

Nuclear magnetic resonance of ^{57}Fe in bismuth–yttrium iron garnets

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Hyperfine magnetic interaction at iron nuclei in a bismuth–yttrium iron garnet system $\text{Bi}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$, $0 \leq x \leq 3$, was studied using nuclear magnetic resonance. ^{57}Fe NMR spectra were measured by spin echo technique at 4.2 K in zero external magnetic field. The spectrum of bismuth iron garnet film $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ prepared by ion beam sputtering corresponds to the iron garnet structure having magnetization along [111] direction: two a -lines at 74.00 MHz and 75.05 MHz with the intensity ratio 1 : 3 assigned to octahedral iron sites and a single d -line at 66.46 MHz of tetrahedral iron sites. The resonant frequencies are slightly shifted in comparison with yttrium iron garnet $\text{Y}_3\text{Fe}_5\text{O}_{12}$. Satellite lines or line broadening appear in spectra of partially substituted samples due to a distribution of Y^{3+} and Bi^{3+} cations in dodecahedral sites.

1. Introduction Nuclear magnetic resonance (NMR) is a method sensitive to the local properties of magnetic materials. It has been applied to YIG containing various substituents or intrinsic substituting defects on iron and yttrium cation sites [1–6]. NMR spectrum of ^{57}Fe nuclei for an ideal YIG structure contains a single d -line assigned to iron ions in tetrahedral crystallographic sites and two lines a_1 and a_2 having integral intensity ratio 1 : 3 which correspond to octahedral sites. Spectrum of a -sites splits into two lines because of the magnetic nonequivalency of a -sites with respect to the [111] direction of magnetization. Resonant frequencies are proportional to the local magnetic field at iron nuclei by gyromagnetic ratio 1.377 MHz/T.

Cationic substitution modifies hyperfine magnetic field at nuclei in its vicinity. Low concentration of substitution gives rise to the characteristic satellite lines which appear in the spectrum besides the main lines (corresponding to the nuclei with no substituent in their vicinity) supposing that the induced change of frequency exceeds the linewidth. In case of a 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 paper we report on ^{57}Fe NMR spectra dependence on the replacement of Y^{3+} in dodecahedral sites by Bi^{3+} . The Bi^{3+} substitution is well known to modify iron garnets magnetic properties and especially to enhance magneto-optical effects. Because of the considerable difference in ionic radii of Y^{3+} (0.1019 nm) and Bi^{3+} (0.117 nm) [7] a bulk sample of bismuth iron garnet (BIG) cannot be

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synthesized. Nevertheless, techniques of film preparation by direct epitaxial growth from vapour phase proved to be successful [8].

2. Experimental BIG single crystal film and bismuth–yttrium iron garnet single crystal film of high Bi concentration ($x = 2.75$) were prepared by ion beam sputtering (IBS). Characteristics of these samples are given in Table 1. Three comparative samples with low x were used: pure single crystal YIG film grown onto gadolinium gallium garnet substrate by liquid phase epitaxy (LPE), bulk single crystal ($x = 0.02$) grown from flux and polycrystalline sample ($x = 0.15$) prepared by ceramic technique.

NMR spectra were recorded at 4.2 K in zero external magnetic field. Spin echo pulse sequence with coherent data summation and Fourier transformation was employed.

3. Results and discussion Spectra of $\text{Bi}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$ ($x = 0, 0.02, 0.15, 2.75$ and 3) are plotted in Fig. 1. 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 $\sim 1 : 3$) assigned to iron in a -sites. This scheme of a spectrum is characteristic for an iron garnet having magnetization direction along $\sim [111]$. Comparison of resonant frequencies of BIG and YIG films is given in Table 2. 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.

Keeping in mind that NMR yields more precise values of the hyperfine fields, a good agreement is found between the hyperfine field on iron nuclei in BIG as well as in YIG obtained from our NMR spectra at 4.2 K and by Mössbauer conversion electron spectroscopy at 6 K [9].

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 [3, 4]. 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 case of the a -spectrum the isotropic part is a weighted mean of the a_1 and a_2 resonant frequencies and the anisotropy can be expressed by means of the splitting δ_a between a_1 and a_2 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.

X-ray diffraction performed for yttrium-bismuth [10] and bismuth iron garnets [11] indicates that replacement of Y^{3+} by Bi^{3+} leads to a shortening of $\text{Fe}-\text{O}^{2-}$ 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 in-

Table 1 Characterisation of iron garnet films prepared by IBS.

x	3	2.75
Target composition	$\text{Bi}_3\text{Fe}_5\text{O}_{12}$	$(\text{Y}_{0.25}\text{Bi}_{2.75})_{2.44/3}\text{Fe}_{4.56}\text{O}_{12}$
Substrate ((111) plane)	$\text{Nd}_3\text{Ga}_5\text{O}_{12}$	$(\text{GdCa})_3(\text{GaMgZr})_5\text{O}_{12}$
Substrate lattice constant (nm)	1.2509	1.2499
Thickness (μm)	2.75	1.75
Lattice constant (nm)	1.2629	1.2638
Faraday rotation ($^\circ/\mu\text{m}$) at 635 nm, room temperature	−5.35	−5.1

Table 2 Comparison of ^{57}Fe NMR spectral parameters of BIG and YIG films

	f_d (MHz)	Δ_d (MHz)	f_{a1} (MHz)	Δ_{a1} (MHz)	f_{a2} (MHz)	Δ_{a2} (MHz)	I_a (MHz)	δ_a (MHz)
BIG	66.46	0.57	74.00	~ 0.40	75.05	0.50	74.79	1.05
YIG	64.96	0.025	75.06	0.023	76.06	0.041	75.81	1.00

($f_d, f_{a1}, f_{a2} \dots$ resonant frequencies of d, a_1 and a_2 lines; $\Delta_d, \Delta_{a1}, \Delta_{a2} \dots$ linewidths;
 $I_a = (f_{a1} + 3 f_{a2})/4$, $\delta_a = f_{a2} - f_{a1}$)

creasing 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 a Bi substituent in the nearest c -neighbourhood of the resonating iron. 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 a_1 -main line (shifted by -0.215 MHz), and three satellite lines near a_2 , two of them overlap (shifted by -0.16 MHz and, for the double satellite, by -0.31 MHz).

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 Bi^{3+} . 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 inhomoge-

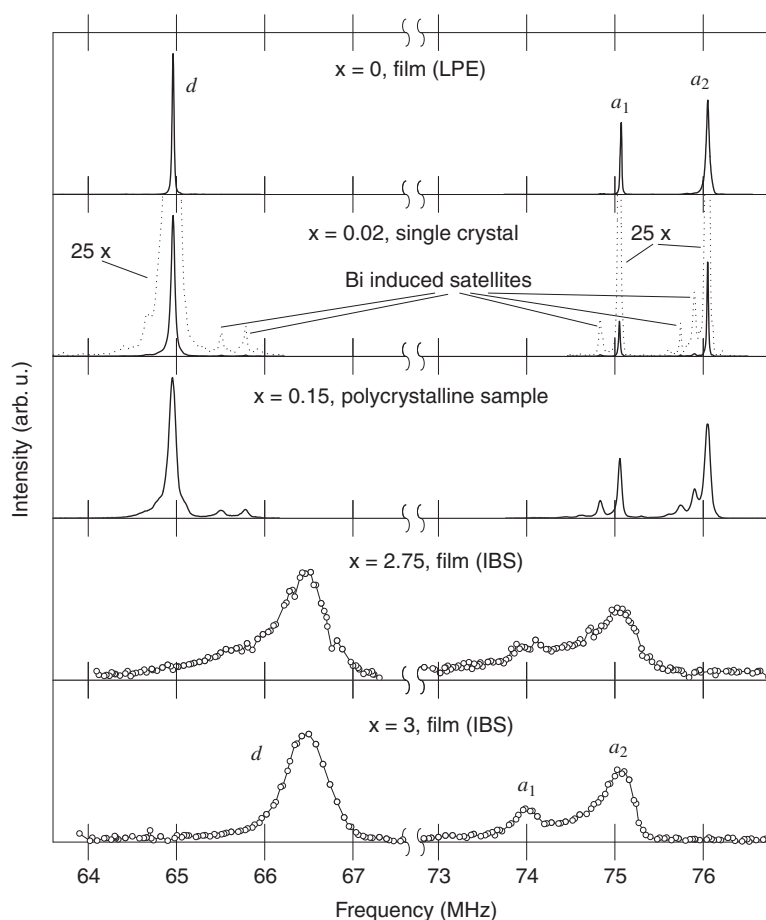


Fig. 1 ^{57}Fe NMR spectra of iron garnets $\text{Bi}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$ measured at 4.2 K in zero external magnetic field.

neous line broadening in the spectrum of a film with $x \sim 2.75$ disables detailed analysis, yet still the mirror position of satellite lines is evident at least in the spectrum of d -sites.

Assuming that the additivity principle is valid for a contribution of individual $\text{Bi} \rightarrow \text{Y}$ substitutions in the neighbor c -site of the resonating iron nucleus to its resonant frequency, the NMR frequencies for BIG can be predicted on the basis of the YIG main lines frequencies and the shifts of Bi^{3+} induced satellites observed in spectra of the yttrium-bismuth iron garnets with low Bi content. Considering numbers of the nearest c -neighbours of the d and a iron sites and neglecting small differences in dipolar and Lorentz magnetic fields we obtained for BIG (in MHz): $f_d \equiv I_d = 66.31$, $f_{a1} = 73.76$, $f_{a2} = 74.79$, $I_a = 74.53$, $\delta_a = 1.03$. These values differ somewhat from those obtained from the experiment (see Table 2) predominately in the isotropic parts for which the estimated values are systematically lower.

4. Conclusions The ^{57}Fe NMR spectrum measured in a single crystal film of BIG prepared by IBS reflects the garnet crystal structure having magnetization along $\sim[111]$ direction. The modification of a hyperfine interaction induced by replacement of Y^{3+} with Bi^{3+} was found. It evidences a considerable difference in the electronic structure of these cations.

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