Research Article

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Magnetic behavior of Fe-doped of multicomponent bismuth niobate pyrochlore

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Abstract: Two series of iron-containing solid solutions $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ and $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ of pyrochlore structure were obtained by the traditional solid phase synthesis method. The electronic state and character of exchange interactions of iron atoms in solid solutions were investigated by methods of magnetic dilution and NEXAFS-spectroscopy. According to X-ray spectroscopy and magnetic susceptibility data, iron(III) atoms are distributed mainly in octahedral positions of niobium(V) and in a dominant amount are in the charge state of Fe(III) in the form of monomers and exchange-bonded clusters mainly with antiferromagnetic type of exchange. Differences in magnetic behavior of iron-containing solid solutions of both series have been revealed. Antiferromagnetic and ferromagnetic exchange can be realized between iron atoms, which, with increasing concentration of paramagnetic atoms and averaging structure distortions, becomes less significant. The parameters of exchange interactions in clusters and distribution of iron paramagnetic atoms depending on the concentration of solid solutions have been calculated.

Keywords: magnetic susceptibility, iron, NEXAFS, pyrochlore structural type, solid solutions

1 Introduction

Synthetic pyrochlores have been a source of continued interest for scientists around the world for several decades. Compounds with pyrochlore structure show a wide range of practically useful properties and are promising for microelectronics and some industries. Among pyrochlores are found multiferroics, superconductors, semiconductors, catalysts [1–4]. They exhibit dielectric, magnetic, electrooptical and piezoelectric properties [5–10]. Materials based on pyrochlores have already found application in solid-state devices as thermistors, thick-film resistors and communication elements and are used as components of ceramic forms for radioactive waste. The comparatively low synthesis temperature of some pyrochlores, their dielectric properties and their chemical inertness with respect to Ag-electrodes make them promising materials for the manufacture of multilayer ceramic capacitors, electronic components and devices for the microwave range [11].

Due to the flexibility of the crystal structure pyrochlores meet wide areas of homogeneity of solid solutions [12–17]. By changing the stoichiometric composition of pyrochlore one can significantly vary its physical and chemical characteristics, which allows to study the influence of the chemical composition on its properties.

In the cubic structure of pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ (Fd-3m) two mutually interacting sublattices $\text{A}_2\text{O}'$ and B_2O_6 are distinguished [1, 18]. The B_2O_6 sublattice consists of octahedrons $[\text{BO}_6]$ connected at the apex of an angle; the $\text{A}_2\text{O}'$ sublattice is formed by tetrahedrons $[\text{O}'\text{A}_4]$. The triple pyrochlores containing transition metals attract special attention [12–17, 19, 20]. Their characteristic feature is the location of transition metal cations on two non-equivalent positions A and B. Such peculiarity of the distribution of transition element cations in bismuth niobate with pyrochlore structure is noted in [14–17]. Complex bismuth-bearing pyrochlores have excellent dielectric properties [22–28]. Among them are $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ [8, 22, 23], $\text{Bi}_2(\text{Zn}_{1-x}\text{Ni}_x)_{2/3}\text{Nb}_{4/3}\text{O}_7$ [24], $\text{Bi}_{2-x}\text{La}_x\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ [27], Cu-doped $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ [28].

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Figure 1: X-ray diffraction patterns of the series of the solid solutions $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ (a) and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ (b) at $x=0(1)$, 0.005(2), 0.01(3), 0.03(4), 0.04(5), 0.06(6)

Previously, we studied the possibility of obtaining cobalt-containing solid solutions of bismuth-magnesium niobate with pyrochlore structure when replacing magnesium or niobium atoms. As a result, it has been established that cobalt(II) atoms in both series of preparations mainly replace octahedral positions of niobium(V). This paper shows the results of the study by NEXAFS-spectroscopy and magnetic dilution of the distribution, electronic state and nature of interatomic interactions of iron atoms in Fe-doped of multicomponent bismuth niobate pyrochlore.

2 Experimental

Iron-containing solid solutions $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ and $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ were synthesized by the standard ceramic method from oxides of bismuth (III), niobium (V), magnesium (II) and iron (III) of special purity grade as a result of gradual calcination at 650, 850, 950 and 1100°C. The phase composition of the samples was monitored by means of scanning electron microscopy (electron scanning microscope Tescan VEGA 3LMN, energy dispersion spectrometer INCA Energy 450) and X-ray phase analysis (a DRON-4-13 diffractometer, $\text{CuK}\alpha$ emission). The unit cell parameters of solid solutions were calculated using the CSD software package [29]. The Faraday method was used to measure the magnetic susceptibility of solid solutions in a wide temperature range of 77–400 K and magnetic field strengths of 7240, 6330, 5230 and 3640 Oe. The measurement technique is described in detail in [30]. Samples of solid solutions were studied by X-ray absorption (NEXAFS – Near Edge X-ray Absorption Fine Structure) spectroscopy at the Russian-German channel of the BESSY-II synchrotron source in Berlin. The NEXAFS spectra of solid solutions were obtained using the total electron yield (TEY) method [31].

2.1 X-ray phase analysis and microstructure

The formation of solid solutions of $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ ($x \leq 0.06$) composition was determined by the X-ray phase analysis (Figure 1a, 1b).

In the $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ samples can be present in trace amounts the phases $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ and MgNb_2O_6 [32, 33].

Calculation of the unit cell parameters showed that the lattice constant of diluted solid solutions of both series slightly changes with the growth of iron content: for $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ $a=1.05445$ ($x = 0.03$) and $a = 1.05441$ nm ($x = 0.06$); for $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ $a = 1.05369$ ($x = 0.03$) and $a = 1.05493$ nm ($x = 0.06$) and close to the parameter of bismuth-magnesium niobate with pyrochlore structure [22–24]: $a = 1.056$ nm. Such a change of the cell parameter in the case of solid solutions $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ may be due to isomorphic substitution of niobium (V) atoms by close in size iron atoms Fe(III) ($R(\text{Nb(V)})_{c.n.-6} = 0.64$, $R(\text{Fe(II)})_{c.n.-6} = 0.61$ (L.S.) and 0.78 (H.S.), $R(\text{Fe(III)})_{c.n.-6} = 0.55$ (L.S.) and 0.645 (H.S.)). The smaller parameter of the $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ cell in comparison with undervalued bismuth-magnesium niobate ($a=1.056$ nm) also indicates the presence of iron mainly in the Fe(III) ($R(\text{Bi(III)})_{c.n.-8} = 1.17$, $R(\text{Fe(II)})_{c.n.-8} = 0.92$, $R(\text{Fe(III)})_{c.n.-8} = 0.78$ and $R(\text{Mg(II)})_{c.n.-8} = 0.89$ [34]. Meanwhile, the possibility of placing a part of iron (III) ions in Bi(III) position and the presence of some Fe(II) ions is not excluded.

2.2 NEXAFS-spectroscopy

To determine the charge state of doped iron atoms by NEXAFS (near-edge X-ray absorption fine structure) spectroscopy, Fe, Mg-codoped bismuth niobate pyrochlore and iron oxides FeO [35], Fe_2O_3 and Fe_3O_4 were investigated. Fe2p- absorption spectra are presented in Figure 2. The

Figure 2: NEXAFS Fe2p -spectra of $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$

main components of the spectra of investigated samples practically coincide with each other in both number and energy position of the main absorption bands. Moreover, the Fe2p-spectra of Fe_2O_3 oxide are almost identical. Based on this, we can assume that iron atoms in solid solutions of magnesium-bismuth niobate are mainly trivalent, i.e., they have the charge state of Fe^{3+} . It is interesting to note that in the Fe2p spectrum of the $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ solid solution the band at ~ 708 eV is blurred and its intensity is less than for Fe_2O_3 and $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$. This is possible for two reasons, one of which is the presence of Fe(II) ions and the other is the presence of Fe(III) ions in an oxygen environment other than the octahedral environment. This is possible provided that magnesium cations partially occupy bismuth positions, and if the latter are scarce, there are vacancies for iron ions.

Due to the fact that iron cations in iron oxides (II,III) occupy octahedral positions it can be concluded that iron ions in Fe, Mg-codoped bismuth niobate pyrochlore also have predominant coordination six. Since in solid solutions of $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ there is a large proportion of six-coordinated Fe(III) ions, according to NEXAFS spectroscopy, we can speak, in general, about the desire of iron ions (III) to take octahedral positions [36–42].

2.3 Magnetic properties

Calculation of paramagnetic components of magnetic susceptibility $[\chi^{\text{para}}(\text{Fe})]$ and values of effective magnetic moments $[\mu_{\text{eff}}(\text{Fe})]$ of iron atoms at different temperatures and for different concentrations of solid solutions was carried out (Figures 3a–3d). The main contribution to the magnetic susceptibility is made by paramagnetic iron ions. The cor-

rection from the diamagnetic ions Bi (III), Nb (V), Mg (II) is very small [43]. The methods of measuring magnetic susceptibility and calculation are described in [30]. The dependence of the inverse value of paramagnetic susceptibility $(1/\chi_{\text{Fe}}^{\text{para}})$ on temperature is linear over the entire temperature range and is subject to Curie-Weiss law. The Curie-Weiss constant for both series of solid solutions is negative, which indicates the dominant antiferromagnetic interactions between paramagnetic atoms. For $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ solid solutions, it varies slightly from -15.8 ($x = 0.005$) to -10.8 K (0.06); for $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$, in contrast, it decreases from -11.2 to -26.7 K, respectively.

The change in the Weiss constant indicates that the proportion of antiferromagnetically bonded units increases with the increase in iron atom content in $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$. The difference in Weiss constant values for both series of solid solutions may be due to the presence of some fraction of noninteracting Fe(III) monomers in bismuth positions in $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$. Paramagnetic isotherms of the magnetic susceptibility of iron atoms are typical for diluted antiferromagnetics (Figures 3a, 3c). The value of the effective magnetic moment of single iron atoms in an infinitely diluted solid solution of $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ increases with temperature rise from $7.99 \mu\text{B}$ (90 K) to $8.27 \mu\text{B}$ (320 K). The overshoot of the magnetic moment with respect to the pure spin value of Fe(III) atoms ($\mu_{\text{eff}} = 5.92 \mu\text{B}$, ${}^6\text{A}_{1g}$) and Fe(II) ($\mu_{\text{eff}} = 4.9 \mu\text{B}$, ${}^5\text{T}_{2g}$) may be associated with the formation of exchange-bound units from iron atoms with predominantly ferromagnetic exchange. Apparently, the formation of clusters from iron atoms (III) in an infinitely diluted solid solution helps to stabilize the structure of solid solutions of heterovalent substitution by including oxygen vacancies in the cluster or by localizing the cluster near it. The possibility of ferromagnetic exchange, atypical for iron atoms (III), is due to geometric distortions in the polyhedral environment of iron atoms caused by anionic vacancies. The probability of realization of ferromagnetic exchange is high through cross-exchange channels, for example, $d_{x^2-y^2} \perp p_x \perp d_{xy}, d_{x^2-y^2} \parallel p_x \perp p_y \parallel d_{xy}, d_{xy} \parallel p_y \perp p_z \parallel d_{xz}$ [36–41].

For $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ solid solutions, the effective magnetic moment varies from 5.79 to $6.06 \mu\text{B}$ and is close to the pure spin value of single iron atoms (III) in Fe(III) solid solutions Fe(III) ($\mu_{\text{eff}} = 5.92 \mu\text{B}$, ${}^6\text{A}_{1g}$), which indicates a practically monomeric state of iron atoms in solid solutions at infinite dilution. The isolated state of iron atoms can be realized by assuming that iron atoms occupy cationic bismuth positions. A slight increase in the magnetic moment indicates weak antiferromagnetic interactions between the paramagnetic atoms and is due to the fact that some por-

Figure 3: Isotherms of the paramagnetic component of the magnetic susceptibility of the solid solutions $Bi_2MgNb_{2-2x}Fe_{2x}O_{9-\delta}$ (a) and $Bi_2Mg_{1-x}Fe_xNb_2O_{9+\delta}$ (b); Temperature dependences of the magnetic moment of iron atoms in $Bi_2MgNb_{2-2x}Fe_{2x}O_{9-\delta}$ (c) and $Bi_2Mg_{1-x}Fe_xNb_2O_{9+\delta}$ (d)

tion of iron ions is distributed in the cationic positions of niobium(V).

The decrease in the paramagnetic component of the magnetic susceptibility of iron atoms with an increase in the concentration of solid solutions of both series is associated with the manifestation of antiferromagnetic interactions between iron atoms. The temperature dependence of the effective magnetic moment of iron atoms in solid solutions with different concentrations of paramagnetic atoms is also indicative of this assumption.

Comparison of isotherms of magnetic susceptibility of both series of solid solutions is shown in the Figure 4. We can see from the Figure 4, that in all concentration interval the receptivity of solid solutions of $Bi_2MgNb_{2-2x}Fe_{2x}O_{9-\delta}$ is much more, than for $Bi_2Mg_{1-x}Fe_xNb_2O_{9+\delta}$. This may indicate that the exchange interaction between paramagnetic atoms, e.g., ferromagnetic type, and clusters in $Bi_2MgNb_{2-2x}Fe_{2x}O_{9-\delta}$ solid solutions can be realized compared to $Bi_2Mg_{1-x}Fe_xNb_2O_{9+\delta}$.

In order to clarify the nature of the distribution of iron atoms in both series of solid solutions and describe the exchange interactions in the clusters, the theoretical cal-

Figure 4: A comparison between paramagnetic components of magnetic susceptibility for $Bi_2Mg_{1-x}Fe_xNb_2O_{9+\delta}$ (open symbols) and $Bi_2MgNb_{2-2x}Fe_{2x}O_{9-\delta}$ (close symbols) solid solutions

ulation of susceptibility and comparison of the values obtained with the experimental ones was performed.

Calculation of experimental dependencies of $\chi_{para}(Fe)$ on solid solutions concentration was carried out within the framework of the diluted solid solution model, according to which magnetic susceptibility is defined as the sum of contributions from single paramagnetic atoms and their exchange-bound aggregates. When calculating the mag-

netic susceptibility for $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$, the existence of Fe(II) atoms was neglected. In order to estimate differences in the distribution of iron atoms in both series of solid solutions, we recorded the value of the exchange parameter in the clusters. The general formula for calculating the paramagnetic component of the magnetic susceptibility of iron atoms is a sum of contributions of the magnetic susceptibility of monomers, dimers, trimers and tetramers with antiferro and ferromagnetic type of exchange:

$$\chi_{\text{calc}}^{\text{para}}(\text{Fe}) = a_{\text{Fe(III)}}^{\text{mon}} \chi_{\text{Fe(III)}}^{\text{mon}} + a_{\text{Fe(III)}}^{\text{dim(f)}} \chi_{\text{Fe(III)}}^{\text{dim(f)}} \quad (1)$$

$$+ a_{\text{Fe(III)}}^{\text{dim(aa)}} \chi_{\text{Fe(III)}}^{\text{dim(a)}} + a_{\text{Fe(III)}}^{\text{trim(f)}} \chi_{\text{Fe(III)}}^{\text{trim(f)}} + a_{\text{Fe(III)}}^{\text{trim(ar)}} \chi_{\text{Fe(III)}}^{\text{trim(a)}} \\ + a_{\text{Fe(III)}}^{\text{tetr(ae)}} \chi_{\text{Fe(III)}}^{\text{tetr(a)}} + a_{\text{Fe(III)}}^{\text{tetr(f)}} \chi_{\text{Fe(III)}}^{\text{tetr(f)}}$$

$$a_{\text{Fe(III)}}^{\text{mon}} + a_{\text{Fe(III)}}^{\text{dim(f)}} + a_{\text{Fe(III)}}^{\text{dim(a)}} + a_{\text{Fe(III)}}^{\text{trim(f)}} + a_{\text{Fe(III)}}^{\text{trim(a)}} \quad (2)$$

$$+ a_{\text{Fe(III)}}^{\text{tetr(a)}} + a_{\text{Fe(III)}}^{\text{tetr(f)}} = 1.$$

This is $a_{\text{Fe(III)}}^{\text{mon}}$, $a_{\text{Fe(III)}}^{\text{dim(f)}}$, $a_{\text{Fe(III)}}^{\text{dim(a)}}$, $a_{\text{Fe(III)}}^{\text{tetr(a)}}$, $a_{\text{Fe(III)}}^{\text{tetr(f)}}$, $a_{\text{Fe(III)}}^{\text{trim(a)}}$, $a_{\text{Fe(III)}}^{\text{trim(f)}}$ and $a_{\text{Fe(III)}}^{\text{tetr(ae)}}$ – fraction of monomers, dimers, trimers and tetramers from iron atoms (III) with ferromagnetic - and antiferromagnetic type of interaction, $\chi_{\text{Fe(III)}}^{\text{mon}}$, $\chi_{\text{Fe(III)}}^{\text{dim(f)}}$, $\chi_{\text{Fe(III)}}^{\text{dim(a)}}$, $\chi_{\text{Fe(III)}}^{\text{trim(f)}}$, $\chi_{\text{Fe(III)}}^{\text{trim(a)}}$, $\chi_{\text{Fe(III)}}^{\text{tetr(a)}}$, $\chi_{\text{Fe(III)}}^{\text{tetr(f)}}$ – magnetic susceptibility of monomers, dimers, trimers and tetramers with ferromagnetic - and antiferromagnetic exchange.

According to the Heisenberg-Dirk-Wan-Fleck model [44], the magnetic susceptibility of tetramers consisting of paramagnetic atoms was calculated by formula (3):

$$\chi_{\text{tetr}}^{S_1-S_2} = \frac{1}{4} \frac{\sum_{S'} \sum_{S_{12}} \sum_{S_{34}} g^2(S') S'(S' + 1)(2S' + 1) e^{-E(J, S')/kT}}{8T \sum_{S'} \sum_{S_{12}} \sum_{S_{34}} (2S' + 1) e^{-E(J, S')/kT}} \quad (3)$$

Where $E(J, S') = -J[S'(S' + 1) - 4S_1(S_1 + 1)]$, $S_{12} = S_1 + S_2$, $S_1 + S_2 - 1, \dots, |S_1 - S_2|$, $S_{34} = S_3 + S_4$, $S_3 + S_4 - 1, \dots, |S_3 - S_4|$, $S' = S_{12} + S_{34}$, $S_{12} + S_{34} - 1, \dots, |S_{12} - S_{34}|$.

Here S_1 and S_2 , S_3 and S_4 – the spin values of the atoms that form tetramers, in our case $S_1 = S_2 = S_3 = S_4 = 5/2$ for the tetramer Fe(III)-O-Fe(III)-O-Fe(III)-O-Fe(III), S' and S_{12} and S_{34} – values of total spin and intermediate moments, g – Lande factor for iron atoms (III), J – exchange parameter, T – absolute temperature.

To calculate the magnetic susceptibility of dimers, the following formula is proposed (4):

$$\chi_{\text{dum}}^{S_1-S_2} = \frac{1}{2} \frac{\sum_{S'} g^2(S') S'(S' + 1)(2S' + 1) e^{-E(J, S')/kT}}{8T \sum_{S'} (2S' + 1) e^{-E(J, S')/kT}}, \quad (4)$$

Here $E(J, S') = -J[S'(S' + 1) - S_a(S_a + 1) - S_b(S_b + 1)]$, $S' = S_a + S_b$, $S_a + S_b - 1, \dots, |S_a - S_b|$; S_a , S_b – the spin values of the atoms that form dimers.

After substitution of the values, the formula 4 is converted to the formula 5:

$$\chi_{\text{dum}}^{S_1-S_2} = \frac{1}{4T}. \quad (5)$$

$$\frac{330e^{12.5x} + 180e^{2.5x} + 84e^{-5.5x} + 30e^{-11.5x} + 6e^{-15.5x}}{11e^{12.5x} + 9e^{2.5x} + 7e^{-5.5x} + 5e^{-11.5x} + 3e^{-15.5x} + e^{-17.5x}},$$

Here $x = J/kT$, k – Boltzmann's constant.

The alignment of the calculated and experimental values is achieved by minimizing the function $\sum_i \sum_j (\chi_{ij}^{\text{calc}} - \chi_{ij}^{\text{exp}})^2$, where $\sum_i$ – summation by all concentrations; $\sum_j$ – temperature totalling; χ_{ij}^{calc} , χ_{ij}^{exp} – experimental and calculated values of paramagnetic component of magnetic susceptibility of solid solutions.

Best agreement of experimental and design data for solid solutions $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ obtained at the values of the parameter of antiferromagnetic exchange in dimers $J_{\text{dim}} = -25$

Figure 5: A comparison between calculated (open symbols) and experimental (close symbols) paramagnetic components of magnetic susceptibility for $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ (a) and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ (b) solid solutions

Table 1: The results of calculating the distribution of iron atoms in the solid solutions $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$

x	$a_{\text{Fe(III)}}^{\text{trim(a)}}$	$a_{\text{Fe(III)}}^{\text{mon}}$	$a_{\text{Fe(III)}}^{\text{dim(f)}}$	$a_{\text{Fe(III)}}^{\text{dim(a)}}$	$\chi_{\text{calc}}/\chi_{\text{exp}} \cdot 10^3$, emu/mol				
					90 K	140 K	200 K	260 K	320 K
0	0	0.960	0.010	0.03	47.3/46.2	30.5/31.0	21.4/22.3	16.5/17.4	13.4/14.2
0.005	0	0.952	0.008	0.04	46.8/47.0	30.2/31.9	21.2/23.0	16.3/18.0	13.3/14.8
0.010	0	0.936	0.004	0.06	45.8/43.4	29.6/29.6	20.8/21.4	16.1/16.8	13.1/13.8
0.015	0	0.927	0.003	0.07	45.4/45.1	29.3/29.8	20.7/21.2	16.0/16.4	13.1/13.4
0.020	0	0.918	0.002	0.08	44.9/44.7	29.1/30.1	20.5/21.6	15.9/16.9	13.0/13.8
0.030	0	0.880	0	0.12	43.1/40.6	28.0/27.1	19.9/19.4	15.4/15.1	12.7/12.4
0.040	0	0.840	0	0.16	41.4/41.4	27.0/27.9	19.3/20.1	15.0/15.7	12.4/12.9
0.060	0.01	0.790	0	0.20	39.5/39.6	25.9/27.2	18.5/19.8	14.5/15.5	12.0/12.8

Note 1 – $a_{\text{Fe(III)}}^{\text{mon}}$, $a_{\text{Fe(III)}}^{\text{dim(f)}}$, $a_{\text{Fe(III)}}^{\text{dim(a)}}$ – fractions of monomers, trimers and dimers from iron (III) atoms with antiferro- and ferromagnetic type of exchange

Figure 6: Dependence of portions of the monomers $a_{\text{Fe(III)}}^{\text{mon}}$ (1), dimers with the antiferromagnetic $a_{\text{Fe(III)}}^{\text{dim(a)}}$ (2) and ferromagnetic $a_{\text{Fe(III)}}^{\text{dim(f)}}$ types of exchange (5); trimers with antiferromagnetic $a_{\text{Fe(III)}}^{\text{trim(a)}}$ (3); tetramers with the antiferromagnetic exchange type $a_{\text{Fe(III)}}^{\text{tetr(a)}}$ (4) and ferromagnetic $a_{\text{Fe(III)}}^{\text{tetr(f)}}$ types of exchange (6) on the content of iron atoms in $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ (a) and $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ (b)

cm^{-1} , in trimers $J_{\text{trim}} = -14 \text{ cm}^{-1}$ and tetramers $J_{\text{tetr}} = -9 \text{ cm}^{-1}$; ferromagnetic – $J_{\text{dim}} = 20 \text{ cm}^{-1}$, in trimers $J_{\text{trim}} = 16 \text{ cm}^{-1}$ and tetramers $J_{\text{tetr}} = 11 \text{ cm}^{-1}$. Comparison of experimental and theoretical values of magnetic susceptibility of solid solutions is shown in the Figures 5a, 5b and Table 1.

The distribution of iron atoms depending on the concentration of solid solutions $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_{9+\delta}$ is shown in the Figures 6a, 6b.

As a result of investigations of iron-containing solid solutions of $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ it was found that in an infinitely diluted solid solution iron (III) atoms are mainly in the aggregate state and form dimers, trimers and tetramers with antiferro – and ferromagnetic type of exchange. Despite the large proportion of aggregates in an infinitely diluted solution with ferromagnetic type of exchange, the exchange is generally antiferromagnetic. Apparently, this is due to a more effective overlap of the orbits involved in the exchange of atoms through the channels of antiferromagnetic exchange, and relatively small geometric distortions

of the structure of solid solutions causing ferromagnetic exchange. The share of clusters with ferromagnetic type of exchange with increasing concentration of solid solutions decreases, which is due to the averaging of local structure distortions and the formation of aggregates mainly with antiferromagnetic type of exchange.

In infinitely diluted $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ solid solutions, the magnetic moment value almost corresponds to the pure spin value for Fe(III). Therefore, the fraction of Fe(III) monomers is much larger than in $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$. The small dependence of magnetic moment on temperature is caused by the fraction of antiferromagnetically bound dimers from Fe(III) atoms. This indicates that some of the Fe(III) atoms replace the position of niobium(V), between which antiferromagnetic exchange takes place. This conclusion does not contradict the known data on the distribution of iron atoms on cationic positions in bismuth niobate with pyrochlore structure [16]. With increasing iron atom content, the proportion of monomers decreases and the propor-

tion of clusters increases, which also indicates the location of iron atoms in octahedral positions. It is interesting to note that solid solutions of both series differ significantly in their cluster composition. The share and nuclearity of clusters in $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ solid solutions is higher than in $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$. There may be two reasons for this. The first one is related to the distribution of part of iron(III) atoms in the bismuth(III) position, and the second may be related to the indirect influence of magnesium atoms on Fe(III) clustering.

Relatively low values of exchange parameters in clusters are obviously connected with competition of antiferro and ferromagnetic interactions. According to the theory of exchange channels [45], an indirect exchange of antiferromagnetic type is realized if the angle of connection between paramagnetic atoms is 180° , deviations from this value contribute to the realization of the exchange of ferromagnetic type. In the pyrochlore structure, the octahedrons are connected by the vertices, forming a three-dimensional framework of niobium-oxygen octahedron chains. Within the chains, the Fe-O-Fe connection angle is less than 180° , namely 135° , which greatly reduces $p_\pi \cdot d_\pi$ the overlap between the channels of antiferromagnetic exchange, for example, $d_{xy} \parallel p_y \parallel d_{xy}$. In addition, the introduction of iron atoms into the niobium position leads to local distortions of the octahedron, including in the plane perpendicular to the axis connecting the two atoms through oxygen, then the contribution of the second channel of antiferromagnetic exchange will greatly reduce $d_{xz} \parallel p_z \parallel d_{xz}$.

3 Conclusions

Two series of iron-containing solid solutions $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ and $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ of pyrochlore structure were obtained by solid phase synthesis method. The parameter of the unit cell of solid solutions is close to the constant cell for bismuth-magnesium niobate. As a result of NEXAFS-study of solid solutions and iron oxides it has been established that the main details of the spectra of solid solutions practically coincide with each other both in number and energy position of the main absorption bands and are identical to $\text{Fe}2p$ -spectrum of Fe_2O_3 oxide. Iron(III) cations are distributed mainly in the octahedral positions of niobium(V) and in a dominant amount are in the charge state of Fe(III) in the form of monomers and exchange-bound clusters mainly with antiferromagnetic type of exchange. The main differences in the magnetic behavior of iron-containing solid solutions of both series may be related to the uneven distribution

of cations in bismuth and niobium positions. As a result of calculating the parameters of metabolic interactions in dimers and the distribution of iron paramagnetic atoms as a function of the concentration of $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ and $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$ solid solutions, the presence of high nuclear clusters with antiferro and ferromagnetic type of interaction was established. The share and nuclearity of clusters in $\text{Bi}_2\text{MgNb}_{2-2x}\text{Fe}_{2x}\text{O}_{9-\delta}$ solid solutions is considerably higher than in $\text{Bi}_2\text{Mg}_{1-x}\text{Fe}_x\text{Nb}_2\text{O}_9$.

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