Vol. **118** (2010) *ACTA PHYSICA POLONICA A* No. 5

14th Czech and Slovak Conference on Magnetism, Košice, Slovakia, July 6–9, 2010

Distribution of Zn in Magnetoelectric Y-Type Hexaferrite

K. Kouřil[a,*], V. Chlan[a], H. Štěpánková[a], A. Telfah[a], P. Novák[b], K. Knížek[b],
Y. Hiraoka[c] and T. Kimura[c]

[a]Charles University in Prague, Faculty of Mathematics and Physics
V Holešovičkách 2, 18000, Praha 8, Czech Republic

[b]Institute of Physics ASCR, Cukrovarnická 10, 162 53 Praha, Czech Republic

[c]Division of Materials Physics, Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka 560–8531, Japan

We employ ^{67}Zn NMR to study distribution of Zn^{2+} in cationic sites of magnetoelectric Y-type hexaferrite single crystal, $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$. The experimental data are interpreted by comparison with NMR spectra simulated from *ab initio* calculated hyperfine parameters.

PACS numbers: 61.05.Qr, 75.85.+t, 75.50.Gg, 31.15.E−

1. Introduction

Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ is a noncollinear insulating ferrimagnet, which in external magnetic field undergoes several phase transitions. One of the phases is known to exhibit magnetoelectricity at low temperatures [1]. It is promising that this phase persists up to room temperature [2], however, electrical conductivity increases rapidly with temperature, soon concealing the ferroelectric order.

Y-type hexaferrite structure contains four octahedral and two tetrahedral sites occupied by small cations. The octahedral sites are fully occupied by Fe^{3+}, while the tetrahedral sites contain both Fe^{3+} and Zn^{2+}. The crystal structure can also be viewed as built of alternating spinel (S) and T blocks stacked along the hexagonal axis [3]. Each block contains one type of the tetrahedral site. The distribution of Zn^{2+} and Fe^{3+} between the blocks is described by parameter γ: S block contains γ of Zn^{2+} and $(1-\gamma)$ of Fe^{3+}, while the opposite holds for the T block.

Magnetoelectricity is sensitive to fine alterations of the system, e.g. changes of composition (Ba:Sr ratio), stoichiometry (oxygen content) and cation distribution (γ). It is desirable to explore possibilities of determination and control of these parameters. In this work we focus on the determination of the γ parameter, which is expected to have a strong influence on electrical conductivity of the system [4]. We employed nuclear magnetic resonance of ^{67}Zn nuclei in order to estimate γ and its changes induced by thermal treatment. Further we performed *ab initio* calculations of $Ba_2Zn_2Fe_{12}O_{22}$ electronic structure, which provided us with insight into the experimental data.

2. Experimental

Single crystal of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ was prepared using Na_2O–Fe_2O_3 flux technique in Pt crucibles [5] and cut into two parts of approximately same size. One part was annealed for 7 days in oxygen atmosphere at 900 °C and then slowly cooled (1 °C per minute), while the other part was left as grown for reference. Finally plane parallel plates (≈ 0.5 mm thick and with areas of ≈ 5 mm^2) were prepared from each part. Both plates were characterized by NMR.

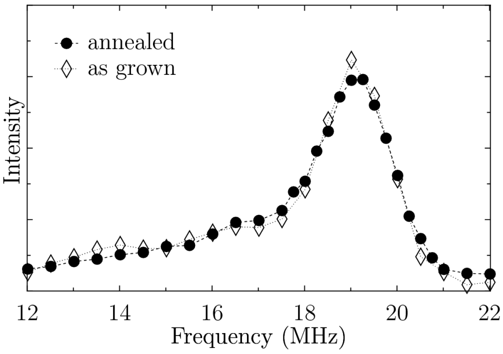

Fig. 1. Experimental NMR spectra of ^{67}Zn. The spectra have been normalized to unit area.

We used pulse coherent NMR spectrometer with the Fourier transform (Bruker Avance) and a homemade tunable NMR probe to measure frequency-swept spectra of

---

[*] corresponding author; e-mail: `karel.kouril@mff.cuni.cz`

^{67}Zn resonance. The spectra were recorded at 4.2 K in zero static external field, rf field was perpendicular to the hexagonal plane of the sample. Experimental NMR spectra of ^{67}Zn resonance are shown in Fig. 1.

3. Simulation of ^{67}Zn NMR spectra

In order to extract the parameter γ from experiment we simulated NMR spectra for various values of γ. The simulations were based on *ab initio* calculations of electron structure of $Ba_2Zn_2Fe_{12}O_{22}$ using WIEN2k [6]. In contrast to our previous paper [7] the crystal structure was fully relaxed — both lattice parameters (c/a and unit cell volume) and internal structural parameters were optimized. The hyperfine magnetic fields and electric field gradients on Zn nuclei were calculated for $\gamma = 0$, 1/2, 1 and linearly interpolated in between. The NMR spectra were simulated from energies and relative intensities of ^{67}Zn nuclear magnetic transitions with suitable line broadening. Simulated NMR ^{67}Zn spectra for varying γ are shown in Fig. 2 with contributions of S and T blocks denoted.

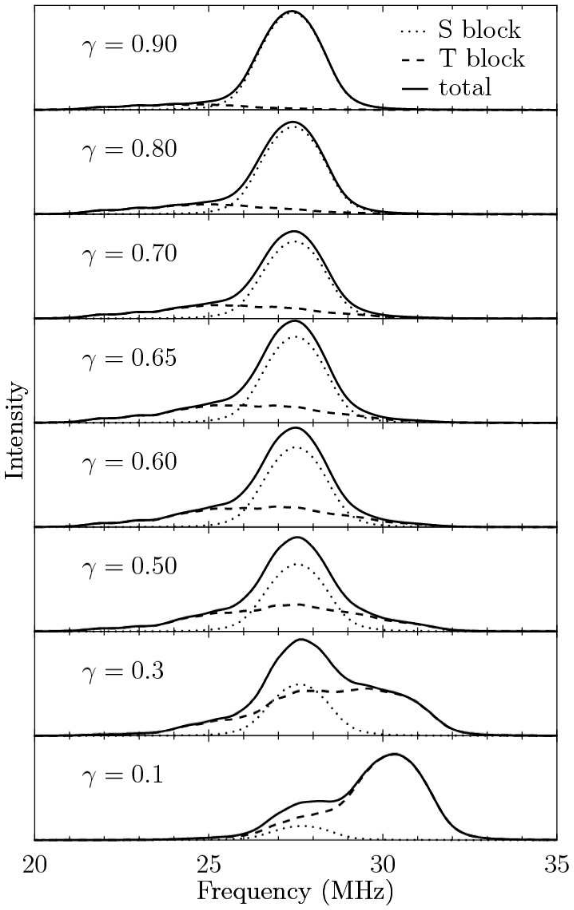

Fig. 2. Simulated ^{67}Zn NMR spectra for various values of γ parameter.

4. Results

The experimental ^{67}Zn NMR spectra (Fig. 1) resemble the shape of simulated NMR profiles (Fig. 2), allowing direct comparison despite the shifted frequency scale. The calculations have shown that resulting ^{67}Zn NMR lineshapes consist of two overlapping components: a narrow one, originating from resonance of the nuclei in the S block, and a broad one, from the nuclei in the T block. Further one can see that the position and width of the S block contribution is nearly insensitive to the value of γ, while the T block contribution varies significantly. The dependence of the spectral shape on γ can be used to determine its value from an experimental lineshape. The experimental data can thus be assigned to the simulated spectrum of $\gamma \approx 0.65$.

5. Conclusions

Comparison of measured NMR spectra and simulated lineshapes based on *ab initio* calculated hyperfine parameters enabled us to estimate the value of the γ parameter. The differences in experimental spectra induced by the performed thermal treatment are subtle and the change of γ probably does not exceed 10%.

Acknowledgments

This work was supported by the project IAA100100803 of the Grant Agency of the AS CR and by the project MS0021620834 of the Ministry of Education of the Czech Republic. The calculations were performed using *dorje* cluster at Institute of Physics of the AS CR.

References

[1] T. Kimura, G. Lawes, A.P. Ramirez, *Phys. Rev. Lett.* **94**, 137201 (2005).

[2] Y.S. Chai, S.H. Chun, S.H. Haam, Y.S. Oh, I. Kim, K.H. Kim, *New J. Phys.* **11**, 073030 (2009).

[3] M. Sugimoto, in: *Ferromagnetic Materials*, Ed. E.P. Wolfharth, Vol. 3, North-Holland, Amsterdam 1982, p. 397.

[4] K. Knížek, P. Novák, M. Küpferling, *Phys. Rev. B* **73**, 153103 (2006).

[5] N. Momozawa, M. Mita, H. Takei, *J. Cryst. Growth* **83**, 403 (1983).

[6] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties*, Karlheinz Schwarz, Techn. Universität Wien, Austria 2001.

[7] K. Kouřil, V. Chlan, H. Štěpánková, P. Novák, K. Knížek, J. Hybler, T. Kimura, Y. Hiraoka, J. Buršík, *J. Magn. Magn. Mater.* **322**, 1243 (2010).