Magnetically inequivalent positions of tin ions in ordered lithium ferrite and anisotropy fields at ^{119}Sn nuclei

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(Submitted 24 March 1986)
Zh. Eksp. Teor. Fiz. **91**, 1744–1754 (November 1986)

The Mössbauer spectroscopy method was used to investigate hyperfine magnetic fields at the ^{57}Fe and ^{119}Sn nuclei in ordered tin-doped lithium ferrite at temperatures 80–950 K. Several magnetically inequivalent positions of diamagnetic tin ions in the octahedral sublattice were observed experimentally. This inequivalence was attributed to an anisotropy of the hyperfine magnetic interaction. Dipole magnetic fields at the tin positions were calculated. The isotropic and anisotropic contributions to the magnetic field at the tin nuclei were separated and estimates were obtained of the contribution made to the anisotropy by the dipole fields and by the fields of the indirect hyperfine interaction. It was established that the anisotropy of the indirect hyperfine interaction of the Sn^{4+} ions was mainly due to orthorhombic distortions of the crystal lattice of lithium ions.

I. INTRODUCTION

Lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ has a completely inverted cubic structure of the spinel $Fe^{3+}[Li^{+}_{0.5}Fe^{3+}_{1.5}]O_4$. The magnetic moment per formula unit is close to the theoretical value 2.5 μ_B, corresponding to a collinear magnetic structure.[1] The Néel temperature of stoichometric lithium ferrite is 913 ± 5 K (Ref. 2).

The distribution of cations in the octahedral B sublattice of lithium ferrite may be disordered or ordered, depending on the heat treatment. In ordered lithium ferrrite (space group $P4_332$) the distributions of the Li^+ and Fe^{3+} ions at the B sites alternate in the ratio 1:3 between crystallographic directions of the ⟨110⟩ type. Lithium ions are located at trigonally distorted octahedra (4b positions) and are surrounded by six B iron ions (Fig. 1, positions I). The environment of lithium ions is symmetric relative to axes of the ⟨111⟩ type. Each iron ion is located at a 12d position and its immediate octahedral environment includes two lithium ions for four iron ions (Fig. 1, positions II). For any direction of the ⟨111⟩ type there are three variants of such an environment, which transform from one to the other by rotation through 120° about the ⟨111⟩ axis. In other words, the environment of the B iron ions is symmetric relative to two-fold axes of the ⟨100⟩ type, which are perpendicular to the ⟨111⟩ axes.

One can expect the ordered distribution of lithium ions to give rise to three magnetically inequivalent positions of iron ions along the ⟨111⟩ direction of easy magnetization of the B sublattice. Such inequivalent positions have indeed been observed by the NMR method in zero external magnetic fields.[3] Dorman *et al.*[4] also obtained three values of magnetic hyperfine fields at the nuclei of the iron atoms at the B sites of lithium ferrite by numerical analysis of the Mössbauer spectra of the ^{57}Fe nuclei. However, it has not been possible to resolve directly the lines in the spectra representing the different positions of the B iron ions.

We shall report an investigation of the magnetically inequivalent positions in the structure of ordered lithium ferrite by Mössbauer spectroscopy of a diamagnetic nulcear probe in the form of tin impurity atoms. New data were obtained on the anisotropy of the hyperfine magnetic fields due to structural and magnetic inequivalence.

2. EXPERIMENTAL METHODS AND RESULTS

Polycrystalline tin-doped lithium ferrite $Li_{0.5}Fe_{2.5}O_4$:^{119}Sn(~0.01 at % Sn) was synthesized by ceramic technology using the method of coprecipitation of hydroxides. The single-phase nature and the cubic ordered structure of the lithium spinel with the unit cell parameter $a_0 = 8.331 \pm 0.003$ Å were determined by x-ray diffraction. The Mössbauer effect was investigated for the ^{57}Fe and ^{119}Sn nuclei in the temperature range 80–950 K. The sources of gamma radiation were ^{57}Co in a chromium matrix and ^{119m}Sn in $BaSnO_3$.

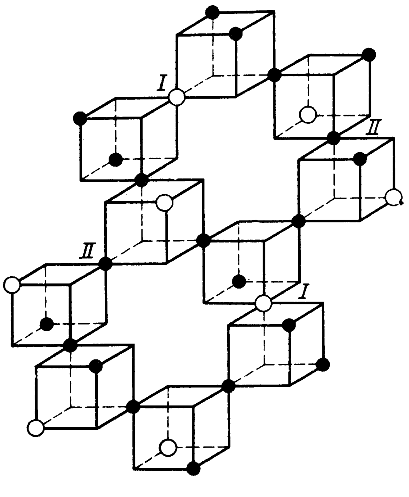


FIG. 1. Distribution of the Fe^{3+} and Li^+ cations at the B sites of ordered lithium ferrite $Li_{0.5}Fe_{2.5}O_4$. The black dots are the atoms of iron and the white ones are the atoms of lithium. Two different positions of the tin ions are: I) Sn^{4+} replacing Li^+; II) Sn^{4+} replacing Fe^{3+}.

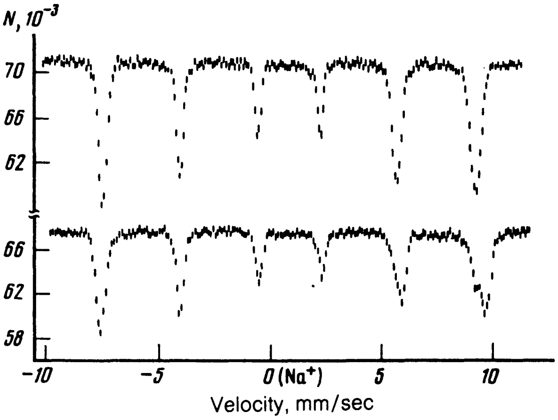


FIG. 2. Mössbauer spectra of the ^{57}Fe nuclei in ordered tin-doped lithium ferrite $Li_{0.5}Fe_{2.5}O_4$:^{119}Sn at temperatures 295 K (upper curve) and 173 K (lower curve).

2.1. Spectra of ^{57}Fe nuclei

Figure 2 shows the Mössbauer spectra of the ^{57}Fe nuclei. At room temperature the AB sublattices were practically unresolvable. The splitting of the lines became significant at lower temperatures. A computer analysis of the spectra into two six-line components yielded the following values of the hyperfine magnetic fields at the ^{57}Fe nuclei: $H_A = 492 \pm 3$ kOe and $H_B = 503 \pm 3$ kOe at 300 K; $H_A = 502 \pm 3$ kOe and $H_B = 518 \pm 3$ kOe at 173 K. Measurements in the range 80–950 K were used to plot the temperature dependences $H_A(T)$ and $H_B(T)$ and these were used to find the Néel point of tin-doped lithium ferrite, which was $T_N = 908 \pm 3$ K. The dependences shown in Fig. 3 agreed with the neutron-diffraction data of Ref. 5 for pure lithium ferrite. The cation distribution deduced by the method of Mössbauer line shift in an external magnetic field[6] confirmed the fully inverted nature of the ferrite.

2.2. Spectra of ^{119}Sn nuclei

The spectra of the ^{119}Sn nuclei (Fig. 4) exhibited a magnetic hyperfine splitting of the lines with a complex distribution of the absolute values of the magnetic fields H^{Sn} at the tin nuclei. This was an indication of the existence of several inequivalent positions of the Sn^{4+} ions.

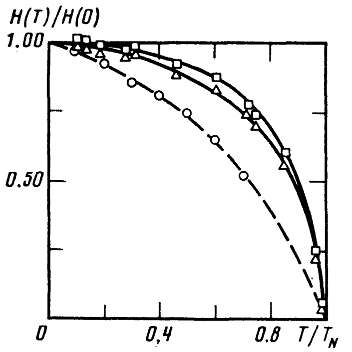


FIG. 3. Hyperfine magnetic fields vs scaled temperature at the ^{57}Fe and ^{119}Sn nuclei in lithium ferrite $Li_{0.5}Fe_{2.5}O_4$:^{119}Sn:□) fields at the nuclei of the Fe^{3+} ions occupying the A sites: △) fields at the nuclei of the Fe^{3+} ions occupying the B sites; ○) average values of the fields at the nuclei of the Sn^{4+} ions at the type II positions. The continuous curves are the neutron-diffraction data on the temperature dependences of the magnetizations of the A and B subslattices.[5]

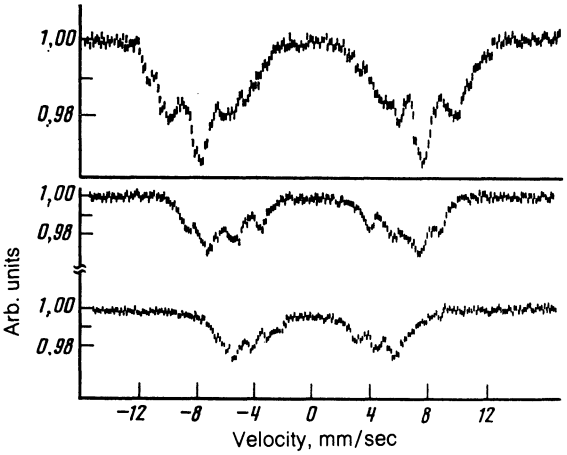


FIG. 4. Mössbauer spectra of the ^{119}Sn nuclei in ordered lithium ferrite at different temperatures: 78, 388, and 641 K (from top to bottom).

An analysis of the symmetry of the spectrum with respect to the center of gravity was made by calculating the third component

$$F_3=\sum_{k=1}^{N} J(k)\,(k-\delta)^3,$$

where $J(k)$ is the difference between the background and the number of pulses in a channel; k is the channel number; δ is the isomeric shift in the channels. It was found that at all temperatures $F_3 \approx 0$ and, consequently, there was no quadrupole splitting.

The distribution functions of the H^{Sn} fields were found using the method of statistical regularization.[7] An analysis was made, assuming that the isomeric shifts at all the positions of the Sn^{4+} ions were equal.

The distribution functions $P(H^{Sn})$ obtained at different temperatures are plotted in Fig. 5. In the range 80–150 K the

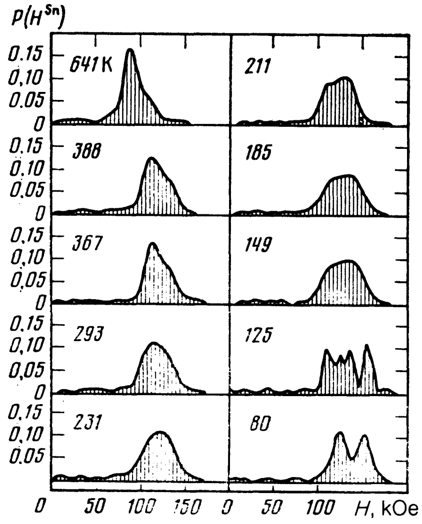


FIG. 5. Distribution functions of the hyperfine magnetic fields at the tin nuclei $P(H^{Sn})$ at different temperatures.

distribution $P(H^{\mathrm{Sn}})$ showed splitting into several groups of lines; for $T > 150$ K there was a complex unresolved distribution and its profile varied with temperature. Analysis of the $P(H^{\mathrm{Sn}})$ indicated that there were at least four inequivalent positions of the tin atoms in the spinel lattice and that the temperature dependence of the H^{Sn} fields was different for each.

3. DISCUSSION OF RESULTS

3.1. Magnetically inequivalent positions of Sn^{4+} ions

Usually the ions of tin occupy the B sites in the spinel structure. Obviously, the Sn^{4+} ions can occupy the positions of the Li^{+} ions (denoted by I in Fig. 1) and of the Fe^{3+} ions (positions II). If the B sites are occupied randomly by the Sn^{4+} ions in ordered lithium ferrite the type I and II positions (Fig. 1) are occupied in the ratio 1:3.

It is shown in Ref. 3 that the type II positions are inequivalent in the magnetic sense because of the anisotropic contribution of the dipole field and the anisotropic component of the hyperfine interaction. For an arbitrary direction of the magnetization all 12 ions at the II positions of one unit cell can be magnetically inequivalent. In the absence of an external magnetic field the magnetic moments of the iron ions are directed along one of the $\langle 111 \rangle$ axes, which is the easy magnetization axis. In this case there should be three equivalent positions of the B ions of the type II, corresponding to three values of the dipole field. Their populations should be in the ratio 3:3:6.

In the case of the type I positions and an arbitrary direction of the magnetization all the four ions in a unit cell are magnetically inequivalent. However, if the magnetization is directed along one of the $\langle 111 \rangle$ axes, two inequivalent positions of the B ions of type I (occupied in the ratio 1:3) should be observed, and they correspond to two values of the dipole field.

Bearing in mind the magnetic inequivalence of all the tin ions at the I and II positions (occupying the lithium and iron sites in the B sublattice), we can expect five components in the ^{119}Sn spectrum and the intensities of these components should be in the ratio 1:3:3:3:6. However, in view of the low intensity of the first component, we can simplify the problem by ignoring this component.

3.2. Temperature dependences of hyperfine magnetic fields at tin nuclei

In view of the existence of four inequivalent positions of the tin ions, we analyzed the distribution curve $P(H^{\mathrm{Sn}})$ into four components with intensities in the ratio 3:3:3:6. This analysis was carreid out by the least-squares method on the assumption that each component is described by a Gaussian curve. In those cases when the functions $P(H^{\mathrm{Sn}})$ are poorly resolved (at temperatures $T \geqslant 149$ K), the results of this analysis were used as the initial approximation for the expansion of the spectra of the ^{119}Sn nuclei into four components with intensities given in the ratio above. In a computer analysis of the spectra we calculated also the error in the determination of the hyperfine fields (see Table I). The results were used to plot the temperature dependences of the fields H^{Sn} for each of the components (Fig. 6).

TABLE I. Hyperfine magnetic fields at ^{119}Sn ($T = 80$ K) and ^{57}Fe ($T = 4.2$ K) nuclei at B type II positions in ordered lithium ferrite.

Type B site	H^{Sn}, kOe	H^{Fe}, kOe from Ref. 3
II − 1	131±1	530.3
II − 2	143±1	535.4
II − 3	154±1	539.4

The elaborate redistribution of the intensity in the function $P(H^{\mathrm{Sn}})$ accompanied resulting from a change in temperature can be explained by the fact that for each of the components (with a relative intensity of 3) the field H^{Sn} undergoes an anomalous reduction at temperatures $T < 230$ K. This anomaly may appear because of the existence of two contributions to the field H^{Sn} with opposite signs and different temperature dependences (Ref. 8). We shall assume that this component should be attributed to the tin ions in the type I position for the following reasons.

As shown in Ref. 8, the field H^{Sn} in the spinel structure is mainly due to two contributions: *a*) a negative contribution due to the intersublattice indirect exchange interaction of the A–O–B type [indirect transfer of the hyperfine magnetic field along the Fe(A)–O–Sn(B) chain]; *b*) a positive contribution due to the intrasublattice direct B–B exchange [direct overlap of the orbitals of the magnetic and diamagnetic ions: Sn(B)–Fe(B)]. The existence of direct bonds in lithium ferrite is supported by the fairly large isomeric chemical shift of the ^{119}Sn spectra: at 80 K it amounts to + 0.46 mm/sec relative to SnO_2 and decreases to + 0.15 mm/sec at 640 K. This is evidence that the interaction (*b*) contributes substantially to the creation of the magnetic field at the nuclei.

Measurements carried out in an external magnetic field indicated that H^{Sn} was negative at both the I and II positions, i.e., this field was antiparallel to the total magnetic moment of the ferrite and it coincided with the direction of the moment of the A sublattice. Consequently, the contribution (*a*) due to the intersublattice interaction A–O–B predominated. The contribution (*b*) due to the B–B interaction plays an important role only at low temperatures and it decreases rapidly with temperature. Since the tin ions at the I

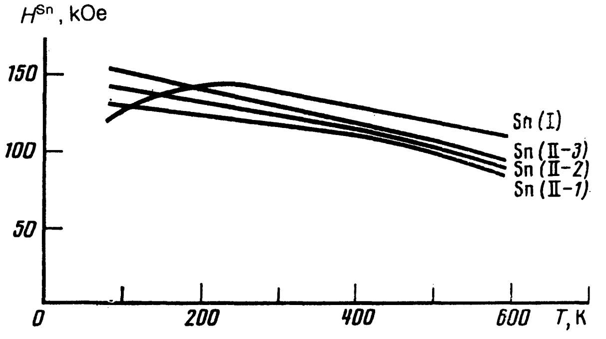
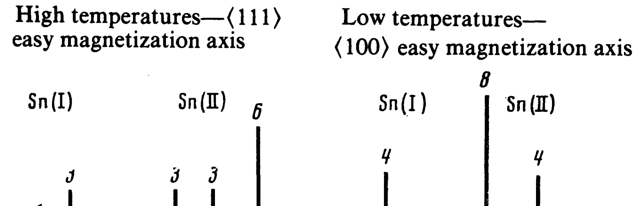


FIG. 6. Temperature dependences of four components of the hyperfine magnetic field H^{Sn} found from the distribution functions.

positions have six Fe^{3+} ions in the immediate B environment, the contribution of (*b*) is greater for these tin ions and it determines the anomalous nature of the temperature dependence $H^{Sn}(T)$. The Sn^{4+} ions at the II positions have only four B ions in the Fe^{3+} environment so that the contribution (*b*) for these ions plays a less important role and is probably significant at lower temperatures.

The observed redistribution of the intensities in the functions $P(H^{Sn})$, as a function of temperature can be explained also in a different way. The redistribution may be attributed to the presence of the Fe^{2+} ions in an amount sufficient for a strong influence on the magnetocrystalline anisotropy.[1] These divalent iron ions can form, for example, because of incomplete neutralization of the charge contributed by the Sn^{4+} impurity ions. Then, at low temperatures we can expect a reorientational phase transition of the $\langle 111\rangle \leftarrow\rightarrow \langle 100\rangle$ type, which has an important influence on the distribution of the dipole fields at the ^{119}Sn nuclei. When the easy magnetization axis is directed along $\langle 100\rangle$, there should be one dipole field for the Sn^{4+} ions at the I positions, and two dipole fields with line intensities in the ratio 8:4 for the II positions. The distribution of the line intensities in the case of such reorientation can be represented schematically as follows:



3.3. Influence of an External Magnetic Field

Figure 7 shows the distributions of the fields H^{Sn} in an external magnetic field. It is worth noting how the profile of the distribution function changes when an external magnetic field is applied. The $P(H^{Sn})$ curve becomes resolved into two peaks, which differ considerably in amplitude and width. The weaker peak clearly represents the Sn^{4+} ions in the I positions replacing the Li^{+} ions. The stronger peak is the average distribution function of the Sn^{4+} ions at the II positions replacing the Fe^{3+} ions. As already pointed out, in the case of an arbitrary direction of the magnetization (set by the external field) relative to the crystallographic axes we can generally expect twelve inequivalent values of the field for the Sn^{4+} ions at the II positions and four values of the field at the I positions. This results in a specific distribution of the dipole fields at the ^{119}Sn nuclei. Clearly, to lowest order we can assume that the peak profiles are described by the distribution laws of H^{Sn}.

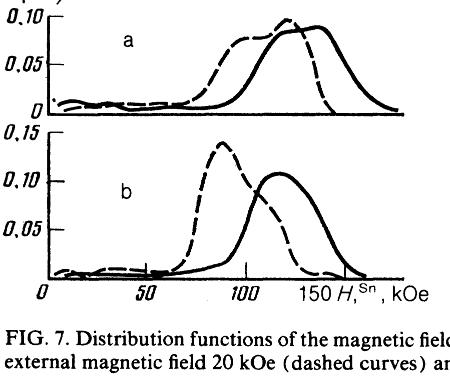


FIG. 7. Distribution functions of the magnetic field at the tin nuclei in an external magnetic field 20 kOe (dashed curves) and in the absence of an external field (continuous curves): a) 173 K; b) 193 K.

3.4. Estimates of fields H^{Sn} at I and II positions

We used the results of Refs. 8 and 9 to estimate approximately the average values of the fields H^{Sn} at 0 K at the I and II positions. It follows from the data on manganese ferrite[8] that one Fe^{3+} B-ion creates a field of the order of $H^{B} = \pm 113$ kOe at tin. The field at tin due to one Fe^{3+} A-ion can be obtained from the data on magnetite[9]: $H^{A} = -117$ kOe.

The field induced at an ion can be written in the form

$$H^{Sn}=mH^{A}+nH^{B},$$

where m and n are the numbers of the Fe^{3+} ions in the nearest A and B environment. Then, for the type I positions in lithium ferrite we obtain

$$H^{Sn(I)}=6H^{A}+6H^{B}=-24\text{ kOe},$$

and for the type II positions

$$H^{Sn(II)}=6H^{A}+4H^{B}=-250\text{ kOe}.$$

These estimates agree in order of magnitude and sign with our experimental data extrapolated to 0 K and they confirm the first variant of Sec. 3.2 accounting for the anomalies in the temperature dependences of the fields at the tin nuclei.

3.5. Anisotropy of H^{Sn} fields

The most interesting result of the present study is the detection of different fields at the tin nuclei located at three inequivalent type II positions (Fig. 5). In our opinion this difference is due to the anisotropic contribution of the dipole field and also due to the anisotropy of the supertransport field associated with the anisotropic component of the exchange interaction.

The magnetic field at a tin nucleus can be represented in the form

$$H^{Sn}=H^{is}_{STHF}+H^{an}_{STHF}+H^{an}_{d},$$

where H^{is}_{STHF} and H^{an}_{STHF} are the isotropic and anisotropic components of the indirect hyperfine interaction and H^{an}_{d} is the dipole field.

Table I lists the values of H^{Sn} for three inequivalent type II positions and the corresponding values at the iron nuclei obtained by the NMR method in Ref. 3. It is clear from this table that the anisotropic component of the magnetic field at the tin nuclei is approximately twice as large as at the iron nuclei.

We shall assume that H_d^{an} is the same for the ^{57}Fe and ^{119}Sn nuclei in the corresponding positions and also that the situation is not affected by doping of lithium ferrite with tin. Then, the increase in the anisotropic field at the tin nuclei is determined by the contribution $H_{\mathrm{STHF}}^{\mathrm{an}}$.

3.6. Calculation of the dipole field

In general, the dipole field can be written in the form[3]

$$H_{di}=D_{ik}\mu_k,$$

where

$$D_{ik}=\sum_a r_a^{-5}(3x_a^i x_a^k-r_a^2\delta_{ik})$$

is a dipole tensor which depends only on the spatial distribution of the magnetic moments. Here, $\mathbf{r}_a$ is the vector drawn from a given site to a site with a magnetic moment μ_a; x_a^i and x_a^h are the coordinates of the vector $\mathbf{r}_a$ $(i,k=1,2,3)$; $\delta_{ih}=1$ if $i=k$ and $\delta_{ih}=0$ if $i\neq k$.

In the case of the B sites, we have

$$H_d^{\mathrm{B}}=-(\mu/a_0^3)D_{ik}^{\mathrm{B}}n_i n_k,$$

where $\mathbf{n}$ is the unit vector of $\mathbf{M}_s=\mathbf{M}_\mathrm{B}-\mathbf{M}_\mathrm{A}$: $\mu=\mu^\mathrm{A}=\mu^\mathrm{B}=5\mu_\mathrm{B}$ is the magnetic moment of the Fe^{3+} ions; a_0 is the lattice parameter of lithium ferrite, which amounts to 8.33 Å; $\mu/a_0^3=80.2$ Oe.

For example, for an ion with the coordinates (1, 5, 1) expressed in units of $(1/8)a_0$ (an Sn ion in one of the II positions) the tensor D_{ik}^{B} can be written in the form of two tensors, one of which represents an axisymmetric dipole field due to the trigonal environment typical of the B sites in the spinel, whereas the second is due to an orthorhombic field associated with the presence of lithium:

$$D_{ik}^{\mathrm{B}}=\begin{vmatrix}0 & D_\mathrm{B} & D_\mathrm{B}\\ D_\mathrm{B} & 0 & D_\mathrm{B}\\ D_\mathrm{B} & D_\mathrm{B} & 0\end{vmatrix}+\begin{vmatrix}D & 0 & A\\ 0 & -2D & 0\\ A & 0 & D\end{vmatrix}.$$

Therefore, the dipole fields at the II positions are governed by three parameters: D_B, A, and D. The calculated values of these parameters are given below:

Parameter	D_B	D	A	D_B'
Calc. in sphere $r_a\leqslant 10a_0$	53.9	11.7	34.1	89.8

For all the 12 type II ions the projections of the magnetic field along the hyperfine field direction can be written as follows:

$$\begin{aligned}
H_d(1,2)&=-(\mu/a_0^3)2D_\mathrm{B}(\pm n_1n_2+n_2n_3\pm n_3n_1)\\
&\quad+2An_2n_3+D(1-3n_1^2),\\
H_d(3,4)&=-(\mu/a_0^3)2D_\mathrm{B}(\pm n_1n_2-n_2n_3\mp n_3n_1)\\
&\quad-2An_2n_3+D(1-3n_1^2),\\
H_d(5,6)&=-(\mu/a_0^3)2D_\mathrm{B}(\pm n_1n_2\pm n_2n_3+n_3n_1)\\
&\quad+2An_1n_3+D(1-3n_2^2),\\
H_d(7,8)&=-(\mu/a_0^3)2D_\mathrm{B}(\mp n_1n_2\pm n_2n_3-n_3n_1)\\
&\quad-2An_1n_3+D(1-3n_2^2),\\
H_d(9,\ 10)&=-(\mu/a_0^3)2D_\mathrm{B}(+n_1n_2\pm n_2n_3\pm n_3n_1)\\
&\quad+2An_1n_2+D(1-3n_3^2),\\
H_d(11,12)&=-(\mu/a_0^3)2D_\mathrm{B}(-n_1n_2\pm n_2n_3\mp n_3n_1)\\
&\quad-2An_1n_2+D(1-3n_3^2).
\end{aligned}\tag{1}$$

In the absence of an external magnetic field, i.e., when the magnetic moments of the iron ions are oriented in ⟨111⟩ directions (which are the easy magnetization axes), we can use Eq. (1) to obtain three values of the dipole field for the line positions with intensities in the ratio 3:3:6:

$$\begin{aligned}
H_{d1}&=-(\mu/a_0^3)(2D_\mathrm{B}+2A/3),\\
H_{d2}&=-(\mu/a_0^3)(-2D_\mathrm{B}/3+2A/3),\\
H_{d3}&=-(\mu/a_0^3)(-2D_\mathrm{B}/3-2A/3).
\end{aligned}\tag{2}$$

Substituting in Eq. (2) the values given above, we obtain three dipole fields:

$$H_{d1}=-80.2[107.8+68.2/3]\approx-10.5\ \mathrm{kOe},$$

$$H_{d2}=-80.2[107.8/3+68.2/3]\approx+1.0\ \mathrm{kOe},$$

$$H_{d3}=-80.2[-107.8/3-68.2/3]\approx+4.7\ \mathrm{kOe}.$$

For an ion with the coordinates (5, 5, 5) expressed in units of $(1/8)a_0$ (representing the Sn^{4+} ions at type I positions), the trigonal symmetry of the environment makes it possible to write down the tensor $D_{ik}^{\prime\mathrm{B}}$ in the form

$$D_{ik}^{\prime\mathrm{B}}=\begin{vmatrix}0 & D_\mathrm{B}' & D_\mathrm{B}'\\ D_\mathrm{B}' & 0 & D_\mathrm{B}'\\ D_\mathrm{B}' & D_\mathrm{B}' & 0\end{vmatrix}.$$

The calculated value of the parameter D_B' is also given above.

For the four type I ions the projections of the dipole field along the direction of the hyperfine field can be written as follows:

$$\begin{aligned}
H_d'(1,2)&=-(\mu/a_0^3)2D_\mathrm{B}'(+n_1n_2\pm n_2n_3\pm n_3n_1),\\
H_d'(3,4)&=-(\mu/a_0^3)2D_\mathrm{B}'(-n_1n_2\pm n_2n_3\mp n_3n_1).
\end{aligned}\tag{3}$$

If the directions of easy magnetization are the ⟨111⟩ axes, it follows from Eq. (3) that the dipole field has two values. The corresponding intensities are in the ratio 1:3:

$$H_{d1}'=-(\mu/a_0^3)2D_\mathrm{B}',\quad H_{d2}'=-(\mu/a_0^3)(2D_\mathrm{B}'/3).\tag{4}$$

Substituting in Eq. (4) the value $D_\mathrm{B}'=89.8$, we find two numerical values of the dipole field

$$H_{d1}'=-80.2\cdot2\cdot89.8=-14.4\ \mathrm{kOe},$$

$$H_{d2}'=80.2\cdot2\cdot89.8/3=4.8\ \mathrm{kOe}.$$

3.7. Estimates of contributions to the field H_{STHF}

We can separate the contributions $H_{\mathrm{STHF}}^{\mathrm{is}}$, $H_{\mathrm{STHF}}^{\mathrm{an}}$, and H_d^{an}. The isotropic contribution made to the field by the indirect hyperfine interaction at the II positions can be found as the center of gravity of three lines with the intensities in the ratio 1:1:2:

$$H_{\mathrm{STHF}}^{\mathrm{is}}=(131+143+2\cdot154)/4=145.5\ \mathrm{kOe}.$$

TABLE II. Contributions to parameters of tensor D_{ik}^{B} by dipole and anisotropic indirect hyperfine interaction (IHFI) fields.

	D_b, kOe	A, kOe	D, kOe
Calculation for $r_a \leqslant 10a_0$	4.34	2.74	0.94
Experiment for Fe^{3+} (B)	2,02	2.89	1.62
Anisotropy of IHFI	−2,32	0.15	0.68
Experiment for Sn^{4+}	4.50	8.25	–
Anisotropy of IHFI	0,16	5.51	–

Now, knowing the component $H_{\mathrm{STHF}}^{\mathrm{is}}$ and the values of the dipole field, we can readily determine the anisotropic component due to the exchange hyperfine interaction for each of the three inequivalent positions. Using the relationship $H_{\mathrm{STHF}}^{\mathrm{an}} = H_{\mathrm{exp}}^{\mathrm{Sn}} - (H_{\mathrm{STHF}}^{\mathrm{is}} + H_{d}^{\mathrm{an}})$, we obtain

Type of B site	II – 1	II – 2	II – 3
H_{STHF}^{an}, kOe	−4	−3,5	+4

It therefore follows that the fields $H_{\mathrm{STHF}}^{\mathrm{an}}$ at all three type II positions have approximately the same intensities but different signs: in the positions II–III the sign of the anisotropic component of the field is opposite to the corresponding component at the positions II-1 and II-2.

It is interesting to determine the contributions made by the anisotropy of the indirect hyperfine interaction to the parameters of the tensor D_{ik}^{B}. When the experimental values of the fields taken from Table I are substituted into Eq. (2), we obtain

$$H_{d2}-H_{d1}=(\mu/a_0^3)(8D_B/3)=12\ \mathrm{kOe},$$

$$H_{d3}-H_{d2}=(\mu/a_0^3)(4A/3)=11\ \mathrm{kOe}$$

Hence we can easily calculate the parameters D_B and A.

Table II gives the values of these parameters (in kilooersted) and also the corresponding contributions made by the anisotropy of the indirect hyperfine interaction obtained from our experiments on Sn^{4+} and from the NMR measurements on Fe^{3+} (Ref. 3).

It is clear from Table II that in the case of Sn^{4+} the anisotropy of the indirect hyperfine interaction is manifested more strongly by the parameter A, i.e., in this case the orthorhombic distortions of the lattice by the lithium ions play a greater role. On the other hand, in the case of Fe^{3+} the influence of the trigonal environment is more important.

4. CONCLUSIONS

Our investigation has demonstrated once again the high efficiency of the diamagnetic nuclear probe method for tackling fine spectroscopic details. The extreme sensitivity of the nuclei of diamagnetic ions to structural and magnetic environments has made it possible not only to establish clearly the magnetic inequivalence of atoms in the structure of ordered lithium ferrite, but also to reveal the anisotropy of the hyperfine magnetic fields at the tin nuclei. One should mention particularly that for the first time the anisotropy of the indirect hyperfine interaction has been investigated in its pure form, whereas studies of the anisotropy of the local fields at the nuclei of magnetic ions (such as ^{57}Fe) fail to distinguish the contributions of the indirect hyperfine interaction and of the intrinsic (intraatomic) hyperfine interaction.

[1)] Within experimental error, we found no Fe^{2+} ions in the sample, so that this variant will be regarded as less probable but fundamentally possible.

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Translated by A. Tybulewicz