Temperature Mössbauer study of the spatial spin-modulated structure in the multiferroic $BiFeO_3$

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Abstract. ^{57}Fe Mössbauer detailed study of the spatial spin-modulated structure of the multiferroic $BiFeO_3$ was carried out in a wide temperature range including the temperature of magnetic phase transition. The Mossbauer spectra have been analysed by fitting in terms of the anharmonic spin cycloid mode. It is established that at temperatures below ~330 K a magnetic anisotropy of the "easy axis" type is realized and above is the magnetic anisotropy of the "easy plane" type. An explanation for the change in the type of magnetic anisotropy is proposed, based on taking into account the different temperature dependences of the two contributions to the effective uniaxial magnetic anisotropy constant: a crystal anisotropy of net antiferromagnet and a weak ferromagnetism.

1 Introduction

The bismuth ferrite $BiFeO_3$ is known to possess multiferroic properties, being both antiferromagnetic and ferroelectric. High antiferromagnetic Neel temperature (643 K) and ferroelectric Curie temperature (1103 K) of the ferrite are of great interest in many fields of science and technology [1]. Bismuth ferrite has a rhombohedral distorted perovskite crystal structure (space group R3c) [2] in which Fe^{3+} and Bi^{3+} cations are displaced along the hexagonal [001]-axis, leading to a spontaneous polarization in this direction. In accordance with neutron diffraction investigations [3], $BiFeO_3$ has a spatial spin-modulated structure (SSMS). It was established that there existed a magnetic cycloid spiral with a long period of 620 Å incommensurate with the lattice parameter, in which G-type antiferromagnetic ordered moments of Fe atoms rotate in the direction $[110]_{hex}$ of wave propagation in the plane containing hexagonal symmetry axis of the rhombohedral ferrite cell. The existence of SSMS in BiFeO3 was theoretically explained in [4, 5], where it was shown that spatial dependence of the angle ϑ between antiferromagnetism vector and symmetry axis on the distance x along the propagation direction, was described by the elliptic Jacobi sn-function.

The temperature-dependent evolution of the magnetic structure in BiFeO3 is an important subject for investigation with several currently unresolved issues. ^{57}Fe Mössbauer spectroscopy was used in studying $BiFeO_3$ in several papers [6 – 11] that were devoted to analysis of the magnetic structure features in terms of the cycloid type incommensurate anharmonic SSMS model. In analyzing the Mössbauer spectra, the dependence of the angle ϑ on the coordinate x corresponded to the magnetic anisotropy of the "easy plane" type, was used in [6]. Thus the values of the anharmonicity parameter $m = 0.5$ at RT and $m = 0.6$ at 90 K were obtained [6]. It was shown [7] that at low temperatures a magnetic anisotropy of the "easy axis" type is realized. In this case the anharmonicity parameter m obtained from the Mössbauer spectrum ($m = 0.26 \pm 0.06$ at 4.85 K) was close to the value obtained from the NMR spectrum ($m = 0.25 \pm 0.07$ at 4.2 K). In subsequent papers [8 – 11] it was assumed that magnetic anisotropy of the "easy axis" type is realized in the entire temperature range of SSMS existence. As a result of an analysis of the Mossbauer spectra, it was shown on this assumption that with increasing temperature, the anharmonicity parameter m remained virtually constant up to $T \sim 150$ K and then decreased, tending to zero at 350 – 400 K and until the system reaches the harmonic state ($m = 0$). It was noticed in [10, 11] that with increasing temperature in the region $T > 350$ K when the value of the anharmonicity parameter equal zero, description of the spectrum deteriorates and the Chi-square functional increases.

The purpose of this work was the detailed temperature Mössbauer study of the feature of the spatial spin-modulated structure of multiferroic $BiFeO_3$.

2 Methods

2.1 Synthesis

Polycrystalline sample of $BiFeO_3$ with relative content stable isotope ^{57}Fe at 10% was prepared by the solid ceramic technology method. The mixture of oxide powders of the components compound in the proper proportions pressed into tablets, which were annealed for one day at a temperature equal to 700-830°C in air (with

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an intermediate triple milling and compression into tablets). At T = 830°C, final annealing was performed and then rapidly cooling the sample in air.

Phase composition of samples was characterized by X-ray diffraction using Panalytical Empyrean powder diffractometer in Bragg-Brentano geometry (step size – 0.026°, scan step time – 200 s) using nickel-filtered Cu(Kα) (λ = 1.5406Å) radiation. As shown X-ray measurements, the obtained single-phase sample $BiFeO_3$ have rhombohedral structure with parameters: a = 3.963 Å and α = 89.43º, space group R3c.

2.2 ^{57}Fe Mössbauer spectroscopy

Mössbauer studies were carried out using a spectrometer operating in constant acceleration mode with a triangular shape changes in Doppler velocity of the source relative to the absorber. The source is ^{57}Co performed in the matrix Rh. Mössbauer spectrometer calibration was performed at room temperature using a standard absorber α-Fe. Measurements were carried out at temperatures in the range of 4.85 – 700 K using a closed cycle helium cryostat SHI-850-5, compact cryogenic complex produced by VNIIFTRI and Mössbauer furnace MBF-1100-TR.

For processing and analysis of the Mössbauer spectra we used methods of recovery hyperfine parameter distributions and fitting in the SSMS cycloid type model implemented in the program SpectrRelax [12, 13].

3 Result and discussions

3.1 Study of the spatial spin-modulated structure

According to papers [4, 5] the spatial dependence of angle $\vartheta(x)$ 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:

$$\cos\vartheta(x) = \mathrm{sn}\left(\frac{4K(m)}{\lambda}x, m\right) \text{ at } K_u > 0 \text{ ("easy axis")}, \quad (1)$$

$$\sin\vartheta(x) = \mathrm{sn}\left(\frac{4K(m)}{\lambda}x, m\right) \text{ at } K_u < 0 \text{ ("easy plane")}, \quad (2)$$

where x is the coordinate along the direction of wave propagation, λ is the anharmonic spin modulation wavelength, $0 \le m < 1$ is the (anharmonicity) parameter of Jacobi's elliptic function, and $K(m)$ is a complete elliptic integral of the first kind.

The results of the analysis of Mössbauer spectra of nuclei ^{57}Fe in $BiFeO_3$ at $T < T_N$ in the context of the cycloid type SSMS model are presented in Fig. 1. One can see a model envelope curve fitting well experimental Mössbauer spectrum (Fig. 1a). 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.

As we can see (Fig. 1b), the distributions $p(H_n)$ contain two distinct local maxima with different intensities with depressions between them. The partial spectra related to these local maxima have almost the same shifts, but different in the magnitude and sign of the quadrupole shift. For the multiferroic $BiFeO_3$ the maxima of the intensity of the distribution $p(H_n)$ with large field values correspond to the orientations of the magnetic moment of the iron atoms parallel to the axis of symmetry of the crystal ($H_\parallel$), and the maxima with lower field values – perpendicular to this axis ($H_\perp$) [7, 14].

The distribution profiles of $p(H_n)$ allow us to judge not only the existence of SSMS in the studied compound, but also on the degree of anharmonicity of SSMS. When $m \to 0$, the SSMS becomes harmonic (sinusoidal). This means that the $p(H_n)$ distribution will have a symmetrical shape with equal height peaks at the edges and a minimum in the middle. If $m \to 1$, then the anharmonicity of the SSMS increases, and the difference in the intensities of the maxima increases.

A comparison of the distributions $p(H_n)$ shown in Fig. 1, indicates a very important experimental fact, namely, as the temperature increases, the ratio of the intensities of the maxima of the distribution $p(H_n)$ changes. At temperatures of 80, and 300 K, the left maximum in the distribution $p(H_n)$ is of lower intensity, and the right-hand maximum is of higher intensity, while for the spectra measured at temperatures of 350 and 500 K, the right-hand maximum of $p(H_n)$ already has a smaller, and the left one – most intensity. This means that with increasing temperature the relative number of Fe atoms that have magnetic moments oriented perpendicular to the axis of symmetry of the crystal, increases, and the relative number of Fe atoms with the orientation of the moments along the axis of symmetry decreases.

The fitting of the spectra showed that for the temperature range 4.85–300 K the best description of the experimental spectrum was achieved using the equation (1), which corresponds to a uniaxial magnetic anisotropy ($K_u > 0$), and in the region 350 – 585 K – of the equation (2), which corresponds to a magnetic anisotropy of the easy plane type ($K_u < 0$). A change in the sign of the magnetic anisotropy constant with an increase in temperature means a change in the type of magnetic anisotropy with "easy axis" on the "easy plane".

The values of the anharmonicity parameters m of the cycloid type SSMS, obtained as a result of fitting the Mössbauer spectra of $BiFeO_3$, measured in the temperature range 4.85–585 K, are shown in Fig. 2. With increasing temperature in the region T < 330 K, in which a magnetic anisotropy of the "easy axis" type exists, the parameter m decreases, the ratio of the intensities of the maxima in the distribution $p(H_n)$ and SSMS becomes more harmonious. At $T \to 330$ K, the anharmonicity parameter $m \to 0$, which corresponds to a harmonic SSMS. With a further increase of the temperature in the region T > 330 K, in which there is a magnetic anisotropy of the "easy plane" type, the parameter m increases and the SSMS becomes more anharmonic.

We estimate the values of the magnetic anisotropy constant K_u as a function of temperature for the multiferroic $BiFeO_3$, using the experimental values of the parameter m obtained by us.

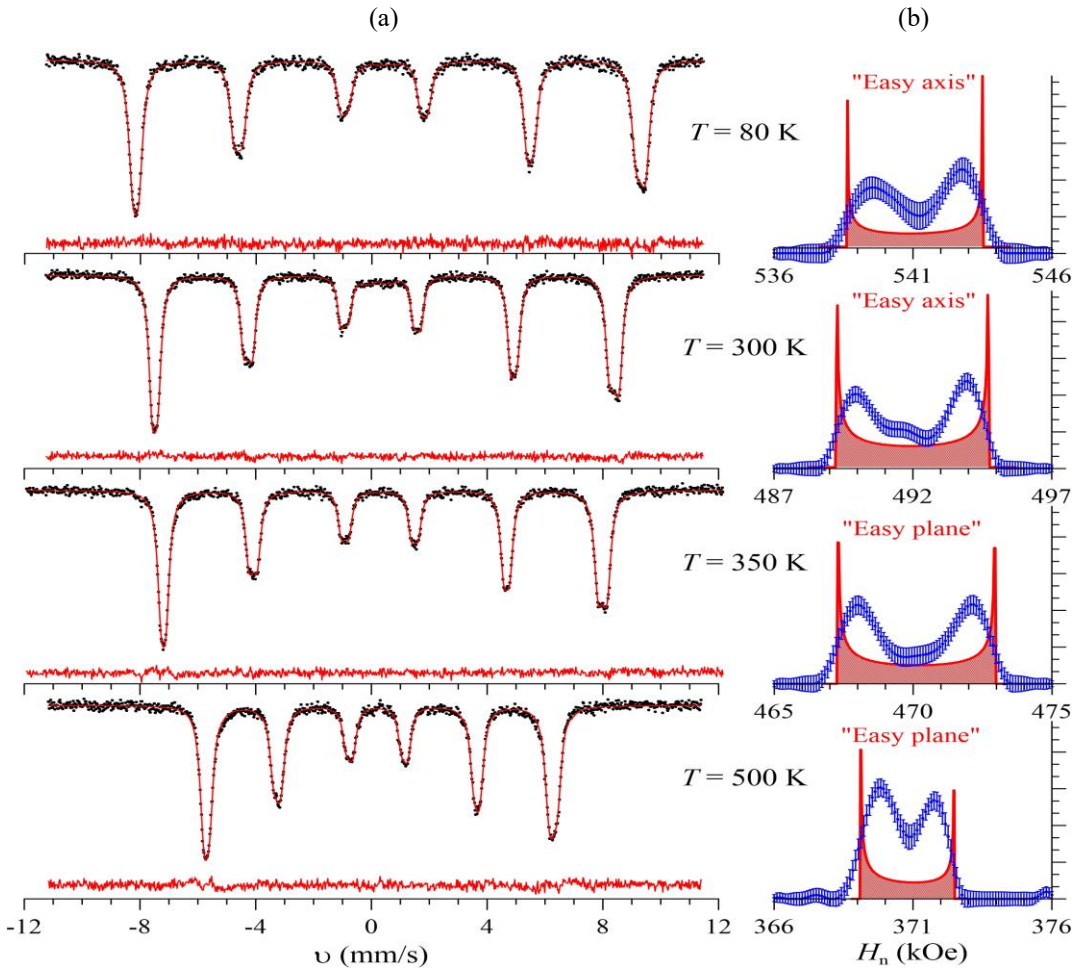

Fig. 1. ^{57}Fe Mössbauer spectra (a) and results of its processing using the method of the reconstruction of the hyperfine parameter distributions and within the model of the cycloidal type SSMS for $Bi^{57}Fe_{0.10}Fe_{0.90}O_3$ at various temperatures. (b) Distribution of the hyperfine magnetic field $p(H_n)$ (points with standard deviation are the result of distribution reconstruction; solid line with shaded area is $p(Hn)$ distribution calculated in the terms of cycloid type SSMS model).

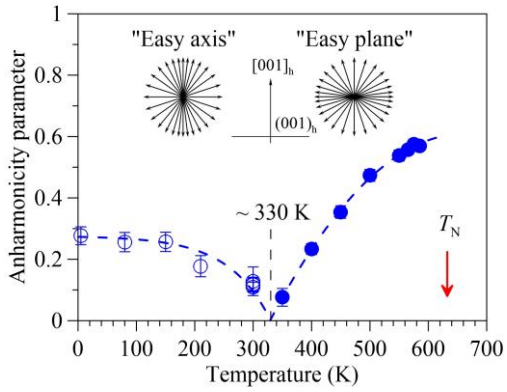

Fig. 2. The anharmonicity parameter m of the cycloid type SSMS as a function of temperature. The insets schematically show the spin spatial variation in the cycloids with ″easy axis″ and ″easy plane″ anisotropy.

For this purpose, we use the relations connecting the magnetic anisotropy constant K_u, the anharmonicity parameter m, the SSMS wavelength λ, the Néel temperature T_N and the distance between the nearest iron atoms $a_{Fe\text{-}Fe}$ [14].

When estimating the magnetic anisotropy constant K_u the length of the cycloid in $BiFeO_3$ was assumed to be λ = 620 Å (according to [3]) and only slightly change with temperature [15], the value of T_N was taken equal to 633.1 K [10], the distance $a_{Fe\text{–}Fe}$ was set to 4 Å [14].

As a result, it was found that at T = 4.85 K the anisotropy constant is $K_u \approx 1.0 \cdot 10^6$ erg/cm^3, at $T \rightarrow 330$ K $K_u \rightarrow 0$, then changes sign and increases in absolute value to $3.0 \cdot 10^6$ erg/cm^3 at T = 580 K.

3.2 Mechanism of changing the type of magnetic anisotropy

The temperature induced switching of the magnetic anisotropy type from easy plane to easy axis one observed in the experiment can be explained by the competition of several contributions to the effective anisotropy of bismuth ferrite:

$$K_{u\_eff} = K_u - \chi_\perp \frac{H_{DM}^2}{2} - \chi_\perp \frac{H^2}{2} \qquad (3)$$

where K_u is the anisotropy constant of antiferromagnetic system, the second term is the contribution of weak ferromagnetism, the third one appears in external magnetic field H; $\chi_\perp = 4.7 \cdot 10^{-5}$ is magnetic susceptibility in the direction perpendicular to the moments in antiferromagnetic lattices, and H_{DM} is Dzyaloshinskii-

Moriya field responsible for the weak ferromagnetism. At low temperatures ($T = 4.2$ K) the constant values are: $K_u = 6.6 \cdot 10^5$ erg/cm^3, $H_{DM} = 120$ kOe [16] and the resultant anisotropy in the absence of external magnetic field is the easy axis one.

The high magnetic field experiments [16-18] show that at some critical field the spin cycloid state is suppressed and the phase transition occurs to the homogeneous magnetic state with the in-plane orientation of the magnetic moments.

Noteworthy that this critical field strongly depends on the temperature [18] decreasing from 18 Tesla to several Tesla in the vicinity of Neel temperature. Since the perpendicular susceptibility $\chi_\perp$ is temperature independent this fact denotes the different temperature dependence of the first and second terms in (3). At some temperature, the second term in (3) can outbalance the first term and the magnetic anisotropy becomes the easy-plane one even in the absence of the external magnetic field.

We can estimate this critical temperature using the graph from [18] and the condition of spin cycloid suppression [16]:

$$K_{u\_eff} < -\Delta W_{cycloid} \quad (4)$$

where $\Delta W_{cycloid}$ is the energy gain due to the cycloid formation.

At critical temperature, the first two terms in (3) compensate each other and the phase transition condition (4) takes the form:

$$\chi_\perp \frac{H_c^2}{2}\bigg|_{T=T_c} = \Delta W_{cycloid}. \quad (5)$$

$\Delta W_{cycloid}$ can be estimated as ~ 500 kerg/cm^3 [19] that in accordance with (5) corresponds to the H_c ~ 15 Tesla. Using the graph in Fig. 3 [18] we obtain the corresponding critical temperature about 350 K that is close to the value 330 K for pure bismuth ferrite and lies within the range of critical temperatures for substituted compounds (300-400 K).

4 Conclusions

The temperature-dependent evolution of the spatial spin-modulated structure in multiferroic $BiFeO_3$ was detailed study by ^{57}Fe Mössbauer spectroscopy. The Mossbauer spectra have been analyzed by recovery of hyperfine parameter distributions and fitting in the SSMS cycloid type model methods. It is established that at temperature ~330 K, the type of magnetic anisotropy from the "easy axis" to the "easy plane" changes. With increasing temperature in the region $T < 330$ K, in which there is a magnetic anisotropy of the "easy axis" type, the anharmonicity parameter m decreases, and SSMS becomes more harmonious. At $T \rightarrow 330$ K, the anharmonicity parameter $m \rightarrow 0$, which corresponds to a harmonic SSMS. With a further increase of the temperature in the region $T > 330$ K, in which there exists a magnetic anisotropy of the "easy plane" type, the parameter m increases and the SSMS becomes more anharmonic. The magnetic anisotropy constant K_u as a function of temperature has been derived from the observed anharmonicity.

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