# CHIRAL MAGNETIC STRUCTURE OF Y-TYPE $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ HEXAFERRITE IN INTERMEDIATE PHASE

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## Abstract

Magnetic structure in intermediate-II and intermediate-III phases of Y-type hexaferrite single crystal $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ was investigated using neutron diffraction with polarization analysis. It was found that both phases have chiral magnetic structures. This shows that in contrast to previous assumptions, intermediate-II phase has transverse conical spin structure similar to the intermediate-III phase. Therefore, magnetic field induced ferroelectric state may exist also in the intermediate-II phase of Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite. Obtained results provide important insight into the recent observations of room temperature magnetoelectric coupling in Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite.

## 1. Introduction

Hexaferrites are ferrites with hexagonal structures with alkaline earth metal and transition metal sites, extensively used in permanent magnets and in microwave absorber applications [1]. High temperature (above 100 K) magnetoelectric coupling discovered during last decade in this class of compounds generated possibility of numerous applications in data storage with added flexibility of tuning magnetoelectric properties by substituting the transition metal as well as alkaline earth metal sites [2, 3]. Hexaferrites divided into different classes M, Y, Z, X, U, and W with rich magnetic phase diagram, were reported to exhibit magnetoelectric coupling at much higher temperature. Out of these compounds Y-type $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ was the first hexafferite in which a magnetic field-induced ferroelectric phase with significant magnetoelectric (ME) coupling was found [4].

The crystal structure of Y-type hexaferrite consists of alternately stacked spinal (S) and tetragonal (T) blocks crystallizing in $R\bar{3}m$ space group [4]. Magnetic structure is best described in terms of the block spin model, where crystallographic unit cell is divided into large ( $\mu_L$ ) and small ( $\mu_S$ ) spin blocks. Superexchange interactions at the spin block boundary can be modified either by transition metal site substitution or by changing the alkaline earth metal sites.

In $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$, due to the Sr substitution magnetic structure changes from collinear to in plane spiral ordering [4]. Upon applying field perpendicular to (001) , six metamagnetic steps in the magnetization curves were observed [5]. The centrosymmetric space

group does not allow any polarization, but scenario changes when magnetic field is applied perpendicular to *c*-axis. Magnetic field driven ferroelectric polarization was observed in the intermediate-III metamagnetic phase where a "2-fan" planner structure shown in **Figure 1a** was earlier reported [**5, 6**]. However, later it was shown that the magnetic field driven ferroelectricity cannot be explained in the proposed fanlike structure [**6**]. Instead, it can exist in a transverse conical spin structure shown in **Figure 1b**. Such magnetic structure has chirality which is consistent with the inverse Dzyaloshinski–Moriya mechanism of ferroelectricity [**2**].

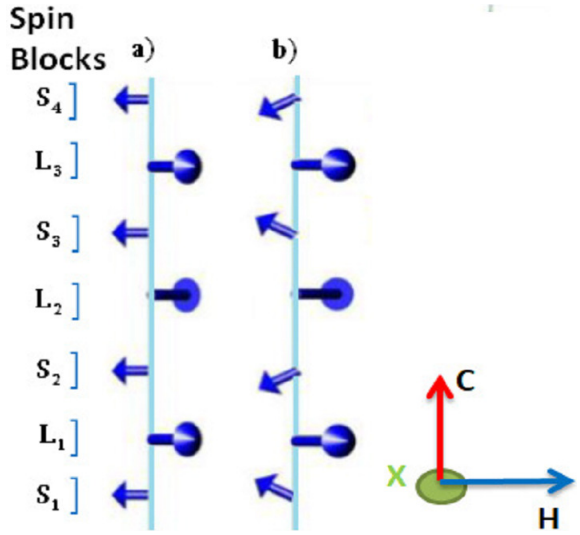


**Figure 1.** Schematic of proposed "2-fan" magnetic structures in intermediate-II and intermediate-III phases **(a)** and transverse conical spin structure in ferroelectric phase for Y-type $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ hexaferrite **(b)**.

Recently we reported ME effect at room temperature in single-crystal Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite [**7**]. This result indicates that the intermediate-II phase, similar to intermediate-III, is ferroelectric in this compound. If this is the case, intermediate-II phase should also have a transverse conical spin structure with corresponding chirality. Neutron diffraction with polarization analysis is a powerful tool for investigating chirality of magnetic structures in multiferroic oxides. Therefore, we performed the polarized neutron diffraction experiments to study magnetic structure in the intermediate-II and intermediate-III phases of magnetoelectric Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite single crystal.

## 2. Experimental details

Single crystal of Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite was prepared by flux growth method from high purity starting materials $BaCO_3$, $SrCO_3$, ZnO, $Fe_2O_3$ and $Na_2CO_3$ used as a solvent [**8**]. The exact composition was determined by refinements of single crystal X-ray diffraction data in an Oxford diffraction instrument from Rigaku. The refined lattice parameters were found to be 5.85 and 43.42 Å in $R\bar{3}m$ space group with hexagonal settings. For neutron scattering experiments in the present work we used crystal with dimensions 3 × 1.5 × 0.3 mm.

The scattering cross section of the polarized neutrons is sensitive to spin chirality [**9**]. Therefore, the polarized neutron scattering technique is very well suited to study the magnetic

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chirality. The scattering cross-section for polarized neutrons is given by Blume–Maleyev equation [10, 11]:

$$\sigma_Q = |N_Q|^2 + |M_Q^{\perp}|^2 + P\left(N_{-Q}M_Q^{\perp} + M_{-Q}^{\perp}N_Q\right) + iP\left(M_{-Q}^{\perp} \times M_{+Q}^{\perp}\right).$$

Here, $\sigma_Q$ is a scattering cross-section for polarized neutrons, $\boldsymbol{Q}$ is a scattering vector, $N_Q$ and $M_Q$ are nuclear and magnetic scattering amplitudes for a given $\boldsymbol{Q}$ and $\boldsymbol{P}$ polarization of a neutron beam, respectively.

In above equation, only the last two terms depend on polarization of the incoming neutrons, and describe nuclear–magnetic interference scattering and chirality. In our case, according to soft X-ray diffraction experiment (P. Thakuria, et al. – *in preparation*) there is no nuclear scattering present at $(1, 0, 0.5)$ reflection. Therefore, in that equation we need only last chiral therm. Polarization dependent neutron scattering is a very useful probe of the magnetic chirality in the spin networks [9]. In the present work we used polarized incident neutron beam without polarization analysis of the scattered beam (so-called half polarized experiment). By measuring the difference

$$\Delta I(\omega, Q) = I^{\uparrow}(\omega, Q) - I^{\downarrow}(\omega, Q)$$

for incident neutron polarizations parallel $I^{\uparrow}(\omega, Q)$ and antiparallel $I^{\downarrow}(\omega, Q)$ to the scattering vector $Q$, chiral magnetism was determined.

Polarized neutron diffraction measurements were performed at the Institut Laue–Langevinon the IN12 cold triple-axis spectrometer in the temperature range 5 – 100 K at different horizontal magnetic fields ( $H < 2$ T ). We used full polarization analysis to separate the possible position of magnetic and structural peaks. Half polarized experiment was used to get access to the magnetic chirality. For both methods we needed the polarization in the scattering plane, therefore horizontal magnetic field was used. For the transverse conical spin structure, in case of the vertical magnetic field the modulation of the magnetic moments in the scattering plane is restricted, which implies no chiral scattering.

### 3. Results and discussions

**Figure 2** shows full polarized analysis neutron scattering spectra of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite single-crystal for spin-flip and non-spin-flip intensities at 5 K. These measurements were performed for some selected reflections in a horizontal magnetic field configuration $H = 0.5$ T . For further measurements we selected $(1, 0, 0.5)$ reflection where one of the clear differences was observed between spin-flip and non-spin-flip intensities (see **Figure 2d**). For this reflection we explored chiral magnetism by performing half polarized experiments at different temperatures and magnetic fields.

**Figure 3a** shows $\omega$-scans across the $(1, 0, 0.5)$ reflection at $T = 100$ K in $H = 0.6$ T horizontal magnetic field ( $\boldsymbol{H} \perp \boldsymbol{c}$ ). One can see that the intensity is higher with neutron spin parallel ( $I^{\uparrow}$ ) to the scattering vector $\boldsymbol{Q}$ compared to neutron spin antiparallel ( $I^{\downarrow}$ ). The difference ( $I^{\uparrow} - I^{\downarrow}$ ) is plotted in **Figure 3b**. Such behavior is typical for the spiral magnets [12]. Observed intensity difference provides evidence for the presence of chiral magnetism in intermediate-II phase. Therefore, one can conclude that the intermediate-II phase in Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite can be ferroelectric in addition to the intermediate-III phase. This deviates from the conclusion derived by Kimura, et al. [4] based on macroscopic measurements. However, it is in agreement with our recent results obtained by ferromagnetic resonance [7] and soft X-ray chiral scattering (P. Thakuria, et al. – *in preparation*) techniques.

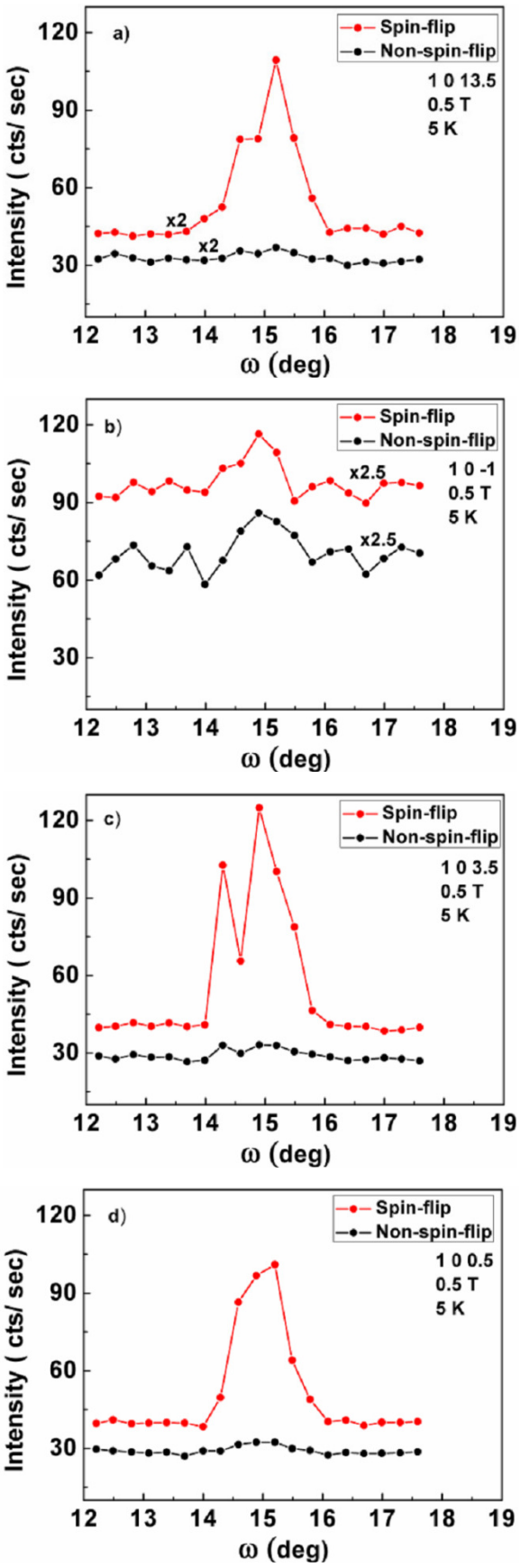


**Figure 2**. Examples of full polarized analysis neutron scattering spectra for some selected reflections of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite single-crystal for spin-flip and non-spin-flip intensities at $T = 5$ K in horizontal field $H = 0.5$ T configuration.


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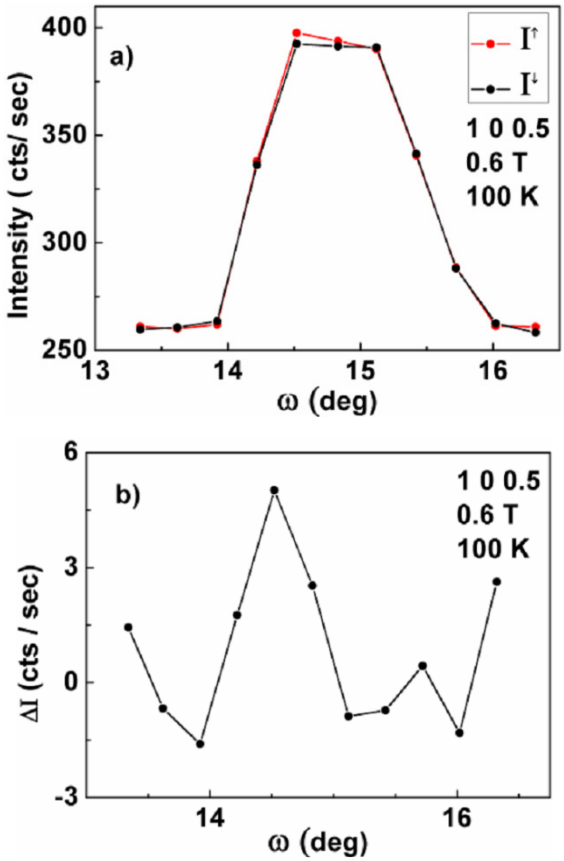


**Figure 3.** $\omega$-scans across $(1, 0, 0.5)$ reflection at $T = 100$ K in $H = 0.6$ T horizontal magnetic field ( $\boldsymbol{H} \perp \boldsymbol{c}$ ) for positive ( $I^{\uparrow}$ ) and negative polarized ( $I^{\downarrow}$ ) neutrons **(a)** and difference $\Delta I = I^{\uparrow} - I^{\downarrow}$ between intensities of positive and negative polarized neutrons **(b)**.

We also performed similar neutron diffraction measurements at $T = 5$ K and in horizontal magnetic fields $H = 0.3 - 1.3$ T . In this field and temperature range Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite is in intermediate-III phase **[2]**. This phase is known to be ferroelectric. Indeed, we observed that in the intermediate-III phase, intensity of positive polarized neutrons ( $I^{\uparrow}$ ) is higher than negative polarized neutrons ( $I^{\downarrow}$ ). This confirms transverse conical spin structure also in intermediate-III phase. Therefore, we can conclude that the magnetic structure in both intermediate-II and intermediate-III phases allows the existence of magnetic field-induced ferroelectricity.

### 4. Summary and conclusions

To summarize, we studied chiral magnetic structure in single crystal of Y-type $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite by using neutron diffraction with polarization analysis. A wide range of the temperature and magnetic field was explored, which includes intermediate-II and intermediate-III phases of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$. Chiral magnetism was detected in both of these phases. It shows that in contrast to previous assumptions, intermediate-II phase also has transverse conical spin structure similar to the intermediate-III phase. This magnetic structure has chirality which is consistent with the inverse Dzyaloshinskii–Moriya mechanism of ferroelectricity and therefore magnetic field induced ferroelectricity is possible. Obtained

results justify the presence of magnetoelectric coupling in intermediate-II phase of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite, which was reported recently by using electrically modulated ferromagnetic resonance [7].

## References


[1] R. C. Pullar. Prog. Mater. Sc., 2012, 57, 1191.
[2] T. Kimura. Ann. Rev. Cond. Matter Phys., 2012, 3, 93.
[3] Y. Tokura, S. Seki, N. Nagaosa. Rep. Prog. Phys., 2014, 77, 076501.
[4] T. Kimura, G. Lawes, A. P. Ramirez. Phys. Rev. Lett., 2005, 94, 137201.
[5] N. Momozawa, Y. Yamaguchi, H. Takei, M. Mita. J. Phys. Soc. Jpn., 1985, 54, 771.
[6] N. Momozawa, Y. Yamaguchi. J. Phys. Soc. Jpn., 1993, 62, 1292.
[7] G. Khazaradze, P. Thakuria, D. Daraselia, D. Japaridze, M. Angst, A. Shengelaya. J. Magn. Magn. Mater., 2020, 498, 166177.
[8] N. Momozawa, M. Mita, H. Takei. J. Crys. Growth, 1987, 83, 403.
[9] V. P. Plakhty, J. Kulda, D. Visser, E. V. Moskvin, J. Wosnitza. Phys. Rev. Lett., 2000, 85, 3942.
[10] M. Blume. Phys. Rev., 1963, 130, 1670.
[11] S. V. Maleyev, V. G. Baryakhtar, P. A. Suris. Fiz. Tv. Tela, 1962, 4, 3461.
[12] Y. Yamasaki, H. Sagayama, T. Goto, M. Matsuura, K. Hirota, T. Arimaand, Y. Tokura. Phys. Rev. Lett., 2007, 98, 147204.



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