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Hyperfine interactions in magnetic iron oxides with nonmagnetic substitutions

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1. Introduction

Magnetic materials, including **magnetic iron oxides**, are important for different technical applications as well as for basic research in condensed matter field. Their physical properties can be sufficiently affected by the presence of defects or substitutions. Many of these defects can be hardly studied by conventional methods giving information about a system as a whole. As a consequence, the role of a specific defect, especially when more types of defects are present in the system, can be found out by methods providing information on local properties of a magnetic material and could therefore be used as an effective tool to monitor changes caused by different types of defects. The method offering the best resolution is the Nuclear Magnetic Resonance (NMR). It provides a possibility to study separately resonant responses from different crystallographic positions in a given structure.

Proposed thesis is focused on the study of **hyperfine interactions** in magnetic iron oxides by means of NMR techniques. The thesis takes into consideration two basic magnetic iron oxides/ferrites: yttrium iron garnet (YIG, chemical formula $Y_3Fe_5O_{12}$) and magnetite (Fe₃O₄). The matter of interest is hyperfine interactions in nominally pure materials as well as the changes induced in the systems in question by substitutions in different crystallographic positions. The goal is to investigate changes in NMR spectra and relaxations induced by different substitutions and to contribute to explanation of the influence of the substitutions on the change of hyperfine parameters and some macroscopic properties of the materials.

2. Fundamental properties of yttrium iron garnet (YIG) and magnetite

Yttrium iron garnet (YIG) is a ferrimagnetic material which is widely used in various microwave and optical-communication devices and other applications - mainly due to its suitable magnetic and magneto-optical properties.

According to a structure analysis [Gell57] yttrium iron garnet belongs to a space symmetry group O_h^{10} (Ia-3d), i.e. it has a body-centered cubic Bravais lattice. Its unit cell contains eight formula units {Y₃} [Fe₂] (Fe₃) O_{12} . Different brackets { }, [], () are used to denote three different cation sites or types of coordinations to oxygen. The Y³⁺ ions occupy dodecahedral or {c}-sites, while Fe³⁺ ions occupy octahedral or [a]-sites and tetrahedral or (d)-sites. The lattice constant *a*=12.2376 Å at 4.2K [Levi66].

The only ions possessing magnetic moments in YIG system are Fe^{3+} ions which form *a* and *d* magnetic sublattices. The exchange between individual magnetic moments is carried out by superexchange interaction by means of oxygen anions [Kram34]. The theory predicts maximum superexchange interaction for an angle Fe^{3+} - O^{2-} Fe^{3+} of 180 degrees and small Fe^{3+} - O^{2-} distance. In the case of YIG the strongest interaction occurs between $Fe^{3+}(a)$ and $Fe^{3+}(d)$ ions for which the $Fe^{3+}(a) - O^{2-} - Fe^{3+}(d)$ angle is 125.9° [Wink81]. The magnetic moments of $Fe^{3+}(a)$ and $Fe^{3+}(d)$ ions are antiparallel below Curie temperature Tc=560K [Gell64]. Because there are $3Fe^{3+}(d)$ and $2Fe^{3+}(a)$ ions per formula unit, there should be a net magnetic moment corresponding to one Fe^{3+} ion, i.e. $5\mu_B$.

Magnetite Fe_3O_4 is a member of spinel ferrites family. Despite it is the earliest discovered magnet (~1500 B.C.) and one of the best known magnetic compounds, this mixed-valence system hitherto is not completely understood and the investigation of the physical properties of magnetite is still an intriguing field of research, especially, the properties in relation to the electronic ordering of the Fe²⁺ and Fe³⁺ ions below and above the Verwey transition, and the phase transition itself.

Magnetite exhibits a variety of properties, depending on its temperature. There are three main regions of temperatures where magnetite behaves differently: first region- between 0K and

the Verwey transition temperature T_V (of about 120-125K, depending on purity and internal stresses), second region - from T_V up to T_C (the Curie temperature, which is of about 840K) and the third one - above T_C . In the last region magnetite behaves as a paramagnet. At T_C magnetite turns from paramagnetic to ferrimagnetic phase, in temperature region $0K - T_C$ it is a collinear ferrimagnet. At the Verwey temperature T_V , Fe₃O₄ undergoes a metal-insulator transition, accompanied by a structure transition from cubic to monoclinic. This the so-called Verwey transition is characterized by a large decrease in conductivity (of about two orders of magnitude) and a drop of the magnetization as well as by a heat capacity anomaly at the transition temperature. Just above the Verwey temperature T_V magnetite undergoes another transition – the so-called spin-reorientation transition, when the easy direction of magnetization is changing. In pure Fe₃O₄ this transition occurs at $T_{SR} \sim 130$ K. The conductivity of Fe₃O₄ at room temperature is relatively high (about $2x10^4$ (Ωm)⁻¹) compared to the rather low values ($\sim 10^{-5}(\Omega m)^{-1}$) of "normal" spinels such as Co₃O₄ and Mn₃O₄[WalzO2].

Magnetite crystallizes into the cubic spinel structure (space symmetry group Fd3m- O_h^7 , a lattice parameter a=8.398Å [Brab95]) above the Verwey transition temperature (~120-125K). It has an inverse spinel structure and its formula unit is usually written as $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ to distinguish the first A-type tetrahedrally coordinated Fe^{3+} ions from the bracketed Fe^{2+} and Fe^{3+} ions in B-type octahedral sites.

Magnetic moments of A and B sublattices are aligned anti-parallel. This arrangement gives rise to the net magnetic moment of 4 μ_B per formula unit, when taking 5 μ_B per Fe³⁺ and 4 μ_B per Fe²⁺. Fe³⁺ ion has half-filled 3d electron shell (electron configuration 3d⁵) and zero angular momentum in the ground state. On the other hand, the ground state of the free Fe²⁺ ion (electron configuration 3d⁶) is ⁵D and considerable orbital momentum remains even when this term is split by the crystal field. Besides the superexchange interactions in magnetite, Fe³⁺ and Fe²⁺ ions in octahedral sites are ferromagnetically coupled via a double-exchange mechanism associated with inter-ion electron transfer [Cox92].

3. ⁵⁷Fe NMR in YIG and magnetite

An essential role for the NMR spectra interpretation plays the local symmetry of a crystal. The local fields (and consequently the corresponding resonance frequencies) on nuclei of differently positioned iron ions can be different, so each site in fact has its own subspectrum, which can be divided into several lines, distant up to several MHz. The structure of subspectrum (the number of lines, their relative intensities and splitting) is given by a symmetry of the corresponding crystallographic position and crystal structure, magnetic structure and anisotropy of a local field on nuclei (i.e. its dependence on a direction of the magnetic moment of an ion).

The ⁵⁷Fe nuclei disposed in *d* and *a* sites of **yttrium iron garnet** possess S₄ and C_{3i} symmetry, respectively. As was shown in [Robe62], the resonant frequency of NMR in YIG can be described by the expression: $v_{hf} = v_I + v_{AN} (3\cos^2\theta - 1)$, where v_I , v_{AN} are isotropic and anisotropic constants of a resonance frequency, θ is the angle between magnetization direction and a local symmetry axis.

In the case when magnetization lies along the easy axis (directions of <111> type) all S₄ symmetry axes of *d*-sites (lying along directions of <100> type) make the same angle θ = 54.74° with the magnetization direction. Therefore, all *d* sites have equal NMR frequencies and only one NMR line corresponding to the resonance of ⁵⁷Fe nuclei in *d*-positions can be observed in NMR spectrum. In the case of *a*-sites there are two magnetically inequivalent sets of *a*-positions: *a*₁ with the local C₃ symmetry axis parallel to the magnetization direction θ_{a1} =0° and *a*₂ when the local three-fold symmetry axis and magnetization lie along different body diagonals θ_{a2} =70.53°.

The ⁵⁷Fe NMR spectrum of yttrium iron garnet then consists of two *a* lines with the ratio of intensities a_1 : $a_2 = 1$: 3 (Figure 1).



Figure 1. NMR spectrum of ⁵⁷Fe nuclei in pure YIG at 4.2 K in zero external magnetic field. Signal from the domains. Maximal amplitudes in the spectra were adjusted to 100 [Engl98].

⁵⁷Fe NMR spectra of **magnetite** exhibit a more complicated structure compared to YIG. According to a character of a change of NMR spectra of magnetite in temperature range $4.2K \le T \le 430K$ (how it was measured and reported in [StepHT99]) one can mark out three different regions:

1) $4.2K \le T < T_V$. The monoclinic cell of Fe₃O₄ contains 32 formula units with 32 Apositioned and 64 B-positioned iron ions. However, the number of crystallographically inequivalent sites is reduced by C_C symmetry to 8 of A-type and 16 of B-type sites. Easy direction of magnetization at low temperatures is [001] and it does not reduce the symmetry, so there are 8 and 16 magnetically inequivalent iron ions on A and B sites respectively. As a consequence, 8 Fe(A) lines and 16 Fe(B) lines are predicted in the NMR spectrum below T_V. In Figure 2 the ⁵⁷Fe NMR spectrum of magnetite single crystal of high purity (T_V=123.9K), measured at T = 4.2K at zero external magnetic field, is displayed [StepHT99].



Figure 2. ⁵⁷Fe NMR spectrum of magnetite single crystal measured at T=4.2 K (T_v=123.9 K) [StepHT99].The upper spectrum is 8 times magnified.

2) $T_V < T < T_{SR}$. Above T_V and close to this temperature the spectrum is drastically simplified, being reduced to two lines, as expected for the cubic symmetry and magnetization direction along the <001> direction (in absence of an external magnetic field) leading to the

unification of the iron ions on B-sites. For M \parallel [001] all Fe ions on octahedral (B) sites are magnetically equivalent. All tetrahedral (A) sites are magnetically equivalent for M \parallel [001] too. So the spectrum consists of a single Fe(A) line (very narrow line at 69.590 MHz) and single Fe(B) line (66.297 MHz) (Figure 3) [StepHT99], [Nova00].



Figure 3. ⁵⁷Fe NMR spectrum of magnetite single crystal (T_v=121.5 K) at 122 K [StepHT99].

3) $T_{SR} < T < 430$ K. Between 125 and 131K magnetite undergoes the spin-reorientation transition: magnetization changes its direction from <001> to <111>. Then above T_{SR} there are two magnetically non-equivalent B sites: for the sites B₁ the axis of local trigonal distortion is parallel to the magnetization, while for sites B₂ trigonal distortion and magnetization point along different body diagonals. It leads to the splitting of the Fe(B) line to two lines (B₁ and B₂) with the ideal intensity ratio 1:3. The line at lower frequency corresponds to B₁ sites, while the higher frequency line to B₂ sites [StepHT99], [Nova00]. All tetrahedral (A) sites are magnetically equivalent for M || <111>. Then the spectrum of magnetite above the spin-reorientation transition is expected to consist of 3 lines: two B and one A lines with the ideal ratio of integral intensities I(B₁):I(B₂):I(A) = 1:3:2 (Figure 4) [StepHT99].



Figure 4. ⁵⁷Fe NMR spectrum of magnetite single crystal (T_v=121.5 K) at 134 K [StepHT99].

4. Experimental technique

NMR spectra have been measured by the spin echo method using the pulse phasecoherent spectrometer with an averaging technique and Fast Fourier Transformation (FFT). The measurements have been performed on a high resolution NMR spectrometer S.M.I.S. (adapted for NMR measurements in magnetics) at the Faculty of Mathematics and Physics of Charles University in Prague. The block scheme of the spectrometer is shown in Figure 5.



Figure 5. Block scheme of the pulsed NMR spectrometer used for the measurements.

The whole spectrometer is governed by the PC. The RF generator produces continuous radiofrequency signals with the frequency f_0 and $f_0 + f_B$. Afterwards continuous signal with the frequency f_0 is modulated by a pulse sequence produced by the pulse generator and is amplified by the RF amplifier (power output 300W). The attenuator establishes optimal (for obtaining of the spin echo signal) magnitude of the pulses. Pulses of optimal value go to a probe. The measured samples have been placed either in a coil of the tuned resonant circuit or the broadband probe has been used. After the pulses had been applied the echo signal was detected. The echo signal is then sent to the low-noise broadband preamplifier and to the mixer, where the spin echo signal is mixed with the reference continuous signal of the frequency $f_0 + f_B$ received from the RF generator. The result of the mixing is the spin echo signal modulated on the intermediate frequency f_B . The spin echo signal, amplified in the intermediate-frequency amplifier, is then digitized by the AD converter. Digitized spin echo signal is averaged in the PC memory in order to improve the signal/noise ratio. The resulting signal/noise ratio is proportional to $n^{1/2}$, where n is the number of averaged signals. NMR signal spectrum is obtained by the fast Fourier transformation of the averaged time dependent spin echo signal.

Frequency range	10 MHz - 300 MHz		
Maximal output of excitation pulses	300 W		
Length range of the excitation pulses	0.1 μs – 40 μs		
Repetition time range of the pulse series	0.01 s – 327s		
Pulse separation range	7 µs – 3200 µs		

Basic technical parameters of the pulse coherent spectrometer used in the measurements are collected in Table 1.

Table 1. Basic technical characteristics of the pulse phase coherent NMR spectrometer.

The temperature dependence measurements have been carried out using a continuous flow helium cryostat CF 1200 (Oxford Instruments) with temperature controller ITC4 (Oxford Instruments). In order to control temperature on the sample more precisely additional temperature monitor "Lake Shore" model 218 has been used with temperature sensor attached directly to the sample (the temperature accuracy was better than 0.1 K).

5. Main experimental results, calculations and discussions

In the YIG concerning part of the thesis, the results of the study of hyperfine interactions and relaxation parameters in substituted YIG (YIG:Al, YIG:In, YIG:La, YIG:Ca, YIG:Bi) and BiIG are presented. The part devoted to the magnetite deals with Al and Ga substituted systems.

5.1. Effect of aluminum substitution in YIG on ⁵⁷Fe hyperfine field anisotropy

A series of Y₃Al_xFe_{5-x}O₁₂ single crystal films with increasing content of Al substitution has been studied. ⁵⁷Fe NMR spectra have been measured at 4.2K. Besides the main lines corresponding to a resonance of nuclei of ions with ideal nearest neighbourhood, in NMR spectra of samples with substitutions there are also satellite lines corresponding to the resonance of nuclei of those ions which have a substitution or defect in their nearest neighbourhood.

⁵⁷Fe NMR spectra of the *a*-sites in the samples with (111) substrate orientation are shown in Figure 6. The assignment of the satellites induced by the Al³⁺ substitution is based on their intensity dependence on the amount of Al₂O₃ in the flux assuming that the substitution into *d*-site influences predominately the resonant frequency of nuclei in the nearest *a*-sites. The amount of Al in the YIG samples given in Fig. 6 has been determined from the relative integral intensities of the satellites and the main lines. Satellites caused by the intrinsic 'antisite' defects (Y³⁺ on *a*sites) identified previously [Step98A] in YIG samples are also pronounced in the spectra.



Figure 6. ⁵⁷Fe NMR spectra (a-sites) of Y₃Fe_{5-x}Al_xO₁₂ epitaxial films measured at zero external field at 4.2 K. Satellites induced by the Al substituents and Y antisite defects are denoted.

The film with the x=0.017 (Fig.6) and (110) substrate orientation has then been picked out for the studying of changes of the hyperfine field tensor induced by the presence of Al. This film has been measured at 4.2K in the external magnetic field of 0.1T applied consecutively in 16 different directions parallel to the plane (110) of the film. The dependence of resonant frequencies of main and satellite lines on the angle ϑ between magnetization direction and the

direction [001] has been studied. The angles ϑ have been identified according to the known angular dependence of the main *a* and *d* lines. The satellites induced by the presence of Al³⁺ ions in the nearest *d*-neighborhood of *a* sites have been identified after elimination of the Y³⁺ antisite defects satellites with known angular dependences.

The angular dependences of the resonant frequencies corresponding to the main a and d lines are shown in Figure 7.



Figure 7. The angular dependences of the resonant frequencies of the main *a* and *d* lines measured at 4.2K in the external field of 0.1T on the sample $Y_3Al_xFe_{5-x}O_{12}$ with x=0.017.

The angular dependences of the resonant frequencies corresponding to the *a*-main lines and to the Al^{3+} induced satellite lines are shown in Figure 8.



Figure 8. The angular dependences of the 57 Fe (a-sites) NMR frequencies of $Y_3Al_xFe_{5-x}O_{12}$ with x=0.017. ϑ is the angle between magnetization direction and [001]. Experimental points (open circles correspond to the main lines, full circles – to satellites) and fitted curves.

Analysis of the angular dependences has been performed for the sets of main lines (of both d and a iron sites) and for the complete set of the satellites corresponding to all

crystallographically equivalent configurations of the resonating iron on the *a*-site and the Al^{3+} substituent on one of its nearest *d*-sites. Resonant frequencies within a particular set (f_w) depend on the magnetization direction *n* according to the formula:

$$f_{(w)} = I + \mathbf{n}\mathbf{A}_{(w)}\mathbf{n} = I + \mathbf{n}\mathbf{G}_{(w)}^{-1}\mathbf{A}\mathbf{G}_{(w)}\mathbf{n}$$
⁽¹⁾

neglecting terms with higher powers of *n*. *I* is the isotropic term and *A* is the second-order traceless symmetric tensor describing the hyperfine field anisotropy for the reference configuration (w=1) of the set. The matrices $G_{(w)}$ represent point-symmetry operations transforming the reference configuration to the other configurations of the set.

Considering the Ia $\bar{3}$ d space group of the YIG crystal structure, local symmetries of the sites with the resonating irons and general direction of *n*, equation (1) predicts three main *d*-lines, four main *a*-lines and 24 satellite lines of *a*-sites having one Al³⁺ ion on the nearest *d*-site, and for *n* in (110) plane it predicts two main *d*-lines, three main *a*-lines and 12 satellite lines of *a*-sites having one Al³⁺ ion on the nearest *d*-site.

The values of I and components of A have been obtained by a least-square fit of Eq. (1) to the experimental data (Figures 7 and 8). The results of the fitting procedure for the main lines:

$$I^{d,main} = 64.966MHz, \qquad A^{d,main} = \begin{cases} 51 & 0 & 0 \\ 0 & 51 & 0 & kHz, \\ 0 & 0 & -102 \end{cases}$$
(2)
$$I^{a,main} = 75.798MHz, \qquad A^{a,main} = \begin{cases} 0 & -375 & -375 \\ -375 & 0 & -375 & kHz \\ -375 & -375 & 0 \end{cases}$$
(3)

are very close to those found previously for the nominally pure YIG single crystal [Koho97, Step98A] and Ga:YIG film [Koho99]. The tensors are given in the coordinate system of an elementary cell and correspond to the *d*-sites having its S₄ local symmetry axis along [0,0,1] direction and to the *a*-sites with their local symmetry axis S₆ along [1,1,1].

For *a*-sites with Al in their nearest neighbourhood one has been obtained:

$$I^{a,sat} = 75.111MHz, \qquad A^{a,sat} = \begin{cases} 273 & -76 & -361 \\ -76 & -533 & -583 & kHz \\ -361 & -583 & 260 \end{cases}$$
(4)

While the isotropic term is supposed to be modified predominately by the change of electron transfer to the 4s levels of the Fe³⁺ ion, the anisotropic part depends also on the transfer to 3d and 4p levels but contains also a contribution of a dipolar magnetic field of iron magnetic moments. To obtain the only contribution of the electron transfer modification, the change $\Delta A^{a,dip}$ of the dipolar field connected with the replacement of the neighbour iron with a nonmagnetic ion should be eliminated. The dipolar field for any position of the resonating iron nucleus and the replaced neighbouring Fe³⁺ can be calculated using the crystallographic data [Step00]. Unfortunately it is not possible to choose unambiguously the corresponding tensor from the set of

$$A_{(w)}^{a,sat} = G_{(w)}^{-1} A^{a,sat} G_{(w)}$$
(5)

tensors (to decide to which of 24 possibilities it corresponds) without an additional assumption. To solve this problem we have used the superposition model [Engl85]. The all 24 possibilities have been tested and only one of them was close to the prediction of the superposition model.

After its diagonalization, the principal values (421, -246, -175) kHz have been obtained. The first one corresponds to the principal axis deviated by only 1.1° from the Fe-O direction. The second principal value differs only slightly from the third one. The tensor is therefore nearly (however not exactly) uniaxial. We can conclude that the situation studied (resonating iron nucleus on *a* site, substituent (Al) on the nearest *d* site) together with analogous cases of Ga and Ge substitutions complies with the "independent bond" model.

These results together with those previously obtained for Ga³⁺ [Koho99] and Ge⁴⁺ [Koho00] substitutions form a basic set of hyperfine parameters enabling us to consider the influence of (i) different ionic radii of trivalent nonmagnetic substitution, (ii) replacement of the magnetic ion Fe³⁺ by a nonmagnetic one, and (iii) the influence of different valencies of the nonmagnetic substituents. All the three nonmagnetic substituents decrease the isotropic term for iron nuclei in their nearest a-sites. The effect of the valence change is somewhat smaller but comparable to that due to the replacement of iron by a nonmagnetic trivalent cation with similar ionic radius. The results concerning ⁵⁷Fe NMR in Al substituted YIG have been published [Gama02-1] together with the analysis and comparison of hyperfine fields modifications induced by Al, Ga and Ge cation substitutions.

5.2. Nuclear magnetic relaxation in YIG films with nonmagnetic trivalent substitutions

Besides a direct observation of effects of cation substitutions in NMR spectra in form of satellite structure, another but less explored effect of impurities is their influence on the nuclear magnetic spin–lattice and spin–spin relaxations. However, relaxation studies on magnetic oxides meet difficulties in both the theoretical analysis of the relaxation mechanisms [Beem68] and in an experimental verification. The only systematically studied changes of the relaxation rates in YIG epitaxial films have been carried out on YIG with some nonmagnetic non-trivalent (charged) cation substitutions [Wagn96]. The aim of the present study is to estimate the direct impact of the substitution. It should be then investigated in systems where the valence of the substituent is the same as that of the replaced cation. Three sets of samples (epitaxial films) have been studied. Our choice covers all cation sites of the garnet structure, i.e. the nonmagnetic Al³⁺ that prefers tetrahedral sites of ferric ions, In³⁺ occupying octahedral sites, and La³⁺ that replaces yttrium in dodecahedral sites.

Relaxation rates have been measured in zero external magnetic field at 4.2K for all the three main lines, i.e. *d*; *a1* and *a2*. The spin– lattice relaxation rate T_1^{-1} has been determined from the dependence of NMR signal on the repetition time of the two-pulse spin echo pulse sequence. The spin–spin relaxation rate T_2^{-1} has been measured by two techniques: (1) from the signal intensity dependence of the two-pulse spin echo on the delay between pulses and (2) from the decay of the individual echoes in the multiple pulse Carr-Purcell-Meiboom-Gill (CPMG) sequence.

Analyses of the time dependences have been made by a least square fit assuming a single-exponential behaviour. An effect of substitution has been characterized by the induced change of the relaxation rate:

$$\Delta \frac{1}{T_i} = \frac{1}{T_i^{subst}} - \frac{1}{T_i^{pure}}, \qquad i = 1, 2.$$
(6)

The changes of the spin–lattice relaxation rate obtained are shown in Figure 9. All the three types of impurities influence ΔT_1^{-1} within the studied concentration range in a similar way, i.e. the increase of their concentrations leads to the reduction of the relaxation rate. The decrease seems to stop when the concentration of about x= 0.1 is reached. The ΔT_1^{-1} values obtained for the same amount of the substituent per formula unit are quite comparable, although the

substitutions concern magnetic (Al, In replacing ferric ions) as well as nonmagnetic (La replacing yttrium) sublattices. The only common feature then seems to be an increased perturbation of the crystal structure periodicity caused by the presence of cations with different ionic radii.



Figure 9

Figure 10

- Figure 9. Dependence of ⁵⁷Fe nuclear relaxation rates T_1^{-1} of main lines for Y₃Fe_{5-x}Al_xO₁₂, Y₃Fe_{5-x}In_xO₁₂ and Y_{3-x}La_xFe₅O₁₂ on x-axis, plotted as differences between the values of the substituted and the pure sample. Symbols: circle=d-site, triangle up=a1-site, triangle down=a2-site. Relaxation rates T_{1pure}^{-1} of the pure sample for d; a1; a2 main lines are respectively 16, 20, 20 s⁻¹.
- Figure 10. Dependence of ⁵⁷Fe nuclear relaxation rates T_2^{-1} of main lines for Y₃Fe_{5-x}Al_xO₁₂, Y₃Fe_{5-x}In_xO₁₂ and Y_{3-x}La_xFe₅O₁₂ on x-axis, plotted as differences between the values of the substituted and the pure sample. Open symbols correspond to the T_2^{-1} (1). full to the T_2^{-1} (2); circle=d-site, triangle up=a1-site, triangle down=a2-site. Relaxation rates $T_{2,pres}^{-1}$ (1) of the pure sample for d; a1; a2 main lines are respectively 15, 16, 24 s⁻¹, relaxation rates $T_{2,pure}^{-1}$ (2) are 16, 16, 19 s⁻¹.

The nuclear magnetic spin–lattice relaxation mechanisms proposed for magnetic oxides [Beem68] assume that the energy dissipation is enabled by the hyperfine and dipole–dipole coupling between nuclear and electron magnetic moments. Our results might relate to the influence of the disturbed crystal and electron structure periodicity on the electron spin dynamics. The principal role of other effects of the substitution, like possible influence on the domain wall properties or magnetic dilution in iron sublattices by In and Al, cannot however be excluded.

Figure 10 displays the results obtained for the spin–spin relaxation rates. In certain cases significantly different values have been obtained from the two techniques used - the two-pulse spin echo and the multiple pulse Carr-Purcell sequence. For this reason we refer $T_2^{-1}(1)$ to the former and $T_2^{-1}(2)$ to the latter method. The $T_2^{-1}(2)$ relaxation rates are comparable to the T_1^{-1} values of the same samples and also exhibit similar dependence on the amount of substitution.

The $T_2^{-1}(1)$ for the Al and La substitutions follow more or less the $T_2^{-1}(2)$ values, but a substantial difference is seen for the In substitution where after reaching x~0.05 the $T_2^{-1}(1)$ sharply increases. Following Ref. [Ghos71], the time dependences of the signal intensities obtained by the two methods in solids may differ by a diffusion-like terms as a consequence of a different reflection of frequency fluctuations in the methods used for relaxation measurements. Also, it is worth to point out the anisotropy pronounced for the octahedral sites by a significant

difference between the $T_2^{-1}(1)$ values of *a1* and *a2* main lines. These results have been published [Gama02-2].

5.3. NMR spectra and relaxations of ⁵⁷Fe in calcium-doped yttrium iron garnet films

If the charge of cationic substitution in YIG is different from 3+, compensation is needed to balance the extra charge. These impurities are therefore called charged impurities. If the charge cannot be balanced by the present impurities, the formation of charged intrinsic defects like Fe²⁺ and Fe⁴⁺ takes place. Since the presence of a small quantity of nontrivalent Fe ions is difficult to detect directly, only indirect methods can be used to prove their existence.

Ca²⁺ is supposed to replace Y³⁺ in c-sites. Charge compensation can be reached by paired substitutions (e.g. Ca²⁺-Ge⁴⁺, Ca²⁺-Si⁴⁺). On the other hand, Y_{3-x}Ca_xFe₅O₁₂ samples without charge compensation doping can also be prepared. The following series of epitaxial films have been used for the study: YIG:Ca prepared from lead oxide flux, YIG:Ca–Ge, YIG:Ca–Si and YIG:Ca prepared from barium oxide flux. NMR spectra and for YIG:Ca samples prepared from barium oxide flux also relaxation rates have been measured at 4.2K in zero external magnetic field.

Comparing the ⁵⁷Fe NMR spectra of various series of Ca substituted samples (YIG:Ca, YIG:Ca–Ge and YIG:Ca–Si) and considering their changes with the increasing Ca content in a flux, a pronounced satellite line induced by Ca has been identified at 65.6 MHz in the *d*-site spectral region. The second satellite line expected from the crystal and magnetic structure analyses, has not been observed being presumably hidden by the main d-line. The content of Ca per formula unit (x_{NMR}) has been estimated from the ratio of the Ca-induced satellite and the main d-line integral intensities.

The impact of the Ca substitution in YIG:Ca samples on relaxation rates has been also studied. Relaxation parameters have been measured for main d-lines at 4.2 K. The spin–lattice relaxation rate T_1^{-1} has been determined from the dependence of a two-pulse spin echo on a repetition time. Spin-spin relaxation rate T_2^{-1} has been measured from the dependence of a two-pulse spin echo on a time delay between pulses and alternatively from the decay of individual echoes in a Carr–Purcell- Meiboom-Gill multiple pulse sequence. As the time dependences may differ probably due to the diffusion-like term we refer $T_2^{-1}(1)$ to the former and $T_2^{-1}(2)$ to the latter method. The results are plotted in Figure 11. With increasing Ca²⁺ concentration, the formation of Fe²⁺ should be then more and more suppressed. Fe²⁺ is a strong NMR relaxation rates [Wagn96]. The decrease has been really observed in our series of YIG:Ca films prepared from barium flux, but only for x_{NMR} higher than ~0.002. It indicates that for lower content of Ca when the relaxation rates remain approximately constant, the charge compensation is reached by other mechanisms. These results have been published [Step04].



Figure 11. Dependence of ⁵⁷Fe NMR relaxation rates on Ca content for the main d-line in a series of YIG:Ca films prepared from Ba flux on GGG substrate. (110) orientation, T = 4:2K. Circles= T_1^{-1} , triangles down = T_2^{-1} (1), triangles up = T_2^{-1} (2). 5.4. **NMR of** ⁵⁷Fe in bismuth-yttrium iron garnets

In a case of complete replacement of Y^{3+} in dodecahedral (c) cation sites the pattern of the spectrum is expected to be analogous to that of YIG (provided magnetization direction remains parallel to [111]), with possible shifts of the resonant frequencies. In the present paragraph we will dwell upon ⁵⁷Fe NMR spectra dependence on the replacement of Y^{3+} in dodecahedral sites by Bi³⁺. Because of the considerable difference in ionic radii of Y^{3+} (0.1019 nm) and Bi³⁺ (0.117 nm) [Shan76] a bulk sample of bismuth iron garnet (BIG) cannot be synthesized. Nevertheless, techniques of film preparation by direct epitaxial growth from vapour phase proved to be successful [Okud01].

BIG single crystal film and bismuth–yttrium iron garnet single crystal film of high Bi concentration (x=2.75) have been prepared by ion beam sputtering (IBS) [Okud01] by T.Okuda et al. Three comparative samples with low x have been used: pure single crystal YIG film prepared by liquid phase epitaxy (LPE), bulk single crystal (x = 0.02) and polycrystalline sample (x = 0.15). NMR spectra were measured at 4.2 K in zero external magnetic field.

Spectra of $Bi_xY_{3-x}Fe_5O_{12}$ (x = 0, 0.02, 0.15, 2.75 and 3) are plotted in Figure 12. The spectrum of BIG consists of a single line centered at 66.46 MHz which corresponds to iron nuclei in d-sites and of two lines at 74.00 MHz and 75.06 MHz (with relative integral intensities ~1:3) assigned to iron ions in a-sites. This scheme of a spectrum is characteristic for an iron garnet having magnetization direction along ~ [111]. The spectral lines of BIG sample exhibit more than an order higher inhomogeneous broadening in comparison with YIG epitaxial films and the lines shape is asymmetric with the slower decrease towards lower frequencies. The most probable reason for the line broadening is a higher amount of intrinsic defects, nevertheless, a distribution of magnetization directions close to [111] or distribution of demagnetizing fields cannot be excluded.

Resonant frequency of a given iron crystallographic site can be described as a sum of two contributions: a dominating isotropic part I and a small anisotropic part, i.e. a contribution dependent on the magnetization direction with respect to the local coordinate system of the site. For magnetization parallel to [111] the resonant frequency of d-spectrum equals directly to the isotropic part and a parameter characterizing the anisotropy cannot be determined from this spectrum. In the case of a-spectrum the isotropic part is a weighted average of the a1 and a2 resonant frequencies and the anisotropy can be expressed by means of a splitting δ_a between a1 and a2 lines. Comparison of BIG and YIG, given in Table 2, shows that in BIG the isotropic part is higher for d-sites while it is smaller for a-sites. The splitting of a-lines does not change considerably.

	$f_{\vec{a}}$ (MHz)	∆j (MHz)	∫ _{a1} (MHz)	₄ (MHz)	f _{at} (MHz)	∆₂ (MHz)	I _a (MHz)	δ _a (MHz)
BIG	65.46	0.57	74.00	~0.40	75.05	0.50	74.79	$1.05 \\ 1.00$
YIG	64.96	0.02 <i>5</i>	75.06	0.023	76.06	0.041	75.81	

 $(f_{a}, f_{a}, f_{a}, \dots$ resonant frequencies of d, a_{1} and a_{2} lines; A_{a}, A_{a}, \dots linewidths; $I_{a} = (f_{a} + 3 f_{a})/4, \delta_{a} = f_{a} - f_{a}$)

Table 2. Comparison of ⁵⁷Fe NMR spectral parameters of BIG and YIG films.

X-ray diffraction performed for yttrium-bismuth [Gell75] and bismuth iron garnets [Tora95] indicates that replacement of Y^{3+} by Bi^{3+} leads to a shortening of Fe– O^{2-} distances in the tetrahedron while in the octahedron they lengthen. In this respect the comparison of iron hyperfine fields in BIG and YIG is interesting since the higher covalency related to the shorter

interatomic distances is believed to lower resonant frequencies. The found spectral shifts of BIG in respect to the YIG reveal, however, just an opposite tendency, i.e., decrease in resonant frequency with increasing size of the octahedron, and increasing frequency in case of the decreasing tetrahedron. This indicates a substantial impact of the bismuth electron structure on electron transfer in Fe–O-cation triads.

In samples with x = 0.02 and 0.15 we have detected resolved satellites in spectra induced by the presence of Bi substituent in the nearest c-neighbourhood of the resonating iron (Fig.12). Two satellite lines are pronounced in the *d*-spectrum (shifted by 0.54 and 0.81 MHz from the main d-line). *a*-spectrum contains one satellite line close to a1-main line (shifted by -0.215MHz), and three satellite lines near a2, two of them overlap (shifted by -0.16 MHz and, for the double satellite, by -0.31 MHz).



Figure 12. ⁵⁷Fe NMR spectra of bismuth-yttrium iron garnets $Bi_xY_{3-x}Fe_5O_{12}$ with x = 0, 0.02, 0.15, 2.75 and 3 measured at 4.2K in zero external magnetic field.

For high values of x (close to 3) a mirror structure of spectra is expected. It means that the spectra contain satellites corresponding to the resonating irons with a single Y^{3+} cation in their nearest *c*-neighbourhood regularly occupied (in BIG) by Bi³⁺. These satellite lines should be shifted from the BIG main lines in an opposite direction than satellites in YIG with small concentration of Bi. The inhomogeneous line broadening in the spectrum of the film with x ~ 2.75 disables detailed analysis, however the mirror position of satellite lines is still evident at least in the spectrum of d-sites. These results have been published [Step03].

5.5. ⁵⁷Fe NMR of Al³⁺ substituted magnetite below the Verwey transition

To study the effect of Al-impurities on the electronic structure of magnetite several synthetic single crystals of $Fe_{3-x}Al_xO_4$ have been used with aluminum contents x = 0.005, 0.01, 0.02, 0.03. T_v 's of_the substituted samples have been estimated by means of NMR technique in our research. They were found to be decreasing with increasing Al content in agreement with [Brab98]: $T_v(x=0.005) \le 121$ K, $T_v(x=0.01) \le 117$ K, $T_v(x=0.02) < 105$ K, $T_v(x=0.03) < 100$ K.

In Figure 13 NMR spectra of Al-substituted magnetite measured at liquid helium temperature are presented for different aluminum contents, namely x=0; 0.005, 0.01, and 0.03. The differences between the pure and substituted magnetite spectra are that the former spectra have lines of A and B-types visually broadened. The broadening depends on aluminum content: the more substitutions - the broader NMR lines are.

Figure 13. ⁵⁷Fe NMR spectra of pure magnetite Fe_3O_4 (according to [Nova00]) and Al-substituted magnetite $Fe_{3-x}Al_xO_4$ with increasing aluminum content x measured at T=4.2K. In the frequency region 33-57 MHz, the spectra are drawn also magnified (dotted lines) for clearness.

The character of magnetite spectrum having superimposed many of B and A-lines within the frequency range 68-72MHz and additional systematic lines broadening caused by the presence of Al^{3+} ions makes impossible to reveal satellites in the vicinity of A-lines, caused by the substitution of nearest neighbor Fe ions of B-type by Al^{3+} ions at such content.

Resonance frequencies of tetrahedral (A) iron sites for aluminum substituted samples with x=0, 0.005, 0.01, 0.02 and 0.03 are plotted in Figure 14 as functions of temperature.

Apparently positions of the main lines of tetrahedral iron sites at a given temperature do not depend on Al concentration and are the same as those of the pure samples reported in [Nova00].

In Figure 15 the temperature dependences of resonance frequencies of octahedral (B) iron sites for the samples with aluminum contents x=0, 0.005, 0.01, 0.02 and 0.03 are presented. Since some of B-lines are not always well resolved in spectra the fitting procedure is not reliable enough for them. As a consequence, only those B-lines have been taken into consideration,

which could be reliably fitted. The most problematic spectra in that sense were ones at approximately 23K and 55K because of the behavior of spin-spin relaxation times within the region close to those temperatures

Figure 14. Temperature dependences of resonance frequencies of the main lines for tetrahedral (A) iron sites below the Verwey transition. Data for pure magnetite (x=0) are taken from [Nova00] and plotted as open circles. Black symbols designate the resonance frequencies of the samples with aluminum contents 0.005, 0.01, 0.02 and 0.03.

The temperature dependences in question did not reveal any changes in the values of hyperfine fields on iron sites, giving rise to main lines of magnetite below T_v , in the presence of Al substitution up to x=0.03. These results together with ⁵⁷Fe NMR spectra of Al-substituted magnetite with increasing aluminum content have been published [Koho04].

Measurements of Al-substituted magnetite samples below the Verwey transition revealed that the temperature behavior of relaxation times of substituted magnetite is in rough outline similar to that of the pure magnetite [NovaICF00], however some significant differences occur. The effect of increasing Al content revealed itself the most in lowering by an order of magnitude of the spin-lattice relaxation times T₁ at T=4.2K as for A and for B lines. A noticeable difference has been observed in the temperature behavior of T_1 and T_2 relaxations of the substituted sample with x=0.005 below the Verwey transition with respect to the pure magnetite. T₁ relaxations of substituted sample at T<20K were twice longer than ones of pure magnetite, while T₂ relaxations were found to be faster than those of the pure magnetite within the same temperature region. As T_1 and T_2 relaxations of the substituted sample within \approx 30-80K have been observed to be much faster than those of the pure sample. Minimum of T₂ relaxations of A positioned iron ions is at least by 3 orders of magnitude lower than for the pure sample, while the minimum of T_1 relaxation of the same ions is twice lower than for the pure magnetite. Concerning B-positioned iron ions, their both T_1 and T_2 relaxations are at least by an order of magnitude faster than ones of the pure magnetite. In the temperature region from \approx 80K up to T_V both T₁ and T₂ relaxations of A-line did not change significantly. The possible reasons of main differences in temperature behaviour of relaxations of pure and Al substituted samples have been pointed out comparing presented data with other experimental results and estimations (see discussions in the complete text of the thesis).

Figure 15. Temperature dependence of resonance frequencies of the main lines of octahedral (B) iron sites below the Verwey transition. Data for pure magnetite (x=0) are taken from [NovaICF00] and plotted as open circles. Black symbols designate the resonance frequencies of the samples with aluminum contents x=0.005, 0.01, 0.02 and 0.03.

5.6. ⁵⁷Fe NMR spectra of Al³⁺ substituted magnetite above the Verwey transition

In Figure 16 ⁵⁷Fe NMR spectra for three studied compounds, taken at temperatures close to 240K (well above the Verwey transition) are displayed. In the spectra of x= 0.005 and x= 0.03 compounds the satellite lines are clearly seen, their amplitudes increase with the nominal concentration of Al. Symmetry analysis of this situation shows that the A line has two satellites with an amplitude ratio 1:2 for M||[001] ($T_V < T < T_{SR}$), while for M||[111] ($T > T_{SR}$) three satellite lines exist in the ratio 1:1:2.

As in the case of NMR spectra of Al substituted magnetite below the Verwey transition, Al doping leads to broadening of main (and satellite) lines. The difference of the spectra of x= 0.005 crystal and the pure magnetite is small, indicating that Al doping at low concentration has only a small effect on the electronic structure of magnetite. Eventual larger differences, which might exist close to T_v , are obscured by the presence of the spin-reorientation transition. Close to this transition ($T_{SR}\approx128$ K), the lines are additionally broadened and considerable information is lost, in particular, the satellites caused by Al are no longer resolved. However, the satellites reappear below T_{SR} .

The temperature dependences of NMR frequencies of the main and corresponding satellite lines of tetrahedral Fe³⁺ ions for pure and substituted samples are shown in Figure 17. The decrease of the resonance frequencies of the satellite lines with increasing T is slightly faster compared to the corresponding main line. This is expected, as for the Fe (A) with a nearest Al neighbor, one of the Fe (A)–oxygen–Fe (B) superexchange interactions is missing (there are 12 such interactions in an ideal environment).

The next Figure 18 presents temperature dependence of NMR frequencies for octahedral B lines above the Verwey transition. As in the case of tetrahedral lines, one can see no difference in temperature dependencies of the frequencies of octahedral lines for pure and substituted samples, i.e. aluminum content up to x=0.03 does not affect the temperature behavior of NMR frequencies of the main lines of magnetite.

Figure 16. ⁵⁷Fe NMR spectra of Fe₃O₄ (T = 250.4 K), Fe_{2.995}Al_{0.005}O₄ (T = 240 K) and Fe_{2.97}Al_{0.03}O₄ (T = 240.3 K) single crystals.

Figure 17. Temperature dependence of the resonance frequencies of the main line and satellite lines of tetrahedral Fe³⁺ ions for Fe_{3-x}Al_xO₄ with x=0; 0.005 and 0.03 above the Verwey transition. The line with the highest frequency corresponds to Fe (A) with only Fe-nearest neighbors on the B sublattice. Remaining lines are satellites (one neighbour Fe substituted by Al).

Figure 18. Temperature dependence of the resonance frequencies of the main lines of octahedral (B) iron ions for $Fe_{3-x}Al_xO_4$ with x=0; 0.005 and 0.03 above the Verwey transition.

Temperature dependences of the halfwidths Δ of A and B resonance lines taken at a half of their amplitudes are displayed in Figure 19 for pure and substituted samples.

In a broad interval of temperatures, the Δ (T) dependence is flat. The linewidths for x=0.005 are slightly larger compared to x=0. The linewidths of x=0.03 crystal are considerably larger compared with x=0 and x=0.005 crystals. Moreover, they are much stronger temperature-dependent at temperatures above the spin-reorientation transition and their values cannot be explained by the anisotropy of the hyperfine field, provided that the anisotropy is similar as in compounds with lower content of Al. The most likely scenario is that with lowering of the temperature, the electron density in x=0.03 compound becomes inhomogeneous, leading to a

broader distribution of the hyperfine fields. The results presented have been published [Gama02].

Figure 19. Fe_{3-x}Al_xO₄. Temperature dependences of the widths Δ of the resonance lines taken at a half of their amplitudes for Fe_{3-x}Al_xO₄ with x=0; 0.005 and 0.03. Triangles and circles for B sites correspond to temperatures below and above the spin-reorientation transition, respectively. Dotted symbols correspond to the Al concentration x=0.03; full symbols to x=0.005 and open symbols to x=0.

5.7. NMR of ⁵⁷Fe, ⁶⁹Ga and ⁷¹Ga in Ga substituted magnetite

The influence of Ga substitution is very interesting with regard to its trivalent state. It was surprising that substitution of Ga lowers T_V much weaker than trivalent Al substitution, for example. This fact was explained by the assumption that Al^{3+} ions occupy preferentially B sites while Ga^{3+} ions enter preferentially A-sites.

The single crystal $Fe_{3-x}Ga_xO_4$, x=0.05 has been measured in zero external magnetic field at temperatures T = 4.2K, 77K and 273K. The NMR spectrum measured in our gallium substituted sample at 273 K, well above the Verwey temperature, is shown in Figure 20.

Comparing with the spectra of the pure sample [Nova00] one can unambiguously resolve the ⁵⁷Fe NMR lines of A-, B₁-, and B₂-sites. For additional two lines at 70.78 MHz and 55.74 MHz one can calculate the frequency ratio $f_{70} / f_{55} \cong 1.27$. This value exactly corresponds to the ratio of γ -factors of both Ga isotopes: ⁷¹ $\gamma / {}^{69}\gamma \cong 1.27$. In addition, taking into account that the ratio of the line amplitudes agrees with the ratio of natural isotopic abundance of both isotopes, we have assigned those lines to ⁷¹Ga and ⁶⁹Ga in tetrahedral A sites. The weak broadening of both lines could be explained by a quadrupolar interaction caused by the local failure of the cubic symmetry of A-sites induced by the Ga substitution.

The small satellite S_1 at 62.1 MHz corresponds to the iron resonance in B_1 site in the nearest vicinity of which one A-sited iron was replaced by Ga. We can conclude that in our sample Ga ions are predominantly located at *a* sites. The concentration of Ga ions entering B sites has been estimated to be less than 0.006 [Chlan].

The ⁵⁷Fe NMR spectra measured in Ga substituted sample below the Verwey transition at 77 K and 4.2 K revealed the structure very similar to those measured in the pure magnetite [NovaICF00].

Figure 20. The 69 Ga, 71 Ga and 57 Fe NMR spectra of the single crystal Fe_{3-x}Ga_xO₄ with x=0.05 measured at 273 K.

Figure 21. The ⁶⁹Ga, ⁷¹Ga NMR spectra of the single crystal Fe_{3-x}Ga_xO₄, x=0.05 at 4.2 K and 77 K.

NMR spectra of Ga measured at 77K and 4.2K are shown in the Figure 21. The line structures in the middle part of the spectra (68-74 MHz) and at the lower frequency side (49-51 MHz) are created by signals of both Ga and Fe nuclei. Remaining lines in the Fig.21 have been most likely induced by Ga nuclei. One can easily identify two groups of those lines (see Fig.21) connected by the ratio of γ -factors of two Ga isotopes. The pattern constituted by these lines is very similar to that of iron lines from A-sites. So it seems that the structure of the Ga spectrum is, similarly to the iron spectrum, created by the differences of the local A-sites surroundings below the Verwey temperature. These results have been published [Koho05, Chlan].

6. Summary

The present thesis is devoted to the studying of hyperfine interactions in magnetic iron oxides, namely YIG and magnetite, by means of Nuclear Magnetic Resonance method. The subject of the thesis is to find out and interpret a response induced by nonmagnetic substitutions (Al³⁺, In³⁺, La³⁺, Ca²⁺, Bi³⁺, Ga³⁺) in NMR spectra and relaxations and to contribute to explanation of the influence of the substitutions on a change of hyperfine parameters of the systems. The studied substitutions have been chosen to enter different cationic sublattices of the systems.

In the case of YIG system:

1) An effect of Al substitution on ⁵⁷Fe hyperfine field anisotropy has been systematically studied by means of NMR measurements in an external magnetic field. Analysis of the data yielded the changes of hyperfine parameters induced by Al and enabled to compare the influences of changes in ionic radii and valencies.

2) Effects of trivalent cation substitutions (Al³⁺(*d*), In³⁺(*a*), La³⁺(*c*) on nuclear magnetic relaxations of ⁵⁷Fe nuclei have been studied by measurements in zero external magnetic fields.

Decrease of spin-lattice and spin-spin (except for the higher In content) relaxation rates with increasing concentrations of substituents has been found.

3) Effect of $Ca^{2+}(c)$ substitution on ⁵⁷Fe NMR spectra and relaxations has been studied. After an initial constant region, a decrease of a spin-lattice relaxation rate has been observed with increasing Ca content. The onset of the relaxation rate decrease is supposed to correspond to an induced decrease of an amount of Fe²⁺ ions, while charge compensation is supposed to be reached by other mechanisms for lower calcium contents.

4) Hyperfine interaction at iron nuclei in a bismuth-yttrium iron garnet system $Bi_xY_{3-x}Fe_5O_{12}$ has been studied. The ⁵⁷Fe NMR spectrum of the film (prepared by IBS) with nominal composition of completely substituted, i.e. bismuth iron garnet (BIG), has been obtained and has confirmed the garnet structure of the sample. It was expected according to the X-ray diffraction experiments, that the replacement of Y^{3+} (*c*) by Bi^{3+} would lead to a shortening of Fe-O distances in the tetrahedrons while in octahedrons they would lengthen. In this respect the comparison of iron hyperfine fields in BIG and YIG was interesting since the higher covalence related to shorter interatomic distances is believed to lower resonant frequencies. The found spectral shifts of BIG with respect to YIG revealed, however, just the opposite tendency, indicating a substantial impact of the bismuth electron structure on electron transfer in Fe-O-cation triads.

In the case of magnetite system:

1) Symmetry consideration has been performed predicting the number and relative intensities of satellite lines in ⁵⁷Fe NMR spectra of substituted magnetites.

2) Spectra of Al-substituted magnetite below, around and above the Verwey transition have been studied. Below the Verwey temperature, the broadening of the main lines with increasing Al content has been detected, their temperature dependencies have been obtained. The decrease of the Verwey temperature with increasing Al content was found to be in agreement with electric conductivity measurements. It has been also found that the Al substitution significantly affects the relaxation times of resonating iron nuclei. The possible reasons of differences in temperature behaviour of relaxation times of pure and substituted magnetite have been pointed out comparing presented data with results of other experimental methods and estimations. Above the Verwey transition, temperature dependences of main and satellite lines of Al substituted magnetite have been systematically studied as well as their behaviour in the vicinity of spin-reorientation transition. Studying of temperature dependences of linewidths of main resonance lines revealed that for higher Al contents their values cannot be explained by the anisotropy of the hyperfine field. As the most likely scenario it was suggested that the electron density becomes inhomogeneous as $T \rightarrow T_V$.

3) The studying of Ga substituted magnetite below and above the Verwey transition temperature (T_v) has revealed a well-resolved structure of Ga lines, assigned to ⁶⁹Ga and ⁷¹Ga isotopes. The Ga lines found as well as ⁵⁷Fe spectra indicate a preference of Ga substitution for the tetrahedral *a* sites. These results on Al and Ga substituted magnetites support the assumption of stronger effect of Al substitution on the Verwey transition because of the preference of Al substitution for octahedral *b* sites in contrast to Ga substitution.

The experimental results obtained in this thesis and their analyses present a rich set of new information on the behavior of a ferrimagnetic iron oxides containing nonmagnetic substitutions as well as advanced information on hyperfine interactions and NMR in these systems. The collected data and findings can be used in future investigations of electronic structure and exchange interactions in magnetic oxides.

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