Quadrupole effects and magnetic anisotropy in the NMR spectra of Jahn–Teller Mn^{3+} ions in lithium ferrite

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In our experiments we have observed a strong magnetic anisotropy in the NMR spectra of nuclei of the Jahn–Teller Mn^{3+} ions in lithium ferrite (intrinsic or impurity), similar to what was observed previously in manganese ferrite and yttrium iron garnet. We have also noted that quadrupole effects appear in the individual spectra. In our theoretical discussion, we use simple notions concerning the local fields at the nuclei of the ions in the magnets, as well as symmetry considerations.

1. INTRODUCTION

The physical properties of crystals containing Jahn–Teller ions, i.e., ions with ground states that are orbitally degenerate in a cubic crystal field, differ considerably from the properties of compounds that do not contain these ions. Such compounds often exhibit structural phase transitions, complex magnetic structures, anomalous magnetostriction, and magnetic anisotropy. All of these features are usually associated with the Jahn–Teller (JT) effect, in which the orbital degeneracy of the ground state of an ion is lifted by distortions of the crystal structure in its immediate neighborhood.[1]

Among the various experimental methods used to study the JT effect, the NMR method in particular can provide very interesting information. Although the JT effect essentially involves hyperfine electron–nuclear interactions in the crystal, it must undoubtedly contain information regarding the Jahn–Teller effect itself.

At present, there are a number of publications whose topic is the study of hyperfine interactions of Jahn–Teller ion nuclei in magnetoelastic crystals by the NMR method.[2–4] In Ref. 2 a strong anisotropy of the local fields was observed for nuclei of the Jahn–Teller ions Mn^{3+} in manganese ferrite, and the possibility was entertained that quadrupole interactions could show up in NMR spectra. The authors of Ref. 3 reported similar features of Jahn–Teller Mn^{3+} ions in yttrium iron garnet (YIG). A recent publication[4] contains the results of a study of these features in the NMR spectrum of Jahn–Teller Mn^{3+} ions in manganese zinc ferrites.

In this paper the NMR method is used to study hyperfine interactions at nuclei of Jahn–Teller ions in ordered lithium ferrite. The goal of the article is to identify those features in the NMR spectrum of magnetoelastic crystals which reveal the presence of the JT effect.

2. EXPERIMENTAL RESULTS

The NMR spectrum was measured using spin-echo spectrometers, with working regions from 2 to 200 and from 200 to 700 MHz. The measurements were carried out both in zero magnetic field and in external magnetic fields up to 6 kOe at temperatures 4.2 K. The samples under investigation belonged to a series of polycrystalline lithium ferrites doped with manganese, and corresponding to the formula $Li_{0.5}Fe_{2.5-x}Mn_xO_4$, with $x = 0$ to 0.07. In addition, single-crystal samples of lithium ferrite doped with manganese (1.5 mass %) grown from solution in a melt of $PbO–B_2O_3$ were investigated. X-ray analysis showed that all the samples were single-phase lithium ferrospinels.

The NMR spectrum of single-crystal and polycrystalline samples of $Li_{0.5}Fe_{2.5-x}Mn_xO_4$ in zero external magnetic field consists of four groups of lines in the frequency ranges 46 to 50, 71 to 75, 410 to 450, and 560 to 600 MHz. The NMR lines in the range 46 to 50 MHz belong to the oxygen ions,[5] while the lines in the range 71 to 75 MHz belong to ions of iron in the tetrahedral (A) and octahedral (B) sites.[6] It should be noted that the shape of the NMR spectrum of Fe^{3+} and the value of the resonance frequency are practically independent of the concentration of manganese ions up to $x = 0.07$. This indicates that doping of $Li_{0.5}Fe_{2.5}O_4$ with ions of manganese up to $x = 0.07$ does not destroy the order of the lithium and iron ions in the B positions.

The NMR lines in the frequency regions 410 to 450 and 560 to 600 MHz are observed only in samples of lithium ferrite doped with manganese; the intensity of these signals grows as the manganese concentration increases. The association of these two groups of lines with the manganese ions was established on the basis of measurements of the nuclear gyromagnetic ratios. The dependences of the resonant NMR frequencies on the value of the external magnetic field were measured. As the field increased, the values of the resonant frequencies of the lines in the frequency interval 560 to 600 MHz increased, while in the region 410 to 450 MHz they decreased. Using the magnitude of the frequency shift, we determine the gyromagnetic ratios, which turned out to equal 1.03 ± 0.03 MHz/kOe for both groups of lines. The tabulated value of the gyromagnetic ratio of the ^{55}Mn nucleus comes to 1.055 MHz/kOe. Taking into account the sign of the shift of the NMR lines of ^{55}Mn (Ref. 6), we can assign the lines in the region of frequencies 560–600 MHz to manganese ion in the A site, while the lines in the region 410–450 MHz correspond to those in the B sites. The center of gravity of the NMR spectrum of the manganese ions in the A site corresponds to a local field 550 kOe at the nucleus, which is characteristic for divalent manganese ions.[7]

The NMR spectrum in the frequency region 410 to 450 MHz (Fig. 1) belongs to ^{55}Mn nuclei located within domains, as follows from the choice of conditions for excitation

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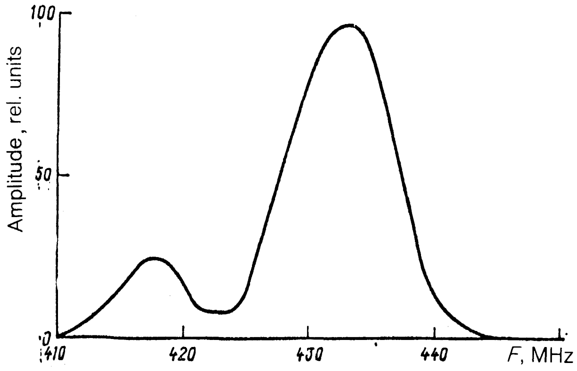

FIG. 1. NMR spectrum of Mn^{3+} (B) in single-crystal $Li_{0.5}Fe_{2.5}O_4$:Mn for $H_0 = 0$, $T = 4.2$ K.

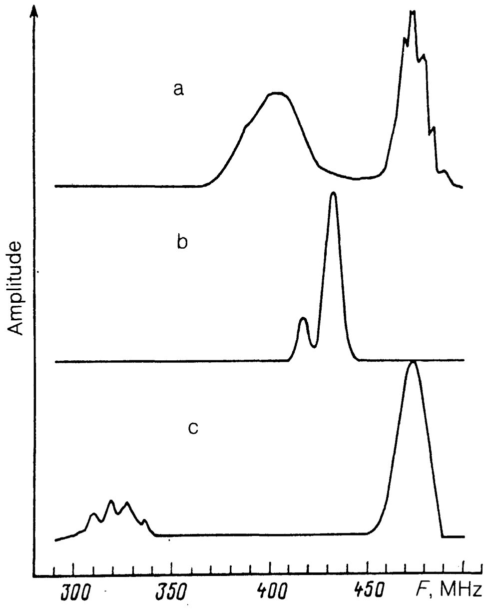

FIG. 2. NMR spectrum of Mn^{3+} (B) at 4.2 K for M‖[110] (a), [111] (b), and [001] (c).

of the NMR signals. We used high-frequency pulses of lengths 0.5 and 1 μsec and amplitudes ≈ 300 V. Using short excitation pulses of equal length (0.2 μsec) and amplitudes ≈ 20 V, we recorded the NMR signals belonging to nuclei in the domain walls. The NMR spectrum from nuclei in the domain walls occupies a considerably larger range of frequencies (370 to 490 MHz) compared to the 410–450 MHz for nuclei in the domains. The larger width of the NMR spectrum from nuclei in the domain walls indicates a considerable anisotropy in the local field component for nuclei of these manganese ions.

In order to determine the isotropic and anisotropic components of the local field for manganese ion nuclei, which corresponds to the NMR lines in the frequency range 410–450 MHz, we measured the NMR spectrum of a single-crystal sample for various directions of the magnetization with respect to the crystallographic axes. The measurements were carried out on a single crystal of $Li_{0.5}Fe_{2.5}O_4$: Mn shaped like an octahedron. The sample was rotated around the [001] axis in an external magnetic field of 3 kOe perpendicular to this axis. The magnetization vector rotated in the plane (001).

In Fig. 2 we show the NMR spectra measured for directions of the magnetization **M** along the three principal axes: [100], [111], and [110]. The NMR spectrum belonging to **M**‖[111] was measured at $H_0 = 0$. As is clear from Fig. 2, the NMR spectra obtained for various directions of the magnetization differ radically from one another. In order to verify that these spectra actually belong to one and the same manganese ion, they were also measured in a sample whose spins were reoriented from the [111] axis to the [100] axis by an external field. This was accomplished by orienting the sample in such a way that the [100] axis was parallel to the external magnetic field. We measured the spectra as functions of the external field. As H varied from 0 to 3 kOe, a reorientation of **M** took place from [111] to [100]; in this case the NMR lines in the 410 to 450 MHz region smoothly split into two lines with resonant frequencies 319 and 474 MHz.

The character of the change in the spectrum as **M** rotates in the plane (100) is shown in Fig. 3. It is clear from Figs. 2 and 3 that we are observing a strong dependence of the resonant frequencies of the NMR lines on the direction of magnetization with respect to the crystallographic axes, which points to a large value of the anisotropic component of the local field at the nuclei of the manganese ions under investigation. Similar dependences of the resonant frequencies were observed for nuclei of Mn^{3+} in the octahedral positions of manganese[2] and manganese-zinc ferrites.[4] Therefore, we can also assign the NMR spectra shown in Figs. 1–3 to the Mn^{3+} ions in the octahedral positions of lithium ferrite. A calculation of the isotropic and anisotropic components of the local field for Mn^{3+} nuclei will be presented below.

From Figs. 2 and 3 it is clear that when **M**‖[100] the low-frequency line in the NMR spectrum of Mn^{3+} (B)

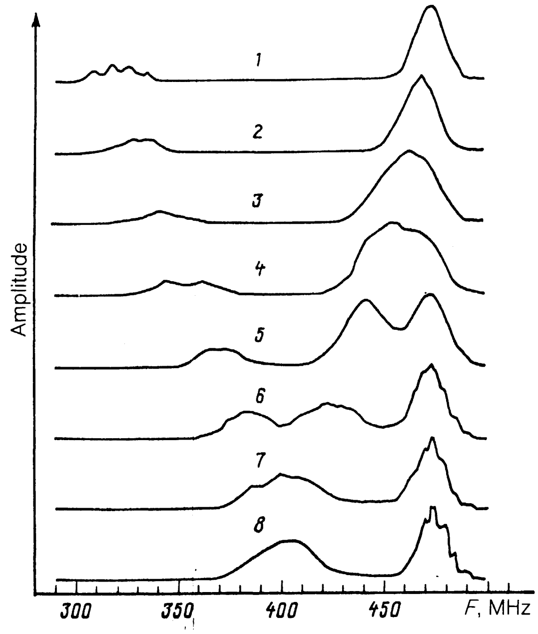

FIG. 3. NMR spectrum of Mn^{3+} (B) at 4.2 K for various angles between the magnetization and the [100] axis: (1)—0°, (2)—11°, (3)—17°, (4)—26°, (5)—29°, (6)—35°, (7)—41°, (8)—45°.

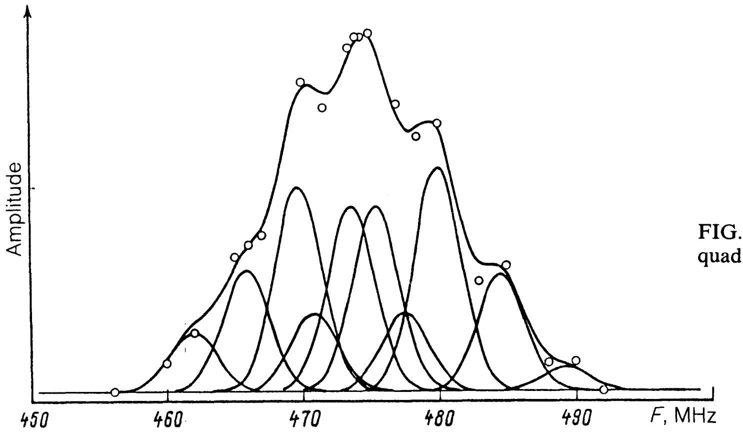

FIG. 4. Resolution of the NMR spectrum of Mn^{3+} for $\mathbf{M}\parallel[110]$ into two quadrupole-split lines.

(i.e., the range of frequencies 295 to 350 MHz) is a superposition of five equidistant lines with a spacing of 8.5 MHz between them. In view of the fact that the ^{55}Mn nucleus possesses a nuclear spin $I = 5/2$, each line in the spectrum should consist of five equidistant components. Apparently, the observed splitting of the NMR spectrum in the frequency range 295 to 350 MHz is caused by quadrupole interactions. Quadrupole interactions can also be observed in the spectra of the high-frequency lines (455–495 MHz) when $\mathbf{M}\parallel[110]$. However, in this case the number of visually resolved lines is more than five. It is natural to assume that we are observing a superposition of two closely-spaced quadrupole-split spectra. With a goal of confirming this assumption we resolved the spectra into components using a computer. Figure 4 shows the synthesized spectrum in the frequency range 455 to 495 MHz. From this resolved spectrum it follows that the experimentally observed spectrum actually can be represented as a superposition of two quadrupole-split lines, the resonant frequencies of the central component of which equal 469.7 and 480 MHz. The spacings between the quadrupole satellites for the first line was 3.9, while for the second it was 4.6 MHz.

3. ANALYSIS AND DISCUSSION

It follows from the experimental data presented in the preceding section that the NMR spectrum from impurity Mn^{3+} ions in the octahedral positions of ordered lithium ferrite possess strong magnetic anisotropy: their shape changes rapidly when the crystal is remagnetized from one direction to another. Analogous results were obtained earlier in investigating the NMR spectra of Mn^{3+} in other ferrimagnetic crystals: YIG, $MnFe_2O_4$, and $Mn_{0.82}Zn_{0.18}Fe_2O_4$. These results suggest that strong magnetic anisotropy is a general feature of all the NMR spectra of Jahn–Teller ions in cubic ferromagnets.

For a qualitative description of the experimental results presented here, we propose in this paper to use an approach based on the customary representations of the local magnetic fields at the nuclei of the ions in a magnetically ordered crystal and on symmetry considerations. As for the Jahn–Teller effect, in these compounds we will assume that it is manifested only by distortions of the neighboring oxygen environment of the impurity Mn^{3+} ions. Since we are discussing ions in octahedral positions in the spinel structure, we will assume that an almost regular octahedron of oxygen ions in the neighborhood of the impurity ion Mn^{3+} undergoes a compression or extension along one of the directions of type [100] of the cubic crystal, and that this takes place despite the fact that the neighborhoods of iron and manganese ions in octahedral positions of lithium ferrite possess very low symmetry (the only symmetry element is rotation around a twofold axis in the directions of type [110]). These Jahn–Teller distortions have the following consequences: first of all, they entirely lift the orbital degeneracy of the electronic state of the Mn^{3+} ion, and secondly, they give rise to strong anisotropy in the hyperfine interactions with the impurity ion. Because the measurements were carried out at helium temperatures, we may assume that the impurity ions are in the ground state, with the maximum projection of spin on the quantization axis coinciding with the direction of magnetization of the crystal.

If we neglect the quadrupole effects, the operator for the interaction energy of the nuclei of the impurity ion Mn^{3+} with the electrons can be written in the form

$$\mathscr{H}=-\boldsymbol{\mu}\mathbf{H}, \tag{1}$$

where $\boldsymbol{\mu} = \gamma_n \hbar \mathbf{I}$ is the magnetic moment of the nucleus, γ_n is the nuclear gyromagnetic ratio, and $\mathbf{H}$ is the magnetic field at the nucleus. This simple expression is a consequence of the customary assumptions about magnetic fields at the nuclei of ions in crystals. Generally speaking, such assumptions are not justified for all crystals; however, in magnetically ordered compounds, where ordering of the spins is due to strong exchange interactions, they turn out to be quite useful.

As a consequence of the hyperfine interaction (1) there occurs a splitting of the ground state of the impurity ion into $2I + 1$ components with energies

$$E_m=-\hbar\gamma_n H_m.$$

The resonance absorption, as is well-known, is connected with transitions between neighboring levels of the hyperfine structure and occurs at a frequency

$$\omega_0=\gamma_n H.$$

The NMR spectrum from impurity ions would be extremely simple if the positions of these ions in the crystal were equivalent in all respects. In actuality, they are equivalent only crystallographically, and the presence of magnetic order removes this equivalence. This circumstance complicates the observed NMR spectrum and its anisotropy.

Let us consider, to be specific, an impurity ion Mn^{3+} in an octahedral position with a twofold symmetry axis in the direction $[1\bar{1}0]$, and assume that the Jahn–Teller distortion does not disrupt the symmetry in the immediate neighborhood of the impurity ion. Then, assuming a tensor relation between the magnetic field at the nucleus of the impurity ion and the magnetization of the crystal, we write

$$\mathbf{H}=\hat{T}\mathbf{n},\quad \mathbf{n}=\mathbf{M}/M, \tag{2}$$

where $\hat{T}$ is a symmetric second-rank tensor that is independent of the direction of the magnetization; in a system of coordinates with axes along directions of type [100] this tensor can be represented by a matrix of the following form:

$$T_{\alpha\beta}=\begin{pmatrix} c-\Delta & h & d \\ h & c-\Delta & d \\ d & d & c+2\Delta \end{pmatrix} \tag{3}$$

where c is an isotropic constant, while the quantities Δ, d, and h are parameters that characterize the anisotropy of the hyperfine and dipole interactions.

In this case, we obtain for the magnetic field at the nucleus of the ion, in the position under discussion, the expression:

$$H=\{[(c-\Delta)n_1+hn_2+dn_3]^2+[(c-\Delta)n_2+hn_1+dn_3]^2 + [(c+2\Delta)n_3+d(n_1+n_2)]^2\}^{1/2}, \tag{4}$$

where n_1, n_2, and n_3 are the components of the vector $\mathbf{n}$. Replacing the components n_α of the vector n in this expression by the components of unit vectors in the equivalent directions, we obtain an ensemble of magnetic-field values at the nuclei of the impurity ions for all other octahedral positions. For an arbitrary direction of the vector n we obtain 12 different values of H in all, which corresponds to a multiplicity 12d of the particular positions in lithium ferrite. Consequently, in the general case, the NMR spectrum of Mn^{3+} is a superposition of 12 resonance lines. The number of lines in the NMR spectrum can be smaller when the magnetization of the crystal is directed along [100], [110], or [111].

Thus, e.g., for the case $\mathbf{n}\|[001]$ we should observe no more than two resonance lines in the NMR spectrum, because there are only three directions of type [100] and two of them transform into each other by a rotation around the symmetry axis. For $\mathbf{n}\|[111]$ the spectrum consists of three resonance lines, because among the four directions of type [111] two transform into themselves by a rotation around the symmetry axis and the others transform into each other. If, however, $\mathbf{n}\|[110]$, we should observe four lines in this spectrum, because among the six directions of type [110] two transform into themselves under a rotation around the symmetry axis, while the remaining two pairs transform into each other. All the cases we have listed are encountered when the direction of the vector n is varied smoothly in the plane $(1\bar{1}0)$. The corresponding angular dependences of the resonance frequencies were described previously in Ref. 6 in connection with the study of NMR spectra of Fe^{3+} in octahedral positions of lithium ferrite. For the NMR spectra of Mn^{3+} they are shown in Fig. 5. The parameters required for this calculation were determined by comparing the theoretical dependences with the experimental data. In Table I we show the values of the parameters c, Δ, d, and h for the Mn^{3+} ions and also for the Fe^{3+} ions as determined according to the data of Ref. 6. For convenience in comparing the calculated dependences with the experimental, we have also listed in the table the values of the parameters in frequency units.

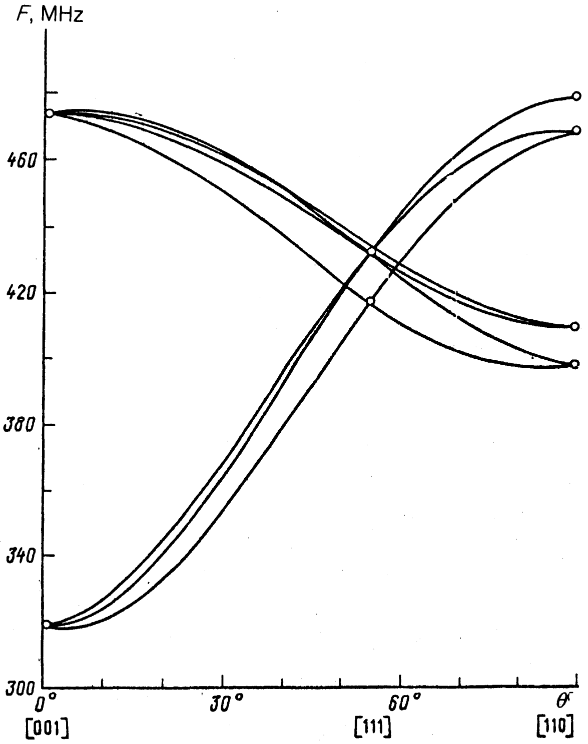

FIG. 5. Angular dependence of the resonance frequencies of the central components of the quadrupole-split NMR lines of Mn^{3+} in single-crystal $Li_{0.5}Fe_{2.5}O_4$:Mn at 4.2 K in an external field of 3 kOe; θ is the angle between the magnetization and the [001] axis.

For directions along the principal axes of the crystal, this number of lines in the NMR spectrum will be observed only for nuclei with spin $I=1/2$. Since the ^{55}Mn nucleus possesses spin 5/2, the quadrupole interactions should be manifested in the spectra, and this is also observed in experiment (see, e.g., Fig. 4).

To take the quadrupole interactions into account, the energy operator (1) for the electron-nuclear interactions was replaced by

$$\mathscr{H}=-\boldsymbol{\mu}\mathbf{H}+\frac{1}{6}\sum_{\alpha,\beta}\varphi_{\alpha\beta}Q_{\alpha\beta}, \tag{5}$$

where $Q_{\alpha\beta}$ is the quadrupole tensor of the nucleus:

$$Q_{\alpha\beta}=\frac{3eQ}{2I(2I-1)}\left[I_\alpha I_\beta+I_\beta I_\alpha-\frac{2}{3}I(I+1)\delta_{\alpha\beta}\right],$$

while $\varphi_{\alpha\beta}$ is the tensor of electric field gradients (EFG) at the nucleus, and its form is determined by symmetry considerations:

TABLE I. Values of the parameters that describe the local fields at the Mn^{3+} and Fe^{3+} nuclei.

Ion	Measurement units	*c*	Δ	*d*	*h*
Mn^{3+}	MHz	−422,3	52	6	5,1
	kOe	−400,2	49,3	5,7	4,8
Fe^{3+}	MHz	−73,93	−0,22	0,277	0,65
	kOe	−535,7	−1,69	2	4,7

$$\varphi_{\alpha\beta}=eq\begin{pmatrix}-1 & \varepsilon & \delta\\ \varepsilon & -1 & \delta\\ \delta & \delta & 2\end{pmatrix}. \tag{6}$$

We calculated the resonance frequencies in the presence of quadrupole interactions using first-order perturbation theory, and obtained the following expressions:

$$\nu_k=\nu_0+k\delta\nu,\quad k=0,\ \pm1,\ \pm2, \tag{7}$$

where

$$\delta\nu=\frac{\nu_Q\varphi_{zz}'}{eq},\qquad \nu_Q=\frac{3e^2Qq}{2hI(2I-1)},$$

$$\varphi_{zz}'=\frac{1}{H^2}\sum_{\alpha\beta}\varphi_{\alpha\beta}H_\alpha H_\beta$$

$$=\frac{eq}{H^2}[(2H_z^2-H_x^2-H_y^2)+2H_z(H_x+H_y)\delta+2H_xH_y\varepsilon].$$

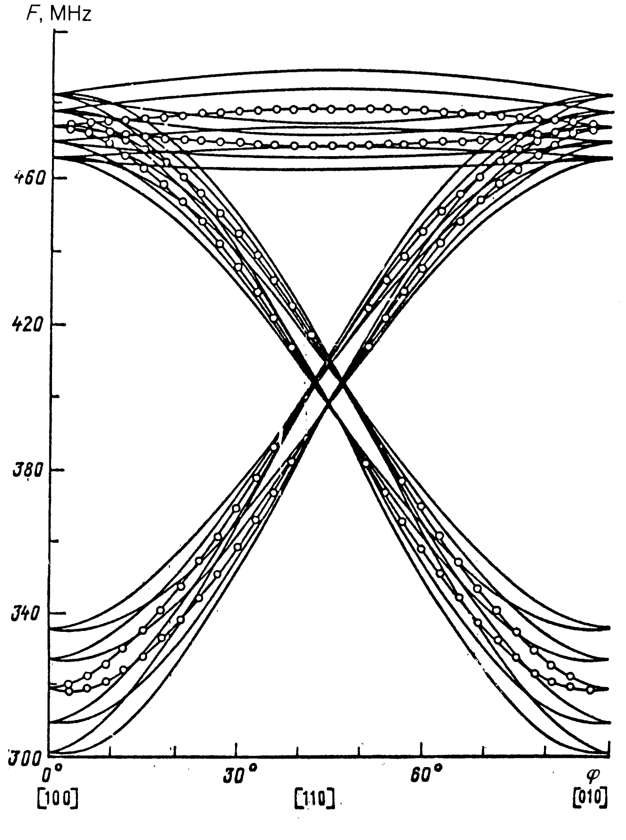

FIG. 6. Calculated angular dependences of the NMR frequencies of Mn^{3+} in the (001) plane in single-crystal $Li_{0.5}Fe_{2.5}O_4$:Mn; here φ is the angle between the magnetization and the [100] axis. The curves with marks on them correspond to central components of the quadrupole-split NMR lines.

The quadrupole interactions lead to a splitting of each resonance line into five equivalent lines.

Using the experimental data presented in Sec. 2 for the quadrupole splitting of certain lines in the NMR spectrum of Mn^{3+}, the parameters of the EFG at the nuclei of the impurity Mn^{3+} ions: were found to be $\nu_Q=4.25$ MHz, $\nu_Q\varepsilon=0.35$ MHz, and $\nu_Q\delta=0.4$ MHz. The calculated angular dependences of the NMR resonance frequencies taking into account quadrupole interactions in the [001] plane are presented in Fig. 6. Comparison of the NMR spectra of Fig. 3 and the theoretical angular dependences (Fig. 6) shows qualitative agreement of the theory and experiment. This agreement confirms the correctness of our assumption that the JT effect does not change the local symmetry of the Mn^{3+} ions. However, a comparison of the corresponding parameters that describe the anisotropic local field at nuclei of trivalent iron and manganese in the octahedral positions (see Table I) shows clearly that the parameters *h* and *d* for both ions are roughly the same, while the parameter Δ is roughly 30 times larger for the Mn^{3+} ions than it is for the iron ions. Taking into account that Δ characterizes the tetragonal distortion of the local symmetry of the ions in the octahedral positions, we may conclude that the large value of Δ is caused by the static Jahn–Teller effect. Of course, the real picture of how the Jahn-Teller effect is manifest in the NMR experiments can be more complicated than what we describe here, as the more detailed investigations in manganese zinc ferrites indicate.[4] However, our case should be simpler than that of $Mn_{1-x}Zn_xFe_2O_4$, because there is no strong source of random field in $Li_{0.5}Fe_{2.5}O_4$ when the concentration of impurities in the form of Mn ions is small.

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