Spin reorientation in $ErFeO_3$ under uniaxial compression: An NMR study

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Nuclear magnetic resonance of ^{57}Fe nuclei is used to study the effect of uniaxial compression parallel to the *c* axis of an erbium orthoferrite crystal on the temperature dependence of the NMR frequency spectrum in the temperature range of the spin-reorientation phase transition Γ_4—Γ_2. An abrupt change is discovered in the transition temperature as the stress is varied. This is accompanied by a change in the nature of the spin-reorientation transition: from $\Gamma_4-\Gamma_2$ for $P<P_{cr}$ to $\Gamma_4-\Gamma_4+\Gamma_{42}(\theta=\frac{1}{4}\pi)$—$\Gamma_{42}(\theta=\frac{1}{4}\pi)$—$\Gamma_{24}(\theta=\frac{1}{4}\pi)+\Gamma_2$—$\Gamma_2$ for $P>P_{cr}$. *© 1995 American Institute of Physics.*

1. INTRODUCTION

In view of the complexity of the experiments and of fabricating high-quality samples, there are very few studies of the effect of uniaxial stress on spin-reorientation (SR) phase transitions in magnetic substances. For example, the effect of uniaxial stress on SR transitions in orthoferrites has only been studied by Belov *et al.*[1] for $TmFeO_3$. Stress in the direction of the *c* axis was found to affect the temperature shift of the SR transition. However, measurements of the temperature dependence of the magnetization do not provide complete and conclusive information about the nature of the SR transition.

In this paper we employ NMR of ^{57}Fe nuclei to study how uniaxial compression parallel to the *c* axis of the crystal affects the SR transition in $ErFeO_3$.

Erbium orthoferrite $ErFeO_3$ is a compound with orthorhombic symmetry belonging to the $D_{2h}^{16}-P_{bnm}$ spatial group. Magnetically, $ErFeO_3$ is a weak ferromagnet below T_N and possesses the magnetic configuration Γ_4. As the temperature is lowered to the 90–100 K range, spontaneous spin reorientation (even rotation of the spins of Fe^{3+} ions) takes place in the orthoferrite through two second-order magnetic phase transitions from the high-temperature magnetic configuration $\Gamma_4(F_zG_x)$ to the low-temperature magnetic configuration $\Gamma_2(F_xG_z)$. In the absence of stress in erbium orthoferrite, the ^{57}Fe NMR spectrum in the SR range exhibits a characteristic line splitting effect (formation of a "loop"), which is a consequence of the magnetic nonequivalence of iron nuclei; Fig. 1a.[2-4] The size of the splitting of NMR ^{57}Fe frequencies in the SR region is directly determined by the spin orientation angle θ in Fe^{3+} ions ($\Delta F\sim\sin 2\theta$), which makes it possible to effectively use this quantity to study SR transitions and magnetic structures.

2. SAMPLES AND THE METHOD

Our experiment used a single crystal of $ErFeO_3$ grown along the *c* axis by crucible-free floating-zone melting with optical heating and enriched with the ^{57}Fe isotope ($\sim 10\%$). The sample was 6 mm in diameter and 10 mm long.

NMR studies of ^{57}Fe nuclei were conducted with a semiautomatic pulse NMR spectrometer operating in the 5–100 MHz frequency range by the spin-echo (Hahn) method. The length of the exciting pulses was $\tau_1=4\ \mu$m and $\tau_2=8\ \mu$m, the lag between the pulses was $\tau_{12}=100\ \mu$m, and the pulse repetition frequency was $f_r=250$ Hz. The absorption linewidth ΔF was roughly 60 kHz.

The directions of the crystallographic axes were determined and the crystal was oriented during processing with a DRON-1,5 x-ray diffractometer. Uniaxial stress in the sample was maintained by the method described in Ref. 5, in which a bellows press[6] was employed. The medium acting as the stress mediator was gaseous helium, and pressure measurements were done by a reference pressure gauge. The experimental errors were as follows: $\Delta F=\pm 20$ kHz in frequency measurements, $\Delta T=\pm 0.1$ K in temperature measurements, and $\Delta P=\pm 3$ % in pressure measurements.

3. DISCUSSION

Uniaxial compression applied along the *c* axis does not change the nature of the SR transition up to pressures of 0.126 GPa but gives rise to a substantial shift of the SR region up the temperature scale at a rate of 45 K GPa^{-1}. Thus, compression along the *c* axis lowers the energy of the magnetic configuration Γ_2. For $P>0.126$ GPa the shape of the NMR spectrum changes dramatically. A reduction to $T=T_2$ in the temperature is accompanied by the sudden appearance, in addition to the line corresponding to the high-temperature phase, of two lines whose positions coincide with those of the two lines in the $ErFeO_3$ NMR spectrum for $P=0$ or $P<0.126$ GPa at the center of the SR transitions, i.e., when the rotation angle θ of the spins of iron ions is $\frac{1}{4}\pi$. As the temperature decreases below T_2, the central line of the high-temperature phase gradually disappears, and in its place the central line corresponding to the low-temperature phase appears. As the pressure is increased, the central line of the high-temperature phase gradually begins to change into the central line of the low-temperature phase. The edge lines in the NMR spectrum, exhibiting practically no change with respect to the central line, are observed up to the temperature T_1, where they suddenly disappear (Figs. 1b and c).

Applying external mechanical stress (pressure) leads to elastic deformation of the sample. Under uniaxial compres-

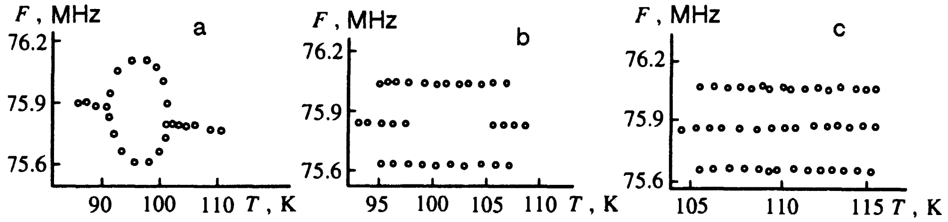

FIG. 1. The temperature dependence of the ^{57}Fe NMR frequencies in ErFeO$_3$ in the region of the SR transition Γ_4—Γ_2: (a) $P=0$, (b) $P=0.126$ GPa, and (c) $P=0.19$ GPa.

sion along the c axis the components of the elastic strain tensor for a rhombic crystal are determined by the expression

$$\varepsilon_{ij}=-PS_{ijzz}\delta_{ij}, \tag{1}$$

where S_{ijkl} is the elastic compliance tensor. For a rhombic crystal under hydrostatic stress we have

$$\varepsilon_{ii}=-P\sum_j S_{iijj}. \tag{2}$$

Hydrostatic stress or compression along the crystallographic axes a, b, and c of a rhombic crystal does not alter the symmetry of the lattice. Because of the magnetoelastic bonds, it only changes the anisotropy constant K_1:

$$\Delta K_1=L_a\varepsilon_{aa}+L_b\varepsilon_{bb}+L_c\varepsilon_{cc}$$

$$=\begin{cases} -P\sum\limits_i L_iS_{ii33}\,(\text{compression along the } c \text{ axis}),\\ \\ -P\sum\limits_{ij} L_iS_{iijj}\,(\text{hydrostatic stress}).\end{cases} \tag{3}$$

The presence of a shear component in the mechanical stresses changes the rhombic symmetry of the crystal and induces an orientational phase transition in the strain plane for an arbitrarily low level of shear.

Let us write the magnetic energy of the crystal, including the magnetoelastic energy, in the form

$$\Phi=K_1\sin^2\theta+K_2\sin^4\theta$$

$$+(L_a\varepsilon_{aa}+L_b\varepsilon_{bb}+L_c\varepsilon_{cc})\sin^2\theta+\tfrac{1}{2}\,\mu_2\varepsilon_{ac}\sin 2\theta, \tag{4}$$

where K_1 and K_2 are the first and second magnetic anisotropy constants; θ is the angle at which the magnetic moments are oriented in relation to the c axis of the crystal; L_a, L_b, L_c, and μ_2 are the magnetoelastic coupling constants; and ε_{aa}, ε_{bb}, ε_{cc}, and ε_{cc} are the components of the strain tensor of a rhombic crystal.

In the absence of shear stresses, as shown earlier, the effect of pressure reduces solely to a change in the magnetic anisotropy constants and, as a result, to a shift of the beginning and end of SR with no change in the SR range. If we assume that K_2, L_a, L_b, and L_c are approximately temperature-independent and K_1 is a linear function of temperature specified as[7]

$$K_1(T)=2K_2\frac{T-T_2}{T_2-T_1}, \tag{5}$$

where T_1 and T_2 are the beginning and end of the SR range, we have

$$\frac{\partial T_1}{\partial P}=\frac{\partial T_2}{\partial P}=-\frac{(T_2-T_1)}{2K_2}\frac{\partial K_1}{\partial P}. \tag{6}$$

In the presence of elastic strain we can introduce an effective anisotropy constant as follows:

$$K_1^{\text{eff}}=K_1+\Delta K_1,\quad \Delta K_1=L_a\varepsilon_{aa}+L_b\varepsilon_{bb}+L_c\varepsilon_{cc}. \tag{7}$$

Using the experimental data on the elastic constants of TmFeO$_3$ (Ref. 8), we find that

$$S_{1133}=-0.22\times10^{-2}\ \text{GPa}^{-1},$$

$$S_{2233}=-0.21\times10^{-2}\ \text{GPa}^{-1},$$

$$S_{3333}=+0.65\times10^{-2}\ \text{GPa}^{-1}.$$

Hence under uniaxial compression along the c axis in TmFeO$_3$ the following strains emerge:

$$\varepsilon_{aa}\simeq0.22\times10^{-4}P,\quad \varepsilon_{bb}\simeq0.21\times10^{-4}P,$$

$$\varepsilon_{cc}\simeq-0.65\times10^{-4}P,$$

where P is in units of GPa. The values for erbium orthoferrite are expected to be close. Using the data of Ref. 7,

$$L_a\simeq2.2\times10^6\ \text{J/m}^3,\quad L_b\simeq2.2\times10^6\ \text{J/m}^3,$$

$$L_c\simeq-5.4\times10^6\ \text{J/m}^3,$$

we get $\Delta K=-4.5\times10^3P$, i.e.,

$$\frac{\partial K_1^{\text{eff}}}{\partial P}=4.5\times10^6\ \text{J/m}^3\ \text{GPa}^{-1}.$$

Assuming $\Delta T=T_2-T_1\simeq10$ K and $K_2\simeq5\times10^3$ J/m^{-3}, which is characteristic of ErFeO$_3$ (see Ref. 7), we find that

$$\frac{\partial T_2}{\partial P}=\frac{\partial T_1}{\partial P}\approx+45\ \text{K/GPa}.$$

Thus, the temperatures T_1 and T_2 of the beginning and end of the SR transition grow at the same rate (i.e., without changing the range of the SR transition) as the uniaxial stress along the c axis increases. The qualitative estimates of the rate of growth of T_1 and T_2 with stress, obtained via experimental data on TmFeO$_3$, the closest neighbor of ErFeO$_3$, agree completely with data obtained in measurements for $P<0.126$ GPa.

As noted earlier, under hydrostatic pressure the elastic strains in the crystal are described by Eq. (2). Using the data on TmFeO$_3$ of Ref. 8,

$$S_{11}=0.18\times10^{-2}\ \text{GPa}^{-1},\quad S_{22}=0.15\times10^{-2}\ \text{GPa}^{-1},$$

$$S_{33}=0.23\times10^{-2}\ \text{GPa}^{-1},$$

we get

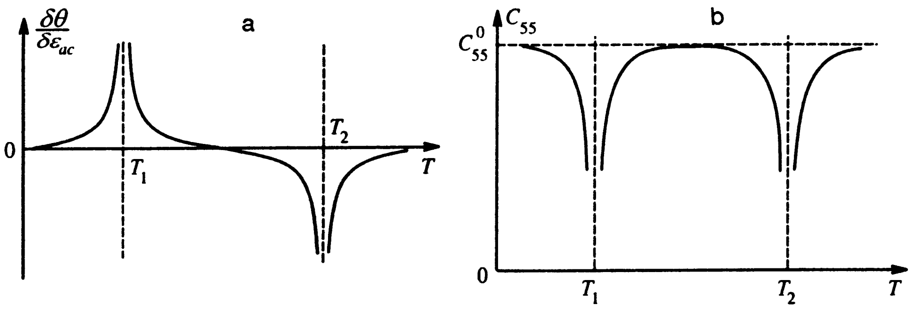

FIG. 2. A schematic of the temperature dependence of the shearing magnetic susceptibility (b) and the shearing elastic constant (b) in the region of the SR transition Γ_4—Γ_2.

$$\frac{\partial K_1^{\text{eff}}}{\partial P_{\text{isotr}}} = -0.5\times 10^4\ \text{J/m}^3\cdot\text{GPa}^{-1}$$

and

$$\frac{\partial T_1}{\partial P_{\text{isotr}}} \approx \frac{\partial T_2}{\partial P_{\text{isotr}}} \approx 5\ \text{K/GPa}.$$

Our investigations of the effect of hydrostatic stress on the SR transition in $ErFeO_3$ have shown that up to pressures of 1.3 GPa the nature of the transition does not change; only its temperature range shifts up the temperature scale at a rate of about 1.5 K/GPa, which agrees with the predictions of the simplest model theory.

According to Ref. 7, the shift in the SR temperature under hydrostatic pressure is proportional to the sum of strains along the principal axes of the crystal. Allowing for the fact that in SR in $TmFeO_3$ the magnetostriction strains are negative along the a and b axes and positive along the c axis, one should expect a decrease in the effect on the shift of the SR temperature from hydrostatic pressure in comparison to uniaxial pressure; this was observed in experiments with $TmFeO_3$ in Ref. 1 and in $ErFeO_3$ in our experiments.

We believe that shear, homogeneous or inhomogeneous, which emerges either because of the inaccuracy in the orientation of crystallographic axes along the stress axis or because of the presence in the sample of various defects in crystal structure, plays an important role in determining the nature of the SR transition in the presence of uniaxial stress. The unique property of mechanical shear stresses is the possibility of inducing spontaneous reorientation in any plane of the orthoferrite. For instance, in the $\Gamma_4(G_x)$ configuration, "shear" stress in the ac plane induces ac-reorientation, and "shear" stress in the ab plane induces ab-reorientation. In the $\Gamma_2(G_z)$ configuration, "shear" stress in the ac plane induces ac-reorientation, and "shear" stress in the bc plane induces bc-reorientation. But if uniaxial stress is applied in the temperature range where an angular phase, say Γ_{24}, occurs, the spatial angular configuration Γ_{124} may be obtained. This requires applying "shear" stress either in the bc plane or in the ab plane.

Minimizing the thermodynamic potential (4) in angle θ, we find that in the presence of shear in the ac plane the equilibrium value of the orientation angle of the spins of iron ions in $ErFeO_3$ is determined by the equation

$$\tan 2\theta = -\frac{\mu_2\varepsilon_{ac}}{K_1^{\text{eff}} + 2K_2\sin^2\theta} \tag{8}$$

(for $\cos 2\theta \neq 0$).

For the "magnetoelastic" susceptibility we have

$$\left.\frac{\partial\theta}{\partial\varepsilon_{ac}}\right|_0 = \begin{cases} -\dfrac{\mu_2}{2K_1}, & \theta=0, \\ -\dfrac{\mu_2}{2(K_1+2K_2)}, & \theta=\dfrac{\pi}{2}, \\ -\dfrac{\mu_2\cos 2\theta}{2K_2\sin^2\theta}, & 0<\theta<\dfrac{\pi}{2}. \end{cases} \tag{9}$$

Thus, the magnetoelastic susceptibility $(\partial\theta/\partial\varepsilon_{ac})|_0$ has a hyperbolic singularity at the beginning (point T_1) and end (point T_2) of the SR transition (Fig. 2a). Note that as ε_{ac} grows, the equilibrium value of the spin orientation angle $\theta = \pi/4$ which under ordinary conditions (in the absence of stress) corresponds to the center of the SR transition and is determined by the peak in the ^{57}Fe NMR frequency splitting.

At the points T_1 and T_2 the hyperbolic divergence is also a characteristic feature of the elastic susceptibility S_{55}, the component of the elastic pliability tensor that determines the response to shear mechanical stress in the ac plane.

In practice it is more customary to use the corresponding component (C_{55}) of the tensor of elastic constants; the critical behavior of this component under ac-reorientation is depicted schematically in Fig. 2b. The sharp decreases in C_{55} at points T_1 and T_2 leads to an appropriate drop in the transverse sound propagation speed, $v_{ac}^T = \sqrt{C_{55}/\rho}$, and to anomalous "softening" of the lattice in relation to shear mechanical stresses in the spin rotation plane.

The emergence of small homogeneous or inhomogeneous shear mechanical stresses σ_{ac} under uniaxial stress results in the appearance of corresponding shear strains ε_{ac}, which acquire exceptionally large values at the beginning (point T_1) and end (point T_2) of the SR transition Γ_4—Γ_2 and in the process induce the angular phase Γ_{42} with $\theta=\pi/4$. Magnetic inhomogeneities, in particular regions inside domains in the phases Γ_4 and Γ_2, may act here as nucleation centers of the Γ_{42} phase ($\theta=\pi/4$).

Note that an important feature of the $\frac{1}{4}\pi$ phase is that the dispersion of the spin orientation angle θ is largest in compounds with fluctuating anisotropy (substituted and defective orthoferrites).[9] This may lead to additional "softening" of the lattice with respect to shear stresses at the center of the SR transition. The latter evidently manifests itself in the anomalous behavior of the transverse sound velocity v_{ac}^T in this region for a number of substituted orthoferrites.[10] Thus, the regions near defects with a fluctuating first anisotropy constant may act as "stabilizers" of the $\pi/4$-phase.

Growth of the nucleation centers of the $\pi/4$-phase probably exhibits a threshold as a function of stress, which is suggested by the existence in our experiments of a critical pressure $P_{\mathrm{cr}}=0.126$ GPa.

The nature of the ^{57}Fe NMR spectra in ErFeO_3 and analysis show that for $P>P_{\mathrm{cr}}=0.126$ GPa the ordinarily smooth SR transition Γ_4—Γ_2 transforms into a first-order phase transition according to the following scheme:

$$\Gamma_4-\Gamma_4+\Gamma_{42}\left(\theta=\frac{\pi}{4}\right)-\Gamma_{42}\left(\theta=\frac{\pi}{4}\right)-\Gamma_{24}\left(\theta=\frac{\pi}{4}\right)$$
$$+\Gamma_2-\Gamma_2, \tag{10}$$

with formation of nucleation centers of the $\pi/4$-phase and a magnetically inhomogeneous state.

As the stresses grow (the experiment was carried out up to 0.19 GPa), the coexistence region of the phases mentioned above broadens (up to 20 K at the point of maximum pressure).

The change in the nature of the SR transition Γ_4—Γ_2 when $P>P_{\mathrm{cr}}$ manifests itself not only in the features of the ^{57}Fe NMR spectra but also in other characteristics and dependences, for one thing, in the temperature dependence of magnetization in the SR transition region.

In conclusion we note that the nature of the transition and primarily such quantities as P_{cr}, the temperature shift, and the phase coexistence region depend essentially on the presence of defects in the sample and the accuracy in orienting the crystal and stresses.

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