—of the $Er^{3+}$ ions).

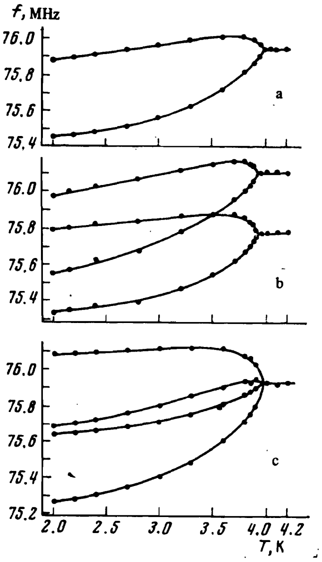

FIG. 3. Temperature dependence of the NMR frequencies of $Fe^{57}$ and $ErFeO_3$: a—$H_0 = 0$, b—$H_0 = 1.2$ kOe along the c axis; c—$H_0 = 2$ kOe along the b axis.

transformed in a magnetic field parallel to the b or c axis of the crystal into two pairs of lines.

## 2. NMR SPECTRA AND THEIR INTERPRETATION

The NMR spectra of $Fe^{57}$ in single-crystal $ErFeO_3$ grown by the procedure described in[16] were obtained with the aid of a spin-echo spectrometer in the temperature range 2—4.2°K. The durations of the exciting pulses satisfied the condition for the excitation of the nuclei in the domains ($\tau_2 = 2\tau_1$) and their values were $\tau_1 = 10$ $\mu$sec and $\tau_2 = 20$ $\mu$sec. The width of the NMR line was ~45 kHz.

The dependence of the resonance frequencies on the temperature, obtained from the aggregate of the recorded spectra, is shown in Fig. 3. In the absence of an external magnetic field (Fig. 3a), the NMR spectrum consists of one line at $T > T_C = 3.98°K$ and of two lines of equal width and intensity at $T < T_C$. The temperature $T_C = 3.98°K$ is close to the ordering temperature of the rare-earth ions $T_{N2} = 4°K$, indicated in[12].

An external magnetic field $H_0$ along the a axis decreases only slightly the temperature $T_C$ at which the splitting of the resonance lines appears, but the NMR spectrum reveals, as before, one line above this temperature and two lines below. This means that the spins of the $Fe^{3+}$ ions are perpendicular to the a axis of the crystal.

In external magnetic fields parallel to the b and c axes of the crystal (Figs. 3b and 3c), each of the spectral lines is split into two lines below $T_C$, as expected. The temperature $T_C$ in a field $H_0 \parallel b$ remains practically unchanged, and in a field $H_0 \parallel c$ it decreases. When the temperature drops below $T_C$, the splitting of the resonance lines decreases in a field $H_0 \parallel c$ and increases in a field $H_0 \parallel b$. This is evidence of the smooth rotation of the spins from the c axis to the b axis of the crystal.

Formulas describing the behavior of the resonant frequencies in the region of the ordering of the Re ions can be obtained from the following considerations:

Assume that $H_0 = 0$ and that the local fields at the nuclei of the $Fe^{3+}$ ions are connected with the magnetic moments of the cations by the linear relations

$$\mathbf{H}_i = \sum_k A(i, k)\boldsymbol{\mu}_k - A_0\boldsymbol{\mu}_i, \quad i=1,2; \quad k=1,2,\ldots,8. \tag{1}$$

Here $A_0$ is the hyperfine interaction constant for the $Fe^{3+}$ ions, $\mu_k$ are the magnetic moments of the cations, and A(i, k) are certain tensors that depend only on the structure of the crystal. The magnetostriction distortions of the rhombic structure of the crystal, which are possible in principle in the case of spin flip, will be ignored.

It is known that the environment of the ions 2 differs from that of the ions 1 in that $R_3$ is rotated through 180° about the c axis and in that the ions undergo the permutation P given by

$$1 \leftrightarrow 2; \; 3 \leftrightarrow 4; \; 5 \leftrightarrow 6; \; 7 \leftrightarrow 8. \tag{2}$$

This means that in the reference frame K′ the distribution of all the ions, without exception, is exactly the same as in the system K (Fig. 1). In this case there is every reason for writing down in the system K′

$$\mathbf{H}_2' = \sum_k A(1, k)\boldsymbol{\mu}_{Pk}' - A_0\boldsymbol{\mu}_2'. \tag{3}$$

In the system K this relation takes the form

$$\mathbf{H}_2 = \sum_k B_k\boldsymbol{\mu}_k - A_0\boldsymbol{\mu}_2 \tag{4}$$

where

$$B_k = A(2, k) = R_3 A(1, Pk) R_3. \tag{5}$$

Thus, the local fields at the nuclei of the nonequivalent $Fe^{3+}$ ions are determined only by the aggregate of the tensors A(1, 1), ..., A(1, 8).

After determining the local fields at the nuclei of the $Fe^{3+}$ ions, we can now calculate the resonant frequencies from the formula

$$\omega(i) = \omega_0 - \gamma_n \sum_k \mu_k(\mathbf{n}_i, A(i, k)\mathbf{n}_k), \tag{6}$$

where

$$\omega_0 = \gamma_n \mu_{Fe} A_0 \tag{7}$$

is the frequency corresponding to the isotropic hyperfine field at the nuclei of the $Fe^{3+}$ ions, and $n_k$ are unit vectors along $\mu_k$. After a number of simple transformations, assuming the magnetic structure of Fig. 1a, we obtain the following expression for the splitting of the NMR frequencies and their mean value:

$$\omega(1) - \omega(2) = F\sin 2\theta + \gamma_n\mu_R G\cos\theta, \tag{8a}$$

$$\tfrac{1}{2}[\omega(1) + \omega(2)] = C + D\cos 2\theta + \gamma_n\mu_R E\sin\theta. \tag{8b}$$

Here C, D, E, F, and G are certain parameters that are uniquely connected with the components of the tensors A(i, k), and $\mu_R$ is the magnetic moment of the $Er^{3+}$ ions. Since the structure of the crystal is practically unchanged after the reorientation, we can assume the parameters C, D, ..., to be constant.

It is obvious furthermore that in a magnetic field $H_c$ along the c axis each of the resonance lines is split:

$$\omega(i) \to \omega_c^{\pm}(i) = \omega_c(i) \pm \gamma_n\mu_{Fe}H_c\cos\theta_c. \tag{9}$$

A similar splitting occurs also in a magnetic field $H_b$ along the b axis:

$$\omega(i) \to \omega_b^{\pm}(i) = \omega_b(i) \pm \gamma_n\mu_{Fe}H_b\sin\theta_b. \tag{10}$$

In (9) and (10), $\omega_{b,c}(i)$ are frequencies determined by relations (8), and $\theta_{b,c}$ are the angles between the moments of the $Fe^{3+}$ and the c axis of the crystal in the presence of external magnetic fields. From (9) and (10) it follows that

$$\Delta\omega_b(i)=\omega_b^+(i)-\omega_b^-(i)=2\gamma_n\mu_{Fe}H_b\sin\theta_b, \tag{11a}$$

$$\Delta\omega_c(i)=\omega_c^+(i)-\omega_c^-(i)=2\gamma_n\mu_{Fe}H_c\cos\theta_c. \tag{11b}$$

Thus, from the splitting of the NMR frequencies in the magnetic field we can determine $\theta_b$ and $\theta_c$.

Turning to the experimental results (Figs. 3b and 3c), we observe that the values of the splitting of the two resonance lines in the magnetic field, $\Delta\omega(1)$ and $\Delta\omega(2)$, are different. This difference, however, is insignificant and can be attributed to the weak spatial splitting of the spins of the nonequivalent iron ions (Fig. 2b), which appears as a result of the mixing of the $C_{yz}$ mode. Figure 4 shows the temperature dependences of the angles $\theta_b$ in a magnetic field of 1 kOe, obtained from the experimental data of Fig. 3c in formula (11a) for i = 1 and 2. The difference between $\theta_1$ and $\theta_2$ is negligible and reaches approximately 3–4 deg at 2°K.

Notice should be taken of the fact that a magnetic field parallel to the b axis of the crystal does not cause any noticeable change in the magnetic structure of the orthoferrite. This is evidenced by the fact that the splitting of the resonance lines, due to this field, depends linearly, at a fixed temperature, on $H_0$ (Fig. 5), and $T_c$ remains constant. Neglecting the difference between $\theta_1$ and $\theta_2$ (Fig. 4) and using the dependence of the resonance frequencies and of $\theta$ on the temperature, we can determine from (8), in principle, the parameters C, D, ..., and the temperature dependence of $\mu_R$.

## 3. CONCLUSIONS

Our investigations of the NMR of $Fe^{57}$ in $ErFeO_3$ in the temperature range where the Re ions are ordered establishes unequivocally the fact that the spins of the $Fe^{3+}$ are continuously rotated in the bc plane. The high accuracy of the measurements by the NMR method has made it possible to observe the onset of a noncomplanar magnetic structure of the iron ions in $ErFeO_3$ at low temperatures.

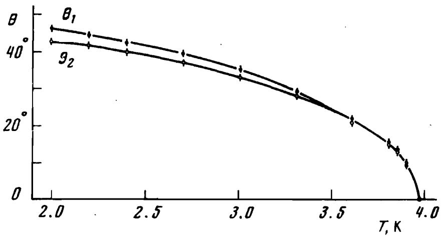

FIG. 4. Dependence of the direction of the magnetic moments of the $Fe^{3+}$ ions on the temperature.

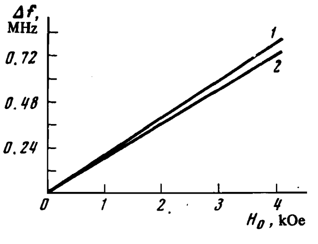

FIG. 5. Dependence of the splittings of the resonant frequencies $\Delta f_{1,2}$ on the external magnetic field $H_0$ applied along the b axis at T = 2°K.

The expressions obtained for the resonance frequencies (8) can be reconciled with the experimental results if the parameters C, D, ..., are suitably chosen. The magnitude of the splitting of the resonant frequencies (8a) depends, on the one hand, on the direction of the spins of the $Fe^{3+}$ ions in the bc plane and, on the other, on the value of the magnetic moments of the $Er^{3+}$ ions, as was assumed in[17]. This makes it possible in principle, on the basis of only the NMR data on $Fe^{57}$, to obtain information on the temperature dependence of the magnetic moments of the $Er^{3+}$ ions, which is of considerable interest in connection with investigations of the ordering of Re ions in orthoferrites and in similar compounds.

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