Induced hyperfine interactions at the nuclei of the O^{2-} ions in ferrite spinels

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Local fields at the ^{17}O nuclei in $Mn_{1-x}Zn_xFe_2O_4$ ferrites with a natural abundance of the ^{17}O isotope were determined by the NMR method at helium temperatures. Three groups of NMR lines of the O^{2-} ions differed with respect to the immediate tetrahedral environment. The isotropic and anisotropic components of these local fields at the ^{17}O nuclei were determined. The isotropic components of the local fields were then used in a calculation of the parameters representing transfer of the spin density along the Nn^{2+}–O^{2-} and Fe^{3+}–O^{2-} bonds in spinels: f_s(Mn–O) = 0.61%; f_s(Fe_B–O) = 1.13%; f_s(Fe_A–O) = 1.31%. A change in the oxygen parameter in spinels had a considerable influence on the anisotropic component of the local field at the ^{17}O nuclei.

1. INTRODUCTION

The hyperfine interactions at the anion nuclei in magnetically ordered compounds are important for understanding the role of ligand ions in the exchange interactions and for determining the nature of the local fields at the nuclei of these ions. Moreover, investigations of these interactions can provide important information on the local magnetic and crystallographic structure of magnetic materials. Much work has been done already on the induced hyperfine interaction in pairs consisting of an F^- anion and a magnetic cation.[1] However, there have been only a few investigations of the O^{2-} anions. For example, the ENDOR method was used in Refs. 2 and 3 in a study of the induced hyperfine interaction in systems formed from ^{17}O, on the one hand, and Fe^{3+}, Mn^{3+}, or Cr^{3+}, on the other, in the MgO matrix. The investigations of magnetically ordered oxide compounds are limited only to a determination of the NMR of ^{17}O in $K_2CuCl_4 \cdot 2H_20$ enriched with the ^{17}O isotope[4] and observations of the NMR of ^{17}O in unenriched samples of $MnFe_2O_4$ ferrites.[5]

We determined the local fields at the O^{2-} nuclei in $Mn_{1-x}Zn_xFe_2O_4$ ferrites by the spin echo method at liquid helium temperatures. We checked the single-phase nature of single-crystal and polycrystalline samples of manganese zinc ferrites with a natural abundance of the ^{17}O isotope.

2. EXPERIMENTAL RESULTS

The NMR signal of ^{17}O in manganese zinc ferrites was investigated in a wide frequency range (5–700 MHz) at 1.8 K using single-crystal and polycrystalline samples. It was found that the NMR spectrum of these ferrites included not only the lines due to the $Fe^{3+}(B)$ (68–71 MHz), $Fe^{3+}(A)$ (71.5–72.1 MHz), $Mn^{3+}(B)$ (340–460 MHz), $Mn^{2+}(A)$ (580–600 MHz), and Zn^{2+} (17–19 MHz) ions, but also lines at frequencies 47–52 MHz, 56–61 MHz, and 73–85 MHz. The lines in the last three groups were at least two orders of magnitude weaker than the NMR line of the Fe^{3+} (B) ions.

We established earlier[5] that the NMR line of $MnFe_2O_4$ at 58.0 MHz was due to oxygen ions with the NMR spectrum consisting of two lines at 58.0 and 68.2 MHz [the latter coincided in frequency with the NMR spectrum of $Fe^{3+}(B)$]. Our studies showed that the NMR spectra of ^{17}O reported in Ref. 5 were typical of $MnFe_2O_4$ samples containing the Fe^{3+} ions at the tetrahedral (A) positions in amounts less than 5% (the concentration of Fe^{3+} at the A positions was deduced from the integrated intensities of the NMR lines of Fe^{3+} at the A and B positions). Manganese and manganese zinc ferrites with high concentrations of Fe^{3+} at the A positions had NMR lines at 47–52 MHz. The NMR lines at 74–84 MHz were observed only for samples containing zinc ions. The intensities of these lines were proportional to the concentration of Zn^{2+} and independent of the concentration of Fe^{3+} at the A positions.

The 47–52, 56–61, and 79–85 MHz lines were attributed to oxygen on the basis of the measured nuclear gyromagnetic ratios. The errors in the determination of these ratios, which could arise because of the dependence of the NMR frequency on the angle between the directions of an external magnetic field and the crystallographic axes, were avoided by orienting a spherical $Mn_{0.82}Zn_{0.18}Fe_2O_4$ single crystal so that the ⟨111⟩ axis coincided exactly with the direction of the external field. This was because the ⟨111⟩ directions were the easy magnetization axes at helium temperatures. The measured nuclear gyromagnetic ratios were 0.57 ± 0.02

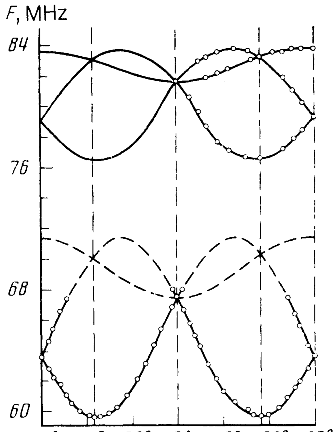

FIG. 1. Angular dependence of the NMR frequencies of ^{17}O in an $Mn_{0.82}Zn_{0.18}Fe_2O_4$ crystal subjected to an external field $H_0 = 5$ kOe; here, α is the angle between the magnetization and the ⟨001⟩ axis.

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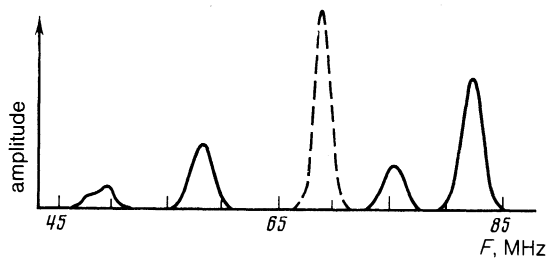

FIG. 2. Spectrum of the NMR of ^{17}O in an $Mn_{0.82}Zn_{0.18}Fe_2O_4$ single crystal in the absence of a magnetic field.

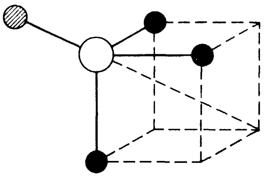

FIG. 3. Immediate cation environment of O^{2-} in the spinel structure: the white circle is the oxygen ion, the shaded circle is the cation at the *A* position, and the black dots are the cations at the *B* positions.

MHz/kOe for all the lines, in agreement with the tabulated value of this ratio for the ^{17}O nuclei (0.5772 MHz/kOe). The NMR frequencies of ^{17}O increased as a function of the external magnetic field, indicating that the direction of the local field at the ^{17}O nuclei was identical with the direction of the magnetization of a crystal.

The local symmetry of the oxygen ions was determined from the dependence of the NMR frequencies on the direction of the magnetization relative to the crystallographic axes. These measurements were made at 1.8 K using a cylindrical single crystal of $Mn_{0.82}Zn_{0.18}Fe_2O_4$ in which one of the $\langle 110 \rangle$ axes coincided with the cylinder axis. This sample was rotated about the cylinder axis in a field of 5 kOe directed at right-angles to this axis. Since the field exceeded the saturation value along the difficult magnetization axis, this rotation rotated the magnetization vector in the (110) plane.

The angular dependence of the NMR frequencies of ^{17}O is plotted in Fig. 1. We were unable to determine the NMR of ^{17}O at 69–72 MHz because of the overlap, on the frequency scale, with the NMR lines of Fe^{3+} (*B*). Moreover, we were unable to record the angular dependence of the NMR lines of ^{17}O at frequencies 47–52 MHz because these lines were too weak. A comparison of the angular dependences of the NMR frequencies of ^{17}O at 59–68 MHz and 76–84 MHz with the angular dependences reported in Ref. 5 indicated that the local symmetry of the O^{2-} ions was the same for all these lines. We were therefore able to extrapolate the angular dependence of the resonance frequencies above 68 MHz (the results of this extrapolation are represented by the broken trace in Fig. 1) and to reconstruct the complete NMR spectrum of ^{17}O in $Mn_{0.82}Zn_{0.18}Fe_2O_4$ (Fig. 2).

The angular dependence of the NMR frequencies in Fig. 1 correspond to ions with the axial local symmetry and threefold axes directed along $\langle 111 \rangle$. They are described by the following expression:

$$f=f_{\text{is}}+f_{\text{an}}(1-3\cos^2\theta), \qquad (1)$$

where f_{is} and f_{an} are proportional to the isotropic and anisotropic components of the local field at the ^{17}O nuclei, whereas θ is the angle between the local trigonal symmetry axis of a specific ion and the direction of magnetization of the whole crystal.

Each oxygen ion in a ferrite spinel is surrounded directly by one cation at the *A* position and three cations at the *B* positions (Fig. 3). The magnetic cations at the *A* and *B* positions are antiferromagnetically ordered. In manganese zinc ferrites the most probable octahedral environment is in the form of three O^{2-} ions. The tetrahedral environment in $MnFe_2O_4$ most probably consists of Mn^{2+} ions. The probability of the appearance of an Fe^{3+} ion in the *A* environment is proportional to the concentration of such ions at the *A* positions, which for our samples was at most 15%. As pointed out already, in the case of $MnFe_2O_4$ the NMR lines of ^{17}O at 56–72 MHz were considerably stronger than the NMR lines of ^{17}O at frequencies 47–52 MHz, which were practically undetectable in samples with the $Fe^{3+}(A)$ ion concentration amounting to 5%. Bearing in mind the probability of a specific environment of O^{2-} in $MnFe_2O_4$ and the ratio of the intensities of the NMR lines of ^{17}O, we attributed the 47–52 MHz lines to oxygen with the $Fe^{3+}(A) - 3Fe^{3+}(B)$ environment, whereas the 56–72 MHz lines were due to O^{2-} with the $Mn^{2+}(A) - 3Fe^{3+}B$ environment. Since the NMR lines of O^{2-} at 73–85 MHz were observed only for samples containing Zn^{2+}, it was natural to identify them as the O^{2-} ions with the $Zn^{2+}(A) - 3Fe^{3+}(B)$ environment.

It is clear from Fig. 3 that replacing the Mn^{2+} ions at the *A* positions with Fe^{3+} or Zn^{2+} did not alter the local symmetry of O^{2-} and, therefore, the angular dependences of the NMR frequencies of O^{2-} with different *A* environments should be described by the same expression (1). The known NMR frequencies of O^{2-} were used to find the isotropic and anisotropic components of the local fields at the nuclei of these ions in $Mn_{0.82}Zn_{0.18}Fe_2O_4$ (Table I). The values of the isotropic components of the local fields at the O^{2-} nuclei with different immediate tetrahedral environments were used to find the fields per bond of the O^{2-}–$Fe^{3+}(A)$, O^{2-}–$Fe^{3+}(B)$, or O^{2-}–Mn^{2+}(A) type (Table II). The local fields are given in Tables I and II again in frequency units for ease of comparison with the data obtained by the ENDOR method.[2,3]

TABLE I. Local fields at the nuclei of the O^{2-} ions in $Mn_{0.82}Zn_{0.18}Fe_2O_4$ with different types of environment.

Type of O^{2-} environment	$Fe^{3+}(A) - 3Fe^{3+}(B)$	$Mn^{2+}(A) - 3Fe^{3+}(B)$	$Zn^{2+}(A) - 3Fe^{3+}(B)$
H_{is}, kOe	85.76	114.97	139.67
H_{is}, MHz	49.5	66.36	80.62
H_{an}, kOe	1.30	6.55	4.34
H_{an}, MHz	0,75	3.78	2.51

TABLE II. Local fields at the nuclei of the ^{17}O ions per one bond.

Type of bond	O^{2-} — Fe^{3+} (A)	O^{2-} — $Fe^{3+}(B)$	O^{2-} — Mn^{2+} (A)
H_{is}, kOe	53.92	46.56	24.71
H_{is}, MHz	31.12	26.87	14.26

3. THEORY

The local field at the nucleus of a nonmagnetic anion induced by the neighboring magnetic s-type ion (Fe^{3+}, Mn^{2+}) can be represented in a form

$$\mathbf{H}=-\frac{1}{\gamma_n}\hat{A}\mathbf{S}, \tag{2}$$

where γ_n is the nuclear gyromagnetic ratio and S is the spin of a magnetic ion. The tensor $\hat{A}$ of the induced hyperfine interactions includes the following three main contributions[1]:

1) an isotropic contact contribution $A_{ij}=A_s\delta_{ij}$, which is due to the effects of spin density transfer and of the spin polarization of the filled ns shells of a nonmagnetic ion

$$A_s=\frac{f_s}{2s}A_s^{(0)}, \quad A_s^{(0)}=\frac{16}{3}\pi\mu_B\gamma_n\hbar|\varphi_{ns}(0)|^2, \tag{3}$$

where f is the parameter representing transfer of the spin density along an s bond and $|\varphi_{ns}(0)|^2$ is the probability density of detection of an ns electron at a nucleus;

2) an anisotropic covalent contribution

$$A_{ij}^{\text{cov}}=3A_p^{\text{cov}}\left(n_in_j-\frac{1}{3}\delta_{ij}\right), \tag{4}$$

where $\mathbf{n}$ is a unit vector in the direction of a bond along a line joining the nucleus of an anion with that of an impurity ion and the parameter A_p^{cov} is given by

$$A_p^{\text{cov}}=\frac{f_\sigma-f_\pi}{2s}A_p^{(0)}, \quad A_p^{(0)}=\frac{4}{5}\mu_B\gamma_n\hbar\left\langle\frac{1}{r^3}\right\rangle_{np}, \tag{5}$$

where $f_{\sigma,\pi}$ are the spin density transfer parameters along the σ and π bonds and $\langle 1/r^3\rangle_{np}$ is the radial average for the np shell (this anisotropic covalent contribution is related to the transfer of the spin density and polarization of the np shells of the anion);

3) an anisotropic dipole contribution

$$A_{ij}^d=3A_d(n_in_j-{}^1/_3\delta_{ij}), \quad A_d=\gamma_n\gamma_s/R^3, \tag{6}$$

where γ_s is the spin gyromagnetic ratio and R is the anion–magnetic ion distance.

The spin density transfer parameters $f_{s,\sigma,\pi}$ represent many of the most important characteristics of a magnetic cation–anion bond in a crystal, including the effective magnetic moment at a cation, the crystal field intensity, the cation–anion–cation superexchange interaction, etc. These parameters depend on both the electron structure of the cation and anion and the bond length R. It is usual to employ an empirical relationship

$$df/f=-\alpha\, dR/R \tag{7}$$

with the dimensionless parameter α varying within the range 5–10. The following experimental values were reported in Ref. 3:

$$A_s=-9.98 \text{ MHz } (^{17}O-Fe^{3+}),$$
$$A_s=-7.51 \text{ MHz } (^{17}O-Mn^{2+}),$$
$$A_p=-2.23 \text{ MHz } (^{17}O-Fe^{3+}),$$
$$A_p=-1.17 \text{ MHz } (^{17}O-Mn^{2+}).$$

The theoretical values of $A_s^{(0)}$ and $A_p^{(0)}$ for O^{2-} (including contributions of only the $2s$ and $2p$ electrons)[3]

$$A_s^{(0)}=-4309.0 \text{ MHz} \qquad A_p^{(0)}=-92.3 \text{ MHz}$$

were used in Ref. 3 to find also the spin density transfer parameters

$$f_s=1.05\%, \quad f_\sigma-f_\pi=5.7\% \qquad (O^{2-}-Fe^{3+}),$$
$$f_s=0.8\%, \quad f_\sigma-f_\pi=0.8\% \qquad (O^{2-}-Mn^{2+}).$$

Undoubtedly all these data, suitably corrected, could be used in a quantitative analysis of the NMR data for ^{17}O in ferrite spinels.

If the low-temperature magnetic order is collinear, the expression for the local field at the ^{17}O nucleus can be represented conveniently in the form

$$\mathbf{H}=\frac{1}{\gamma_n}\hat{a}\mathbf{m}, \tag{8}$$

where $\mathbf{m}$ is the reduced magnetic moment and the tensor $\hat{a}$ obtained ignoring the covalent reduction in the spin moment can be related to the tensors of the induced hyperfine interaction

$$\hat{a}=\sum_B\hat{A}(B)S(B)-\sum_A\hat{A}(A)S(A), \tag{9}$$

where the summation is carried out over all the magnetic ions at the appropriate positions.

The anisotropic part of the tensor $\hat{a}$, governed by the covalent and dipole contributions described by Eqs. (4) and (6), can be deduced from symmetry considerations and is given by

$$\hat{a}\,(\text{aH.})=\begin{pmatrix} a_\perp & 0 & 0 \\ 0 & a_\perp & 0 \\ 0 & 0 & a_\parallel \end{pmatrix} \tag{10}$$

(the Z axis is directed along the local trigonal axis), where $a_\perp=-1/2a_\parallel$.

Without allowance for weak nuclear quadrupole interactions of ^{17}O ($I=5/2$) the NMR frequency can be represented[3] in the form of Eq. (1) (assuming that the local fields at the O^{2-} nuclei are weakly anisotropic) with the components

$$f_{\text{is}}=|a_0|, \quad f_{\text{an}}=a_\perp \operatorname{sign} a_0, \tag{11}$$

where a_0 is the isotropic part of the tensor $\hat{a}$:

$$a_0 = \sum_B A_s(B)S(B) - \sum_A A_s(A)S(A). \qquad (12)$$

In the ideal case when the three equivalent $O^{2-} - Fe^{3+}(B)$ bonds in the spinel are directed along the ⟨100⟩ crystallographic axes, the total contribution of these bonds to the anisotropic (covalent and dipole) part of the tensor $\hat{a}$ (and consequently, to the value of f_{an}) vanishes. In the case of real crystals the displacement of the oxygen ion by δ along the trigonal axis results in decompensation of the anisotropic contribution of the immediate B environment. Then, we can use Eqs. (4), (6), (9), and (11) to obtain readily (in the case when $\delta \ll a$) the following expression for the contribution to f_{an}:

$$\Delta f_{an} = 12\sqrt{3}\frac{\delta}{a}(A_p^{cov} + A_d)\,\mathrm{sign}\,a_0 \qquad (13)$$

where $A_p^{cov} + A_d = A_p$ is the parameter of the anisotropic induced hyperfine interactions for a single $O^{2-} - Fe^{3+}(B)$ bond. Therefore, the displacement of O^{2-} in the direction of the B positions increases f_{an} when the sign of A_p and A_s is the same.

An important problem in analyzing of the anisotropy of the local field at the ^{17}O nuclei in ferrite spinels is that of allowing for the long-range magnetic-dipole interaction of the ^{17}O nuclei with the magnetic moments of ions in the second and more distant configuration spheres. The magnitude of the corresponding contribution to f_{an} is difficult to calculate quantitatively, especially as in the case of ferrite spinels with cations of different valences (Fe^{3+}, Mn^{2+}, Zn^{2+}), we cannot exclude the possibility that the short-range order effects will appear, which will give rise to a dependence of the average dipole field of the more disant spheres at the ^{17}O nucleus on the nature of the immediate environment.

Finally, ferrite spinels differ from matrices of the MgO type because the O^{2-} ions occupy noncentrosymmetric positions, giving rise to strong electric fields that induce the so-called *sp* hybridization, i.e., partial mixing of the ns and np states. This effect can alter the parameters of the cation–anion transfer of the spin density (f_s, f_σ, f_π), dependening on the valence state of the immediate environment of O^{2-}.

4. DISCUSSION OF RESULTS

4.1. Isotropic induced hyperfine interactions

Using the data in Table II on the contributions of the individual cation–anion bonds to the value of f_{is}, we can calculate the corresponding parameters A_s and f_s. For example, in the case of the O^{2-}–$Fe^{3+}(B)$ bond, we obtain $A_s(B) = -10.75$ MHz and $f_s(B) = 1.13\%$. These values are close to the corresponding parameters of the MgO:Fe^{3+} system.[3] In the case of the $O^{2-} - Fe^{3+}(A)$ bond we obtain somewhat larger values, $A_s(A) = -12.45$ MHz and $f_s(A) = 1.31\%$, which is to be expected bearing in mind that the $Fe^{3+}(A) - O^{2-}$ distance is considerably less than the $Fe^{3+}(B) - O^{2-}$ distance (1.89 Å against 2.03 Å—see Ref. 6). In the case of the O^{2-}–$Mn^{2+}(A)$ bond we find that $A_s(A) = -5.70$ MHz and $f_s(A) = 0.61\%$ These values are somewhat less than the corresponding values for the MgO:Mn^{2+} system,[2,3] which may be due to the large $Mn^{2+}(A) - O^{2-}$ distance in the spinel compared with the corresponding distance in MgO or with the sp hybridization effect.

In calculation of the quantities $A_a(A)$ and $f_s(A)$ for the $O^{2-} - Mn^{2+}(A)$ and O^{2-}–$Fe^{3+}(A)$ bonds, we assumed that the $O^{2-} - Fe^{3+}(B)$ bonds are unaffected in all three cases under discussion. In reality, the presence of Mn^{2+} instead of Zn^{2+} at the A position clearly reduces the $O^{2-} - Fe^{3+}(B)$ distances and, consequently, it results in an increase of the contribution of the $Fe^{3+}(B)$ ions to f_{is}. The effect is the opposite of that for Fe^{3+} at the A position. Consequently, the real values of $A_s(A)$ and $f_s(A)$ for the O^{2-}–$Fe^{3+}(A)$ bond is somewhat less, whereas for the O^{2-}–$Mn^{2+}(A)$ bond it should be somewhat greater than the values we found, which brings these values even closer to the parameters typical of the MgO matrix.

In spite of the small differences, in all cases the parameters of the isotropic induced hyperfine interaction of the ^{17}O nuclei in spinels and MgO are in satisfactory agreement, confirming once again our interpretation of the NMR spectra of ^{17}O.

4.2. Anisotropic induced hyperfine interactions

The value $f_{an} = 2.51$ MHz, corresponding to the ^{17}O nuclei, which have the Zn^{2+} ion in the immediate A environment, represents the magnetic-dipole contribution of the distant spheres and/or the "decompensation" of the anisotropic hyperfine interactions with three $Fe^{3+}(B)$ ions. The contribution of the second mechanism can be estimated using Eq. (13) and the results of Ref. 3, according to which in the case of the O^{2-}–Fe^{3+} bond in MgO we have $A_p = -2.23$ MHz. We then obtain

$$\Delta f_{an} = 12\sqrt{3}\cdot 2.23\frac{\delta}{a} \approx 48\frac{\delta}{a}\ \text{MHz},$$

which for $\delta/a \sim 0.01$ corresponds to $\Delta f_{an} \sim 0.5$ MHz. Bearing in mind the large ionic radius of Zn^{2+}, we cannot exclude the possibility that a displacement of the O^{2-} ion along the $Fe^{3+}(B)$ direction will make a relatively large contribution and cause an anisotropic hyperfine interaction of ^{17}O with three $Fe^{3+}(B)$ ions to arise.

The replacement of nonmagnetic Zn^{2+} in the A position closest to ^{17}O with a magnetic Mn^{2+} ion increases f_{an} ($f_{an} = 3.78$ MHz, see Table I), which naturally can be attributed to the anisotropic contribution of the ^{17}O–$Mn^{2+}(A)$ bond. Using the results of Ref. 3 to estimate the corresponding parameter A_p ($A_p = -1.17$ MHz), we obtain the anisotropic contribution $^{17}O - Mn^{2+}(A)$ bond to f_{an} and we find that this contribution is 2.9 MHz. It therefore follows that the contribution of the ^{17}O–$Mn^{2+}(A)$ bond to f_{an} represents a major part compared with the contribution of the "distant dipoles" and/or the "decompensation" effect which also should make a considerable contribution to f_{an} because of the large radius of the Mn^{2+} ion.

The $^{17}O - Fe^{3+}(A)$ bond makes a large contribution to the anisotropy of the hyperfine interaction. If we use Eq. (3), we find that the relevant term contributes $f_{an} = 5.6$ MHz. The experimental value of f_{an} for ^{17}O, which has only the Fe^{3+} ions in the immediate environment, is almost an order of magnitude less: $f_{an}^{exp} = 0.75$ MHz. This may be due to reversal of the sign of the dipole contribution of the distant nuclei or due to the "decompensation" effect. In fact, replacing the large Mn^{2+} and Zn^{2+} ions with the relatively small Fe^{3+} ion should shift the O^{2-} ion toward the A position, thus decompensating the anisotropic contribution made by all three $Fe^{3+}(B)$ ions to f_{an}. If δ is negative, the sign of the term in f_{an} will be negative.

It therefore follows that the use of the known data on the anisotropy of the induced ^{17}O–Mn^{2+} and ^{17}O–Fe^{3+} hyperfine interactions in MgO, and also allowance for the singularities of the crystal and magnetic structures of ferrite spinels, should provide a semiquantitative explanation of the observed anisotropy of the NMR spectra of ^{17}O.

5. CONCLUSIONS

A comprehensive experimental and theoretical investigation of the NMR spectra of ferrite spinels permitted us to identify reliably, for the first time, the various lines in the spectrum of ^{17}O. These lines were identified on the basis of the relationships they obeyed, considered as a function of the intensity and concentrations of various ions, utilizing measurements of the gyromagnetic ratios and of the angular dependences of the NMR frequencies, and also including the results of numerical calculations of the NMR frequencies in agreement with the published ENDOR data.

Our theoretical analysis not only enabled us to interpret the observed features of the NMR spectra of ^{17}O, but also to calculate the number of induced hyperfine interaction parameters for the transfer of the spin density in the case of the O^{2-}–Mn^{2+} and O^{2-}–Fe^{3+} bonds. We found that a more detailed investigation of the NMR spectra of ^{17}O in ferrite spinels should give information on the local distortions of the crystal structure, particularly on the local parameter representing the displacement of the O^{2-} ions. The values of the parameters of transfer of the spin density along the O^{2-}–Fe^{3+} bonds can be used also to calculate the exchange interactions and to predict the isotropic local fields at the ^{17}O nuclei in different ferrites: spinel, garnet, and orthoferrite.

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