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Magnetic interactions in Aurivillius phase $Bi_5FeTi_3O_{15}$ structure

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This paper analysis the temperature dependence of FC and ZFC magnetization for $Bi_5FeTi_3O_{15}$ multiferroic. It has Aurivillius four-layer phase structure. The analysis evidence on the influence of the grains of this material on its overall magnetic properties. The lack of a dramatic temperature threshold in the FC(ZFC) dependences may result in spin canting induced by the Dzyaloshinskii–Moriya interaction.

Keywords: Aurivillius phases, perovskites, magnetic properties.

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1. Introduction

Aurivillius phase-structured $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ multiferroics are prospective materials for ferroelectric random access memory (FeRAM) as materials for spintronics and photovoltaics [1–4].

In general, the crystal structure of Aurivillius phases is an alternation of $F = \{(Bi_2O_2)^{2+}\}_\infty$ bismuth-oxygen layers and $P = \{(Bi_{m+1}Fe_{m-3}Ti_3O_{3m+1})\}^{2-}$ perovskite-like units composed of different numbers of layers m based on the $BiFeO_3$ multiferroic. Accordingly, the unit cell of $Bi_5FeTi_3O_{15}$ contains $m = 4$ layers in a perovskite-like unit (Fig. 1).

It was established in [3–5], that the distribution of Fe/Ti ions in the Aurivillius phase structure with $m \leq 5$ is ordered and cations of iron occupy mainly $B(1)$ positions in the internal layers of the perovskite-like unit, while titanium cations occupy $B(2)$ positions on its external layers (Fig. 1). The character of this distribution affects the stability of materials based on them and correlates with changes in their functional (including magnetic) characteristics [2–4,6–8]. As of today, the magnetic behavior of Aurivillius phases is a subject under discussion, because despite of the gained experimental data (see, for example, the review [1] and references in it), there is no single interpretation of the observed magnetic response. Therefore, the study of local interaction of magnetic cations in such structures is a topical problem.

The experimental results presented in [4,9–11] uncover the difficulties of synthesis of materials based on $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ with $m > 5$ compounds regardless the chosen technology. The formation of impurity phases in these materials on the basis of the Bi_2O_3-Fe_2O_3 system [12] makes it difficult to interpret the magnetic response. Therefore, from the fundamental point of view, the $Bi_5Ti_3FeO_{15}$ four-layer compound is a convenient model object to clarify the peculiarities of Aurivillius phase magnetization, because materials based on this compound yield maximum output of the target product.

As shown in [4,5], the $Bi_5FeTi_3O_{15}$ compound is paramagnetic at room temperature, and near magnetic ordering is typical for it. In [7] the magnetic behavior of $Bi_5FeTi_3O_{15}$ is described as a short-range (localized) antiferromagnetic interaction. As noted in many studies (see, for example, the

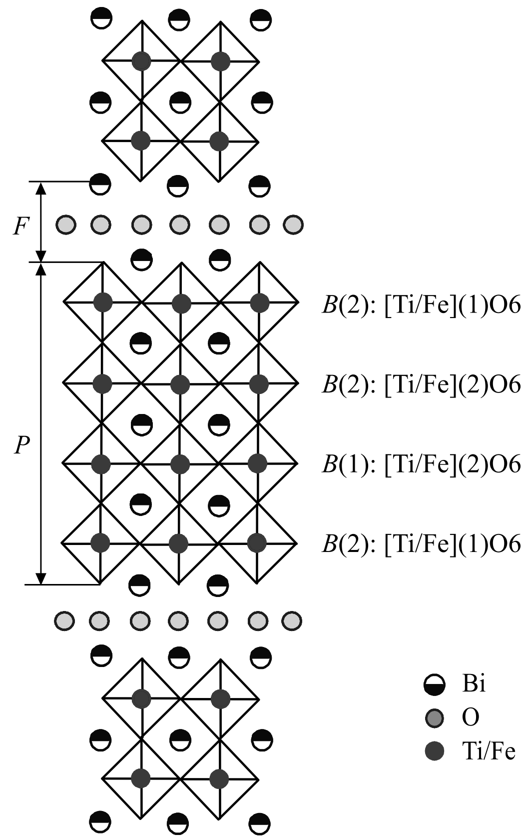

Figure 1. Scheme of layers arrangement in the $Bi_5FeTi_3O_{15}$ structure.

review [1] and references in it), prospective materials for technical applications are those where magnetic order can be achieved at temperatures higher than room temperature. At the same time, a suggestion is made that the Aurivillius phase $Bi_5FeTi_3O_{15}$ with $m = 4$ is not among these materials. There are relatively few theoretical models of $Bi_5FeTi_3O_{15}$ magnetization. The main models are presented in [7,8] and describe the peculiarities of Fe^{3+} ions bonds in the structure with neighbor atoms contributing to the magnetization.

This work is the first to perform analysis of the experimental dependence of $Bi_5Ti_3FeO_{15}$ magnetization on temperature in comparison with theoretical data and to discuss the nature of this dependence.

2. Experimental procedure

The material is synthesized by the method of solid phase chemical reactions. Initial reagents for the synthesis were oxides of bismuth, ferrum (III), and titanium (IV), taken in the stoichiometry of the $Bi_5FeTi_3O_{15}$ compound. For detailed description of this technology, see [9]. To change the magnetization, a sample was used in the form of polycrystal powder.

Phase composition was determined using Shimadzu XRD-7000 diffractometer. We used CuK_α radiation with a wave length of $\lambda = 1.541$ Å. Refinement of x-ray diffraction pattern by the method of fundamental parameters has shown good agreement of the line profile with the experimental data. Parameters of the rhomboidal unit cell are in agreement with the known data and presented in Fig. 2.

The composition of elements was determined by the method of energy dispersive microanalysis (FEI Quanta 200 scanning electron microscope with EDAX accessory). The

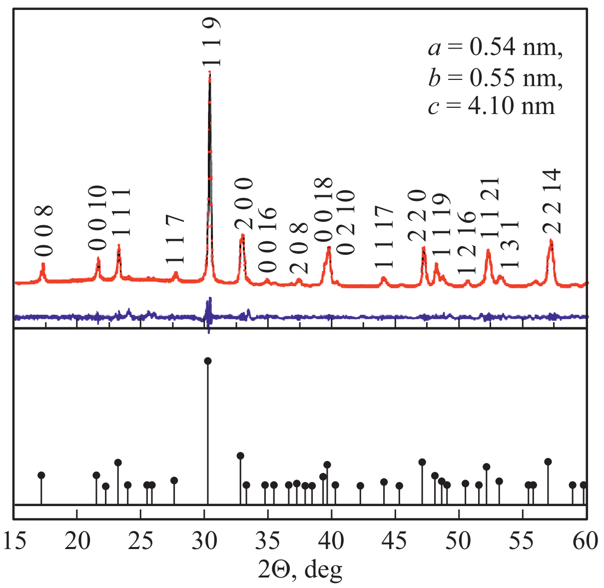

Figure 2. X-ray diffraction pattern of $Bi_5FeTi_3O_{15}$. Top panel — experimental data, bottom panel — reference data for position of peaks (JCPDS Card No. 01-089-8545), spatial group A21*am*.

data of x-ray diffraction analysis and element analysis have shown that the produced material is a single-phase material and composition of the target product is compliant with the stoichiometric composition.

Magnetic measurements were conducted on PPMS Quantum Design vibrating magnetometer in the temperature range of 5–300 K. Temperature dependencies of specific magnetization M in zero field cooling (ZFC) and field cooling (FC) modes were recorded in the external field of $H = 500$ Oe.

3. Experimental results

Results of the magnetic experiment for the obtained material are shown in Fig. 3, 4. To interpret magnetic interactions in the $Bi_5FeTi_3O_{15}$ structure, we use the following chain of reasoning. To qualitatively describe the magnetic characteristics, a model of unordered quasi-two-dimensional Heisenberg magnet at weak interaction between cations of neighbor layers is used: in the case of $Bi_5FeTi_3O_{15}$ its unit cell contains four perovskite-like layers (Fig. 1). At the same the case of diluted magnet is implemented because cations of ferrum involved in the antiferromagnetic interaction are substituted by cations of titanium, which results in their ferromagnetism.

In fact, in the case if the nearest neighbors of ferrum are the Fe^{3+} ferrum ions themselves (with an electron configuration of $d5$), interacting with each other through the oxygen anion, then so called superexchange interaction is manifested between them according to the Goodenough–Kanamori rule [13,14], which results in formation of the antiferromagnetic bond. Titanium cations are non-magnetic and, therefore, in the case of their neighborhood with Fe^{3+} the superexchange interaction is broken, and ferrum cation becomes ferromagnetic. Since in the ideal case each of the four layers in the perovskite-like unit can be described by simple cubic lattice with four layers along the c axis, each position of the magnetic cation in it is filled with a probability of x. In [7] a suggestion is made that Fe^{3+} ions occupy their positions in a random way, while in [4,5] it is established that in the structure of $Bi_5FeTi_3O_{15}$ compound they are localized in an ordered manner and predominantly in the internal positions of the perovskite-like unit (Fig. 1)

The conditions of percolation by the example of the cubic cell are considered in [7,8], where it is shown that the critical concentration of magnetic cations for its implementation must be $x_c \approx 0.312$. According to structural features of $Bi_5FeTi_3O_{15}$, the percolation threshold for this compound is as low as $x = 0.25$. Therefore, the authors of [7] study the magnetism of localized states, assuming the percolation is impossible due to the difference between the theoretical and experimental values of x. Within the assumptions made, the authors also have quantitatively estimated the temperature behavior of magnetization dependence and the temperature of transition to non-magnetic state, which

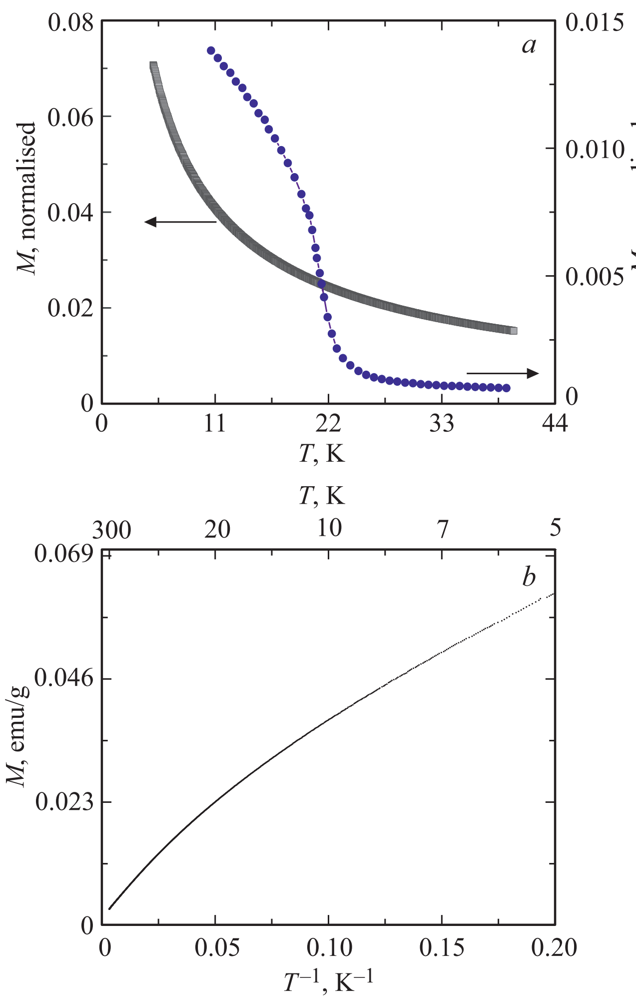

Figure 3. (*a*) Dependencies of FC/ZFC magnetization (coincident) on temperature (5–300 K) normalized to the area under the relevant curve, in the range of 4.2–40 K. Squares — experiment of this study, circles — calculated data of [7] for the following system: $8n \times n \times n$ unit cells with $n = 4$. (*b*) Experimental dependencies of FC/ZFC (coincide) on inverse of temperature.

is approximately equal to $T \sim 22$ K. The dependence of magnetization on temperature obtained in our work, as can be seen from Fig. 3, *a*, however, is considerably different from the theoretical forecasts of [7]. In particular, there is no any abrupt drop of magnetization at $T \sim 22$ K observed on the experimental dependence. The differences between the experiment and the theoretical calculation are most likely manifested due to the contribution into the behavior of the dependence from other effects, different from those considered in [7]. Indeed, according to literature sources [15–17] they may be explained by several mechanisms, such as spin quantization caused by Dzyaloshinsky–Moriya (DM) interactions, exchange ferromagnetic bond between Fe^{2+} and Fe^{3+} ions and with enriched Fe nanodomains, as well as the role of the exchange interaction between F-centers can not be ruled out [15–17]. Since in the $Bi_5FeTi_3O_{15}$ material under consideration the ions of ferrum are in the Fe^{3+} state [5], the observed effects may be related mainly to spin quantization, caused by the DM interaction.

Let us consider more specifically the mechanisms of magnetization. For this purpose, let us refer to Fig. 3, *b* that shows the dependence of magnetization M plotted as a function of inverse of temperature to rule out the contribution of paramagnetism. As known, the paramagnetic response of material is described by Langevin formalism, and in the case of its manifestation the $M(1/T)$ curve would have the form of logistic dependence. However, the obtained experimental dependence can not be described in this way. Also, note that temperature dependencies of magnetization measured for the case of presence of an external field (FC) and for the case of absence of such a field (ZFC) are coincident. This may be related to the manifestation of spontaneous

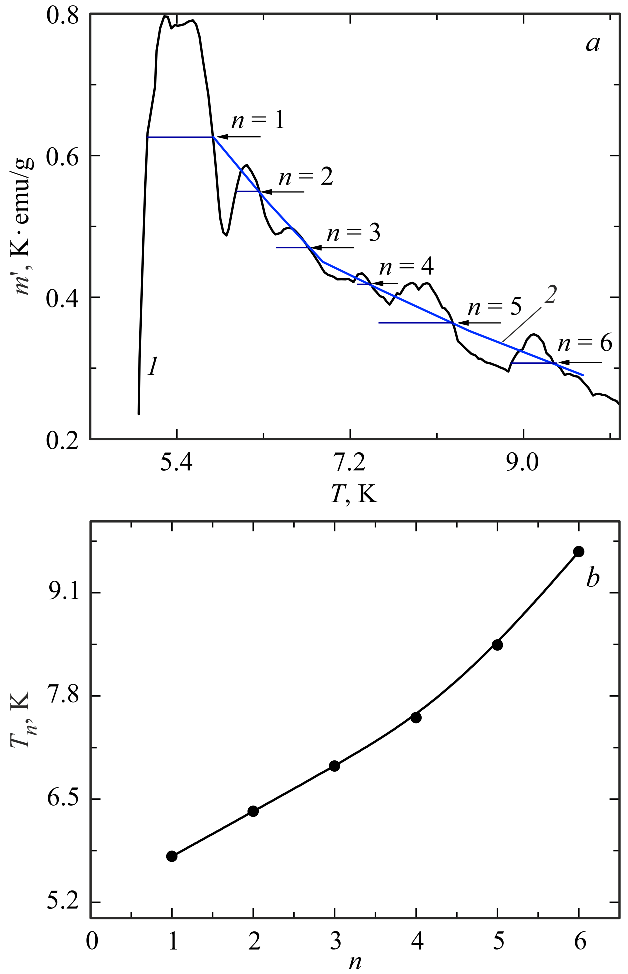

Figure 4. (*a*) The temperature dependence of first derivative m' of $M(T^{-1})$, represented in Fig. 3, *b* in the region of features manifestation — curve *1*. Shelves in the figure — geometric mean between neighbor points of maxima and minima. Curve *2* — result of geometric smoothing of maximum and minimum values of oscillations. The arrows show intersection points of the smoothed and non-smoothed dependencies. (*b*) Energy for intersection points of Fig. 4, *a* marked with arrows depending on their sequential numbers. Solid line — parabolic approximation.

magnetization, that can not be counteracted by the magnetic field of 500 Oe.

It can be seen in Fig. 3, that the shown dependence — the superposition of an oscillating function and a function that monotonously decrease with increase in temperature, a weak ferromagnetism is remained contrary to the forecasts of theoretical work [7], until room temperature. At the same time similar dependencies of FC and ZFC are monotone functions of inverse of temperature (see Fig. 3).

Figure 4, *a* shows the first derivative of magnetization with respect to inverse of temperature m'. It should be noted that with the differentiation to smooth out the noise inherent to the experimental setup, the experimental points were smoothed by the Savitzky–Golay method [15] using a polynomial of degree two over a window with ten reference points, and the degree of polynomial and the number of points were selected empirically.

The oscillations could be related to the contribution to magnetization from the magnons subjected to geometric confinement by suitable granules of powder of the material in question, exhibiting ferromagnetic properties. Such a localization could result in oscillations on the $m'(1/T)$ dependence, which are observed in the experiment. In this case the magnons could be excited by the mechanism of their interaction with phonons of the material's lattice. This interaction is covered in [19].

Let us test this hypothesis. It is known that dispersion equation for magnons has the following form:

$$\varepsilon = Ak^2, \tag{1}$$

where $k = 2\pi/\lambda$ — wave vector of the magnon, and λ — wave length of the magnon, A — constant value.

In case of the simplest model of localization of a magnon on a branch of percolation cluster with a length of L, a half-integer number of wave lengths can be fitted on it, i. e.

$$L = n\,\frac{\lambda}{2}, \tag{2}$$

$$k_n = n\,\frac{\pi}{L}, \tag{3}$$

$$\varepsilon = Ak_n^2. \tag{4}$$

It follows from equation (4) that in the case of confinement the spectrum of magnons is quantized. If we assume that the generation of magnons is related to the lattice temperature and takes place due to the relation between magnons and phonons, then the magnetization dependence on temperature should have peaks at the temperatures equal to permitted magnon energies. Also, note that at low values of k the dependence (4) is close to linear.

To test the hypothesis of the impact of magnon spectrum quantization on the magnetization, let us consider the following approach. As noted above, the dependence of derivative on temperature is a function that monotonously decreases with increase in temperature, on which oscillations are superimposed. That is the procedure of differentiation allowed us to discover a hidden regularity for the magnetization dependence on temperature.

To refine the temperatures where extremums are observed on the oscillating hidden contribution to the magnetization, it is necessary to highlight a trend in Fig. 4 that is monotonously varying with increase in temperature. For this purpose a geometric filter was applied, being similar to that previously used in [20] to study the interference pattern in thin films. Its essence is that in the interval between successive minima and maxima of an oscillating interference function the value of this function was substituted by the geometrical mean of maximum and minimum, respectively. In this case the straight line section between successive geometrical mean values is the zero reference level of the oscillations. The result of this procedure for our case is shown in Fig. 4 *a*. Arrows and shelves mark the geometrical mean values, for convenience the line of the trend of interest is drawn through the marked values using polynomial approximation.

It is common knowledge that if the first derivative changes its sign from plus to minus when passing through the extremum point, the extremum is a maximum of the oscillating function of magnetization. Note, that it can be seen from Fig. 4, *a* that all the points marked with arrows meet the criterion of sign change when passing from neighboring points of maximum to points of minimum with the trend curve used as a reference. A curve drawn through these points, as shown in Fig. 4, *a*, uncovers a general monotone trend of m' for the behavior of non-oscillating contribution to the magnetization.

At the next stage a dependence shown in Fig. 4, *b* is built depending on the integer number n (with increase in n the energy increases). In the case of magnon confinement this dependence should be an analog of magnon dispersion. However, with this dispersion dependence the zero wave vector should have correspondent zero energy in accordance with (4). Since the zero energy is not reached in Fig. 4, *b*, a conclusion could be made that the oscillations in Fig. 4, *a* are not related to confinement of magnons. However, as it turned out a similar dependence was observed in [21] not that long ago.

Note, that the oscillations of magnetization can be resulted from the interaction of ferromagnetic grains of the $Bi_5FeTi_3O_{15}$ powder under study, because the powder of the material under study contains grains that interact with each other. This interaction is suppressed by temperature. First the most weakly bonded grains are suppressed. Similar model is used in [22] to explain oscillations of ferromagnetic graphite magnetization.

4. Conclusion

This work considers the features of magnetic interactions in the structure of a polycrystalline material based on the $Bi_5FeTi_3O_{15}$ four-layer perovskite-like compound of Aurivillius phase type. It is shown that the behavior of magnetization dependencies for two variation modes, FC and ZFC, is considerably different from the theoretic forecasts. As opposed to the theory, the experimental data in the temperature range of 5−40 K has no an abrupt temperature transition to the non-magnetic state at 22 K. Therefore, when designing materials based on the Aurivillius phase, where the magnetic order can be achieved at temperatures higher than room temperature, it is necessary to take into account the role of different effects, related first of all to the spin quantization caused by Dzyaloshinsky−Moriya interaction.

On the derivatives of experimental FC and ZFC temperature dependencies of magnetization of this material some features are manifested that can characterize the impact on the dependencies caused by the specifics of grains magnetization in the polycrystalline material based on the $Bi_5FeTi_3O_{15}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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