Hyperfine interactions in ordered lithium ferrite: NMR investigations with diamagnetic substitution and hydrostatic compression

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We have performed a detailed investigation of hyperfine interactions (HFIs) in a model crystal belonging to an extensive class of ferrite spinels—ordered lithium ferrite $Li_{0.5}Fe_{2.5}O_4$. To this end, we have studied at $T = 4.2$ K the satellite structure of the ^{57}Fe NMR spectra of tetrahedral (A) and octahedral (B) Fe^{3+} ions of diamagnetically diluted ferrites $Li_{0.5}Fe_{2.5-x}Al_xO_4$ ($0 \leqslant x \leqslant 0.225$) and $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ ($0 \leqslant x \leqslant 0.43$) with easy axes $\langle 111 \rangle$ and cobalt-doped ($\sim 0.2\%$) ferrites with analogous compositions and easy axes $\langle 100 \rangle$; we have also investigated the effect of high pressure, up to 16 kbar, on the NMR frequency. We have determined the magnitudes of the components of the hyperfine (HF) magnetic field on the nuclei of A and B Fe^{3+} ions, namely, the field $H_{\rm COV}$, reflecting the effect of the nearest-neighbor anionic environment, and the field $H_{\rm IHF}$, determined by the transfer of spin density from the surrounding magnetoactive cations. We have also reliably identified the contributions from different cationic spheres. We find that the anisotropy of the HF fields can be explained on the basis of the independent-bond model, whose applicability for studying HFI was established previously only in the case of $Y_3Fe_5O_{12}$ [English *et al.*, J. Magn. Magn. Mater. **50**, 174 (1985)]. In accordance with the characteristic features of the crystal structure of $Li_{0.5}Fe_{2.5}O_4$, we show at a microscopic level that the anisotropy of the HF field at the A sites is determined by the anisotropy of the field $H_{\rm IHF}$, while at the B sites the anisotropy is determined primarily by the anisotropy of the field $H_{\rm COV}$. We find that the concentration dependences of the HF fields are determined not only by radial effects due to the change in the lattice parameter, but also by the effect of diamagnetic substitution in the second cationic coordination sphere. We establish, on the basis of the closeness of the mechanisms of indirect exchange and indirect HFIs, the hierarchy of intersublattice and intrasublattice exchange interactions in lithium ferrite.

1. INTRODUCTION

The method of ^{57}Fe NMR, together with the Mössbauer effect, has been successfully employed for studying hyperfine interactions (HFIs) in magnetically ordered dielectrics by recording the local magnetic field on the ^{57}Fe nuclei, $\mathbf{H}_{\rm LOC} = \mathbf{H}_{\rm HF} + \mathbf{H}_{\rm DIP}$, where $\mathbf{H}_{\rm DIP}$ is the field due to the surrounding magnetic dipoles and the field $\mathbf{H}_{\rm HF}$ is proportional to the electron spin density on the iron nucleus. The source of the main part of the hyperfine (HF) field in $3d$-ions is the exchange spin polarization of closed s-shells by the spin of unpaired $3d$-electrons.[1] The effect of the crystalline environment for predominantly ionic iron compounds is usually regarded as a modification of the field of the free ion [$H_0 \approx -630$ kOe for Fe^{3+} (Ref. 1)] 1) as a result of covalency and overlapping of electronic shells of the central cation and the ligands ($H_{\rm COV}$). The change in the electron structure of the ligands which participate in these effects, primarily their spin polarization by the surrounding cations, is described by introducing the indirect hyperfine (IHF) field $H_{\rm IHF}$:[2]

$$H_{\rm HF} = H_0 + H_{\rm COV} + H_{\rm IHF}. \tag{1}$$

A very informative method for studying magnetic HFI is diamagnetic substitution. When a magnetic vacancy appears in a cation-ligand-cation chain, the local magnetic field on the nucleus of the ion changes, in the general case, as a result of the change in the dipole field, "switching off" of spin-density transfer, and distortion of the crystal field

$$\Delta H_{\rm LOC} = \Delta H_{\rm DIP} + \Delta H_{\rm IHF} + \Delta H_{\rm COV}. \tag{2}$$

For ferrites with spinel structure, in which the cations occupy tetrahedral (A) and octahedral (B) sites, such investigations have been performed by substituting at both A and B sites diamagnetic ions for iron ions.[2–9] Mössbauer and NMR experiments have shown that the field $H_{\rm LOC}$ decreases on ^{57}Fe nuclei at sites whose nearest-neighbor environment contains diamagnetic cations; this decrease was associated primarily with the vanishing of spin-density transfer from the substituted magnetic ion F^{3+}, ($\Delta H_{\rm IHF}$). The spread in the values of the IHF fields found in this manner in different works is very significant. This is due to the low accuracy with which $H_{\rm IHF}$ is determined, in most cases by analyzing the concentration dependence of the average HF fields. In cases when satellites were resolved in the NMR spectrum, $H_{\rm IHF}$ per bond was determined by assuming that the IHF fields are isotropic.[6] Later, however, in an analysis of NMR spectra of diamagnetically substituted yttrium iron garnet, it was shown that the anisotropy of the HF fields must be taken into account.[10] The anisotropy of the field $H_{\rm HF}$ was described with the help of the independent-bond model, previously widely employed in crystal-field theory, according to which the contributions of separate ligands to the HF field on the central cation are independent and given by

$$H_{\rm HF} = H_{\rm HF}^{\rm is} + H_{\rm HF}^{\rm anis} \cos^2 \varphi, \tag{3}$$

where φ is the angle between the magnetization and the central-cation–ligand bond. This model employs the fact that the admixture of ligand electrons to the electronic configuration of the ion is small. For this reason, the correlation be-

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tween the separate bonds can be neglected and it can be assumed that the contributions of the ligands to the HF field on the nucleus of the cation are additive. Each contribution reflects the axial symmetry of the metal-ligand bond, while the HF field can be determined as the sum of the components (3) over all bonds.

In the present work we study the isotropic and anisotropic HFIs with diamagnetic dilution of a model crystal of ferrites with spinel structure—$\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$. The ^{57}Fe NMR spectra are interpreted on the basis of the independent-bond model for the purpose of confirming the applicability of this model in iron spinels. We also present the results of measurements of local fields on ^{57}Fe nuclei in lithium ferrite under hydrostatic compression. Such measurements are necessary in order to study the subtle effects due to HFIs.

2. MAGNETIC AND CRYSTAL STRUCTURE OF $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$

Lithium ferrite is most suitable for investigations of HFIs, since it has extremely narrow NMR lines thanks to the completely ordered magnetic and crystalline structure. The only type of magnetic ion it contains is Fe^{3+}, which has $3d^5$–^6S electronic configuration with a purely spin magnetic moment $\mu_0 \approx 5\mu_B$ and is antiferromagnetically ordered at the *A* and *B* sites. The space group of the ordered lithium ferrite is $P4_332$ (Ref. 11). But lithium ferrite can also be regarded with adequate accuracy as a spinel (space group $Fd3m$) with ordering of the Li^+ and Fe^{3+} cations at 1:3 octahedral positions,[12] so that the cation distribution can be written in the form $(\mathrm{Fe}^{3+})\,[\mathrm{Fe}^{3+}_{1.5}\mathrm{Li}^{+}_{0.5}]\mathrm{O}_4^{2-}$. In such a structure the cations have particular positions, while the position of the anions is characterized by the oxygen parameter u. The lattice constant and the oxygen parameter determine the position of all ions in the cell. For $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$ ($a = 8.330$ Å and $u = 0.3834$) the *A–O–B* bond is characterized by the angle 122.7° and the *B–O–B* bond is, correspondingly, characterized by the angle 93.6°. In lithium ferrite each Fe^{3+} (*A*) ion is bound, through four oxygen ions, with 12 *B*-ions ($9\mathrm{Fe}^{3+}$ and $3\mathrm{Li}^+$), while each $\mathrm{Fe}^{3+}(B)$ ion is bound, through six oxygen ions, with six $\mathrm{Fe}^{3+}(A)$ ions and six *B*-ions ($4\mathrm{Fe}^{3+}$ and $2\mathrm{Li}^+$). These and other more distant environments of *A* and *B* Fe^{3+} ions are presented in Table I.

The local crystallographic symmetry of the tetrahedral *A* sites in the structure of normal spinel is cubic, but the presence of two types of ions in the *B* sublattice of inverted lithium ferrite lowers the symmetry, so that each $\mathrm{Fe}^{3+}(A)$ ion has one of four $\langle 111\rangle$ directions as a trigonal symmetry axis. In accordance with this, for magnetization along the $\langle 111\rangle$ direction, which is the easy axis of $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$, there are two types of magnetically inequivalent *A* sites in the ratio 3:1; this results in the presence of two lines in the NMR spectrum of *A* sites of ^{57}Fe. For magnetization along the $\langle 100\rangle$ direction all *A* sites are equivalent and the NMR spectrum consists of a single line. The *B* sites in the lattice of normal spinel are trigonally distorted with $\langle 111\rangle$ symmetry axes. The presence of Li^+ ions in lithium ferrite results in additional nonequivalence of $\mathrm{Fe}^{3+}(B)$ ions due to orthorhombic distortions. As a result, each $\mathrm{Fe}^{3+}(B)$ ion has two two-fold $\langle 110\rangle$ symmetry axes. Since the symmetry of the *B* sites is lower than that of the *A* sites, the number of lines in the NMR spectrum of the *B* sites of Fe^{3+} is greater than for *A* sites [three for $\mathbf{M}\|\langle 111\rangle$ and two for $\mathbf{M}\|\langle 100\rangle$ (Ref. 13)].

3. EXPERIMENT AND RESULTS

The NMR investigations were conducted using single crystals of the ferrites $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5-x}\mathrm{Al}_x\mathrm{O}_4$ ($0 \leqslant x \leqslant 0.225$) and $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5-x}\mathrm{Ga}_x\mathrm{O}_4$ ($0 \leqslant x \leqslant 0.43$) with $\langle 111\rangle$ easy axes of magnetization as well as ferrites with similar compositions doped with cobalt ($\sim 0.2\%$), which, as is well known,[14] results in reorientation of the easy axis toward directions of the type $\langle 100\rangle$. The samples were grown by the method of spontaneous crystallization from a solution in a melt. The results of the determination of the lattice constant, the cation distribution, and the saturation magnetization for these samples

TABLE I. Interionic distances in $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$.

Central ions	Surrounding ions			Remarks
	N	r, Å	type of ion	
Fe^{3+} (A)	4	1,92	O^{2-}	
	9	3,45	Fe^{3+} (B)	nearest-neighbor cationic environment
	3	3,45	Li	
	4	3,61	Fe^{3+} (A)	
	12	5,41	Fe^{3+} (B)	next-to-nearest neighbor Fe^{3+} environment
	9	6,83	»	
	12	5,89	Fe^{3+} (A)	
	12	6,91	»	
Fe^{3+} (B)	6	2,02	O^{2-}	
	4	2,95	Fe^{3+} (B)	Nearest cationic environment
	2	2,95	Li	
	6	3,45	Fe^{3+} (A)	
	10	5,10	Fe^{3+} (B)	Next-to-nearest Fe^{3+} environment
	8	5,89	»	
	8	6,59	»	
	8	5,41	Fe^{3+} (A)	

TABLE II. Characteristics of $Li_{0.5}Fe_{2.5-x}M_xO_4$ samples.

Samples	x	x_A	x_B	a, Å	T_c, °C	$M_S(T=0)$, G
$Li_{0,5}Fe_{2,5}O_4$	0	0	0	8,330	911	313
$(Fe_{1-x_A}Al_{x_A})[Li_{0,5}Fe_{1,5-x_B}Al_{x_B}]O_4$	0,1	0,010	0,090	8,314	–	273
	0,164	0,017	0,147	8,305	851	241
	0.225	0,029	0,196	8,291	833	216
$(Fe_{1-x_A}Ga_{x_A})[Li_{0,5}Fe_{1,5-x_B}Ga_{x_B}]O_4$	0,06	0,037	0,023	8,328	853	330
	0,16	0,112	0,048	8,325	823	367
	0,22	0.162	0,058	8,323	789	389
	0,43	0,308	0,122	8,316	705	433

are summarized in Table II.[15] The NMR spectra were recorded by the spin-echo technique. The NMR spectra consisted of the average amplitude of the spin-echo signal as a function of the filling frequency of the excitation pulses. An incoherent NMR spectrometer with a gated integrator with frequency pulling, was employed. The conditions under which the signals were excited and recorded were chosen so that only the intradomain nuclei were observed and there was no instrumental broadening of the spectra. All measurements were performed at $T=4.2$ K without applying an external magnetic field.

The NMR spectra of diamagnetically substituted lithium ferrites are presented in Figs. 1 and 2. A characteristic feature of the spectra of the Li–Al ferrites with weak diamagnetic dilution is the presence of a pronounced satellite structure for iron at the A sites. As the aluminum concentration increases the intensities of the satellites a_1–a_7 increase while the positions of the satellites with respect to the principal lines remain unchanged. Since at low concentrations Al occupies predominantly the B sites of the spinel structure (Table II), these satellite lines must be assigned to the nuclei of $Fe^{3+}(A)$ ions, in whose nearest-neighbor B environment Al^{3+} – ions appear, i.e., they must be attributed to diamagnetic substitutions in the chains

$$Fe^{3+}(B)\uparrow \rightarrow O^{2-} \rightarrow Fe^{3+}(A)\downarrow.$$

In the spectra of $Fe^{3+}(B)$ ions of Li–Al ferrites only one resolved satellite b_1 is observed, but the substantially greater broadening of the principal lines of the B sites than those of A sites indicates the presence of unresolved satellites in the spectrum of $Fe^{3+}(B)$ ions, which, like the b_1 satellites, are due to the diamagnetic substitution in the chains

$$\begin{tikzcd}
& O^{2-} \arrow[dr] & \\
Fe^{3+}(B)\uparrow \arrow[ur] \arrow[dr] & & Fe^{3+}(B)\uparrow . \\
& O^{2-} \arrow[ur] &
\end{tikzcd}$$

The NMR spectra of Li–Ga ferrites for Ga concentrations $0 \leqslant x \leqslant 0.22$ are also observed to contain satellites whose intensities increase and positions relative to the principal lines remain unchanged as x increases. The "rise" of the spectra of Li–Ga ferrites above 74 MHz, increasing as a function of Ga content, is associated with the superposition of a wider line of the ^{69}Ga NMR spectrum on the ^{57}Fe NMR spectrum.[16] In contrast to Al^{3+} ions, a significant fraction of the Ga^{3+} ions ($\sim$60–75%, see Table II) replaces iron at the A sites, and for this reason the presence of b_2-b_9 satellites in the spectra of $Fe^{3+}(B)$ ions in Li–Ga ferrites can be associated with diamagnetic substitution in the chains

$$Fe^{3+}(A)\downarrow \rightarrow O^{2-} \rightarrow Fe^{3+}(B)\uparrow.$$

The Ga^{3+} ions at B sites, in turn, lead to the appearance of satellites a_3 and a_7, analogous to the stronger satellites of A sites in Li–Al ferrites, in the spectra of $Fe^{3+}(A)$ ions, Finally, the a_8 satellite in the spectra of $Fe^{3+}(A)$ ions of Li–Ga ferrites must be attributed to diamagnetic substitution in the

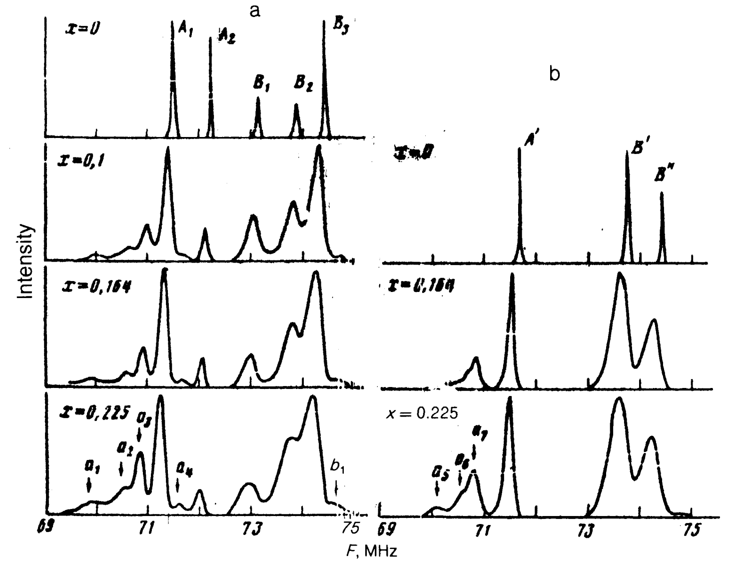


FIG. 1. ^{57}Fe NMR spectra of the ferrites $Li_{0.5}Fe_{2.5-x}Al_xO_4$ at $T=4.2$ K. a) ⟨111⟩ easy axis and b) ⟨100⟩ easy axis.

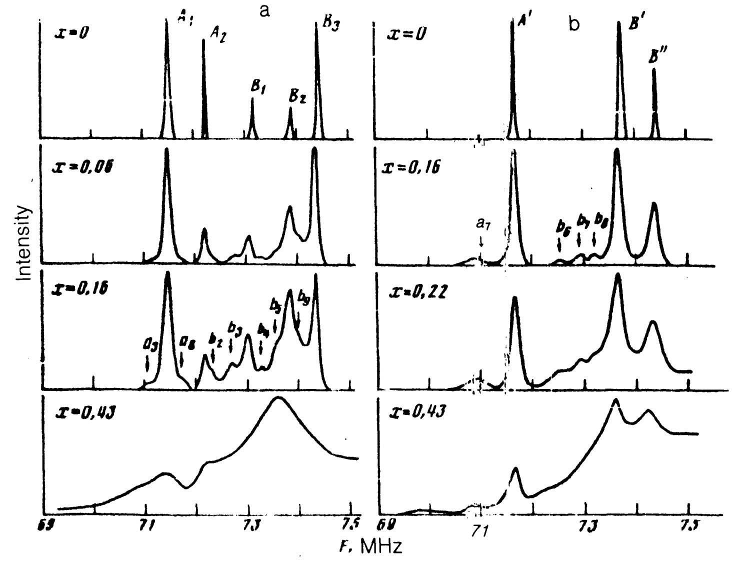


FIG. 2. ^{57}Fe NMR spectra of the ferrites $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ at $T=4.2$ K. a) ⟨111⟩ easy axis and b) ⟨100⟩ easy axis.

nearest-neighbor A environment of $Fe^{3+}(A)$ ions. Thus, by taking into account diamagnetic substitution in Fe–O–Fe chains we can explain qualitatively the satellite structure of the ^{57}Fe NMR spectra of diamagnetically diluted lithium ferrite, and in addition substitution in chains of the form

$$Fe^{3+}(A)\downarrow\text{–}O^{2-}\text{–}Fe^{3+}(B)\uparrow$$

leads, as expected, to stronger changes in the spectra.

Another important feature of the ^{57}Fe NMR spectra is the asymmetric broadening and shift in the direction of lower frequencies of both the principal and satellite lines with increasing Al or Ga content. In view of the concentration dependence of the magnetization $\Delta H_L = 4\pi/3\Delta M_S$ (Table II), we took into account the trivial contribution to the local field, arising due to the change in the Lorentz field. We found that the HF field at ^{57}Fe nuclei decreases with increasing diamagnetic ion concentration for both A and$B$ sites of iron (Fig. 3), and this behavior is not related with diamagnetic substitution in the nearest-neighbor cationic environments, which result, as a rule, in splitting of the NMR lines. The position of the lines can be affected by a coherent change in the lattice parameter accompanying dilution. This is indicated by the significantly greater change in the NMR frequencies for Li–Al ferrites than in the case of Li–Ga ferrites; this corresponds to the greater change in the lattice parameter in Li–Al ferrites (Table II).

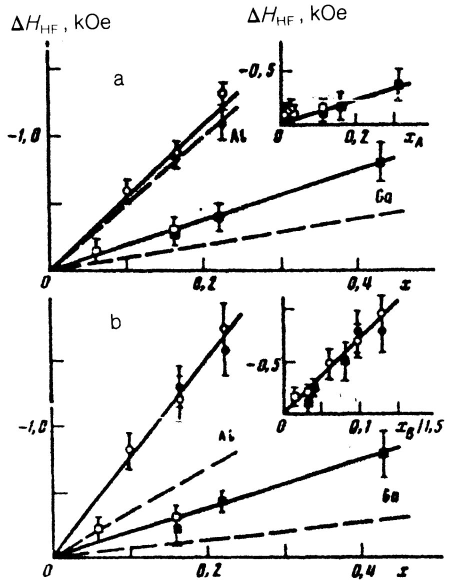


FIG. 3. Concentration dependence of isotropic HF fields at ^{57}Fe nuclei in A and B sites of diamagnetically substituted lithium ferrites: a—ΔH_{HF} (A); b—ΔH_{HF} (B). Notation: ○—Li–Al ferrites with ⟨111⟩ easy axis, ●—same with ⟨100⟩ easy axis; □—Li–Ga ferrites with ⟨111⟩ easy axis; ■—same with ⟨100⟩ easy axis. The changes in the HF fields were obtained from the shifts of the principal lines in the NMR spectra after correction for the change in the Lorentz field. The dashed lines show the contributions of $\Delta H_{HF}(x)$ which are associated with the change produced in the lattice parameter by diamagnetic dilution. Insets: Values of $\Delta H_{HF}(A)$ and $\Delta H_{HF}(B)$, corrected for radial effects, as a function of the degree of substitution of the A and B sublattices, respectively.

In order to take into account radial effects, we performed NMR measurements of the HF fields under conditions of hydrostatic compression of $Li_{0.5}Fe_{2.5}O_4$ at the temperature of liquid helium (the details of the experiment are described, for example, in Ref. 17). The frequencies of the A and B iron ions decrease linearly with pressure in the region 0–16 kbar (Fig. 4). The values of the pressure coefficients of the NMR frequencies of ^{57}Fe (Table III) were determined by least-squares analysis of the separate spectra (three to five measurements for each value of the pressure) and the pressure dependence in the linear approximation in the pressure. For isotropic HF fields at the nuclei of $Fe^{3+}(A)$ and $Fe^{3+}(B)$ ions and their pressure coefficients, corrected for the Lorentz field and the change in this field as a function of the pressure, we have, respectively,

$$\begin{aligned}&|H_{nA}|=520{,}3\ \text{kOe},\\&\partial|H_{nA}|/\partial P=-5{,}00(9)\cdot10^{-2}\ \text{kOe}\cdot\text{kbar}^{-1},\\&|H_{nB}|=539{,}6\ \text{kOe},\\&\partial|H_{nB}|/\partial P=-3{,}38(9)\cdot10^{-2}\ \text{kOe}\cdot\text{kbar}^{-1}.\end{aligned}\qquad(4)$$

Using the value of the compressibility of lithium ferrite $\varkappa=5.78\cdot10^{-4}$ kbar^{-1} (Ref. 18), we used the pressure coefficients to calculate the changes occurring in the HF fields at

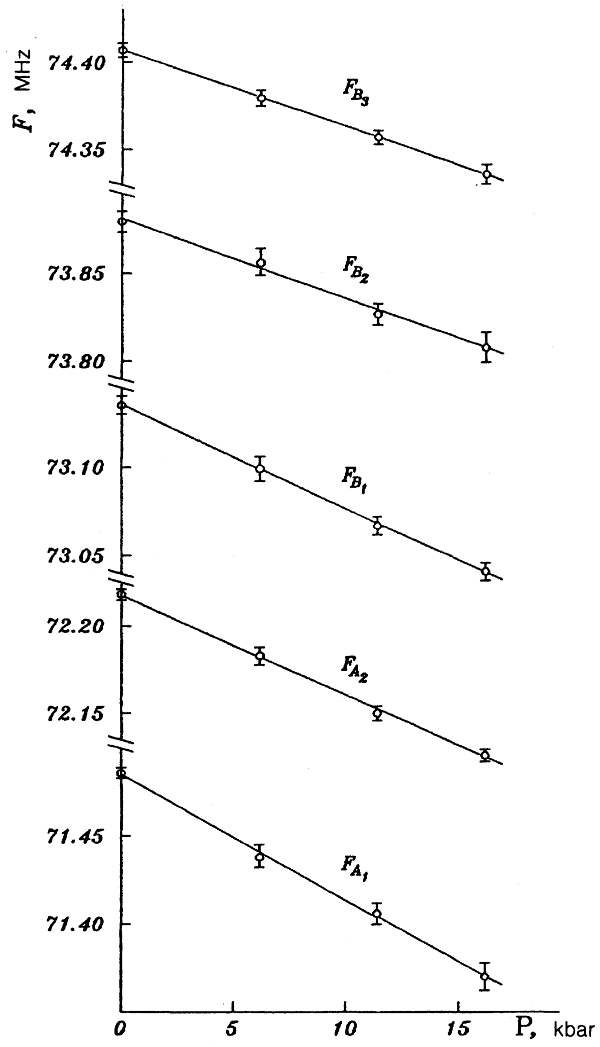


FIG. 4. Pressure dependences of the ^{57}Fe NMR frequencies in lithium ferrite at $T = 4.2$ K.

the nuclei of A and B iron ions owing to the change in the lattice parameter accompanying diamagnetic dilution of $Li_{0.5}Fe_{2.5}O_4$ (dashed lines in Fig. 3). However, the radial effects explain only partially the experimentally observed decrease of the HF fields.

4. ANALYSIS OF EXPERIMENTAL RESULTS

4.1. Diamagnetic substitution in $Fe^{3+}(B)\uparrow \rightarrow O^{2-} \rightarrow Fe^{3+}(A)\downarrow$ chains

The NMR spectra of ^{57}Fe at the A sites of Li–Al ferrites (the easy axis is $\langle 111 \rangle$) were analyzed in Ref. 6, where it was assumed that the change in the HF field accompanying diamagnetic substitution is isotropic and the anisotropic change of the dipole field, in view of its weakness, contributes only to the broadening of the lines. The satellites a_3 and a_4 were referred to the $Fe^{3+}(A_1)$ and $Fe^{3+}(A_2)$ sites, respectively, with a single Al^{3+} ion in the nearest-neighbor B environment, while the satellite a_2 was referred, on the basis of the equal spacing of the lines a_2–a_3 and a_3–A_1, to $Fe^{3+}(A_1)$ sites with double diamagnetic substitution. This approach gave the field $H_{\rm IHF}(A) = 2.8 \pm 0.3$ kOe per bond $Fe^{3+}(B)\uparrow \rightarrow O^{2-} \rightarrow Fe^{3+}(A)\downarrow$. In the present work, together with careful repeated measurements of NMR spectra of Li–Al ferrites with easy access $\langle 111 \rangle$, we also measured the spectra of Co-doped Li–Al ferrites with easy access $\langle 100 \rangle$. It was found that in order to explain the entire collection of experimental NMR spectra of $Fe^{3+}(A)$ ions the components of the local field at the ^{57}Fe nuclei must be taken into account more systematically. Indeed, in the case of the easy axis $\langle 100 \rangle$ the satellite a_7, by analogy with the satellite a_3, can be assigned to $Fe^{3+}(A')$ sites with a single Al^{3+} ion in the nearest-neighbor B environment, while the satellite a_5 can be assigned to $Fe^{3+}(A')$ sites with double diamagnetic substitution. However, the a_3–A_1 splitting and a_7–A' splitting are substantially different, i.e., the change in the local field at ^{57}Fe-nuclei at the A sites depends on the direction of magnetization. Therefore, the anisotropic components of the local field must be taken into account in order to explain the positions of the satellites.

The interpretation given below is based on taking into account the anisotropic change brought about in both the HF field, according to Eq. (3), and the dipole field by substitution:

$$\Delta H_{\rm LOC} = \Delta H_{\rm HF}^{\rm is} + \Delta H_{\rm HF}^{\rm anis} \cos^2\varphi + \Delta H_{\rm DIP}. \qquad (5)$$

We exclude from analysis the satellites a_2 and a_5, which are associated with double substitution in the nearest-neighbor environment of $Fe^{3+}(A)$ ions. The computed ratios of the intensities of such satellites to the intensities of the corresponding single-substitution satellites, the impurity is distributed randomly, are in agreement with the experimental ratios and constitute ~0.16–0.38 for the Al concentrations investigated. We shall analyze the position of the remaining satellites, associated with single substitution, on the basis of the data given in Table IV, where the values of $\cos^2\varphi$ and $\Delta F_{\rm DIP}$ for substitutions in nine nearest $Fe^{3+}(B)$ sites are collected. For A' sites, all Fe–O bonds are equivalent, while there are two values of $\Delta H_{\rm DIP}$. Accordingly, the spectrum of $Fe^{3+}(A)$ sites is observed to contain two close-lying satellites a_6 and a_7, the ratio of whose intensities and whose splitting are in agreement with the expected values. The spec-

TABLE III. Results of statistical analysis of the pressure dependences of ^{57}Fe. NMR frequencies in $Li_{0.5}Fe_{2.5}O_4$ at $T = 4.2$ K ($F_A^{\rm is} = \frac{1}{4}[3F_{A_1} + F_{A_2}]$; $F_B^{\rm is} = \frac{1}{4}[F_{B_1} + F_{B_2} + 2F_{B_3}]$).

	Tetrahedral sites			Octahedral sites			
	A_1	A_2	$A_{\rm is}$	B_1	B_2	B_3	$B_{\rm is}$
F, kHz (P=0)	71 486 (±3)	72 221 (±2)	71 670 (±3)	73 135 (±5)	73 878 (±6)	74 406 (±4)	73 956 (±5)
$\partial F/\partial P$, kHz·kbar^{-1}	−7,1 (±0,13)	−5,9 (±0,08)	−6,80 (±0,12)	−5,9 (±0,12)	−4,5 (±0,12)	−4,3 (±0,12)	−4,75 (±0,12)

TABLE IV. Satellite structure of spectra of $Fe^{3+}(A)$ sites with diamagnetic substitution in the nearest $Fe^{3+}(B)$ sites (substituent ions are Al^{3+} and Ga^{3+}).

Fe^{3+} (A) site	Multiplicity	$\cos^2\varphi$	ΔF_{DIP}, kHz	ΔF_{exp}, kHz		Observed satellite
				Al^{3+}	Ga^{3+}	
$A_1\langle 111\rangle$	2	1,000	−197	−1450	–	a_1
	5	0,111	+28	−430	−420	a_3
	2	0,111	+140	–	–	–
$A_2\langle 111\rangle$	3	1,000	−197	–	–	–
	3	0,111	+28	−410	–	a_4
	3	0,111	+140			–
$A'\langle 100\rangle$	3	0,333	−226	−980	–	a_6
	6	0,333	+113	−660	−680	a_7

trum of $Fe^{3+}(A_1)$ sites can be expected to have only two satellites, since for the observed line widths ~200 kHz the satellite with $\Delta F_{DIP} = 140$ kHz is not resolved. Two such satellites, a_3 and a_1, are observed experimentally. For A_2 sites the pattern of the satellites should be similar to the case of A_1 sites, but, in view of the superposition of the spectra, only one satellite, a_4, is observed. Now the difference between the a_3–A_1 and a_7–A' splittings has a simple explanation, since the different values of $\cos^2\varphi$ (0.11 and 0.33) characterize the corresponding Fe–O bonds.

Only two satellites, a_3 and a_7, associated with diamagnetic substitution in the nearest-neighbor B environment, could be recorded in the spectra of $Fe^{3+}(A)$ ions of Li–Ga ferrites, since the degree of substitution of $Fe^{3+}(B)$ sites by gallium is small ($x_B \approx 0.02$–0.06). Evidently, they correspond to the strongest of the expected satellites. We note that the position of the satellites a_3 and a_7 is close to that of the corresponding satellites in the spectra of Li–Al ferrites.

Thus both the number and amplitude ratio of the satellites of $Fe^{3+}(A)$ sites of diamagnetically substituted lithium ferrites and the position of the satellites can be explained by using the independent-bond model for taking into account the anisotropic change in the HF field together with the anisotropic change in the dipole field. On the other hand, the linear dependence of the change in the HF field on $\cos^2\varphi$, presented in Fig. 5, confirms the applicability of this model for lithium ferrite. With diamagnetic substitution at the B positions of $Li_{0.5}Fe_{2.5}O_4$, a large change is observed in the anisotropic part of the HF field on the nuclei of $Fe^{3+}(A)$ ions with respect to the change in the isotropic part:

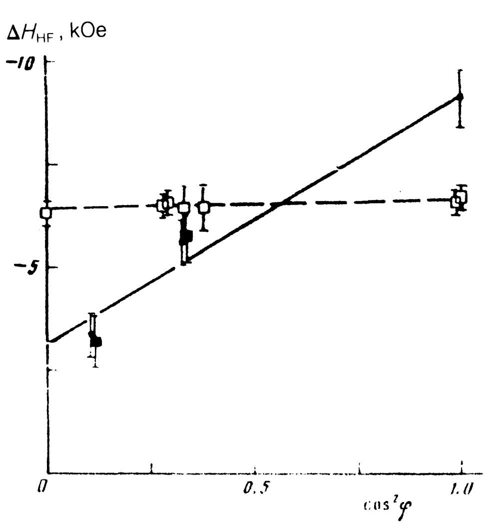


FIG. 5. Change in the hyperfine field accompanying diamagnetic substitution as a function of $\cos^2\varphi$: The circles refer to substitution with Al^{3+} ions, the squares refer to substitution with Ga^{3+} ions; the solid line is the approximation of the change in the HF field at Fe^{3+} (A) sites (dark symbols); and, the dashed line corresponds to the change in the HF field at Fe^{3+} (B) sites.

$$\Delta H^{is}_{HF}(A) = -3.1(5)\text{kOe}, \quad \Delta H^{anis}_{HF}(A) = -6.0(9)\text{ kOe}. \tag{6}$$

4.2. Diamagnetic substitution in $Fe^{3+}(A)\downarrow \rightarrow O^{2-} \rightarrow Fe^{3+}(B)\uparrow$ chains

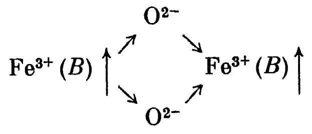
In order to explain the NMR spectra of $Fe^{3+}(B)$ sites in Li–Ga ferrites, we started from the fact that all observed satellites are associated with the substitution of one Fe^{3+} ion by Ga^{3+}, since the probability of double substitutions Ga→Fe at A sites is negligibly small for $x \leqslant 0.16$. According to the data of Table V, which gives the values of $\cos^2\varphi$ and ΔF_{DIP} for substitution of the six nearest $Fe^{3+}(A)$ ions, a similar picture of the spectrum should be expected for the sites $B'(\langle 100\rangle)$ and $B''(\langle 100\rangle)$: each site should have two satellites, whose splitting owing to the HF contribution is equal to $\Delta F_{HF} = -(\gamma/2\pi)\,\Delta H^{anis}_{HF}(B)$ and the splitting owing to the dipole contribution is equal to $\Delta F_{DIP} = 0.338$ MHz. This makes it possible to assign unequivocally the satellites b_6 and b_7 to B' sites and the satellite b_8 to B'' sites. The missing satellite of B'' sites is masked by the wing of the strong B' line. Two possible values of the change in the HF field are obtained formally from the experimental b_7–b_6 splitting $|\Delta F_{exp}| = 0.38$ MHz: $\Delta H^{anis}_{HF}(1) = -0.3(2)$ kOe and $\Delta H^{anis}_{HF}(2) = +5.2(2)$ kOe. The ratio of the intensities of the satellites b_6 and b_7 favors the first variant. Moreover, the satellite structure of the spectra of $Fe^{3+}(B)$ sites of Li–Ga ferrites with easy access $\langle 111\rangle$ (Fig. 6) can be described, using the computed values of the dipole contributions, only in this case. Thus in the case of diamagnetic substitution in the A positions of lithium ferrite the change in the anisotropic part of the HF field at the nuclei of $Fe^{3+}(B)$ ions is very small:

$$\Delta H^{is}_{HF}(B) = -6.3(2)\text{ kOe}, \quad \Delta H^{anis}_{HF}(B) = -0.3(2)\text{ kOe}. \tag{7}$$

TABLE V. Satellite structure of spectra of $Fe^{3+}(B)$ sites with diamagnetic substitution in the nearest $Fe^{3+}(A)$ sites (the substituent ion is Ga^{3+}).

$Fe^{3+}(B)$ site	Multiplicity	$\cos^2\varphi$	ΔF_{DIP}, kHz	ΔF_{exp}, kHz	Observed satellite
$B_1\langle 111\rangle$	6	0,380	+140	−740	b_2
$B_2\langle 111\rangle$	2 4	0,288 0,333	−197 +28	−1100 –	b_3 –
$B_3\langle 111\rangle$	2 4	0,288 0,333	−197 +28	−1090 −850	b_4 b_5
$B'\langle 100\rangle$	2 4	1,000 0,000	−225 +113	−1130 −750	b_6 b_7
$B''\langle 100\rangle$	2 4	1,000 0,000	−225 +113	−1150 –	b_8 –

4.3. Diamagnetic substitution in chains of the form

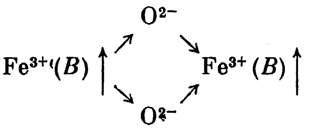


In the spinel structure the $Fe^{3+}(B)$ ion is bound with the nearest $Fe^{3+}(B)$ ion twice by means of different oxygen ions. Since both bonds are identical, in order to take into account the change in the HF field on the basis of the independent-bond model it is sufficient to sum Eq. (3) over the two bonds without increasing the number of parameters. The satellite b_1 in the spectrum of $Fe^{3+}(B)$ sites in Li–Al ferrites with easy access $\langle 111\rangle$ is easy to identify starting from the data in Table VI. It follows immediately from the position of this satellite that

$$\Delta H_{HF}(Al^{3+}\to Fe^{3+}) = 2\Delta H_{HF}^{is} + 0.666\Delta H_{HF}^{anis} = 0.9(2)\ \text{kOe}. \tag{8}$$

We verified the reliability of this value of ΔH_{HF} by decomposing the entire spectrum of the $Fe^{3+}(B)$ sites of Li–Al ferrites (easy access $\langle 111\rangle$) into the principal and satellite lines for different concentrations of the diamagnetic substituent. The decomposition of the spectra was performed using the shape of the resolved line B_1. The number of satellites was determined from the data given in Table VI. The relative position of the satellites and the principal lines was fixed by the computed value of the dipole splitting. However, in view of the fact that $\cos^2\varphi$ has almost the same value for all bonds, the change in the HF field was characterized by the single quantity ΔH_{HF}. As a result, we obtained values of ΔH_{HF} lying in the range 0.8–1.1 kOe, in agreement with the value presented above.

The satellite b_9 in the spectra of the B sites in Li–Ga ferrites could not be explained by taking into account substitution in the chains $Fe^{3+}(A)\downarrow\to O^{2-}\to Fe^{3+}(B)\uparrow$ (Figs. 2 and 6). At the same time, since some of the Ga^{3+} ions occupy B positions, it is natural to identify it with the strongest satellite with substitution in the chains



(Table VI). Then, it follows from the position of the satellite b_9 that

$$\Delta H_{HF}(Ga^{3+}\to Fe^{3+}) = 2\Delta H_{HF}^{is} + 0.621\Delta H_{HF}^{anis} = -0.5(2)\ \text{kOe}. \tag{9}$$

Therefore, with diamagnetic substitution in changes of the type

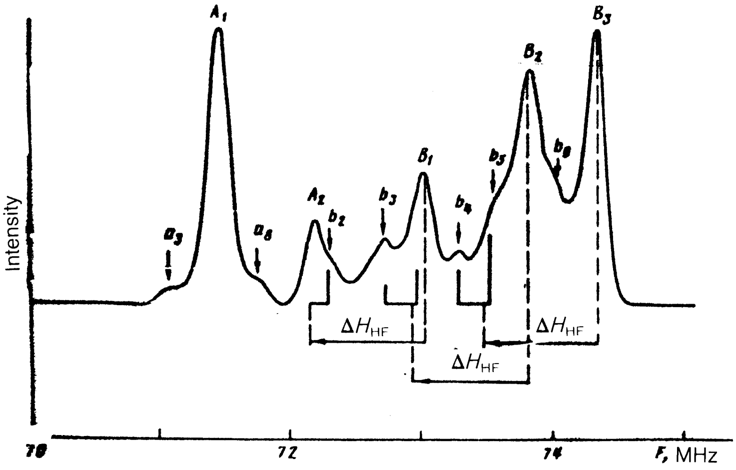
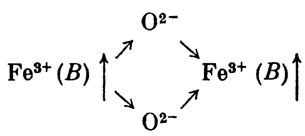


FIG. 6. Comparison of the satellite structure of the spectrum of Fe^{3+} (B) sites of the ferrite $Li_{0.5}Fe_{2.34}Ga_{0.16}O_4$ with the computed positions of the satellites for $\Delta H_{HF} = -6.4$ kOe.

TABLE VI. Satellite structure of spectra of Fe^{3+} (B) sites with diamagnetic substitution in the nearest Fe^{3+} (B) sites.

Fe^{3+} (B) site	Multiplicity	$\cos^2\varphi$	ΔF_{DIP}, kHz	ΔF_{exp}, kHz	Observed satellite
$B_1\langle 111\rangle$	4	0,380 0,380	+248	–	–
$B_2\langle 111\rangle$	2	0,288 0,333	–248	–	–
	2	0,333 0,333	+248	–	–
$B_3\langle 111\rangle$	3	0,288 0,333	–248	–320	b_9
	1	0,333 0,333	+248	+370	b_1
$B'\langle 100\rangle$	1	0,000 0,000	–248	–	–
	3	0,000 1,000	+124	–	–
$B''\langle 100\rangle$	2	0,000 0,000	–248	–	–
	2	0,000 1,000	+124	–	–



the changes in the HF field depend strongly on the substituent ion. This difference will be explained below.

4.4. Effect of diamagnetic substitution in the *A* sites on the NMR spectra of Fe^{3+}(*A*) ions

In lithium ferrite there is no *A*–O–*A* bond between *A* sites via an oxygen ion. For this reason, in the case of substitution of $Fe^{3+}(A)$ ions, the change in the HF field at $Fe^{3+}(A)$ sites should be very small. Indeed, the satellite a_8 (Fig. 2) with close-to-dipole splitting (Table VII) is observed in the spectrum of *A* sites in Li–Ga ferrites. It follows from the position of this satellite that $\Delta H_{HF} = -0.12(15)$ kOe.

4.5. Effect of diamagnetic substitution in distant spheres

In the case of diamagnetic substitution, the NMR frequencies of the principal and satellite lines are observed to decrease. This decrease cannot be explained solely by the decrease produced in the HF field by the change in the lattice parameter (Fig. 3). By analyzing the difference in the experimental concentration dependences $\Delta H_{HF}(A)$ and $\Delta H_{HF}(B)$ (solid lines in Fig. 3) and the dependences determined only by radial effects (dashed lines in Fig. 3), it is possible to observe a correlation between these differences and the degree of substitution in the same sublattice. It was found that the values of $\Delta H_{HF}(A)$ ($\Delta H_{HF}(B)$) corrected for the change in the lattice parameter fall as a function of x_A ($x_B/1.5$) on the same straight line for both Li–Ga and Li–Al ferrites (see insets in Fig. 3). The slopes of the concentration dependences of the HF fields on the iron nuclei at *A* and *B* sites are as follows:

$$\Delta H_{HF}(A\to\ldots\to A)=-1{,}2x_A \text{ kOe},$$
$$\Delta H_{HF}(B\to\ldots\to B)=-7{,}4(x_B/1{,}5) \text{ kOe}. \qquad (10)$$

5. DISCUSSION

5.1. Indirect hyperfine fields in lithium ferrite

Numerous NMR and Mössbauer investigations of diamagnetically substituted ferrites have shown that $|H_{LOC}|$ decreases at ^{57}Fe nuclei in *A* and *B* sites. In interpreting the results, the change in the dipole field was neglected because this field is weak. Neglecting also the local distortions accompanying the substitution $M^{3+}\to Fe^{3+}$, which depend on the difference of the ionic radii of the diamagnetic ion M^{3+} and the ion Fe^{3+} and result in a change in H_{COV}, the changes in the HF field were associated to the "switching off" of spin-

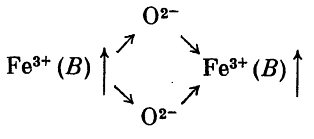
TABLE VII. Satellite structure of spectra of Fe^{3+} (A) sites with diamagnetic substitution in the nearest Fe^{3+} (A) sites.

Fe^{3+} (A) site	Multiplicity	ΔF_{DIP}, kHz	ΔF_{exp}, kHz	Observed satellite
$A_1\langle 111\rangle$	3	–91	–	–
	1	+271	+255	a_8
$A_2\langle 111\rangle$	3	–91	–	–
	1	+271	–	–
$A'\langle 100\rangle$	4	0	–	–

density transfer in the chains $\mathrm{Fe}^{3+}(B)\uparrow\text{–}\mathrm{O}^{2-}\text{–}\mathrm{Fe}^{3+}(A)\downarrow$. This approach made it possible to estimate the magnitude of the IHF field $H_{\mathrm{IHF}}(B)$, induced from $\mathrm{Fe}^{3+}(A)$ ions, at the nuclei of $\mathrm{Fe}^{3+}(B)$ ions and vice versa. In this work we also found that the change produced in the HF field at ^{57}Fe nuclei in $\mathrm{Fe}^{3+}(A)$ sites by substitutions in the B sites $\mathrm{Al}^{3+}\to\mathrm{Fe}^{3+}(\Delta R=-0.110$ Å) and $\mathrm{Ga}^{3+}\to\mathrm{Fe}^{3+}(\Delta R=-0.025$ Å) are virtually identical. It follows from the results (6) and (7) of our analysis that the IHF fields per $\mathrm{Fe}^{3+}(B)\uparrow\text{–}\mathrm{O}^{2-}\text{–}\mathrm{Fe}^{3+}(A)\downarrow$ bond (on the average) for lithium ferrite are[2)]

$$\tilde{H}_{\mathrm{IHF}}(B)=6{,}4(2)\ \mathrm{kOe},\quad \tilde{H}_{\mathrm{IHF}}(A)=5{,}1(6)\ \mathrm{kOe}. \tag{11}$$

At the same time, it was found that in the case of substitution in chains of the type



the change in the HF field depends significantly on the difference of the ionic radii [see Eqs. (8) and (9)]. This result can be easily explained, since in the spinel structure the distance between neighboring $\mathrm{Fe}^{3}(B)$ ions $r_{B-B}=2.95$ Å is significantly shorter than the distance $r_{A-B}=3.41$ Å between the neighboring A and B ions, and the contribution of the local deformation to the change in H_{COV} and the Fe–O–Fe bond angles on substitution can be significant. Extrapolating the dependence $\Delta H_{\mathrm{HF}}(\Delta R)$ to zero difference of the ionic radii of the diamagnetic ion and the iron ion, we can estimate the average IHF field induced at the $\mathrm{Fe}^{3+}(B)$ sites by the nearest $\mathrm{Fe}^{3+}(B)$ ion:

$$\tilde{H}_{\mathrm{IHF}}(B\to B)\approx 0{,}9(2)\ \mathrm{kOe}. \tag{12}$$

For lithium ferrite, which is primarily an ionic compound with a high degree of localization of the electron density, for the more distant environments the changes produced in the HF field by the diamagnetic dilution can be expected to decay rapidly. The results of the present work show that the total change ΔH_{HF}, caused by substitution in the nearest cationic environments, is an order of magnitude higher than ΔH_{HF} due to substitution in the next-to-nearest environments. On the other hand, one can see from our data that in the case of substitutions in the distant spheres ($r_{\mathrm{Fe-Fe}}\geqslant 3.61$ Å) the local distortions can be neglected. For this reason, the change brought about in the HF field by substitution in distant spheres can be interpreted only as a "switching off" of spin-density transfer from Fe^{3+} ions, and we can confine our attention to chains of the form Fe–O–Fe–O–Fe (or Fe–O–Li–O–Fe). Then, for $\mathrm{Fe}^{3+}(A)$ sites one should expect, first of all, changes in the HF field on substitution in the chains $\mathrm{Fe}^{3+}(A)\downarrow\to\mathrm{O}^{2-}\to\mathrm{Fe}^{3+}(B)\uparrow\to\mathrm{O}^{2-}\to\mathrm{Fe}^{3+}(A)\downarrow$ [or $\mathrm{Fe}^{3+}(A)\downarrow\to\mathrm{O}^{2-}\to\mathrm{Li}^{+}(B)\to\mathrm{O}^{2-}\to\mathrm{Fe}^{3+}(A)\downarrow$] and for $\mathrm{Fe}^{3+}(B)$ sites with substitution in the chains $\mathrm{Fe}^{3+}(B)\uparrow\to\mathrm{O}^{2-}\to\mathrm{Fe}^{3+}(A)\downarrow\to\mathrm{O}^{2-}\to\mathrm{Fe}^{3+}(B)\uparrow$, containing 123-degree A–O–B bonds, which, in turn, are responsible for the strongest spin-density transfer in lithium ferrite. This interpretation agrees very well with the dependence, which we observed, of the change in the HF field at ^{57}Fe-nuclei in A and B sites on the degree of substitution of the A and B sublattices, respectively. In lithium ferrite the iron ions could be bound by a different number of chains of the form Fe–O–Fe–O–Fe or Fe–O–Li–O–Fe (from one to six). Taking into account the total number of corresponding chains with substitution of A and B sublattices, the average IHF field per chain of this type can be estimated from the slopes of the concentration dependences of the HF fields (10):

$$\begin{aligned} &H_{\mathrm{IHF}}(B\to\mathrm{O}\to A\to\mathrm{O}\to B)=0{,}2\ \mathrm{kOe},\\ &H_{\mathrm{IHF}}(A\to\mathrm{O}\to B\to\mathrm{O}\to A)=0{,}02\ \mathrm{kOe}. \end{aligned} \tag{13}$$

Diamagnetic substitution of iron ions at the A sites results, as we have already mentioned, in the appearance of a resolved satellite a_8 (Fig. 2) in the NMR spectrum of Li–Ga ferrites. From the position of this satellite we can determine directly, though with low accuracy, $\tilde{H}_{\mathrm{IHF}}(A\to O\to B\to\mathrm{O}\to A)=0.12(15)$ kOe. This result agrees with the value of the IHF field per chain $A\to\mathrm{O}\to B\to\mathrm{O}\to A$ obtained above, since in the spinel structure the nearest $\mathrm{Fe}^{3+}(A)$ ions ($r_{A-A}=3.61$ Å) are bound by six such chains.

Now, using the contributions to the IHF field (11)–(13) and the number of corresponding bonds found above, the total IHF fields at the nuceli of A and B iron ions can be calculated, after which, using the experimental values of the total HF fields (4), the values of H_{COV} can be determined. These values are presented in Table VIII.

We now compare the values obtained in the present work for H_{IHF} in $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$ with the Mössbauer data. In Refs. 4 and 7–9 the IHF fields per $\mathrm{Fe}^{3+}(B)\uparrow\text{–}\mathrm{O}^{2-}\text{–}\mathrm{Fe}^{3+}(A)\downarrow$ bond were determined by substituting diamagnetic ions Sb^{5+}, Ga^{3+}, Al^{3+}, and Zn^{2+}. These values are characterized by a significant spread and, as a rule, they are higher than our data: $\tilde{H}_{\mathrm{IHF}}(A)=4\text{–}10$ kOe and $\tilde{H}_{\mathrm{IHF}}(B)=8\text{–}17$ kOe. We believe that the disagreements are associated with the simplified interpretation of the Möss-

TABLE VIII. Isotropic HF fields (kOe) at ^{57}Fe nuclei in A and B sites in $\mathrm{Li}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4$ ($H_0=-630$ kOe).

Type of field	$\mathrm{Fe}^{3+}(A)$ sites	$\mathrm{Fe}^{3+}(B)$ sites
$H_{\mathrm{IHF}}\ (A\to B)$	–	−38,4
$H_{\mathrm{IHF}}\ (B\to A)$	−45,9	–
$H_{\mathrm{IHF}}\ (B\to B)$	–	−3,6
$H_{\mathrm{IHF}}\ (A\to B\to A)$	−1,2	–
$H_{\mathrm{IHF}}\ (B\to A\to B)$	–	−7,4
$H_{\mathrm{IHF}}^{\mathrm{total}}$	−47,1	−49,4
H_{cov}	+156,8	+139,8

bauer spectra, when the total effect of the decrease in the HF field is attributed to the fields $H_{\rm IHF}(A)$ and $H_{\rm IHF}(B)$, while the change in the lattice parameter accompanying substitution and contributions from more distant environments to $H_{\rm IHF}$ have a definite effect on this decrease.

5.2. Correlation between exchange and indirect hyperfine interactions

The mechanisms of formation of the IHF field and indirect exchange have much in common, since both effects depend on spin-density transfer from one metallic ion to another via a ligand. If, however, the indirect exchange interaction can be interpreted as spin transfer from a $3d$-orbital of one iron ion to the $3d$-orbital of another, taking into account the energy of such a transfer, then in interpreting the IHF field, in addition to the indirect contribution owing to spin transfer into the $3d$-shell, the contribution made by the additional polarization of the s-shells of the central ion to the generation of the spin density at the nucleus must also be taken into account. For this reason, only a qualitative agreement is observed between the ratios of $H_{\rm IHF}$ and exchange integrals for different bonds.[2,19] In lithium ferrite, three exchange constants, J_{AB}, J_{BB}, and J_{AA} are usually considered. These constants characterize the short-range exchange of the nearest-neighbor iron ions and are determined, as a rule, by analyzing the experimental data on the spontaneous magnetization or the paramagnetic susceptibility on the basis of the molecular-field theory. In most such analyses, however, B–B exchange is found to be weaker than the A–A interaction,[20] and this does not agree with the bond geometry in the spinel structure. In Ref. 21 it is shown that for ferrimagnets the molecular-field theory gives values for the intrasublattice exchanges which are too high, especially for the A sublattice. The relative importance of different interactions in the spinel structure can be assessed from the hierarchy, determined in the present work, of IHF fields (see Table VIII):

$$J_{AB} > J_{BB} > J_{AA},$$

which agrees qualitatively with measurements of exchange integrals for $\rm Li_{0.5}Fe_{2.5}O_4$ by the method of inelastic neutron scattering.[22] There is one interesting circumstance: At the octahedral sites the IHF field from the nearest B ions and the next-nearest B iron ions are completely comparable in magnitude. Apparently, when the intrasublattice B–B exchange is taken into account, both indirect exchange between the nearest $\rm Fe^{3+}$ (B) ions through the oxygen ion as well as the exchange interaction in longer chains of the form $\rm Fe^{3+}(\mathit{B})\uparrow\rightarrow O^{2-}\rightarrow Fe^{3+}(\mathit{A})\downarrow\rightarrow O^{2-}\rightarrow Fe^{3+}(\mathit{B})$, must be considered.

5.3. Anisotropy of the HF field at ^{57}Fe nuclei in lithium ferrite

Thus far we have employed the method of independent bonds to describe the changes brought about in the HF field by diamagnetic substitution. If, however, Eq. (3) is summed over all bonds of a given ion, then the total HF field at ^{57}Fe nuclei in unsubstituted $\rm Li_{0.5}Fe_{2.5}O_4$ can be described. In so doing, we determine the number of covalent contributions from the number of nearest $\rm O^{2-}$ ions, and the number of contributions to $H_{\rm IHF}$ depends on the number of bonds of the type Fe–O–Fe. For $\rm Fe^{3+}(\mathit{A})$ sites we have

$$\begin{aligned} H_{\rm HF}(A) = {} & 4H^{\rm is}_{\rm COV} + H^{\rm anis}_{\rm COV} \sum_{i=1}^{4} \cos^2\varphi_i + 9H^{\rm is}_{\rm IHF}(B\rightarrow A) \\ & + H^{\rm anis}_{\rm IHF}(B\rightarrow A) \sum_{j=1}^{9} \cos^2\varphi_j . \end{aligned}$$

If the positions of the ions for the space group $Fd3m$ are taken into account, there should be no anisotropy of $H_{\rm COV}$ for A sites, since $\Sigma_{i=1}^{4} \cos^2\varphi_i = \text{const} = 1.333$, irrespective of the direction of magnetization (Table IV). For the splitting of the NMR frequencies in the case $\mathbf{M}\|\langle 111\rangle$, we can write

$$F(A_2)-F(A_1)=(\gamma/2\pi)\left[\Delta H_{\rm DIP} + 0.889 H^{\rm anis}_{\rm IHF}(B\rightarrow A)\right]. \qquad (14)$$

Since the computed value of the dipole splitting $\Delta H_{\rm DIP} = 0.486$ kOe, determined in Ref. 13 by summing over the lattice, the anisotropy of the IHF field at $\rm Fe^{3+}$ (A) sites can be determined directly from Eq. (14):

$$H^{\rm anis}_{\rm IHF}(A) = 5.47 \text{ kOe}.$$

The good agreement between this result and the value (6), obtained from the position of the satellite of diamagnetically diluted lithium ferrite, confirms the correctness of the foregoing analysis of the satellite structure of the NMR spectra. On the other hand, this result may mean that there is no appreciable contribution of $H_{\rm COV}$ in the splitting of the lines of the A sites, since this contribution is not anisotropic. The point is that the isotropic character of $H_{\rm COV}$ is associated with the absence of distortions of the tetrahedral complex in the spinel structure. Although lithium ferrite, strictly speaking, has the space group $P4_332$, in which the positions of the ions are the same as in spinel, but with some displacements relative to the positions in the spinel structure, the distortions arising in this case are nonetheless so small that they obviously do not make an appreciable contribution to the anisotropy of the HF field at ^{57}Fe nuclei. We note that because of the smallness of the distortions of the oxygen tetrahedron the IHF field induced from $\rm Fe^{3+}$ (A) ions at $\rm Fe^{3+}$ (B) ions is practically isotropic (Fig. 5).

Taking into account the contributions, obtained above, of different interactions to the IHF field, we can write for the HF field at $\rm Fe^{3+}$ (B) sites

$$\begin{aligned} H_{\rm HF}(B) = {} & 6\left[H^{\rm is}_{\rm COV} + H^{\rm is}_{\rm IHF}(A\rightarrow B) + H^{\rm is}_{\rm IHF}(B\rightarrow A\rightarrow B)\right] \\ & + \left[H^{\rm anis}_{\rm COV} + H^{\rm anis}_{\rm IHF}(B\rightarrow A\rightarrow B)\right] \\ & \times \sum_{i=1}^{6} \cos^2\varphi_i + 8H^{\rm is}_{\rm IHF}(B\rightarrow B) \\ & + H^{\rm anis}_{\rm IHF}(B\rightarrow B) \sum_{j=1}^{8} \cos^2\varphi_j . \end{aligned} \qquad (15)$$

The anisotropic HF field at ^{57}Fe nuclei in the B sites can be divided into axial and orthorhombic contributions. This is expressed in Eq. (15) by the presence of two types of angular dependences. The anisotropic part of $H_{\rm COV}$ has axial symmetry owing to the trigonal distortions of the oxygen octahedron in the spinel structure with $u \neq 3/8$ with $\langle 111\rangle$ symmetry axes. The field $H^{\rm anis}_{\rm IHF}(B\rightarrow A\rightarrow B)$ is also axisymmetric, since it reflects the trigonal symmetry of the cationic distortions of the B sites. Correspondingly, both contributions have the same angular dependence. The lowering of the local symmetry at the B sites of lithium ferrite to orthorhombic symmetry is associated with the presence of Li in the nearest-neighbor B environment. Accordingly, the contribution of $H^{\rm anis}_{\rm IHF}(B\rightarrow B)$

has orthorhombic symmetry. When the magnetization vector is directed along the $\langle 100\rangle$ axis, the axial component of $H^{\text{anis}}_{\text{HF}}$ vanishes and from the splitting of the NMR frequencies $F(B'') - F(B') = (\gamma/2\pi)[\Delta H_{\text{DIP}} - H^{\text{anis}}_{\text{IHF}}(B\to B)]$, where $\Delta H_{\text{DIP}} = 2.82$ kOe (Ref. 13), and using Eq. (12) we obtain

$$H^{\text{anis}}_{\text{IHF}}(B\to B) = -2.07\ \text{kOe},$$
$$H^{\text{is}}_{\text{IHF}}(B\to B) = 1.14\ \text{kOe}. \qquad (16)$$

For the easy access $\langle 111\rangle$ the axial component of the anisotropic part of the HF field is maximum and can be determined from the splitting

$$F(B_2) - F(B_1) = (\gamma/2\pi)\{\Delta H_{\text{DIP}} - 0.466 H^{\text{anis}}_{\text{IHF}}(B\to B) - 0.37[H^{\text{anis}}_{\text{COV}} + H^{\text{anis}}_{\text{IHF}}(B\to A\to B)]\},$$

using $\Delta H_{\text{DIP}} = 11.55$ kOe (Ref. 13), Eq. (16)[3] and

$$H^{\text{anis}}_{\text{COV}} + H^{\text{anis}}_{\text{IHF}}(B\to A\to B) = 19.2\ \text{kOe}. \qquad (17)$$

Since $H_{\text{COV}} \gg H_{\text{IHF}}(B\to A\to B)$, the obtained value (17) reflects the high anisotropy of the covalent field at *B* sites.

Thus we have shown that the anisotropy of the HF field differs at *A* and *B* sites of lithium ferrite. For *A* sites it is due to the anisotropy of the indirect (transferred) hyperfine field, while for *B* sites the anisotropy of the characteristics HF field of the Fe^{3+} ion predominates.

5.4. Pressure dependence of the local fields at nuclei

We employed the pressure dependence of the NMR frequencies of $Li_{0.5}Fe_{2.5}O_4$ previously in order to separate empirically the contribution of the radial effects to the concentration dependence of the HF fields of diamagnetically diluted lithium ferrite. We now discuss the effect of hydrostatic pressure on the HFI in $Li_{0.5}Fe_{2.5}O_4$. When the crystal is compressed, both contributions H_{COV} and H_{IHF} to the HF field at the iron nucleus increase because the distances $r_{\text{Fe–O}}$ decrease. Due to the difference in the signs, increases in H_{COV} and H_{IHF} result in a decrease and increase, respectively, of the NMR frequencies. Thus the behavior of the NMR frequencies under conditions of hydrostatic compression is determined by the competition between the radial dependences of these contributions. We shall analyze the behavior of the NMR frequencies at the *B* sites of $Li_{0.5}Fe_{2.5}O_4$ under pressure in comparison with the rare-earth orthoferrites $RFeO_3$, where the Fe^{3+} ions have only octahedral coordination. In Ref. 23 the pressure coefficient of the ^{57}Fe NMR frequency was found to vary strongly in the series of rare-earth orthoferrites due to the variation in H_{IHF}, with H_{COV} staying approximately constant. In the series of orthoferrites the distance $r_{\text{Fe–O}}$ remains practically constant, but the Fe–O–Fe bond angle θ, on which H_{IHF} depends as (with other parameters being fixed)

$$H_{\text{IHF}} = [H_{\text{IHF}}(180^\circ) - H_{\text{IHF}}(90^\circ)]\cos^2\theta + H_{\text{IHF}}(90^\circ)$$
$$\propto (A^2_\sigma - A^2_\pi)\cos^2\theta + A^2_\pi, \qquad (18)$$

where A_σ and A_π are the covalent parameters for σ and π Fe–O bonds, including the corresponding overlap integrals and the transfer parameters,[19] varies significantly. The experimental dependence of the pressure coefficients of the HF fields for $RFeO_3$ (Ref. 23) is described well by the theoretical straight line

$$\partial H_{\text{HF}}/\partial r_{\text{Fe–O}} = (255\cos^2\theta - 155)\ \text{kOe/Å} \qquad (19)$$

in the approximation

$$\partial H_{\text{IHF}}/\partial r_{\text{Fe–O}} \propto (\partial A_\sigma/\partial r) H_{\text{IHF}}, \qquad (20)$$

which follows from Eq. (18), if the bond angle θ and the quantity A^2_π/A^2_σ are insensitive to the pressure. The straight line (19) was obtained using the results of the radial dependences of the HF fields for an undistorted octahedral Fe^{3+} site with $r_{\text{Fe–O}} = 2.01$ Å and taking into account the IHF fields in six Fe^{3+} (octa)↑→O^{2-}→Fe^{3+} (octa)↓ chains.[24]

Comparing our pressure coefficient of the HF field $\partial|H_{nB}|/\partial P = -3.38(9)\cdot 10^{-2}$ kOe·kbar^{-1} for *B* sites of lithium ferrite, characterized by the $Fe^{3+}(B)$↑→O^{2-}→$Fe^{3+}(A)$↓ bond angle $\theta = 122.7°$, with the variation of the pressure coefficients in the series of orthoferrites, we find that it not only agrees in sign with the negative pressure coefficients observed for $RFeO_3$ for $\theta < \theta_{\text{cr}} \approx 140°$, but it satisfies quite well the dependence (19), from which for $\theta = 122.7°$ we have $(\partial|H_{\text{HF}}|/\partial P)_{\text{calc}} = -3.26\cdot 10^{-2}$ kOe·kbar^{-1}, taking into account the compressibility of lithium ferrite $\chi = 5.78\cdot 10^{-4}$ kbar^{-1}. In $Li_{0.5}Fe_{2.5}O_4$ the oxygen octahedra undergo relatively small distortions (the deviations of the O–Fe–O angle from 90° are ~4° for lithium ferrite and ~1–2° for orthoferrites), while the distance $r_{\text{Fe–O}} = 2.02$ Å is virtually identical to the distances in the series $RFeO_3$ ($r_{\text{Fe–O}} = 2.006$–2.014 Å). As a result, the covalent fields in both structures are close: $H_{\text{COV}}(B) = 139.8$ kOe for $Li_{0.5}Fe_{2.5}O_4$ (Table VIII) and $H_{\text{COV}} = 158$ kOe for $RFeO_3$.[19] For this reason, the correlation of the pressure coefficient of the HF field at *B* sites of lithium ferrite with the data for the series of orthoferrites, taking into account Eq. (20), reflects the fact that, in spite of the difference in the formation mechanisms, the magnitude of the IHF field of $Li_{0.5}Fe_{2.5}O_4$ $H_{\text{IHF}}(B) = 49.4$ kOe is described by the angular dependence of H_{IHF} for the orthoferrite series[19] $H_{\text{IHF}}(\theta) = [(104-19.6)\cos^2\theta + 19.6]$ kOe at $\theta = 122.7°$. We note in this connection that the computed values of the parameter A^2_σ for spinel ($r_{\text{Fe–O}} = 2.03$ Å) and orthoferrites $A^2_\sigma = 0.125$ and 0.147, respectively, are close.[25]

The pressure coefficient of the isotropic part of the HF field at *A* sites in lithium ferrite was found to be approximately 1.5 times larger than at *B* sites. The small difference between H_{COV} and H_{IHF} for *A* and *B* sites (Table VIII) cannot be the main reason for this behavior. More important, in our opinion, is the fact that at tetrahedral Fe^{3+} sites the distance $r_{\text{Fe–O}} = 1.92$ Å is significantly shorter than at *B* sites. For this reason, it is not so much the difference of H_{COV} and H_{IHC} at *A* and *B* sites of iron that must be taken into account, as the difference in the slopes of their radial dependences. Unfortunately, at the present time it is impossible to make a quantitative comparison, since no calculations of the radial dependences of the HF fields at the tetrahedral Fe^{3+} sites have been performed. We merely note that higher pressure coefficients at tetrahedral sites than at octahedral sites were also found in iron garnets.[17]

A detailed analysis, the details of which are not presented here, also has shown that the difference in the pressure coefficients of the NMR frequencies of separate lines in the spectra of *A* and *B* sites in lithium ferrite (Table III) reflects the anisotropy of the HF field at these sites.

6. CONCLUSIONS

Thus, thanks to the uniqueness of ordered lithium ferrite among iron spinels, which consists of complete ordering of the crystalline and magnetic structure, as well as the choice of optimal degrees of diamagnetic substitution, in this work we were able to record ^{57}Fe NMR spectra with rich satellite structure. Analysis of these spectra combined with the data from pressure investigations made it possible to study an entire series of previously not studied subtle effects due to HFIs. The data obtained on the delocalization of the spin density can be used to make more accurate interpretations of NMR and Mössbauer spectra in magnetodielectrics—iron spinels—when studying, for example, magnetic phase transitions, cation distribution, local distortions of the crystalline structure, etc.

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1) The negative sign of H_0 reflects the fact that the internal magnetic field at the nucleus is oriented antiparallel to the magnetic moment of the Fe^{3+} ion. In what follows, for convenience we assume formally that it is positive, unless otherwise stipulated.

2) If on substitution the HF field changes as a result of $H_{\rm IHF}$, then the magnitude of the indirect hyperfine field per substituent ion in lithium ferrite is simply related to the parameters of the independent-bond model: $\tilde{H}_{\rm IHF} = -(\Delta H^{\rm is}_{\rm HF} + 0.333 H^{\rm anis}_{\rm HF})$.

3) The splitting $F(B_3) - F(B_2)/(\gamma/2\pi) = 3.88$ kOe is determined virtually completely by the dipole contribution of 3.66 kOe.[13]

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