⁵⁷Fe Mössbauer Study of Spatial Spin-Modulated Structure in BiFeO₃

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Abstract: The method of investigation applied to spatial spin-modulated structure (SSMS) of the cycloid type in multiferroics based on the Mössbauer spectroscopy is discussed. It is shown by the example of bismuth ferrite BiFeO₃ that the usage of Mössbauer spectroscopy can define the anharmonicity parameter of the cycloid type SSMS with preciseness not less than obtained by the NMR-method characterized by much better resolution. The Mössbauer spectroscopy method, sensitive to hyperfine electric quadrupole interaction of nuclei in excited state, makes it possible to obtain additional data on SSMS peculiarities. The anharmonicity parameter for BiFeO₃ has been derived at various temperatures ranging from 4.85 K to 600 K.

Key words: Multiferroic, spatial spin-modulated structure, anharmonicity parameter, Mössbauer spectroscopy.

1. Introduction

Bismuth ferrite BiFeO₃ is a multiferroic, possessing both ferroelectric and antiferromagnetic properties. It is characterized by high antiferromagnetic Neel temperature (643 K) and ferroelectric Curie temperature (1,103 K). Outstanding physical properties of BiFeO₃ arouse a great interest in many fields of science and engineering [1]. At first the information on the existence of spatial spin-modulated structure (SSMS) in bismuth ferrite BiFeO₃ was obtained by a study with high-resolution time-of-flight magnetic neutron diffractometer in 1982 [2]. It was discovered that there existed a magnetic cycloid spiral with a long period of 620 Å incommensurate with the lattice parameter [2], in which G-type antiferromagnetically ordered moments of Fe atoms μ_{Fe} rotate in the direction of wave propagation in the plane containing hexagonal symmetry axis of the rhombohedral ferrite cell. Later the existence of SSMS in BiFeO₃ was

theoretically explained in Refs. [3, 4], where it was shown that spatial dependence of the angle ϑ between antiferromagnetism vector and symmetry axis was described by the elliptic Jacobi sn-function.

Multiferroic BiFeO₃ at various times was studied by plenty of Mössbauer spectroscopy (MS) methods [5-12]. In Ref. [5], for the first time the Mössbauer spectra of sufficient quality for processing and analysis were obtained for ⁵⁷Fe non-enriched ferrite sample. Below the Neel temperature T_N the magnetic splitting of the spectrum into six components was discovered. In more recent papers [6-9], the authors draw attention to the asymmetry of Zeeman sextet below T_N and its inhomogeneous line broadenings. These spectrum peculiarities were supposedly concerned with quadrupole splitting distributions in spectra, caused by presence of inequivalent positions of Fe atoms in crystal structure. Interpretation and fitting of the spectra obtained at $T < T_N$ as a superposition of two Zeeman sextets provided their hyperfine parameters. The values of hyperfine magnetic fields and quadrupole shifts differ significantly in the papers with

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two Zeeman subspectra interpretation along with poor correspondence to data obtained from NMR [13-16].

As a result of the analysis of possible reasons for the peculiarities observed in Mössbauer spectra the authors of Ref. [10] concluded that the asymmetry and broadening of lines of the spectra might be concerned with the presence of SSMS and caused by two different factors. The broadening of lines could be caused by a weak modulation of hyperfine interaction energies provided by changes of angles between magnetic moments μ_{Fe} and main axis of the electric field gradient (EFG) tensor. The asymmetry of spectra is caused by internal anisotropy of magnetic hyperfine interaction in the position with trigonal symmetry.

For the first time in Ref. [11], Mössbauer spectra were interpreted and fitted according to SSMS of the cycloid type theory and not only dependence between hyperfine magnetic field and quadrupole shift and μ_{Fe} orientation were taken into account, but also possibility of presence of additional constant contribution into quadrupole splitting, caused by local magnetoelastic strong interaction. As a result, the authors succeeded in defining hyperfine parameters of spectra corresponding to Fe atom spin orientation along and transversely to hexagonal symmetry axis in BiFeO₃ and estimate anharmonicity parameter $m \cong 0.5$ at room temperature and $m \cong 0.6$ at $T = 90$ K. In totum the results of investigation confirm the magnetic modulation of hyperfine fields observed by NMR, which concerns modulation of magnetic moments μ_{Fe} ordering, also supported by neutron diffraction. However in contradiction with NMR data, hyperfine magnetic field corresponding to spin orientation along the symmetry axis, turned out to be less (494.82 kOe), than in case when the spin is orientated transversely (500.05 kOe). The value of constant additional contribution to quadrupole splitting caused by strong local magnetoelastic interaction, proved to be considerable (0.219 mm/s), and comparable with quadrupole shift above the Neel temperature.

In paper [12], Mössbauer spectra of the same

perovskite BiFeO₃ enriched with 10% isotope ⁵⁷Fe for NMR were measured. Mössbauer spectra were processed using the methods of recovery of the hyperfine parameters distribution and model fitting of spectra. It was shown that magnetic hyperfine field distribution recovered taking into account its linear correlation with quadrupole shift qualitatively confirms the NMR spectrum. The values of hyperfine magnetic fields for two iron atom states with magnetic moments parallel and perpendicular to the symmetry axis of BiFeO₃ were taken from NMR analysis, while isomer shifts, quadrupole shifts and intensities of two subspectra varied. The shifts for both states of ions were found almost equal and the ratio of quadrupole shifts was $\varepsilon_{\perp}/\varepsilon_{\parallel}$. The authors of the paper concluded that for valid description of Mössbauer spectra of multiferroics possessing SSMS NMR data should be taken into account and for investigation SSMS to obtain proper data of parameters in the perovskites one should conduct combined study of these materials, using NMR, Mössbauer and special analytical software.

The literature analysis suggests that nowadays the methods allowing diagnosing and investigating SSMS grow more and more important in studying multiferroics. One of these methods along with neutron diffraction and nuclear magnetic resonance is Mössbauer spectroscopy. At the same time data of hyperfine interaction and spin-wave anharmonicity parameters obtained by the methods of neutron diffraction, NMR and Mössbauer spectroscopy are quite contradictory.

The main purpose of this paper is further development of Mössbauer spectroscopy methods in the field of diagnosing and studying SSMS of the cycloid type in multiferroics by the example of BiFeO₃.

2. Experiments

The investigations were performed by the Mössbauer spectroscopy method at the enriched by 10 percent ⁵⁷Fe isotope sample of BiFeO₃. Polycrystalline

sample was synthesized by the solid-state synthesis method in air [16]. X-ray diffraction (XRD) analysis showed that the synthesized samples are single-phase and crystallize in a rhombohedral structure (space group R3c) with parameters $a = 3.963 \text{ \AA}$ and $a = 89.43^\circ$.

Mössbauer investigations were conducted by spectrometer MS1104Em based on constant acceleration regime with triangle form. ⁵⁷Co/Rh Mössbauer source was used. The spectrometer was calibrated at room temperature by standard absorber α -Fe. Measurements were carried out at temperatures in the range of 4.85–600 K using a closed cycle helium cryostat SHI-850-5 and Mössbauer furnace MBF-1100-TR. The Mössbauer spectra were processed using the recovery of the hyperfine magnetic field distributions $p(H_n)$ and model fitting in terms on the cycloid type of SSMS by program SpectrRelax [17].

3. Results and Discussions

3.1 Mössbauer Spectra and Hyperfine Field Distribution Recovery

In the spectra obtained below the Neel temperature T_N , it was observed asymmetrical Zeeman sextet with inhomogeneous broadening of the resonance lines. As an example, Fig. 1a presents Mössbauer spectra of ⁵⁷Fe nuclei in multiferroic BiFeO₃, measured at 4.85, 80 and 300 K. One can see that the spectra possess the same peculiarities as in the row of papers [8–12] in spectra obtained at temperatures below T_N namely the Zeeman sextets are asymmetrical and their lines are inhomogeneously broadened. The authors [10, 11] explained these peculiarities by the presence of SSMS in BiFeO₃ and in their quadrupole shift ε of resonance lines and hyperfine magnetic fields H_n in subspectra dependence on the angle between the principal axis of the electric field gradient and the spin direction.

It can be seen that the sixth line is less intensive than the first one while the fifth one is more intensive than the second one (Fig. 1a). The character of such an asymmetry explicitly specifies the positive correlation

between ε and H_n . Supposing the presence of linear correlation between all hyperfine parameters of the spectrum: isomer shift δ , quadrupole shift ε and hyperfine field H_n , we recovered the hyperfine magnetic field distribution $p(H_n)$ by the method described in detail in Ref. [18]. One can see in Fig. 1b that in the recovered distributions there are two distinct local maxima (1) and (2) with somewhat different intensities. For example, for the spectrum recorded at 4.85 K these local maxima correspond to the hyperfine magnetic fields $H_n^{(1)} = 545.8 \pm 0.2 \text{ kOe}$ and $H_n^{(2)} = 546.6 \pm 0.2 \text{ kOe}$, to the shifts $\delta^{(1)} = 0.504 \pm 0.002 \text{ mm/s}$ and $\delta^{(2)} = 0.505 \pm 0.002 \text{ mm/s}$ and quadrupole shifts $\varepsilon^{(1)} = -0.08 \pm 0.03 \text{ mm/s}$ and $\varepsilon^{(2)} = 0.20 \pm 0.02 \text{ mm/s}$. The coefficient of linear correlation between quadrupole shift ε and hyperfine field H_n is $(\varepsilon^{(2)} - \varepsilon^{(1)})/(H_n^{(2)} - H_n^{(1)}) = 0.100 \pm 0.006 \text{ mm/s/kOe}$. It should be noted that for these maxima the shifts of lines $\delta^{(1)}$ and $\delta^{(2)}$ are almost equal while the quadrupole shift $\varepsilon^{(1)}$ is about two times smaller than $\varepsilon^{(2)}$ and has opposite sign. This provides a reason to relate the first maximum with the smaller value of field $H_n^{(1)}$ to the case of normal angle between magnetic spin and third order symmetry axis in BiFeO₃ crystal lattice and the second one with the bigger value of field $H_n^{(2)}$ to the case of parallel orientation of Fe atom magnetic moments and this axis. We see that the result of $p(H_n)$ distribution recovery is in accordance with the presence of SSMS in BiFeO₃. The further analysis of Mössbauer spectra was performed by the method of model fitting in terms of cycloid type SSMS.

3.2 Realization of Cycloid Type SSMS Model for Mössbauer Spectra Analysis

According to papers [3, 4] the spatial dependence of angle $\mathcal{A}(x)$ between the antiferromagnetism vector and symmetry axis in bismuth ferrite BiFeO₃ is defined by the two possible solutions, depending on the sign of magnetic anisotropy constant K_u :

$$\cos \mathcal{A}(x) = \text{sn}((4 \cdot K(m)/\lambda) \cdot x, m), K_u > 0 \quad (1a)$$

or:

Fig. 1 ⁵⁷Fe Mössbauer spectra fitted by cycloid type SSMS model (a) and corresponding recovered hyperfine magnetic field H_n distributions $p(H_n)$ (b) for BiFeO₃ at various temperatures. In Fig. 1b: points with standard deviation are the result of distribution recovery $p(H_n)$; solid line with shaded area is $p(H_n)$ distribution calculated in the terms of cycloid type SSMS model.

$$\sin \mathcal{G}(x) = \text{sn}((4 \cdot K(m)/\lambda) \cdot x, m), \quad K_u < 0 \quad (1b)$$

where, x is the coordinate along the cycloid propagation vector, λ is the spin modulation inharmonic wave length, $0 < m < 1$ is the elliptic Jacobi function $\text{sn}(x, m)$ parameter, $K(m)$ is complete elliptic integral of the first order.

In the SpectrRelax program the whole range of coordinate $x \in [0, \lambda]$ variations is divided into a huge amount of intervals of the same length with specific $\mathcal{G}(x)$ value for each. With value of $\mathcal{G}(x)$ known it becomes possible to calculate the hyperfine magnetic field $H_n(\mathcal{G}(x))$ on the nuclei. When the anisotropy of hyperfine interaction is uniaxial and small enough as in case of ⁵⁷Fe nuclei in BiFeO₃, one can write down for the hyperfine magnetic field [13]:

$$H_n(\mathcal{G}(x)) = H_{\parallel} - (H_{\parallel} - H_{\perp}) \sin^2(\mathcal{G}(x)) \quad (2)$$

where, $H_{\parallel}$ and $H_{\perp}$ are desired field values for Fe atom magnetic moment parallel ($\mathcal{G} = 0$) and perpendicular ($\mathcal{G} = \pi/2$) to the symmetry axis correspondingly. The whole range of coordinate changes was divided into 50,000 intervals in order to find the numerical distribution of hyperfine field for Mössbauer spectroscopy. Then partial contributions to the spectra were formed, each on the base of 250 intervals within the range of coordinate changes $x \in [0, \lambda]$. The number of intervals is mutable during the process of analysis.

Every limit of interval for the division of coordinate range $x \in [0, \lambda]$ variations matches up a local line of resonant absorption in the form of Zeeman sextet, whose shapes are described by pseudo-Voigt function which in a linear combination of Lorentz $W_L(z, \Gamma)$ and Gauss $W_G(z, \Gamma)$ functions with the same width Γ :

$$W_{PV}(z, \Gamma) = (1-\alpha) \cdot W_L(z, \Gamma) + \alpha W_G(z, \Gamma) \quad (3)$$

The width Γ and parameter α in Eq. (3) were varied.

In the presence of electric field gradient the Mössbauer resonance lines are shifted. For ⁵⁷Fe nuclei in bismuth ferrite the energy of hyperfine electric quadrupole interaction of nuclei is significantly less than the energy of its magnetic monopole interaction [6], while the asymmetry parameter of EFG tensor equals zero. In this case, the positions ν_i of all resonant lines in sextet in the Doppler velocity scale are provided by formulas [19]:

$$\nu_{1,6}(\mathcal{Q}) = \delta + \varepsilon(\mathcal{Q}) \pm a_+(\mathcal{Q}) \pm \mu_n \frac{3g_{\text{ex}} - g_{\text{gr}}}{2} H_n(\mathcal{Q}) \quad (4a)$$

$$\nu_{2,5}(\mathcal{Q}) = \delta - \varepsilon(\mathcal{Q}) \mp a_-(\mathcal{Q}) \pm \mu_n \frac{g_{\text{ex}} - g_{\text{gr}}}{2} H_n(\mathcal{Q}) \quad (4b)$$

$$\nu_{3,4}(\mathcal{Q}) = \delta - \varepsilon(\mathcal{Q}) \pm a_-(\mathcal{Q}) \mp \mu_n \frac{g_{\text{ex}} + g_{\text{gr}}}{2} H_n(\mathcal{Q}) \quad (4c)$$

The shift δ of Zeeman sextet in the Doppler velocity scale, dependent on the degree of bonds covalence and dynamic features of Mössbauer atoms, was the adjustable parameter equal for all the sextets. Quadrupole shift of resonant lines in first $\varepsilon(\mathcal{Q})$ and second $a_{\pm}(\mathcal{Q})$ orders of smallness in the expansion in series of quadrupole:

$$\varepsilon(\mathcal{Q}) = \varepsilon_{\text{magn}} + \varepsilon_{\text{lat}} \cdot \frac{3 \cos^2 \mathcal{Q} - 1}{2} \quad (5)$$

$$a_{\pm}(\mathcal{Q}) = \varepsilon_{\text{lat}} \frac{3\varepsilon_{\text{lat}}}{g_{\text{ex}} \mu_n H_n} \left(\cos^2 \mathcal{Q} \pm \frac{1}{8} \sin^2 \mathcal{Q} \right) \sin^2 \mathcal{Q} \quad (6)$$

Along with quadrupole shift ε_{lat} , caused by the gradient electric field provided by neighboring atoms (including paramagnetic temperature range) following paper [11], we took into account a possibility of additional shift $\varepsilon_{\text{magn}}$, driven by a local lattice distortion due to a strong magnetoelectric interaction. Here μ_n is nuclear magneton, g_{gr} and g_{ex} are g -factors of base and excited states of the Mössbauer nuclei ⁵⁷Fe.

Pair wise equality of widths (Γ) and intensities (I) of

resonant lines in sextets: $\Gamma_1 = \Gamma_6, \Gamma_2 = \Gamma_5, \Gamma_3 = \Gamma_4$ and $I_1 = I_6, I_2 = I_5, I_3 = I_4$, was hold while looking for optimum values of hyperfine interaction parameters ($\delta, \varepsilon_{\text{lat}}, \varepsilon_{\text{magn}}, H_{\parallel}, H_{\perp}$) and anharmonicity parameter of spin wave (m).

The search for optimal values of model parameters was executed taking into account maximum-likelihood criterion (χ^2 criterion) by Levenberg-Marquardt method, the specific features of implementation of which in case of instability caused by strong correlation of the parameters and for precise determination of partial derivatives for acceleration of convergence of optimization method are described in Ref. [17].

3.3 The Results of the Model Fitting of Spectra in Terms of Cycloid Type SSMS Model

The Mössbauer spectrum was interpreted according to the described above realization of the cycloid type SSMS model. The results of the analysis of Mössbauer spectra of nuclei ⁵⁷Fe in BiFeO₃ at $T < T_N$ in the context of the cycloid type SSMS model are presented in Fig. 1. In Fig. 1a, one can see a model envelope curve fitting well experimental Mössbauer spectrum. In Fig. 1b, the hyperfine field distribution $p(H_n)$, calculated in context of the cycloid type SSMS and the distribution obtained as a result of recovery are provided for comparison. The results of model fitting of Mössbauer spectrum at 4.85 K in context of the cycloid type SSMS at different signs of magnetic anisotropy coefficient K_u are provided in Table 1.

The value of Mössbauer line shift δ obtained as a result of fitting corresponds to the high-spin state of Fe³⁺ cations in octahedral oxygen environment. In case of $K_u > 0$, the expected contribution $\varepsilon_{\text{magn}}$ to the quadrupole shift $\varepsilon(\mathcal{Q})$ (Eq. (5)) caused by lattice local distortion because of strong magnetoelectric interaction practically equals zero. The quadrupole

Table 1 Hyperfine parameters obtained by fitting of the cycloid type SSMS model (at $K_u > 0$ and $K_u < 0$) to the BiFeO₃ Mössbauer spectrum collected at 4.85 K.

K_u	δ (mm/s)	$\varepsilon_{\text{magn}}$ (mm/s)	ε_{lat} (mm/s)	$H_{\perp}$ (kOe)	$H_{\parallel}$ (kOe)	ΔH (κOe)	m	χ^2
> 0	0.505(1)	0.000(2)	0.254(2)	546.9(1)	542.5(1)	4.4(2)	0.26(6)	1.04(4)
< 0	0.505(1)	0.128(2)	-0.254(2)	543.0(1)	546.5(1)	-3.5(2)	0.26(6)	1.05(4)

shift ε_{lat} , caused by EFG induced by atomic environment proved to be positive and fairly high (Table 1). Note that obtained value ε_{lat} (Table 1) is in a good agreement with quadrupole shift value $\varepsilon = 0.2208 \pm 0.0005$ mm/s for the spectrum measured in paramagnetic state at $T = 640$ K. The value ε is slightly less than ε_{lat} which is caused by crystal thermal expansion. In case of $K_u > 0$, the greater field value corresponds to the orientation of Fe atom magnetic moment along the crystal symmetry axis and the smaller one corresponds to perpendicular orientation. The difference between the fields $\Delta H = H_{\parallel} - H_{\perp}$ is positive (Table 1) and slightly less than values obtained from the NMR spectra [15, 16].

Of specific note is the fact that in accordance with the cycloid type SSMS model there exists a linear correlation between the quadrupole shift ε and the hyperfine field H_n (compare Eq. (2) and (5)) whose coefficient equals $(\varepsilon^{(2)} - \varepsilon^{(1)}) / (H_n^{(2)} - H_n^{(1)}) = 3/2(\varepsilon/\Delta H) = 0.087 \pm 0.004$ mm/s/kOe, what is close to the value obtained from the distribution $p(H_n)$ recovery. The difference between the distribution recovery results and the values of hyperfine magnetic field $p(H_n)$ (Fig. 1b) obtained from the calculation of Mössbauer data in context of the cycloid type SSMS model generally depends on the requirement of $p(H_n)$ smoothness [18].

For the Mössbauer spectrum, a change of the model with positive magnetic anisotropy coefficient $K_u > 0$ (Eq. (1a)) to the model with negative value $K_u < 0$ (Eq. (1b)) doesn't make any difference in shift of Mössbauer line δ and width of resonant lines Γ , the value of quadrupole shift $\varepsilon_{\text{magn}}$ changes to $\varepsilon_{\text{magn}} \cong -\varepsilon_{\text{lat}}/2$, the values of hyperfine fields change slightly and exchange their places ($H_{\parallel} \leftrightarrow H_{\perp}$) for mutually perpendicular orientations of magnetic moment μ_{Fe} (the sign of quadrupole shift ε_{lat} and ΔH changes, also value of ΔH changes) at the stable parameter of anharmonicity m and value of standardized functional χ^2 (Table 1). The value of anharmonicity parameter of the cycloid type SSMS obtained from the Mössbauer

spectrum ($m = 0.26 \pm 0.06$) does not contradict that estimated ($m \leq 0.25$) from neutron diffraction [20].

Sufficiently high value of quadrupole shift $\varepsilon_{\text{lat}} = 0.254 \pm 0.020$ mm/s signals of strong gradients influencing ⁵⁷Fe nuclei. We calculated EFG tensor in approximation of point charges (lattice contribution) and estimated quadrupole shift ε using information of atoms localization in BiFeO₃, investigated by neutron diffraction [21] and values of antishielding $\gamma_{\infty} = -9.1$ and shielding $R = 0.32$ Sternheimer parameters [22] (formal charges $Z_{\text{Bi}} = +3$, $Z_{\text{Fe}} = +3$, $Z_{\text{O}} = -2$ and quadrupole moment of nuclei ⁵⁷Fe in excited state $Q = 0.15$ barn [23]). According to the calculations the quadrupole shift proved to be positive and equals $\varepsilon = 0.103$ mm/s. The calculated value is notably less than that one observed in the experiment. Obviously one needs to take into account dipole contribution caused by ion of oxygen polarization and probably electronic contribution caused by overlapping of Fe and O atom orbitals [22]. However in case of high-spin ions Fe³⁺ possessing spherically symmetrical electron shell d⁵ crystal distortion makes the main contribution into EFG and positive sign of calculated shift ε suggest the idea of positive sign of sum-total shift ε_{lat} . In this case it is reasonable to suppose that we observe positive value of magnetic anisotropy constant in bismuth ferrite at low temperatures $K_u > 0$. On the base of our data (Table 1) it is essential to add that in case $K_u > 0$, there is no necessity in postulating strong local distortion of lattice caused by magnetoelectric interaction [11], adding contribution $\varepsilon_{\text{magn}}$ comparable with negative one ε_{lat} (at $K_u < 0$) (Table 1).

Figs. 2 and 3 show the temperature dependence of the anharmonicity parameter m of the spin-wave modulation and the difference ΔH of two hyperfine fields $H_{\parallel}$ and $H_{\perp}$, respectively.

The anharmonicity parameter m which is determined by the ratio of the anisotropy constant to the exchange energy [4, 5] when the temperature increases it is practically constant ($m \sim 0.27$) to $T \sim 150$ K and then decreases tending to zero at 350 K (Fig. 2). As for the

Fig. 2 Temperature dependence of the anharmonicity parameter m of the cycloid type SSMS for BiFeO₃.

Fig. 3 Temperature dependence of the difference ΔH of two hyperfine fields $H_{||}$ and $H_{\perp}$, obtained by Mössbauer spectroscopy (MS) and Nuclear magnetic resonance (NMR) [16].

difference ΔH due to both the dipole-dipole interaction of the nucleus with localized magnetic moments of the atoms and the anisotropy of the hyperfine interactions of the nucleus and the electron shell of an atom of its own, with increasing temperature ΔH first increases slightly and then decreases tending to zero in the temperature range of ~ 600 K. It should be pointed out that there is a good coincidence between the difference ΔH of two hyperfine fields $H_{||}$ and $H_{\perp}$, obtained by Mössbauer spectroscopy (MS) and nuclear magnetic resonance (NMR) [16] in the temperature range 4.2–300 K (Fig. 3).

4. Conclusions

The study carried suggests several useful conclusions.

(1) The anharmonicity parameter of the cycloid type SSMS can be determined by means of Mössbauer spectroscopy with accuracy not less than that obtained

by NMR method with higher resolution;

(2) The Mössbauer spectroscopy method, being sensitive to hyperfine electric quadrupole interaction of nuclei in excited state, offers the possibility of obtaining additional information on peculiarities of SSMS in multiferroics;

(3) Mössbauer spectroscopy together with nuclear magnetic resonance and neutron diffraction is an effective method of study and investigation of cycloid type SSMS.

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