laws become effective starting not with the zeroth momentum, but with P_{eh}.)

One of the possible experimental applications is the study of the dispersion relations of excitons. Besides the traditional methods (e.g., using Raman scattering), observation is possible of dispersion in an electric field $\vec{\mathscr{E}}$ perpendicular to the field H. The point is that, just as in the three dimensional case,[3] in the presence of a field the energy depends on the vector

$$\mathbf{P}'=\mathbf{P}+\frac{Mc}{H^2}[\mathbf{H}\times\vec{\mathscr{E}}].$$

At $P=0$ the momentum characteristic values $P'\sim 1/r_H$ are reached in fields $\mathscr{E}\sim(1/137)(a_0/r_H)H$.

---

1)The energy of e or h in the usual representation $|n_1, m_1; n_2, m_2\rangle$ ($n_{1,2}$ and $m_{1,2}$ are respectively the radial and azimuthal quantum numbers of e and h) is given by

$$\mathscr{E}=(n_1+{}^1/_2)\omega_e+(n_2+{}^1/_2)\omega_h,$$

i.e., it is degenerate in m_1 and m_2. Equation (7) corresponds to the cited expression ($\omega_{e,h}=eH/m_{e,h}c$ at $n=\min(n_1, n_2)$, $m=n_2-n_1$.

2)It is implied that $|\mathbf{P}|\ll|\mathbf{G}|$, where G is the reciprocal-lattice vector. This restriction is inessential, since the dispersion curves are nonmonotonic only in the region $P\sim 1/r_H \ll G$.

3)Since the Coulomb operator is diagonal in m at $P=0$, the position of the centers of the exciton bands relative to the unperturbed levels (7) does not change at any value of γ. Nor does the asymptotic form of the dispersion laws change at $Pr_H\gg 1$.

4)In any state, the exciton mass $M_{nm}\sim 1/E_0 r_H^2$ does not depend on the effective masses e and h at $H=0$. It is seen, however, from the equality $1/E_0 r_H^2\sim(a_0/r_H)M$ (where $a_0=a_e+a_h$ and M is the mass of the exciton as a whole at $H=0$), that $M_{nm}\gg M$.

---

[1]R. J. Elliot and R. Loudon, J. Phys. Chem. Solids 15, 196 (1960).

[2]H. Hasegawa and R. E. Howard, J. Phys. Chem. Solids 21, 179 (1961).

[3]L. P. Gor'kov and I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. 53, 717 (1967) [Sov. Phys. JETP 26, 449 (1967)].

[4]I. V. Lerner and Yu. E. Lozovik, a) Solid State Commun. 23, 453 (1977); b) Zh. Eksp. Teor. Fiz. 74, 274 (1978) [Sov. Phys. JETP 47, 140 (1978)].

[5]I. V. Lerner and Yu. E. Lozovik, Pis'ma Zh. Eksp. Teor. Fiz. 27, 497 (1978) [JETP Lett. 27, 467 (1978)]; J. Low Temp. Phys. 38, 333 (1980).

[6]Y. Kuramoto and C. Horie, Solid State Commun. 25, 713 (1978).

[7]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, 1974 [Pergamon].

[8]S. D. Beneslavskiĭ and A. I. Buzdin, Proc. 2nd All-Union Conf. on Metal-Insulator transitions, Lvov, 1977, p. 231.

[9]Yu. B. Grebenshchikov and V. V. Korneev, Fiz. Tverd. Tela (Leningrad) 19, 2143 (1977) [Sov. Phys. Solid State 19, 1255 (1977)].

[10]É. M. Baskin, L. I. Magarill, and M. V. Éntin, Zh. Eksp. Teor. Fiz. 75, 723 (1978) [Sov. Phys. JETP 48, 365 (1978)].

[11]S. D. Beneslavskiĭ and É. Éntral'go, Zh. Eksp. Teor. Fiz. 68, 2271 (1975) [Sov. Phys. JETP 41, 1135 (1975)].

Translated by J. G. Adashko

NMR investigation of the anisotropy of hyperfine interactions of orthoferrites

A. S. Karnachev, Yu. I. Klechin, N. M. Kovtun, A. S. Moskvin, and E. E. Solov'ev

Donetsk Physicotechnical Institute, Ukrainian Academy of Sciences

(Submitted 23 August 1979)
Zh. Eksp. Teor. Fiz. 78, 1176–1195 (March 1980)

The anisotropy of the hyperfine interactions in a number of rare-earth orthoferrites is investigated experimentally and theoretically on the basis of the singularities produced in the NMR spectrum of ^{57}Fe nuclei in spin-reorientation phase transitions. Both non-substituted orthoferrites and orthoferrites substituted in the rare-earth sublattice are investigated. A phenomenological analysis based on the use of the magnetic symmetry of orthoferrites has made possible a qualitative explanation of all the effects observed in NMR experiments. A microscopic analysis points to a small contribution of the paramagnetic rare-earth sublattice to the anisotropy of the hyperfine interactions (HFI) for the ^{57}Fe nuclei. The most probable mechanism of the HFI anisotropy, explaining all the main features of NMR in the spin-reorientation region is connected with the non-cubic contribution to the crystal field at the Fe^{3+} ions from the next-to-nearest environment, considered within the framework of the point-charge model.

PACS numbers: 75.30.Gw, 76.60.Jx, 75.50.Gg

A few years ago, NMR investigations of phase transitions of the spin-reorientation (SR) type in rare-earth orthoferrites (REO) have led to observation of an interesting phenomenon—violation of the magnetic equivalence of the ions from different sublattices of the iron. This violation consisted in the fact that two values of the local field are produced at the ^{57}Fe nuclei in the SR transitions. In addition, other subtle effects were observed, such as a jump of the local field and the nonsynchronous rotation of the antiferromagnetism vector and the vector of the summary magnetization following the SR.

It was indicated in the first studies that a connection exist between the splitting and shift of the NMR frequencies in the region of the SR transition, on the one hand, and the character of the hyperfine interaction, on the other.[1,2] Allowance for the magnetodipole interactions of the ^{57}Fe nuclei with the surrounding Fe^{3+} ions, however, did not provide a satisfactory quantitative explanation of the observed effect.[3] In addition, no account was taken in the earlier research on the influence of the rare-earth ions. This has made it necessary to explain the experimental data using a model in which the antiferromagnetism and ferromagnetism vectors (**l** and **m**) are not orthogonal in the SR region. Later investigations of mixed orthoferrites containing various rare-earth ions have shown that these effects differ substantially in character, depending precisely on which of the lanthanide-series ion is contained in the given orthoferrite, and at what concentration.

To clarify the physical nature of the observed phenomenon, we have performed as complete as possible theoretical and experimental investigations, using as examples a large number of substituted and non-substituted REO containing rare-earth ions from different parts of the lanthanide series.

The rare-earth orthoferrites are part of a group of oxides having an orthorhombically distorted perovskite structure (space group $D_{2h}^{16}-Pbnm$). Their chemical formula is $RFeO_3$, where R is a rare-earth or yttrium ion. Whereas in an ideal perovskite structure the oxygen ions surrounding the rare-earth ions and the iron ions form undistorted polyhedra, in the REO structure one observes small distortions of the oxygen octahedra surrounding the Fe^{3+} ions, and a rather large distortion of the oxygen polyhedra surrounding the R^{3+} ions. All these distortions increase with increasing atomic number of the rare-earth element.[4] The unit cell of $RFeO_3$ contains four Fe^{3+} ions in the positions $1-(0,\frac{1}{2},0)$, $2-(0,\frac{1}{2},\frac{1}{2})$, $3-(\frac{1}{2},0,\frac{1}{2})$, $4-(\frac{1}{2},0,0)$, as well as $4\,R^{3+}$ ions in the positions $5-(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{4})$, $6-(\frac{1}{2}+x,\frac{1}{2}-y,\frac{3}{4})$, $7-x,-y,\frac{3}{4})$, $8-(x,y,\frac{1}{4})$. These compounds are weak ferromagnets. It is convenient to characterize their magnetic structure by the basis vectors **F** (or m), **G** (or l), **C**, **A** and **f**, **g**, **c**, **a** for the Fe and R sublattices, respectively, with[5]

$$\begin{aligned} 4M\mathbf{F}&=\mathbf{M}_1+\mathbf{M}_2+\mathbf{M}_3+\mathbf{M}_4, \quad & 4M\mathbf{G}&=\mathbf{M}_1-\mathbf{M}_2+\mathbf{M}_3-\mathbf{M}_4,\\ 4M\mathbf{C}&=\mathbf{M}_1+\mathbf{M}_2-\mathbf{M}_3-\mathbf{M}_4, \quad & 4M\mathbf{A}&=\mathbf{M}_1-\mathbf{M}_2-\mathbf{M}_3+\mathbf{M}_4, \end{aligned} \tag{1}$$

where M is the magnetic moment of the Fe^{3+} ion. The basis vectors are defined such that $\mathbf{F}^2+\mathbf{G}^2+\mathbf{C}^2+\mathbf{A}^2=1$. The expressions for **f**, **g**, **c**, and **a** are obtained in analogy with (1) by replacing 1, 2, 3, 4 by 5, 6, 7, 8. For the Fe sublattice[6] $F,C,A \ll G$, thus indicating a G-type structure.

The magnetic structures typical of REO are defined by the set of basis vectors[5] $\Gamma_1(A_x, G_y, C_z; c_z)$, $\Gamma_2(F_x, C_y, G_z; f_x, c_y)$, $\Gamma_4(G_x, A_y, F_z; f_z)$. The spins of the Fe^{3+} below T_{N_1} (~640–700 K) are ordered in the configuration Γ_4, and with decreasing temperature many orthoferrites undergo an SR transition to the configuration Γ_2 (or Γ_1 in the case of $DyFeO_3$).

NMR investigations of rare-earth orthoferrites not only permits the observation and study of the phenomenon of spin reorientation and its accompanying effects of splitting and shift of the NMR frequencies, but also provide practically the only means of studying the anisotropy of hyperfine interaction, an effect which is very weak in the case of the Fe^{3+} ions.

I. EXPERIMENT

The ^{57}Fe NMR signals were excited by a two-pulse procedure using a semi-automatic spin-echo spectrometer with direct automatic recording of the signal. The durations of the exciting signals, depending on the investigated objects, were varied in the ranges $\tau_1=3-10$ and $\tau_2=6-20$ μsec, the interval between the pulses was 150 μsec, and the repetition frequency of the pulse pair was $f=27-98$ Hz. To excite an NMR signal from nuclei inside the domains, the ratio of the durations of the pulses were chosen such that $\tau_2=2\tau_1$. To check that the signal comes from nuclei inside a domain, we used an external constant magnetic field, and also the principle of separating the signals in accord with the amplitude of the exciting voltage.

In view of the large scatter of the phase-transition temperatures in the investigated samples, we used specially developed cryostats and thermostats, in which the coolants were liquid helium, liquid nitrogen, and their vapors. The temperature instability in the range 2–20 K did not exceed 0.05 K, and at temperatures above ~20 K it did not exceed 0.1 K. The error in the measurement of the NMR frequency was ±25 kHz in all cases.

We investigated single-crystal samples of non-substituted orthoferrites $ErFeO_3$, $TmFeO_3$, $YbFeO_3$, $HoFeO_3$, $NdFeO_3$, and also of orthoferrites of mixed compositions: $Er_{1-x}Nd_xFeO_3$ ($x=0.08$; 0.4), $Tm_{1-x}Sm_xFeO_3$ ($x=0.1$; 0.25), $Er_{0.3}Ho_{0.7}FeO_3$, $Er_{0.5}Tm_{0.5}FeO_3$, $Er_{0.8}Dy_{0.2}FeO_3$, $Ho_{0.5}Gd_{0.5}FeO_3$. All the non-substitued orthoferrites, with the exception of $NdFeO_3$, were grown by radiative-heating zone melting without a crucible in the Problem Laboratory of the Moscow Power Institute.

To estimate the structural perfection of the crystals we used x-ray diffraction, metallographic, and microscopic x-ray spectral analysis. The results of the investigations have shown that all the single crystals are single-phase and contain no twins, blocks, or micropores. A chemical analysis has shown that the deviation from stoichiometry does not exceed 1% and the Fe^{2+} ion content is not more than 0.4%. The single crystals were cylinders of 6 mm diameter and 10–15 mm height. The compound $NdFeO_3$ and all the mixed compositions were obtained in the laboratory of optical single crystals of the Crystallography Institute of the USSR Academy of Sciences by spontaneous crystallization from solutions in a $PbO-PbF_2-B_2O_3$ melt. Metallographic and x-ray structure analysis confirmed the absence of extraneous phases. All the single crystals grown by this method had a clearly pronounced perovskite faceting. Their dimensions, depending on the composition, ranged from one to several cubic millimeters.

In the study of the SR transitions in $ErFeO_3$ and $TmFeO_3$ we have observed violation of the magnetic equivalence of the Fe^{3+} ions in the SR temperature interval.[1-3] This violation manifests itself in the NMR spectrum in the form of a smooth splitting of the resonance line into lines of equal intensity and width. The temperature dependence of the NMR frequency in the SR band for $ErFeO_3$ is shown in Fig. 1. Besides the splitting of the resonance lines, the maximum value of which is 510 kHz (≈3.7 kOe), this dependence has one more singularity, namely a jump of the NMR frequency, since the plot of the temperature dependence of the frequency, extrapolated from the region $T>T_2$ into the region $T<T_1$, passes below the analogous curve obtained for the region $T<T_1$ in experiment. The

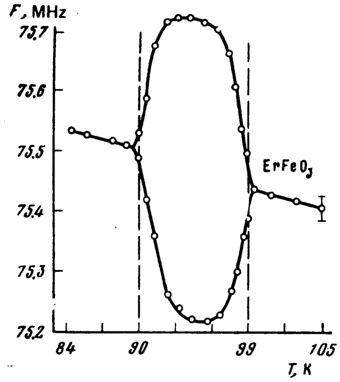

FIG. 1. Temperature dependence of the NMR frequency of ^{57}Fe nuclei in the vicinity of the spin reorientation for $ErFeO_3$.

size of this jump is ~50 kHz (~0.35 kOe). A similar dependence is observed also in $TmFeO_3$.[2]

We have also investigated the SR in $HoFeO_3$ and in $YbFeO_3$. In both cases a splitting of the resonance line into two is also observed, indicating the onset of non-equivalence of the iron ions. In $HoFeO_3$, however, the frequency jump is the reverse of that observed in $ErFeO_3$ and amounts to ≈100 kHz (≈0.7 kOe), while in $YbFeO_3$ there is practically no such jump.

Investigation of neodymium orthoferrite $NdFeO_3$ has shown that in this compound there is no noticeable violation of the equivalence of the iron ions. In this orthoferrite, just as in the one described above, there is spin reorientation in the ac plane, proceeding via two second-order phase transitions. Figure 2 shows the temperature dependence of the NMR frequency in the SR range in $NdFeO_3$. It shows also the temperature dependence of the NMR signal intensity. The highest intensity is reached by the NMR signal at the phase-transition points $T_1 = 112$ K and $T_2 = 187$ K. Inside this temperature range, a smooth rotation of the spins takes place, but no difference is observed between the local fields at the ^{57}Fe nuclei. The NMR line remains single and only broadens slightly, indicating that the NMR frequency splitting does not exceed here 60 kHz (the line half-width).

The singularities in the behavior the resonance frequencies called for a more detailed investigation of the influence exerted on the magnetic nonequivalence of the iron ions by the rare-earth ions. Bearing in mind the large difference in the splitting of the resonance frequencies between $ErFeO_3$ (510 kHz) and $NdFeO_3$ (60 kHz), we have replaced some of the erbium ions by neodymium ions. We have investigated samples of composition $Er_{1-x}Nd_xFeO_3$ with $x = 0.08$ and $x = 0.4$. Table I lists the temperatures of the start (T_1) and end (T_2) of the reorientation for these compositions, and also the values of the splitting ΔF of the NMR line. Since the SR in $NdFeO_3$ occurs at a much higher temperature than in $ErFeO_3$, and occupies a wider temperature region, it was correct to expect the temperature of the reorientation transition to increase with increasing neodymium content, and that its band would broaden. It is seen from Table I that this is in fact the case. In addition, it is seen that with increasing neodymium content the splitting of the NMR frequencies decreases. The composition with $x = 0.4$ has no resolved NMR spectrum in the SR band, so that it is impossible to determine the exact value of the splitting. It can only be stated with assurance that it does not exceed 300 kHz. Thus, addition of neodymium greatly decreases the splitting of the NMR frequencies observed in $ErFeO_3$, and practically no splitting at all is observed in the non-substituted $NdFeO_3$.

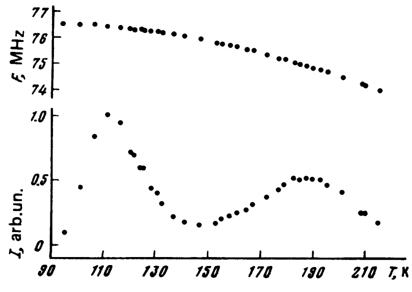

FIG. 2. Temperature dependence of the frequency and intensity of the NMR signal of ^{57}Fe nuclei in the spin-reorientation region for $NdFeO_3$.

TABLE I.

Compound	T_1, K	T_2, K	ΔF, kHz	Compound	T_1, K	T_2, K	ΔF, kHz
$ErFeO_3$	90.0	99.0	510	$Er_{0,3}Ho_{0,7}FeO_3$	61.0	71.6	510
$TmFeO_3$	83.0	98.0	430	$Er_{0,5}Tm_{0,5}FeO_3$	84.5	92.4	450
$HoFeO_3$	53.0	59.0	430	$Er_{0,8}Dy_{0,2}FeO_3$	74.8	83.3	420
$YbFeO_3$	6.8	7.9	400	$Ho_{0,5}Gd_{0,5}FeO_3$	32.5	38.5	355
$NdFeO_3$	112.0	187.0	≤60	$Tm_{0,9}Sm_{0,1}FeO_3$	87.5	104.5	310
$Er_{0,92}Nd_{0,08}FeO_3$	92.0	101.0	480	$Tm_{0,75}Sm_{0,25}FeO_3$	121.0	145.0	220
$Er_{0,6}Nd_{0,4}FeO_3$	97.0	116.0	≤300				

Table I gives the results of the NMR investigation of SR transitions for a number of mixed orthoferrites containing rare-earth ions with radii of close value.[7] A characteristic feature of these curves is the approximately equal splitting of the resonance line, although the SR temperature ranges are different, as are the jumps of the resonance frequency in the SR. To verify that introduction of ions with large ion radius (the left-hand part of the lanthanide series) actually decreases the splitting of the resonance line, we have investigated the mixed orthoferrite $Tm_{1-x}Sm_xFeO_3$ with $x = 0.1$ and $x = 0.25$. It is seen from Table I that, just as in the case of $Er_{1-x}Nd_xFeO_3$, the splitting of the NMR decreases with increasing x, and the SR range broadens and shifts towards higher temperatures.

II. THEORY

1. Magnetic structure and local fields at the ^{57}Fe nuclei

The magnetic field at the nucleus of the Fe^{3+} in $RFeO_3$ can be expressed in terms of the basis vectors of the magnetic structure in the form

$$\mathbf{H} = \sum_B \hat{a}^{(B)}\mathbf{B} + \sum_b \hat{a}^{(b)}\mathbf{b}, \tag{2}$$

where B (or b) is one of the vectors **F**, **G**, **C**, **A** (or **f**, **c**), and the tensors $\hat{a}^{(B)}$ and $\hat{a}^{(b)}$ are determined in terms of the parameters of the various hyperfine interactions. The components of the tensors $\hat{a}^{(B)}$ and $\hat{a}^{(b)}$ for different positions of the Fe^{3+} ions in the unit cell of $RFeO_3$

TABLE II. Ratio of the signs of the components $a_{ij}^{(G)}$ and $a_{ij}^{(f,c)}$ for different positions of the Fe^{3+} ion.

	$a_{ii}^{(G)}, a_{yz,zy}^{(c)}$, $a_{xz,zx}^{(f)}$	$a_{xy,yx}^{(G)}$, $a_{yz,zy}^{(f)}$, $a_{xz,zx}^{(c)}$	$a_{xz,zx}^{(G)}$, $a_{ii}^{(f)}, a_{xy,yx}^{(c)}$	$a_{yz,zy}^{(G)}$, $a_{xy,yx}^{(f)}, a_{ii}^{(c)}$
1	+	+	+	+
2	–	–	+	+
3	+	–	+	–
4	–	+	+	–

may differ in sign. The relations between the signs for the tensors of interest to us are given in Table II.

The main contribution H_0 to the local field at the ^{57}Fe nucleius in $RFeO_3$ is determined by the isotropic contact interactions inside the Fe^{3+} ion ($H_0 \sim 550$ kOe). The remaining anisotropic indirect hyperfine $^{57}Fe-Fe^{3+}$, R^{3+} interactions make a contribution h of the order of 1%. Putting $\mathbf{H}=\mathbf{H}_0+\mathbf{h}$, where $h \ll H_0$, we obtain the value of the local field H in the approximation linear in h/H_0:

$$H=H_0(1+\mathbf{H}_0\mathbf{h}/H_0^2). \tag{3}$$

Using (2), we present for h an expression, valid for the pure configurations Γ_2 and Γ_4 as well as for the region of the spin reorientation $\Gamma_2-\Gamma_4$ θ_G is the angle of orientation of the vector **G**, measured clockwise from the z axis):

$$\begin{aligned}H(\theta_G)=&H_0-a_{xx}^{(G)}\sin^2\theta_G-a_{zz}^{(G)}\cos^2\theta_G-[a_{xz}^{(f)}f_z^{(0)}\sin^2\theta_G\\&+(a_{zx}^{(f)}f_x^{(0)}+a_{zy}^{(c)}c_y^{(0)})\cos^2\theta_G](1-\gamma\cos 2\theta_G)\mp{}^1/_2[a_{xz}^{(G)}+a_{zx}^{(G)}+(a_{xx}^{(f)}f_x^{(0)}\\&+a_{xy}^{(c)}c_y^{(0)}+a_{zz}^{(f)}f_z^{(0)})(1-\gamma\cos 2\theta_G)]\sin 2\theta_G,\end{aligned} \tag{4}$$

where all the parameters $a_{ij}^{(G)}$, $a_{ij}^{(j,c)}$ for the Fe^{3+} ion correspond to position 1, the upper sign corresponds to the ions Fe^{3+} in positions 1 and 3, and the lower to the Fe^{3+} ions in positions 2 and 4. Recognizing that $F, C, A \sim 10^{-2}G$ in orthoferrites, we have retained in the expression for $H(\theta_G)$ only the contribution connected with the vector of the antiferromagnetism of the Fe sublattice. The cited contribution of the R sublattice takes into account the results obtained in the Appendix. In the derivation of (4) we took it into account that the vector $\mathbf{H}_0$ for the ^{57}Fe nuclei in positions 1 and 3 are mutually opposite in direction to **G**.

Thus, in the region of the SR transition a difference is observed between the hyperfine fields at the nuclei of the iron ions from sublattices 1 and 3, on the one hand, and 2 and 4 on the other. This leads to a splitting of the NMR frequency of the ^{57}Fe nuclei. In addition to this effect, a change (shift) in the value of the local field is observed in the region of the SR transition on going from the configuration Γ_4 to the configuration Γ_2 (with a corresponding shift of the NMR frequency). Naturally, there is superimposed on this effect also the usual temperature shift due to the temperature dependence of the field H_0, which can be approximated at low temperatures by the formula

$$H_0(T)/H_0(0)=1-1.59\cdot10^{-3}(kT/J)^2 \tag{5}$$

(a modification of the known Kubo formula for antiferromagnets,[8] J is the exchange integral). The final expression for the shift in the value of the local field in the $\Gamma_4-\Gamma_2$ transition is of the form

$$\begin{aligned}\Delta H(\Gamma_4-\Gamma_2)=&\Delta H_0(\Gamma_4-\Gamma_2)+a_{xx}^{(G)}-a_{zz}^{(G)}\\&+a_{xz}^{(f)}f_z^{(0)}(1+\gamma)-(a_{zx}^{(f)}f_x^{(0)}+a_{zy}^{(c)}c_y^{(0)})(1-\gamma).\end{aligned} \tag{6}$$

The angular (θ_G) dependence of the splitting of the NMR signal is expressed according to (4) by the formula

$$\Delta F=(\alpha+\beta\cos 2\theta_G)\sin 2\theta_G, \tag{7}$$

where α and β are certain constants, with β due only to the contribution of the R sublattice. Equation (7) determines also the temperature dependence of the splitting in the region of the SR transition if we know the $\theta_G(T)$ dependence obtained with the aid of γ-resonance or neutron-diffraction measurements. The experimental data on the $\Delta F(T)$ dependence in $ErFeO_3$ are in good agreement with the data obtained on the basis of the known $\theta_G(T)$ dependence[9] with the aid of the simplified relation (7) at $\beta=0$.

Thus, the temperature or angular dependence of ΔF does not reveal a noticeable contribution from the rare-earth sublattice to the splitting of the NMR frequency. Definite information concerning the character of the anisotropic hyperfine interactions (HFI) can be obtained from an analysis of the angular dependence of the quantity $\bar{F}=(F_1+F_2)/2$ (the arithmetic mean of the NMR frequencies) in the region of the SR. According to (4)

$$\bar{F}=F_0+\alpha_1\cos 2\theta_G+2\beta_1\cos^2 2\theta_G, \tag{8}$$

where F_0, α_1, and β_1 are certain constants, with β_1 determined only by the contribution of the R sublattice. On the whole, the experimental results on the $\bar{F}(T)$ dependence, assuming a smooth function $\theta_G(T)$ of the type observed in $ErFeO_3$ (Ref. 9) and $SmFeO_3$ (Ref. 10), agree well with the simplified $\bar{F}(\theta_G)$ dependence at $\beta_1=0$. However, the data on $Nd_{0.4}Er_{0.6}FeO_3$ (Fig. 3) point to a more complicated character of the $F(\theta_G)$, possibly due to the noticeable contribution of the type $\beta_1\cos^2 2\theta_G$ from the R sublattice to $\bar{F}$, meaning also to the shift of the NMR frequency in the $\Gamma_4-\Gamma_2$ transition.

The use of the NMR procedure for the investigation of the SR region, besides observation of the HFI anisotropy effects, can yield information on the direction of the magnetic-moment vector of $RFeO_3$ in the spin-rotation region. In particular, Bar'yakhtar *et al.*[3] have concluded on the basis of NMR data that the orthogon-

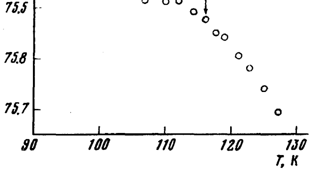

FIG. 3. Temperature dependence of the NMR frequency of ^{57}Fe nuclei in the spin-reorientation region for $Nd_{0.4}Er_{0.6}FeO_3$ (the arrows indicate the temperatures of the start and end of the SR transition).

ality of the ferromagnetic and antiferromagnetic vectors of the iron sublattice is violated in the SR region, and that longitudinal weak ferromagnetism appears. They did not take into account, however, the contribution of the rare-earth sublattice to the total magnetic moment of $RFeO_3$. It is easily seen that when this contribution is taken into account the character of the temperature dependence of θ_m and θ_G—the orientation angles of the summary magnetic moment and of the antiferromagnetism vector of the iron sublattice–can differ substantially, and the simple relation $\theta_G = \theta_m \pm \pi/2$ which is valid for REO such as $YFeO_3$ with nonmagnetic R ion, no longer holds. Actually, when account is taken of the contribution of the R sublattice to the magnetic moment of the REO, the connection between θ_m and θ_G takes within the framework of the "single-doublet" model (see the Appendix) the form

$$\operatorname{tg}\theta_m = \pm\frac{\sigma_0 + \sigma_x^{(R)}(1-\gamma\cos 2\theta_G)}{\sigma_0 + \sigma_z^{(R)}(1-\gamma\cos 2\theta_G)}\operatorname{ctg}\theta_G, \tag{9}$$

where σ_0 is the magnetic moment of the Fe sublattice. Thus, even in the case of a smooth $\theta_G(T)$ dependence in the SR region, the function $\theta_m(T)$ can be most unusual, especially at large values of the parameter γ that characterizes the ratio of the first and second anisotropy constants of the Fe sublattice, and at a greatly differing contribution of the R sublattice to the magnetic moment above and below the SR ($\sigma_z^{(R)}$ and $\sigma_x^{(R)}$, respectively). Thus the different character of the functions $\theta_m(T)$ and $\theta_G(T)$ is a perfectly natural phenomenon, whose explanation does not call for the assumption that the orthogonality of the vectors **F** and **G** is violated.

When an external magnetic field $\mathbf{h}_{ext}$, directed in the ac plane at an angle φ to the c axis, is turned on it is necessary to add to the expression for $H(\theta_G)$ a term $\mp h_{ext}\cos(\theta_G - \varphi)$, whose presence always leads at $|\theta_G - \varphi| \neq \pm\pi/2 \pm \frac{3}{2}\pi$ to a difference between the fields at the ^{57}Fe nuclei in positions 1 and 3, on the one hand, and 2 and 4 on the other. In addition, the presence of an external magnetic field can modify the magnetic structure by shifting the temperatures of the start and end of the SR, and can change the character of the temperature dependence of the orientation angle θ_G of the spins.

We consider by way of illustration the behavior of the local fields in the regions of the $\Gamma_4 - \Gamma_2$ transition,

$$H(\theta_G, h_{ext}) = H(\theta_G) \mp h_{ext}\cos(\theta_G - \varphi)$$

putting $\gamma = 0$ for simplicity and neglecting the shift of H in the transition.

1. External field along the a axis. In this case the splitting of the local fields takes the form

$$\delta H = H_2(\theta_G) - H_1(\theta_G) = (a_{xz}^{(G)} + a_{zx}^{(G)} + a_{xx}^{(f)} f_x^{(0)} + a_{xy}^{(c)} c_y^{(0)} + a_{zz}^{(f)} f_z^{(0)}) \cdot$$
$$\times \sin 2\theta_G + 2h_{ext}\sin\theta_G = a\sin 2\theta_G + 2h_{ext}\sin\theta_G = 2\sin\theta_G(a\cos\theta_G + h_{ext}). \tag{10}$$

The character of the temperature dependence of the splitting $|\delta H|$ in the SR region is determined by three factors: 1) by the sign of the splitting parameter a, 2) by the relative directions of the ferromagnetism and antiferromagnetism vectors **F** and **G**, 3) by the relative direction of the ferromagnetism vector **F** of the iron sublattice and the summary magnetic moment of $RFeO_3$.

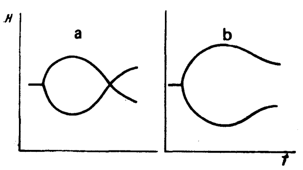

FIG. 4. Temperature dependence of the hyperfine fields at the ^{57}Fe nuclei in the region of the RS transition in an external field h_{ext} parallel to the a axis.

The vectors **F** and **G** are mutually perpendicular, but the sing of the angle $\theta_{FG} = \theta_F - \theta_G = \pm\pi/2$ is not known from experiment. Obviously, in orthoferrites it is determined by the "sign" of the Dzyaloshinskiǐ vectors.[11] Moreover, on the basis of microtheoretical analysis of the magnitude and direction of the Dzyaloshinskiǐ vector in the ion pair $Fe^{3+}-Fe^{3+}$ it was predicted[11] that $\theta_{FG} = +\pi/2$ for all REO.

Figures 4a and 4b show schematically two possible types of temperature dependence of the local fields H_1 and H_2 (at $|a| > h_{ext}$), which are realized for different relations between the signs of the quantities $a, \theta_{FG}, \sigma_a(Fe)/\sigma_a$ (σ_a and $\sigma_a(Fe)$ are respectively the x-components of the magnetization of $RFeO_3$ and of the contribution of the Fe sublattice). The variant shown in Fig. 4a is realized at a negative sign of the product $a\theta_{FG}\sigma_a(Fe)/\sigma_a$. At an Fe^{3+} ion spin-orientation angle determined from the condition $\cos\theta_G^* = -h_{ext}/a$, the splitting δH vanishes. The variant shown in Fig. 4b is realized at a positive sign of the product $a\theta_{FG}\sigma_a(Fe)/\sigma_a$.

2. External field along the c axis. In this case we have

$$\delta H = 2\cos\theta_G(a\sin\theta_G + h_{ext}) \tag{11}$$

and now the character of the temperature dependence of H_1 or H_2 will take the form shown in Fig. 5a even at a positive sign of the product $a\theta_{FG}\sigma_c(Fe)/\sigma_c$. The splitting δH vanishes at an angle θ_G^* defined by the condition $\sin\theta_G^* = -h_{ext}/a$. Figure 5b shows the case realized at a negative sign of the product $a\theta_{FG}\sigma_c(Fe)/\sigma_c$.

Thus, an analysis of the behavior of the local fields at the nuclei ^{57}Fe in $RFeO_3$ in the SR region in an external field yields, besides information on the function $\theta_G(T, h_{ext})$, also in principle information on the sign of the splitting parameter. This means that we can identify the local fields $H_{1,3}$ and $H_{2,4}$, i.e., we can identify the sublattices in a single-domain sample with known direction of the vector of the weak ferromagnetic moment. The experimental data for $ErFeO_4$ point to realization of the variant shown in Figs. 4a and 5b (see Fig.

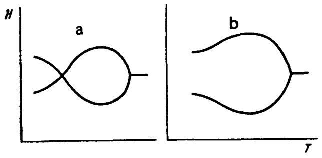

FIG. 5. Temperature dependence of the hyperfine fields at the ^{57}Fe nuclei in the vicinity of the RS transition in an external field h_{ext} parallel to the c axis.

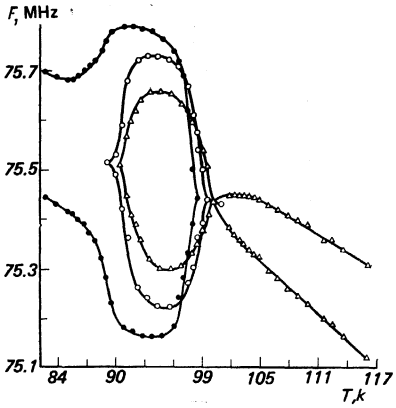

FIG. 6. Temperature dependence of the NMR frequency of the nuclei ^{57}Fe in ErFeO$_3$ in the vicinity of the SR transition in an external field: ●—$h_{ext} \parallel c$, △—$h_{ext} \parallel a$, ○—$h_{ext} = 0$.

6). This is evidence that the splitting parameter is negative, if we assume θ_{FG} to be equal to $+\pi/2$ in accordance with the predictions of Ref. 11, and recognize that the directions of $\sigma_{a,c}$ and $\sigma_{a,c}$ (Fe) coincide in ErFeO$_3$.

Thus, a phenomenological analysis based on the use of the magnetic symmetry of orthoferrite explains qualitatively all the effects observed in experiments on NMR of ^{57}Fe nuclei. It also connects the values of the splitting and of the shift of the resonance line with the parameters that characterize the anisotropy of the HFI. The task of the microscopic theory includes the explanation of both the magnitude of the effect and of a number of regularities observed in experiment. These include the appreciable increase of the splitting parameter a_{xz} on going from light to heavy ions in the RFeO$_3$ series, the much larger splitting of the NMR frequency compared with the frequency shift under SR for the orthoferrites of the second half of the series, and the possibility of different signs of the NMR frequency shift. One of the most important problems is also an explanation of the role of the R ions in the considered effects. Their influence can be either direct, via the anisotropic hyperfine ^{57}Fe–R^{3+} (or ^{57}Fe–O^{2-}–R^{3+}), interaction, or indirect, via changes of the crystallographic parameters, meaning also of the parameters of the anisotropic HFI in the iron sublattice.

2. Elements of microscopic theory of anistropic hyperfine interactions

The problem of the quantitative calculation of the parameters of the anisotropic HFI for ^{57}Fe nuclei and components of the RFeO$_3$ type is complicated, both in view of the large number of mechanisms that contribute to the components of the tensors $a_{ij}^{(B)}$, $a_{ij}^{(b)}$ and because of the difficulties inherent in the quantum-mechanical calculation of the complicated multi-electron system. Certain simplifications can be connected only with the absence of orbital degeneracy in the ground state of the ion Fe^{3+}($^6A_1$). At the same time, an orthogerrite is a system that is convenient for semiquantitative analysis, where most of the mechanisms of the HFI anisotropy can be relatively easily connected with the known parameters of the crystal structure, which varies regularly on going from LaFeO$_3$ to LuFeO$_3$. Thus, the experimentally known dependence of the parameters of the HFI anisotropy on the type of the orthoferrite (the structure–property dependence) can turn out to be decisive when it comes to identifying the basic mechanism of the HFI anisotropy.

We consider below, from precisely these points of view, some different HFI anisotropy mechanisms for ^{57}Fe nuclei in orthoferrites.

1. Anisotropic hyperfine interactions in the iron sublattice

As indicated above, we are considering in this case the largest ("antiferromagnetic") contribution to the anisotropic part of the hyperfine field at the ^{57}Fe nucleus, induced by electrons of its own Fe^{3+} ion or by neighboring Fe^{3+} ions:

$$\mathbf{h} = \hat{a}^{(G)}\mathbf{G}. \tag{12}$$

The energy of the anisotropic interaction of the magnetic moment of the nucleus with the electron spins is conveniently written in the form

$$V_{\text{an}} = ([\boldsymbol{\mu}\times\mathbf{G}]^2 \cdot a^2), \tag{13}$$

where $[\cdot \times \cdot]_q^m$ is an irreducible tensor product of rank m, and the parameters a_q^2 are connected with the components of the tensor $\hat{a}^{(G)}$:

$$\begin{gathered} a_{xx}^{(G)} = 6^{-1/2}a_0{}^2 - \operatorname{Re} a_2{}^2, \quad a_{yy}^{(G)} = 6^{-1/2}a_0{}^2 + \operatorname{Re} a_2{}^2, \quad a_{zz}^{(G)} = -6^{-1/2}a_0{}^2, \\ a_{xy}^{(G)} = -\operatorname{Im} a_2{}^2, \quad a_{xz}^{(G)} = \operatorname{Re} a_1{}^2, \quad a_{yz}^{(G)} = \operatorname{Im} a_1{}^2. \end{gathered} \tag{14}$$

A. Fe–Fe magnetodipole interactions. In this case the parameters a_q^2 are expressed in terms of the lattice sums

$$a_q{}^2 = 2\beta S \sum_j \frac{C_q{}^2(\mathbf{R}_{ij})}{R_{ij}{}^3}\beta_j, \tag{15}$$

where C_q^2 are tensor spherical harmonics ($C_q^2 = (4\pi/5)^{1/2}Y_{2q}$), $\beta_j = +1$ for the Fe^{3+} from sublattices 1 and 3, and $\beta_j = -1$ for Fe^{3+} ions from sublattices 2 and 4. The lattice sums differ from zero only at $q = 0$ or ± 2, this being due to the sufficiently high symmetry of the iron-ion sublattice. We thus have $a_{xz}^{(G)} = a_{yz}^{(G)} = 0$ for the magnetodipole contribution and we obtain no contribution to the splitting of the NMR frequencies in the SR region.

A numerical calculation of the nonzero components $a_i^{(G)}$ was made by the modified Ewald method.[12] The results are listed in Table III. The components $a_{xy}^{(G)} = a_{yx}^{(G)}$ turned out to be negligibly small. The magnetodipole Fe–Fe interaction leads only to a shift of the value of the local field in the SR transition $\Gamma_4 - \Gamma_2$. This shift ranges from ~10 Oe for LiFeO$_3$ to ~400 Oe for the orthoferrites of the second half of the series,

TABLE III. Contribution of the magnetodipole interaction ^{57}Fe – Fe^{3+} to the parameters $a_{xx}^{(G)}$ and $a_{zz}^{(G)}$.

RFeO$_3$	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
$a_{xx}^{(G)}$, Oe	6	78	106	162	194	218	232	252	268	270	278	286	290	304
$a_{zz}^{(G)}$, Oe	−4	−64	−70	−126	−154	−164	−188	−176	−184	−178	−168	−159	−134	−104

and is positive in all cases. Thus the HFI anisotropy mechanism cannot explain the totality of the experimental data, although for the REO of the second half of the series the contribution made to the NMR frequency shift in the $\Gamma_4 - \Gamma_2$ transition is noticeable.

B. Role of noncubic crystal field. The operator of the anisotropic interaction of the electron spins with the nucleus is of the standard form[13]:

$$\hat{V}_{\text{A HFI}} = -2 \cdot 10^{1/2} \beta \sum_i ([\mathbf{S}_i \times C^2(\mathbf{r}_i)]^1 \cdot \boldsymbol{\mu}^1) r_i^{-3} \qquad (16)$$

and for an Fe^{3+} ion in the ground orbitally nondegenerate state ${}^6A_1$ the operator makes a contribution to the energy of the hyperfine interaction in second-order perturbation theory,[1)] with account taken of the noncubic component of the crystal field.

In the semiphenomenological analysis of the role of the noncubic field we distinguish between two contributions, that of the nearest neighbors of the Fe^{3+} ions (six O^{2-} ions forming a weakly distorted octahedron) and the remaining surrounding. In the former case the parameters of the noncubic field are proportional to the corresponding components of the strain tensor of the complex $Fe^{3+}-6O^{2-}$ from the perfect octahedron (this is valid in terms of the local axes of the cubic crystal field). Thus, in the local system of the cubic axes of each $Fe^{3+}-6O^{2-}$ octahedron the HFI anisotropy energy takes the form

$$V_{\text{A HFI}} = \sum_{\gamma = E, T_2} A_\gamma ([\boldsymbol{\mu} \times \mathbf{G}]^{2\gamma} \cdot \varepsilon^{2\gamma}), \qquad (17)$$

where $\varepsilon_y^{2\gamma}$ are the components of the strain tensor and form the basis of the irreducible representation γ (equal to E, T_2) of the point group of the octahedron; A_E and A_{T_2} are certain constants. In the system of the crystallographic axes abc, the expression for the parameters a_q^2 in (13) takes the form

$$a_q^2 = \sum_{\gamma, q'} A_\gamma \alpha_{2q'}^{\gamma v *} \varepsilon_v^{2\gamma} D_{qq'}^{(2)}(\omega_i), \qquad (18)$$

where $D_{qq'}^{(2)}(\omega_i)$ is the rotation matrix,[14] ω_i is the set of Euler angles that determine the transition from the abc frame to the local system of coordinates of the i-th ion Fe^{3+} ($i = 1, 2, 3, 4$), $\alpha_{2q'}^{\gamma v}$ are the coefficients of the transition from the basis of the irreducible representation of the rotation group $D^{(2)}$ to the basis of the irreducible representation γ of the O_h group.

Figures 7a and 7b show the values calculated by us for the contribution of the considered mechanism of the HFI anisotropy to the parameters $a_{xz}^{(G)}$ and $a_{xx}^{(G)} - a_{zz}^{(G)}$, which determine respectively the splitting and the shift of the NMR frequency in the region of the $\Gamma_4 - \Gamma_2$ transitions (all the quantities are in units of $10^{-2}A_E$, $10^{-2}A_{T_2}$). It is easily seen that, taken separately, the contributions of the deformations of the $Fe^{3+}-6O^{2-}$ octahedron, of type E or T_2 [tension (compression) along the x, y, z axes or rotation of the axes, respectively), do not explain the characteristic dependences of the splitting of the NMR frequency on the type of orthoferrite. Nor does a linear combination of the contributions of E and T_2 explain the experimental results if it is recognized that for the second half of the REO series the splitting should exceed the shift substantially (i.e., $|a_{xz}| \gg |a_{xx} - a_{zz}|$). We note that in the point-charge model the parameters A_E and A_{T_2} are equal respectively to $-3 \cdot 6^{1/2} AZe^2/l^3$ and $2 \cdot 6^{1/2} AZe^2/l^3$, where $Z = -2$ is the charge of the O^{2-} ion, l is the average Fe-O distance, and an expression for A is given below. The difficulty of estimating the values of A_E and of A_{T_2} with allowance for the effects of the overlap and the covalence of the $Fe^{3+}-O^{2-}$ and $O^{2-}-O^2$ bonds still leaves unanswered the question of the quantitative estimate of the contribution of the nearest surrounding of the Fe^{3+} ion to the anisotropy of the HFI.

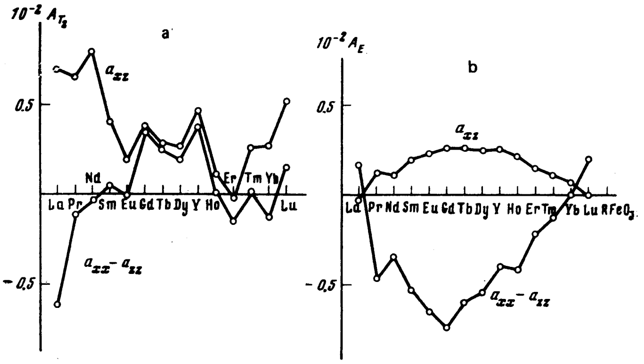

FIG. 7. Dependence of the contribution made to the parameters $a_{xx}^{(G)}$ and $a_{xx}^{(G)} - a_{zz}^{(G)}$, by the deformation of the $Fe^{3+}-6O^{2-}$, octahedron on the type of orthoferrite: a) contribution of deformations of the type T_2, b) contribution of deformations of type E.

The contribution of the remaining surroundings of the Fe^{3+} ions in a noncubic field can be taken into account sufficiently reliably in the model of point charges. In this case the corresponding contribution to the parameters a_q^2 of (13) is proportional to the lattice sums, and for the Fe^{3+} ion in position 1 we have

$$a_q^2 = A \sum_j \frac{Z_j e^2}{R_{ij}^3} C_q^2(\mathbf{R}_{ij}), \qquad (19)$$

where Z_j is the valence of the j-th ion and A is a certain parameter. By way of illustration we present the expression for the parameter A, obtained in second-order perturbation theory with allowance for the contribution of the virtual transitions of the np electrons of the Fe^{3+} ion into empty $n'p$ states under the influence of the noncubic field:

$$A = \frac{6 \cdot 2^{1/2} \beta}{5 \cdot 35^{1/2}} \sum_{nn'} \langle r^{-3} \rangle_{np;n'p} \langle r^2 \rangle_{n'p;np} \Delta E_{{}^6D}^{-1}, \qquad (20)$$

where $\langle r^{-3} \rangle_{np;n'p}$ and $\langle r^2 \rangle_{n'p;np}$ are radial matrix elements, and $\Delta E_{{}^6D}$ is the energy of the $np - n'p({}^6A_1 - {}^6D)$ transition.

The lattice sums of (19) were calculated by us for all the orthoferrites, and the values of the parameters $a_{ij}^{(G)}$ of interest to use are shown in Fig. 8. It is easily seen that the contribution of the considered mechanism to the splitting of the NMR frequency of the ^{57}Fe nuclei in the region of the $\Gamma_4 - \Gamma_2$ transition increases strongly on going from $LaFeO_3$ to $LuFeO_3$, and that for the REO of the second half of the series it will considerably exceed, on the whole, the contribution to the frequency

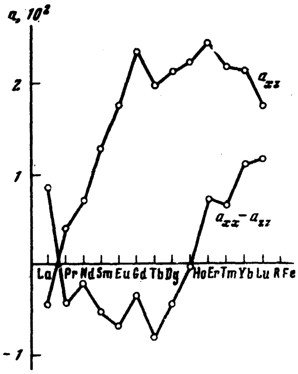

FIG. 8. Dependence of the contribution made to the parameters $a_{xz}^{(G)}$ and $a_{xx}^{(G)}-a_{zz}^{(G)}$ by the noncubic field for the Fe^{3+} ion in the point-charge model on the type of the orthoferrite in the point-charge model (in units of $10^{24}\ e^2A$).

shift. Just as for the preceding mechanism, we note that there is no regular dependence of the shift $a_{xx}^{(G)}-a_{zz}^{(G)}$ on the type of REO. Moreover, this mechanism points clearly to a possibility of a different sign of the shift. All these singularities agree on the whole with the singularities observed in experiment, so that we can conclude that the noncubic field produced by the point charges surrounding the Fe^{3+} ion possibly plays the leading role in the HFI anisotropy.

Rough estimates of the parameter A can be obtained if we choose, quite reasonably, $\Delta E_{6_D}\sim 50$ eV, $\langle r^2\rangle_{n'p;np}\sim 1$ a.u., and $\langle r^{-3}\rangle_{np;n'p}\sim 10^2$ a.u.; then $10^{24}e^2A\sim 10^5$ Oe, and the splitting of the NMR frequency for the ^{57}Fe nuclei in the region of the SR can reach 500–600 kHz (several kOe). The sign of the splitting parameter $a_{xz}^{(G)}$ for $ErFeO_3$ is in this case positive, corresponding to $\theta_{FG}=-\pi/2$, in contrast to the result predicted earlier.[15]

C. Anisotropic indirect HFI *of the type* $^{57}Fe-O^{2-}-Fe^{3+}$. The second coordination sphere of the surroundings of the Fe^{3+} ion (six Fe^{3+} ions) contributes to the anisotropic indirect HFI connected with the indirect transfer of the spin density in the $Fe^{3+}-O^{2-}-Fe^{3+}$ chain and with the polarization of the Fe^{3+}-ions p states, which make the main contribution of the HFI anisotropy. This was precisely the mechanism considered in detail, for example, in Ref. 16 for the chain $^{27}Al-O^{2-}-Fe^{3+}$, Cr^{3+} in $LaAlO_3$ with Fe^{3+} and Cr^{3+} admixture. The authors of that paper proved experimentally the noticeable role of anisotropic indirect HFI in the production of the local field at the nucleus of the diamagnetic ion Al^{3+} in $LaAlO_3:Fe^{3+}$, Cr^{3+}, and obtained also the signs of the corresponding parameters.

The effective Hamiltonian of the anisotropic indirect HFI will be obtained in the second-order perturbation theory with account taken of the operator $\hat{V}_{an}$ (16) and of the operator of the kinetic superexchange interaction connected with the transport of the np electron of the neighboring Fe^{3+} ion to an empty $n'p$ state of the Fe^{3+} ion with simultaneous transfer of an np electron of the Fe^{3+} ion to the d state of the neighboring Fe^{3+} ion. Omitting the intermediate calculations, which are based on a certain modification of the procedure used in Ref. 7 for the analysis of isotropic indirect HFI, we present the final expression for the corresponding contribution to the parameter a_q^2 of (13) (the Fe^{3+} ion is in position 1):

$$a_q^2=B\sum_i C_q^2(\theta_i,\varphi_i), \tag{21}$$

and

$$B=4\left(\frac{3}{5}\right)^{1/2}\beta\sum_{nn'}\frac{\langle r^{-3}\rangle_{np;n'p}}{\Delta E_{np;n'p}}\left\{\frac{b_\sigma b_\sigma'-b_\pi b_\pi'}{U}\right\}, \tag{22}$$

where $\Delta E_{np;n'p}$ is the average energy of the $np\to n'p$ transition in the Fe^{3+} ion, $b_{\sigma,\pi}$ are the integrals of the transfer of the np electron to the d state of the nieghboring Fe^{3+} ion for the σ and π coupling, respectively, $b'_{\sigma,\pi}$ are the integrals of the transfer of the d electron of the neighboring ion Fe^{3+} to the $n'p$ state of the Fe^{3+} ion, and U is a certain mean transfer energy. The angles θ_i and φ_i in the expression for a_q^2 are the polar and azimuthal angles of the vector of the coupling between O^{2-} and the neighboring Fe^{3+} ion in the abc frame, It is interesting that, when summing over all the iron ions that are the neighboring of the ^{57}Fe nucleus, the nonzero components of a_q^2 are $\mathrm{Re}\,a_1^2$ and $\mathrm{Im}\,a_2^2$, and this yields the only nonzero components $a_{xz}^{(G)}=a_{zx}^{(G)}$ and $a_{xy}^{(G)}=a_{yx}^{(G)}$ of the tensor $a^{(g)}$, with

$$a_{xz}^{(G)}=\left(\frac{3}{2}\right)^{1/2}\frac{acx_{O_1}}{l^2}B, \tag{23}$$

where a and c are the corresponding parameters of the unit cell of $RFeO_3$, l is the Fe–O bond length ($l\approx 2.01$ Å), and x_{0_1} is the x component of the displacement of the oxygen ion in the position $4c$.[4]

The value of the parameter $a_{xz}^{(G)}$ in units of B is shown in Fig. 9, which illustrates clearly the growth of $a_{xz}^{(G)}$ on going from $LaFeO_3$ to $LuFeO_3$. The parameter B is positive according to (22), because the σ coupling predominates in the electron transfer ($b_\sigma, b_\sigma' > b_\pi, b_\pi'$), i.e., the quantity $a_{xz}^{(G)}$ is also positive. To estimate the parameter B we use the experimental data of Taylor *et al.*,[16] according to whom the value of B in the chain $^{27}Al-O^2-Fe^{3+}$ in $LaAlO_3$ is approximately one-sixth the value of the induced indirect isotropic hyperfine field at the ^{27}Al nucleus. We use the same relation in the $^{57}Fe-O^{2-}-Fe^{3+}$ chain and, assuming the induced isotropic indirect hyperfine field in this case to be ~10 kOe,[17] we get $B\sim 1.5$ kOe. This leads in accordance with the data of Fig. 9, to a splitting of the order of several kOe of the NMR frequency

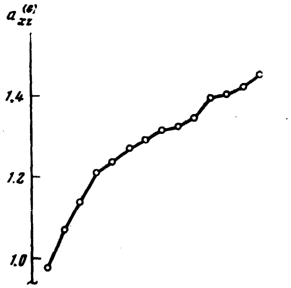

FIG. 9. Contribution of the anisotropic indirect HFI to the splitting parameters (in units of B).

of the ^{57}Fe nuclei in the region of the SR. Thus, the anisotropic indirect HFI make no contribution to the NMR frequency shift in the $\Gamma_4-\Gamma_2$ transition, and make a substantial contribution to the splitting of the NMR frequency in this transition with the "required" dependence of the splitting on the type of REO, although the growth of $a_{xz}^{(G)}$ in the $LaFeO_3 \to LuFeO_3$ transition is less prounounced than in experiment.

D. Concentration of g-factor anisotropy. If the g-factor of the Fe^{3+} ion in $RFeO_3$ is anisotropic, even the main isotropic contact interaction $V_{HFI}=A_S\mathbf{I}\cdot\mathbf{S}$ will contribute to the anisotropic part of the tensor $a_{ij}^{(G)}$:

$$\Delta a_{ij}^{(G)}=\frac{A_S S}{g_n\beta_n}\frac{\Delta g_{ij}}{g}, \tag{24}$$

where g and Δg_{ij} are the isotropic and anisotropic parts of the g-tensor, respectively; g_n and β_n are respectively the nuclear g-factor and the Bohr maneton. The g-factor anisotropy for the Fe^{3+} ion in $RFeO_3$ is small, as attested by the research on the EPR of Fe^{3+} ions in $LaAlO_3$ (Ref. 16) and in $YAlO_3$ (Ref. 18), which are isostructural to the orthoferrites. According to the experimental data[16,18] $|\Delta g_{ij}/g|<10^{-3}$, and this leads to an estimate of the contribution to the anisotropic part of $a_{ij}^{(G)}$ in the form $|\Delta a_{ij}^{(G)}|<500-600$ Oe at $|A_S S/g_n\beta_n|\sim 500-600$ kOe.

Thus, the anisotropy of the g-factor of the Fe^{3+} ion can in principle make a noticeable contribution to the NMR frequency shift in the region of the SR, while the contribution to the splitting of the NMR frequency for the second half of the REO series is inessential.

2. Contribution of rare-earth sublattice to the anisotropy of the HFI for ^{57}Fe nuclei

As indicated above, an investigation of the angular dependence or of the temperature dependence of the splitting of the NMR frequency, or of the average NMR frequency, does not exclude the possibility of a contribution of the R ions to the anisotropy of the HFI for the ^{57}Fe nuclei. Moreover, we have initially noticed a definite correlation between the NMR frequency splitting in the SR region and the quantity $g_J J\beta$, which is the maximum possible magnetic moment of the R ion (Fig. 10). We consider now the main interactions that determine the contribution of the R ions to the anisotropy of the HFI for the ^{57}Fe nuclei, namely the magnetodipole interactions $^{57}Fe-R^{3+}$ and the anisotropic indirect HFI $^{57}Fe-O^{2-}-R^{3+}$.

A. Magnetodipole interaction $^{57}Fe-R^{3+}$. It contributes to all the tensors components $a_{ij}^{(f)}$ and $a_{ij}^{(c)}$. In the SR transition $\Gamma_4-\Gamma_2$, the magnetic structure of the R sublattice changes from $\{f_z\}$ to $\{f_x, c_y\}$, and the c_y component in the Γ_2 configuration is as a rule noticeably larger than the f_x component. The reason is that the effective magnetic fields produced at the R ion by the Fe sublattice have a direction close to the b axis of the crystal.[19]

Table IV lists our calculated values of the components $a_{xy}^{(c)}$ and $a_{zy}^{(c)}$ that determine in accordance with (4) the contribution of the c_y component of the magnetic structure of the R sublattice to the local fields at the

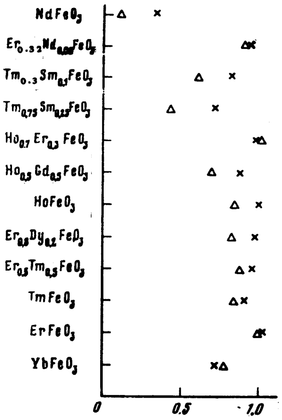

FIG. 10. Correlation between the splitting of the NMR frequency in the RS region and the value of the maximum magnetic moment of the R ion for a number of orthoferrites (in arbitrary units): ×—moment, Δ—ΔF.

^{57}Fe nuclei. The contribution of the considered mechanism to the shift and splitting of the NMR frequency will depend substantially on the magnetic moment of the R ion μ_R in the SR region. Our calculation, based on the experimental data,[19,20] yields $\mu_{Er}\approx 0.05\beta$ for $ErFeO_3$ at $T=90$ K and $\mu_{Ho}\approx 0.8\beta$ for $HoFeO_3$ at $T=50$ K, and in the latter case $|c_y|\approx 0.9$, $|f_x|\approx 0.4$.. Thus, in accordance with the data of Table IV, the magnetodipole interaction $^{57}Fe-R^{3+}$ makes a negligibly small contribution to the NMR frequency shift in the $\Gamma_4-\Gamma_2$ transition in $ErFeO_3$, and a noticeable contribution in the case of $HoFeO_3$(~0.5 kOe). The contribution to the NMR frequency splitting is small in both cases ($a_{xy}^{(c)} \ll a_{zy}^{(c)}$). The sign of the contribution to the splitting parameter of the NMR frequency from the R sublattice is determined both by the sign of the parameters $a_{xy}^{(c)}$, $a_{zy}^{(c)}$ and by the sign of the c_y component of the basis vector of the magnetic structure in the configuration Γ_2, which in turn depends on the direction of the magnetic field produced at the paramagnetic R ion by the Fe sublattice. The main contribution to this field is made by the anisotropic exchange interaction $R^{3+}-O^{2-}-Fe^{3+}$.[19] In particular, the dependence of the magnitude and of the sign of the quasidipole exchange contribution to the effective field on the type of the R ion is determined by the factor[21]

$$\alpha_R=\frac{1}{g_J}\left[\frac{2J+1}{J(J+1)}\right]^{1/2}\begin{Bmatrix} S & L & J\\ S & L & J\\ 1 & 2 & 1\end{Bmatrix}V^{(12)}_{SL;\,SL},$$

where $\{\ \}$ is the $9j$ symbol, $V^{(12)}_{SL;SL}$ is the Racah spectroscopic coefficient[13]; S, L and J are the quantum numbers for the ground $^{2S+1}L_J$ term of the R ion, and g_J is the Landé factor. If we make the perfectly reasonable assumption that the predominant contribution to the ef-

TABLE IV. Values of the components $a_{zy}^{(c)}$ and $a_{xy}^{(c)}$ of the tensor $\hat{a}^{(c)}$ in units of μ_R/β (μ_R is the magnetic moment of the R ion).

$RFeO_3$	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb
$a_{zy}^{(G)}$, Oe	−371	−418	−494	−556	−574	−600	−619	−633	−636	−656
$a_{xy}^{(G)}$, Oe	−14	−18	−26	−35	−37	−41	−45	−47	−49	−51

fective field at the R ion is made by the quasidipole exchange $R^{3+}-O^{2-}-Fe^{3+}$, then the relation between the signs of the component c_y and of the factor α_R in the orthoferrite series will be the same . The factor α_R, for example, reverses sign[21] on going from Er^{3+} to Ho^{3+} and Tm^{3+}, and this leads to a reversal of the sign of c_y on going from $ErFeO_3$ to $HoFeO_3$ and $TmFeO_3$, meaning also to a corresponding change sign of the contribution of the magnetodipole interaction $Fe^{3+}-O^{2-}-R^{3+}$ to the NMR frequency shift.

B. Anisotropic indirect HFI *of the type* $^{57}Fe-O^{2-}-R^{3+}$. The energy of the anisotropic indirect HFI of the type $^{57}Fe-O^{2-}-R^{3+}$ can be represented in the simplest form:

$$V_{A\,\mathrm{IHFI}}^{(\mathrm{Fe-R})}=\sum_{ij} b_{ij}\mu_{n\,i}\cdot\mu_{R\,j}, \tag{25}$$

if the R ion has a well isolated Kramers doublet or isodoublet. A rough estimate of the contribution of this mechanism to the shift and splitting of the NMR frequency in the SR region can be carried out by assuming that the parameters b_{ij} are smaller by approximately one order of magnitude in the corresponding con-constants of the anisotropic indirect HFI in the $^{57}Fe-O^{2-}-Fe^{3+}$ chain, and if we recognize also that as a rule in most cases in the SR region $|\mu_R| \sim (10^{-1}-10^{-2})\mu_B$. In this case the contribution of the considered interactions to the shift and splitting of the NMR frequency does not exceed a quantity of the order of 1 kOe$\times$0.1 $\times$(0.1–1) ~ 0.1–0.01 kOe, i.e., it lies within the limits of the measurement error.

Thus, on the whole the rare-earth ions exert in the main an indirect influence on the HFI anisotropy, and alter the orthorhombic distortions in the orthoferrite lattice and as a consequence the HFI anisotropy in the sublattice of the iron ions. At the same time, in individual cases (for example $HoFeO_3$) they can make also a noticeable direct contribution to the shift of the local field at the ^{57}Fe nucleus. The correlation indicated above between the splitting of the NMR frequency in the SR region and the quantity $g_J J\beta$ is accidental. In a certain sense it reflects the fact that the splitting grows on going from the lighter R ions to the heavier ones, and this growth is accompanied on the one hand by a growth of the orthohombic distortions of the perovskite lattice, and on the other by a change in the type of coupling of the orbital and spin angular momenta for the ground states of the R ions.

CONCLUSION

The NMR method for ^{57}Fe nuclei in rare-earth orthoferrites is not only a large source of extensive information on the character of the spin-reorientation phase transition, but is practically the only source of information on the anisotropy of hyperfine interactions in orthoferrite.

An analysis of the shift and splitting of the NMR frequency in the region of the SR transition, in a number of pure and substituted orthoferrites, points to a definite correlation between the splitting and the orthohombic distortions of the perovskite structure. Application of an external magnetic field makes it possible in principle to identify the magnetic sublattices of the iron ions and to find the sign of the splitting parameter at a known relative direction of the ferro and antiferromagnetism vectors.

The phenomenological analysis based on the known information on the magnetic structure and symmetry of the orthoferrites can explain the observed effects of angular, temperature, and field dependences of the splitting of the NMR frequency. Allowance for the rare-earth contribution to the magnetic moment of the orthoferrites explains qualitatively the observed difference between the temperature dependences of the angles, of the orientation of the spins of the Fe^{3+} ions, and of the summary magnetic moment of $RFeO_3$, without assuming violation of orthogonality of the ferro- and antiferromagnetism vectors of the iron sublattice.

The presented microtheoretical analysis points to a relatively small contribution of the paramagnetic rare-earth sublattice to the anisotropy for the ^{57}Fe nuclei. The most probable mechanism of the HFI anisotropy, which explains all the main singularities of the NMR in the SR region, is the mechanism connected with the noncubic contribution to the crystal field for the Fe^{3+} ions of the next-to-nearest surrounding, and considered within the framework of the model of point charges. For a more detailed quantitative analysis of the HFI anisotropy, however, further NMR investigations are needed, particularly on orthoferrites with substitutes in the iron sublattice.

APPENDIX

The main singularities of the SR phenomenon can be illustrated with the "single-doublet" model as an example. This model considers only the Kramers ground doublet (or quasidoublet) of the R ion. The free energy of the anisotropy of $RFeO_3$ is expressed within the framework of the single-doublet approximation in the form

$$\Phi(\theta)=k_1\cos 2\theta+k_2\cos 4\theta-kT\ln 2\,\mathrm{ch}\frac{\Delta(\theta)}{2kT}, \tag{A.1}$$

where k_1 and k_2 are the first and second anisotropy constants of the iron sublattice and are as a rule assumed to be independent of the temperature in the RS region, and $\Delta(\theta)$ is the splitting of the lower doublet of the R ion in the magnetic field induced by the Fe sublattice.

In the case of reorientation in the *ac* plane we have

$$\Delta(\theta)=\left[\frac{\Delta_a^2-\Delta_c^2}{2}\cos 2\theta+\frac{\Delta_a^2+\Delta_c^2}{2}\right]^{1/2}, \tag{A.2}$$

where $\Delta_{a,c}$ is the splitting of the lower doublet of the R ion in the magnetic configurations G_z and G_x, respectively. The condtion $d\Phi/d\theta=0$ reduces to two equations:

$$1)\ \sin 2\theta=0,\quad 2)\ \alpha\mu-\rho\mu^3=\mathrm{th}(\mu/\tau), \tag{A.3}$$

where we have introduced the following notation:

$$\alpha=1+\gamma\frac{\Delta_a^2+\Delta_c^2}{\Delta_a^2-\Delta_c^2},\quad \rho=\frac{2\gamma}{\mu_{\text{к}}^2-\mu_{\text{н}}^2},$$

$$\gamma=\frac{4k_2}{k_1},\quad \mu=\frac{\Delta(\theta)}{2T_c},\quad \mu_{\text{н}}=\frac{\Delta_c}{2T_c},\quad \mu_{\text{к}}=\frac{\Delta_a}{2T_c},$$

$$T_c=\frac{\Delta_a^2-\Delta_c^2}{16k_1},\quad \tau=\frac{T}{T_c}.$$

The second of these equations describes the region of the spin reorientation; in particular, at $k_2=0$, $\rho=0$, and $\alpha=1$ it goes over into the molecular-field equation well known in the theory of simple ferromagnets, $\mu=\tanh(\mu/\tau)=B_{1/2}(H/\tau)$.

In the region of a continuous SR transition we easily obtain an expression for the magnetic moment of the R ion:

$$\mu_z=\tilde{\mu}_z\sin\theta(1-\gamma\cos 2\theta),\quad \mu_{x,y}=\tilde{\mu}_{x,y}\cos\theta(1-\gamma\cos 2\theta),\tag{A.4}$$

where $\tilde{\mu}_z=g_{zz}^2\beta^2\beta_{zx}/4T_c$

$$\begin{aligned}\tilde{\mu}_x&=\frac{\beta^2}{4T_c}[(g_{xx}\beta_{xz}+g_{xy}\beta_{yz})g_{xx}+(g_{xy}\beta_{xz}+g_{yy}\beta_{yz})g_{xy}],\\ \tilde{\mu}_y&=\frac{\beta^2}{4T_c}[(g_{xx}\beta_{xz}+g_{xy}\beta_{yz})g_{xy}+(g_{xy}\beta_{xz}+g_{yy}\beta_{yz})g_{yy}],\end{aligned}\tag{A.5}$$

g_{ij} are the components of the g tensor of the ground doublet or quasidoublet, and the quantities β_{xz} and β_{yz} determine the magnetic field induced at the R ion by the Fe sublattice:

$$H_x=\beta_{xz}\cos\theta,\quad H_y=\beta_{yz}\cos\theta,\quad H_z=\beta_{zx}\sin\theta.$$

[1] Allowance for the nonorthogonality of the atomic functions of the electrons of Fe^{3+} and of the surrounding O^{2-} ions leads, in first-order approximation, to a contribution to the HFI energy.

---

[1] N. M. Kovtun, A. S. Karnachev, E. E. Solov'ev, A. Ya. Chervonenkis, and A. A. Shemyakov, Fiz. Tverd. Tela (Leningrad) 14, 2150 (1972) [Sov. Phys. Solid State 14, 1856 (1972)].

[2] V. D. Doroshev, A. S. Kharnachev, N. M. Kovtun, E. E. Solov'jov, A. Ya. Chervonenkis, and A. A. Shemyakov, Phys. Status Solidi B 51, K31 (1972).

[3] V. G. Bar'yakhtar, N. M. Kovtun, V. A. Klochan, and E. E. Solov'ev, Fiz. Tverd. Tela (Leningrad) 16, 2058 (1974) [Sov. Phys. Solid State 16, 1336 (1974)].

[4] M. Marezio, J. P. Remeika, and P. D. Dernier, Acta Crystallogr. Sect. B 26, 2008 (1970).

[5] V. E. Naish and E. A. Turov, Fiz. Met. Metalloved. 11, 161 (1961). T. Yamaguchi, J. Phys. Chem. Solids 35, 479 (1974).

[6] A. S. Moskvin and E. V. Sinitsyn, Fiz. Tverd. Tela (Leningrad) 17, 2495 (1975) [Sov. Phys. Solid State 17, 1664 (1975)].

[7] V. V. Vanchikov, A. V. Zalesskiĭ, O. V. Kazakevich, A. S. Karnachev, E. E. Solov'ev, and V. A. Timofeeva, Fiz. Tverd. Tela (Leningrad) 19, 1508 (1977) [Sov. Phys. Solid State 19, 882 (1977)].

[8] R. Kubo, Phys. Rev. 87, 568 (1952).

[9] R. W. Grant and S. Geller, Solid State Commun. 7, 1291 (1969).

[10] G. Gorodetsky and L. M. Levinson, Solid State Commun. 7, 67 (1969).

[11] A. S. Moskvin and I. G. Bostrem, Fiz. Tverd. Tela (Leningrad) 19, 2616 (1977) [Sov. Phys. Solid State 19, 1664 (1977)].

[12] B. R. A. Nijboer and F. W. de Wette, Physica (Utrecht) 23, 309 (1957).

[13] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spectrov (Introduction to the Theory of Atomic Spectra), Nauka, 1977 [Pergamon, 1973].

[14] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, Kvantovaya teoriay uglovogo momenta (Quantum Theory of Angular Momentum), Nauka, 1975.

[15] E. V. Sinitsyn, Candidate's Dissertation, Sverdlovsk, Urals State University, 1975.

[16] D. R. Taylor, J. Owen, and B. M. Wanklyn, J. Phys. C: Solid State Phys. 6, 2592 (1973).

[17] A. S. Moskvin, N. S. Ovanesjan, and V. A. Trukhtanov, Hyperfine Interact. 3, 429 (1977).

[18] R. L. White, G. F. Herrmann, I. W. Carson, and M. Mandel, Phys. Rev. A 136, 236 (1964).

[19] D. L. Wood, L. M. Holmes, and I. P. Remeika, Phys. Rev. 185, 689 (1969).

[20] J. C. Walling and R. L. White, Phys. Rev. B 10, 4748 (1974).

[21] A. S. Moskvin and E. V. Sinitsyn, Fiz. Tverd. Tela (Leningrad) 14, 2535 (1973) [Sov. Phys. Solid State 14, 2198 (1973)].

Translated by J. G. Adashko