Distribution of Zn in Magnetoelectric Y-Type Hexaferrite

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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$_2$Fe$_{12}$O$_{22}$. The experimental data are interpreted by comparison with NMR spectra simulated from ab initio calculated hyperfine parameters.

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1. Introduction

Y-type hexaferrite Ba$_{0.5}$Sr$_{1.5}$Zn$_2$Fe$_{12}$O$_{22}$ is a non-collinear 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 $\gamma$: S block contains $\gamma$ 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 ($\gamma$). It is desirable to explore possibilities of determination and control of these parameters. In this work we focus on the determination of the $\gamma$ 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 $\gamma$ and its changes induced by thermal treatment. Further we performed ab initio calculations of Ba$_2$Zn$_2$Fe$_{12}$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$_2$Fe$_{12}$O$_{22}$ was prepared using Na$_2$O–Fe$_2$O$_3$ 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.](image-url)
In order to extract the parameter $\gamma$ from experiment we simulated NMR spectra for various values of $\gamma$. The simulations were based on \textit{ab initio} calculations of electron structure of Ba$_2$Zn$_2$Fe$_{12}$O$_{22}$ using WIEN2k \cite{6}. In contrast to our previous paper \cite{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 $^{67}\text{Zn}$ nuclear magnetic transitions with suitable line broadening. Simulated NMR $^{67}\text{Zn}$ spectra for varying $\gamma$ are shown in Fig. 2 with contributions of S and T blocks denoted.

![Fig. 2. Simulated $^{67}\text{Zn}$ NMR spectra for various values of $\gamma$ parameter.](image)

### 4. Results

The experimental $^{67}\text{Zn}$ 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 $^{67}\text{Zn}$ 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 $\gamma$, while the T block contribution varies significantly. The dependence of the spectral shape on $\gamma$ 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 \textit{ab initio} calculated hyperfine parameters enabled us to estimate the value of the $\gamma$ parameter. The differences in experimental spectra induced by the performed thermal treatment are subtle and the change of $\gamma$ probably does not exceed 10%.

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### References