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## HYPERFINE FIELD IN YIG WITH CHARGED SUBSTITUTION

J. KOHOUT<sup>a</sup>, H. ŠTĚPÁNKOVÁ<sup>a</sup>, J. ENGLISH<sup>a</sup>, P. NOVÁK<sup>b</sup>, M. KUČERA<sup>a</sup>  
AND K. NITSCH<sup>b</sup>

<sup>a</sup>Faculty of Mathematics and Physics, Charles University  
180 00 Prague 8, V Holešovičkách 2, Czech Republic

<sup>b</sup>Institute of Physics, Academy of Sciences  
Cukrovarnická 10, 16 253 Prague 6, Czech Republic

<sup>57</sup>Fe NMR spectra were measured on thin films of yttrium iron garnet with divalent (Ca<sup>2+</sup>) and tetravalent (Ge<sup>4+</sup>) cation substitutions using the spin echo technique at 4.2 K. A series of Y<sub>3-x</sub>Ca<sub>x</sub>Fe<sub>5-x</sub>Ge<sub>x</sub>O<sub>12</sub> samples with  $0 \leq x \leq 0.05$  was prepared by an epitaxial growth from BaO/B<sub>2</sub>O<sub>3</sub>/BaF<sub>2</sub> flux on gadolinium gallium garnet substrate. Satellite lines corresponding to the iron ions having the Ge<sup>4+</sup> and Ca<sup>2+</sup> in their neighbourhood were identified. The sample with the germanium content of  $x(\text{Ge}) = 0.004$  and (110) substrate orientation was used for a detailed study: NMR spectra of this sample were measured in an external magnetic field of 0.1 T applied along several directions in the plane of the film. The modification of the isotropic part and the anisotropy tensor of the hyperfine interaction caused by the Ge<sup>4+</sup> substituent were obtained from the experimental data. The results were compared with those previously reported for trivalent substitution (Ga<sup>3+</sup>).

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### 1. Introduction

Proportionality between the <sup>57</sup>Fe NMR frequency and the local magnetic field at the resonating nucleus enables determination of the hyperfine field on iron sites in magnetic systems with precision given by the NMR line widths. NMR lines of both octahedral (*a*) and tetrahedral (*d*) Fe<sup>3+</sup> ions in yttrium iron garnet (YIG) are relatively narrow (10<sup>0</sup>–10<sup>1</sup> kHz at liquid helium temperature in the case of high quality, nominally pure crystal) and lie in different frequency regions (≈ 65 MHz for *d*-sites, ≈ 75 MHz for *a*-sites). YIG is therefore a suitable system for studies of the hyperfine field and its changes induced by substituents in the vicinity of the resonating nucleus.

Low concentration of the substitutions in YIG give rise to weak but resolved satellite lines in NMR spectra, corresponding to those <sup>57</sup>Fe nuclei which have a single substituent in their near vicinity. Analysis of the NMR satellite structure

provides information on the modification of the hyperfine field and its anisotropy caused by the substitution. This approach has been used in our previous studies to determine the changes in the hyperfine interaction due to the  $Y^{3+}$  impurity on the  $a$ -site (yttrium antisite defect) [1–3] and  $d$ -sites ( $Ga^{3+}$ ) [4]. In the present paper the effect of the charged substitution on the  $d$ -sites ( $Ge^{4+}$  cation) is described.

## 2. Results and discussion

YIG films with Ge and Ca substitutions were prepared by an epitaxial growth from  $BaO/B_2O_3/BaF_2$  flux on the gadolinium gallium garnet (GGG) substrates of (111), (110) and (100) orientations.  $^{57}Fe$  NMR spectra were measured at 4.2 K using spin-echo technique and subsequent Fourier transform. Selected  $a$ -site spectra from the series of samples, in which the content of  $Ge^{4+}-Ca^{2+}$  was gradually increased, are shown in Fig. 1. The most pronounced satellites are caused by a single substitution either of  $Fe^{3+}$  in the nearest  $d$ -site by  $Ge^{4+}$ , or of  $Fe^{3+}$  in the nearest  $a$ -site by  $Y^{3+}$  (intrinsic antisite defect), or of  $Y^{3+}$  in the nearest dodecahedral ( $c$ -) site by  $Ca^{2+}$ . Assignment of the satellite lines was based on their intensity changes with the increasing  $Ge^{4+}-Ca^{2+}$  content, and on the previously identified satellites caused by the antisite defects and  $Ca^{2+}$  substitution [1, 3, 5, 6]. The interpretation of the satellite structure was confirmed by analysis of the NMR spectra measured in an external magnetic field.

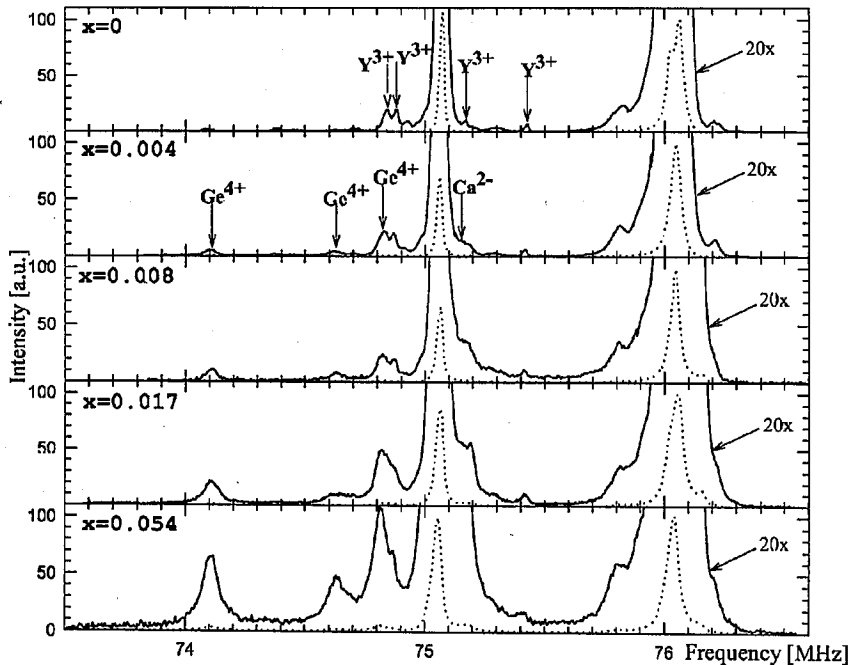


Fig. 1.  $^{57}Fe$  NMR ( $a$ -site) spectra of  $Y_{3-x}Ca_xFe_{5-x}Ge_xO_{12}$  thin films measured at 4.2 K. Satellite lines induced by the  $Ge^{4+}$ ,  $Ca^{2+}$  substituents, and  $Y^{3+}$  antisite defects are denoted.

The sample with the germanium content  $x(\text{Ge}) = 0.004$  and (110) substrate orientation was chosen for study in an external magnetic field. NMR spectra were measured in the field of 0.1 T applied in several directions parallel to the plane of the YIG film. Angular dependencies of the NMR frequencies were analysed for the main lines and for the satellites corresponding to the crystallographically equivalent configurations of the resonating iron on  $a$ -site and  $\text{Ge}^{4+}$  substituent on one of the nearest  $d$ -sites. Resonance frequencies  $f_s$  of the particular set  $s$  depend on the magnetization direction  $n$ :

$$f_s = I + n\hat{G}_s^{-1}\hat{A}\hat{G}_s n, \quad (1)$$

where the terms with higher powers of  $n$  were neglected.  $I$  is an isotropic term and  $\hat{A}$  is a second-order symmetric traceless tensor, that describes local magnetic field anisotropy for the reference configuration ( $s = 1$ ). Matrices  $\hat{G}_s$  represent the point-symmetry operations transforming the reference configuration to the other configurations of the set.

Least-squares fit according to Eq. (1) (Fig. 2) provided the values of  $I$  and  $\hat{A}$  for the  $a$ -sites without substituent in their neighbourhood (denoted by index 0) and for  $a$ -sites having  $\text{Ge}^{4+}$  on one of the nearest  $d$ -sites (index Ge):

$$I_0 = 75.816 \text{ MHz}, \quad I_{\text{Ge}} = 74.681 \text{ MHz}, \quad (2)$$

$$\hat{A}_0 = \begin{pmatrix} 0 & -377 & -377 \\ -377 & 0 & -377 \\ -377 & -377 & 0 \end{pmatrix}, \quad \hat{A}_{\text{Ge}} = \begin{pmatrix} 164 & -82 & -321 \\ -82 & -373 & -451 \\ -321 & -451 & 209 \end{pmatrix} \text{ kHz}.$$

From the fit we simultaneously obtained that the film plane deviates by an angle of  $2.0^\circ$  from the nominal orientation (110).

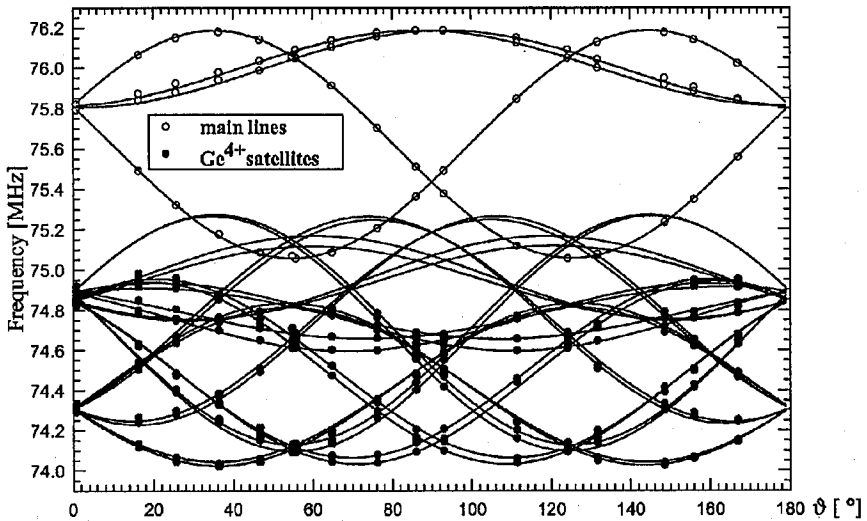


Fig. 2. Angular dependence of the  $^{57}\text{Fe}$  ( $a$ -site) NMR frequencies in  $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Ge}_x\text{O}_{12}$ ,  $x = 0.004$  (experimental points and fitted curves;  $\vartheta$  is the angle between the magnetization and [001] direction).

The local magnetic field on iron nucleus is a superposition of the hyperfine and the dipolar field. The tensor of the latter interaction can be directly calculated, and by subtracting it, the tensor of hyperfine field anisotropy can be obtained. The experiment does not, unfortunately, allow us to decide unambiguously which matrix (from the set of  $\hat{G}_s^{-1}\hat{A}\hat{G}_s$  matrices) corresponds to the configuration of the resonating nucleus and Ge substituent, chosen for the calculation of  $\hat{A}_{\text{dip}}$ . We tried to solve this problem in a similar way as in [4] where an analogous ambiguity occurs. The six possible hf anisotropy tensors were confronted with an "independent bond" model [7], according to which the difference  $\Delta\hat{A}_{\text{hf}}$  between the hf anisotropy tensor of the main and the satellite line should be a uniaxial tensor with the axis lying in the Fe-O direction of the Fe-O-Ge triad. Just one of the possibilities, corresponding to the  $\Delta\hat{A}_{\text{hf}}$  value

$$\Delta\hat{A}_{\text{hf}} = \begin{pmatrix} -103 & -57 & -109 \\ -57 & -53 & 74 \\ -109 & 74 & 155 \end{pmatrix} \text{ kHz} \quad (3)$$

did not contradict excessively to the "independent bond" model, having the principal values of 224, -152, and -72 kHz and the principal axis (corresponding to the largest principal value) declined by 11° from the Fe-O direction.

Comparing our results with those previously obtained in [4] for the Ga<sup>3+</sup> substitution on *d*-sites, we can conclude that the "charged" Ge<sup>4+</sup> substitution induces slightly larger change of the isotropic part of the hyperfine interaction, but the hyperfine field anisotropy is less modified.

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