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## **NEXAFS–Spectra and Magnetic Susceptibility of Nickel and Chromium Doped of Bismuth Niobate**

**Irina E. Vasilyeva<sup>a</sup>,  
Sergey V. Nekipelov<sup>b</sup>, Boris A. Makeev<sup>c</sup>,  
Alexey G. Krasnov<sup>d</sup> and Nadezhda A. Zhuk<sup>a\*</sup>**

*<sup>a</sup>Syktывkar State University  
Syktывkar, Russian Federation*

*<sup>b</sup>Institute of Physics and Mathematics  
of the Komi Science Center UB RAS  
Syktывkar, Russian Federation*

*<sup>c</sup>Institute of Geology of the Komi Science Center UB RAS  
Syktывkar, Russian Federation*

*<sup>d</sup>Institute of Chemistry of the Komi Science Center UB RAS  
Syktывkar, Russian Federation*

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*Abstract.* The electronic state and character of exchange interactions of nickel and chromium atoms in solid solutions of  $\text{Bi}_5\text{Nb}_{3-3x}\text{M}_{3x}\text{O}_{15-\delta}$  (M-Cr,Ni) was researched by methods of magnetic susceptibility and NEXAFS-spectroscopy. NEXAFS spectra of nickel and chromium oxides were obtained. According to X-ray spectroscopy in solid solutions, chromium atoms are mainly in the charge state of Cr(III), and nickel atoms in the high-spin state of Ni(II) in octahedral coordination. In solid solutions, paramagnetic chromium and nickel atoms are present in the form of monomers and clusters with a common antiferromagnetic type of exchange.

*Keywords:* NEXAFS-spectroscopy, magnetic dilution method, exchange interactions.

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## NEXAFS-спектры и магнитная восприимчивость ниобата висмута, допированного никелем и хромом

И.Э. Васильева<sup>а</sup>, С.В. Некипелов<sup>б</sup>,  
Б.А. Макеев<sup>в</sup>, А.Г. Краснов<sup>г</sup>, Н.А. Жук<sup>а</sup>

<sup>а</sup>Сыктывкарский государственный университет  
Российская Федерация, Сыктывкар

<sup>б</sup>Институт физики и математики Коми НЦ УрО РАН  
Российская Федерация, Сыктывкар

<sup>в</sup>Институт геологии Коми НЦ УрО РАН  
Российская Федерация, Сыктывкар

<sup>г</sup>Институт химии Коми НЦ УрО РАН  
Российская Федерация, Сыктывкар

*Аннотация.* Методами магнитной восприимчивости и NEXAFS-спектроскопии исследовано электронное состояние и характер обменных взаимодействий атомов никеля и хрома в составе твердых растворов  $\text{Bi}_5\text{Nb}_{3-3x}\text{M}_{3x}\text{O}_{15-\delta}$  (M-Cr,Ni). Получены NEXAFS-спектры оксидов никеля и хрома. По данным рентгеновской спектроскопии, в твердых растворах атомы хрома находятся преимущественно в зарядовом состоянии Cr(III), а атомы никеля – в высокоспиновом состоянии Ni(II) в октаэдрической координации. В твердых растворах парамагнитные атомы хрома и никеля присутствуют в форме мономеров и кластеров с общим антиферромагнитным типом обмена.

*Ключевые слова:* обменные взаимодействия, NEXAFS-спектроскопия, метод магнитного разбавления.

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### Introduction

The Aurivillius phases are a large family of bismuth-containing layered perovskite-like compounds whose composition is described by the general formula  $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$ , where  $\text{Bi}_2\text{O}_2$  are bismuth oxygen layers and  $\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$  are perovskite-like fragments consisting of bounded tops of octahedrons  $\text{BO}_6$  with placement of large cations A in cuboctahedral voids between them [1-7]. The value of the coefficient n in this formula corresponds to the number of octahedrons  $\text{BO}_6$  by the thickness of a perovskite-like fragment and can vary from 1 to 5 and more. Along with usual layered compounds there are also so-called mixed or hybrid layered compounds  $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})\dots(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$ , in the structure of which the perovskite-like fragments of different thickness alternate. Bismuth niobate  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  belongs to the mixed layered compounds, whose structure is characterized by an ordered alternation of fragments one and two niobium thick –

oxygen octahedron, so that its structure can be described as  $(\text{Bi}_2\text{O}_2)(\text{NbO}_4)(\text{Bi}_2\text{O}_2)(\text{BiNb}_2\text{O}_7)$ , when  $n=1$  и  $m=3$  [4, 7-11].

Continuing interest for several decades in layered compounds like  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  is due to the prospects of their practical use as catalysts, elements of devices of non-volatile ferroelectric memory (FRAM), ion conductors and multiferroics. The wide range of possible applications of Aurivillius phases is determined by low dielectric permeability, high Curie temperatures and low degradation rates of materials based on them [7-10].

Previous studies of solid solutions of bismuth niobates with a layered perovskite-like structure have led to the assumption that heterovalent substitution of niobium by less valence atoms is accompanied by partial oxidation of paramagnetic atoms, while in concentrated solutions, stabilization of the structure occurs through the formation of aggregates from paramagnetic atoms [12, 13]. Information on the charge state of paramagnetic atoms was obtained earlier from EPR studies and analysis of magnetic behavior of solid solutions. The presented work shows the results of investigation of the electronic state and exchange interactions between paramagnetic atoms in solid solutions based on  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  by magnetic dilution and NEXAFS-spectroscopy.

### Objects and methods of research

Synthesis of samples of solid solutions of bismuth niobate was carried out by a standard ceramic method from bismuth oxides (III), niobium (V), nickel (II) and chromium (III) by step-by-step firing at temperatures of 650, 850 and 1050 °C. The phase composition of the studied preparations was controlled by X-ray analysis (DRON-4-13,  $\text{Cu}_{K\alpha}$ -radiation); parameters of solid solutions elementary cell were calculated using CSD package [14]. The magnetic susceptibility of solid solutions was measured by Faraday method in the temperature range 77 – 400 K at 16 fixed values of temperature and magnetic field strength 7240, 6330, 5230 and 3640 E. The accuracy of relative measurements was 2%. Samples of solid solutions were studied by X-ray absorption spectroscopy (NEXAFS – Near Edge X-ray Absorption Fine Structure) using synchrotron radiation from the BESSY II storage device (Berlin, Germany). NEXAFS spectra were obtained using Total electron yield (TEY) [15].

### Results and discussion

The chromium (nickel)-containing solid solutions  $\text{Bi}_5\text{Nb}_{3-3x}\text{M}_{3x}\text{O}_{15-\delta}$  (M-Ni, Cr) have been studied with  $0.005 \leq x \leq 0.06$ . The single-phase nature of the samples was proved by the methods of scanning electron microscopy and X-ray analyses (Figs. 1, 2). Solid solutions of  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  ( $x \leq 0.02$ ) can be crystallized in tetragonal syngony (sp. gr.  $P4/mmm$ ), unit cell parameters with  $x=0.005$  are:  $a=0.5471$ ,  $c=2.0960$  nm ( $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ , sp. gr.  $P4/mmm$ ,  $a=0.547$ ,  $c=2.097$  nm [4]); as nickel content increases, monoclinic distortion of the unit cell emerges at  $0.02 < x \leq 0.06$ . Monoclinic distortion of the tetragonal cell of the solid solutions  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  was established in previous works [16, 17] and is associated with formation of atomic defects in the structure. The X-ray patterns of the solid solutions were interpreted based on the space group  $P2/m$  [16, 17]. The unit cell unit cell parameters with  $x=0.06$  are:  $a=0.5482$  nm,  $c=2.1020$  nm,  $b=0.5458$  nm, the  $\alpha$  angle changes from  $90^\circ$  to  $90.70^\circ$ . Solid solutions of  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$  ( $x < 0.02$ ) can be crystallized in tetragonal syngony (sp. gr.  $P4/mmm$ ), unit cell parameters with  $x=0.005$  are:  $a=0.5469$ ,  $c=2.0960$  nm. The unit cell unit cell parameters with  $x=0.06$  are:  $a=0.5473$  nm,  $c=2.099$  nm,  $b=0.5463$  nm, the  $\alpha$  angle changes from  $90^\circ$  to  $90.44^\circ$ .

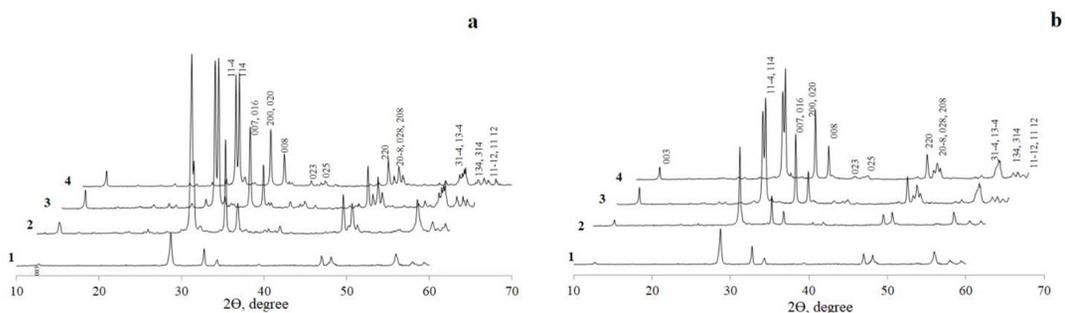


Fig. 1. X-Ray pattern for  $\text{Bi}_5\text{Nb}_{3-3x}\text{M}_{3x}\text{O}_{15-\delta}$  (M-Cr (a) and Ni (b)) at  $x=0$  (1), 0.01 (2), 0.02 (3), 0.04 (4)

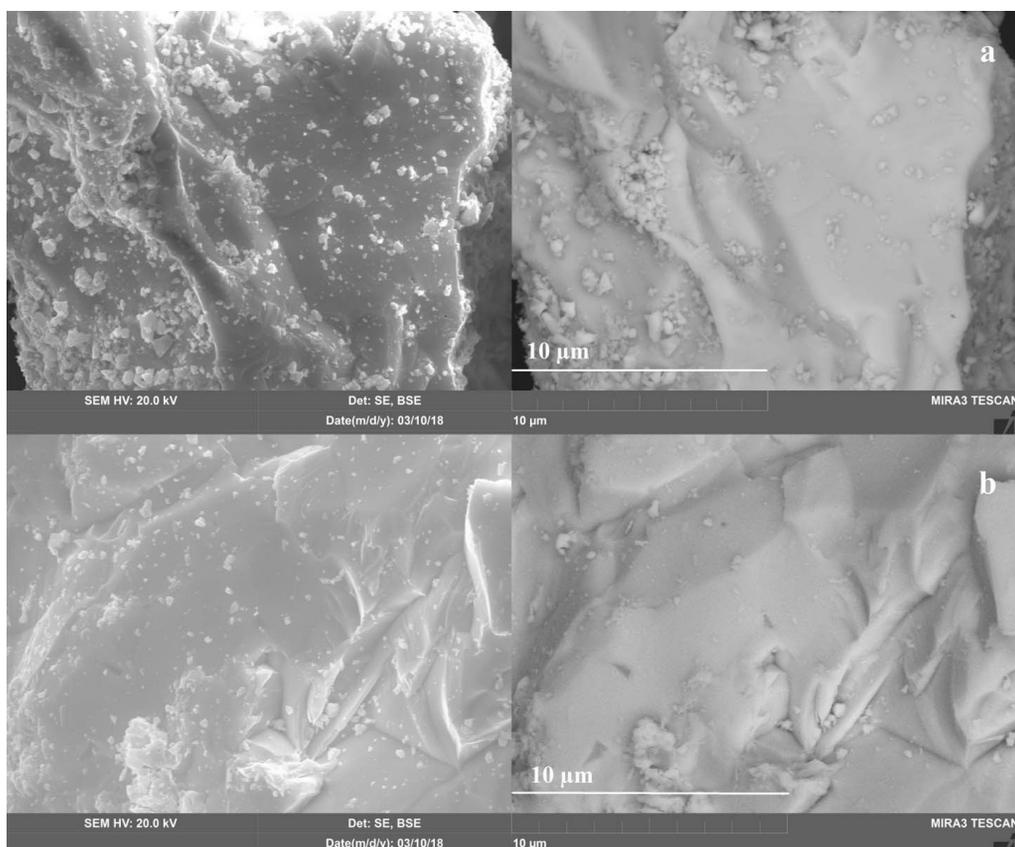


Fig. 2. Microphotographs of the surface of the samples  $\text{Bi}_5\text{Nb}_{2.88}\text{M}_{0.12}\text{O}_{15-\delta}$  (M-Cr (a) и Ni (b)) in the mode of secondary and elastically reflected electrons

To determine the charge state of chromium and nickel atoms, samples of solid solutions were examined using NEXAFS-spectroscopy using a BESSY-II synchrotron source. All NEXAFS spectra were recorded in total electron yield (TEY) mode. Figure 3a shows the absorption spectra of nickel atoms in  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  and nickel oxide(II). As can be seen, the spectrum of nickel in bismuth niobate is similar in intensity and energy position of the main peaks with corresponding details of  $\text{Ni}_{2p_{3/2}}$  spectra NiO. Comparison of the theoretical spectrum given in paper I. Preda et al. [18], with the

experimental allows to conclude that the NEXAFS spectrum of nickel in  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  has the same line form with the spectrum of high-spin Ni(II) atoms in octahedral environment. It is important to note that nickel atoms are characterized by the crystal field of octahedral symmetry, which means that the position of niobium(V) is replaced. The shift of Ni2p<sub>3/2</sub>-spectra for  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  to the region of larger photon energy values may be due to a smaller value of the crystal field parameter, as indicated in [18].

NEXAFS Cr2p spectra are shown in Fig. 3b. The spectra of oxides Cr<sub>2</sub>O<sub>3</sub> and CrO<sub>2</sub>, CrO<sub>3</sub> [19] are given for comparison. As can be seen from the figure, the main details of the Cr2p spectrum for  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$  coincide with the Cr<sub>2</sub>O<sub>3</sub> spectrum both in terms of the energy position of the main bands (A – D) and their relative intensity. Moreover, in Cr<sub>2</sub>O<sub>3</sub> oxide (corundum structure) chromium atoms have octahedral environment, while in CrO<sub>2</sub> and CrO<sub>3</sub> chromium has tetrahedral environment.

Meanwhile, in the Cr2p spectrum for  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$  there is an additional influx of E (580.5 eV), which is absent in Cr<sub>2</sub>O spectrum, but its energy position correlates well with the position of the corresponding intensive peak in CrO<sub>3</sub> spectrum. This suggests that chromium atoms may be in crystalline fields of different symmetry and charge states (III) and (VI). The largest fraction of chromium atoms in solid solutions is in the octahedral state Cr(III), i.e. at positions Nb(V).

In order to study the nature of metabolic interactions and the electronic state of nickel and chromium atoms, magnetic susceptibility of samples of diluted solid solutions was studied. Paramagnetic components of magnetic susceptibility and values of effective magnetic moments of nickel and chromium atoms at different temperatures and for different concentrations of solid solutions were calculated based on measurements of magnetic susceptibility of solid solutions. Diamagnetic corrections in the calculation of the paramagnetic component of the magnetic susceptibility have been introduced taking into account the susceptibility of the  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  bismuth niobate matrix measured in the same temperature range.

It is established that the dependence of the inverse value of the paramagnetic component of the magnetic susceptibility calculated for one mole of paramagnetic atoms on the temperature for all solid solutions is subject to the Curie-Weiss law in the investigated temperature range. Constant Weiss

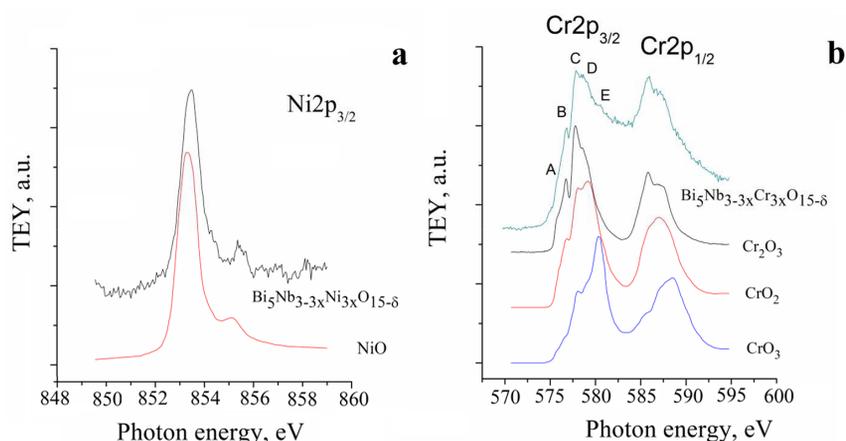


Fig. 3. a) NEXAFS Ni2p-spectra NiO and  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  ( $x=0.04$ ); b) Cr2p-spectra  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$  ( $x=0.04$ ) and CrO<sub>3</sub> [28], CrO<sub>2</sub> [29], Cr<sub>2</sub>O<sub>3</sub>

for both series of solid solutions takes negative values that is a sign of antiferromagnetic exchange interactions.

Paramagnetic isotherms of the magnetic susceptibility of nickel [ $\chi^{para}(\text{Ni})$ ] atoms in  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  solid solutions are typical for antiferromagnetics (Fig. 4a). The value of the effective magnetic moment of nickel atoms calculated as a result of extrapolation of concentration dependencies of [ $\chi^{para}(\text{Ni})$ ] on infinite dilution of solid solutions increases with temperature from  $\mu_{\text{eff}}(\text{Ni}) = 4.43 \mu\text{B}$  (90 K) to  $4.82 \mu\text{B}$  (320 K) and exceeds the purely spin magnetic moment values of nickel (II) atoms ( $2.87 \mu\text{B}$ ),  $\text{Ni(III)}_{3/2}$  ( $3.87 \mu\text{B}$ ) or  $\text{Ni(III)}_{1/2}$  ( $1.87 \mu\text{B}$ ). Such a behavior of the magnetic moment of nickel in solid solutions can only indicate that in infinitely diluted solid solutions are formed exchange-bound units with antiferro- and ferromagnetic types of exchange from nonvalent atoms  $\text{Ni(III)}_{5-3/2}$  and  $\text{Ni(II)}$ . A similar situation was observed earlier for nickel-containing solid solutions of barium-bismuth niobate  $\text{Bi}_2\text{BaNb}_{2-x}\text{Ni}_x\text{O}_{15-\delta}$  [20]; the effective magnetic moment of nickel atoms in them is much larger and varies from  $5.15 \mu\text{B}$  (90 K) to  $5.46 \mu\text{B}$  (293 K). Such high values of the magnetic moment of nickel were explained by the formation of dimers with ferromagnetic type of exchange due to local distortions of the polyhedral environment, which then collapse into a tetramer with a common antiferromagnetic type of exchange. It is noteworthy that such strong cluster formation is observed for barium-containing niobates, once again confirming the thesis about the influence of barium on the degree of clusterization of paramagnetic atoms in the structure of barium-bismuth niobate [13]. In solid solutions based on  $\text{Bi}_5\text{Nb}_3\text{O}_{15}$  everything is limited to the formation of dimers with ferromagnetic type of exchange, the proportion of which decreases with increasing concentration of solid solutions, yielding to dimers from  $\text{Ni(II)}$  atoms with antiferromagnetic type of exchange (Fig. 4b).

Thus, nickel atoms in solid solutions are mainly in the form of monomers and aggregates from  $\text{Ni(II)}$  atoms in the high spin state. In highly diluted solid solutions, nickel atoms are partially oxidized to the  $\text{Ni(III)}$  state and aggregated into clusters of heterovalent nickel atoms with a common ferromagnetic type of exchange. With increasing concentrations of solid solutions, dimers are aggregated in clusters with a common antiferromagnetic type of exchange, or inferior to the number of dimers with antiferromagnetic type of exchange, the appearance of which is favorable to the peculiarities of the crystal structure of solid solutions.

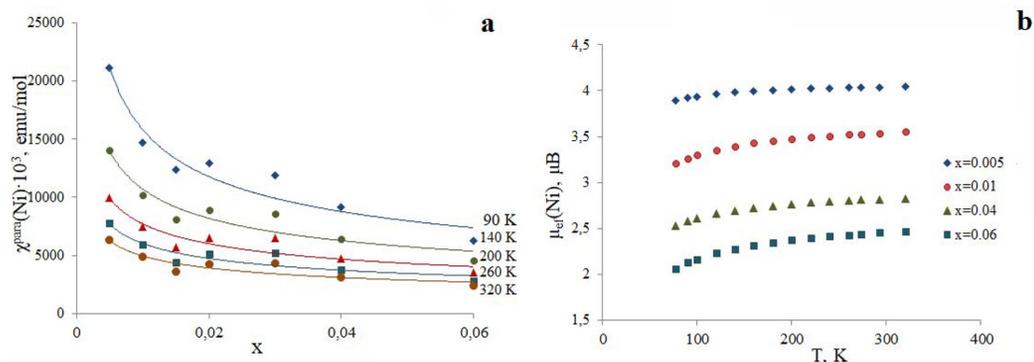


Fig. 4. a) Paramagnetic component isotherms of the magnetic susceptibility of nickel in the solid solutions of  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$ ; b) Temperature dependencies of the effective magnetic moment of nickel atoms in  $\text{Bi}_5\text{Nb}_{3-3x}\text{Ni}_{3x}\text{O}_{15-\delta}$  at  $x=0.005, 0.01, 0.04$  and  $0.06$

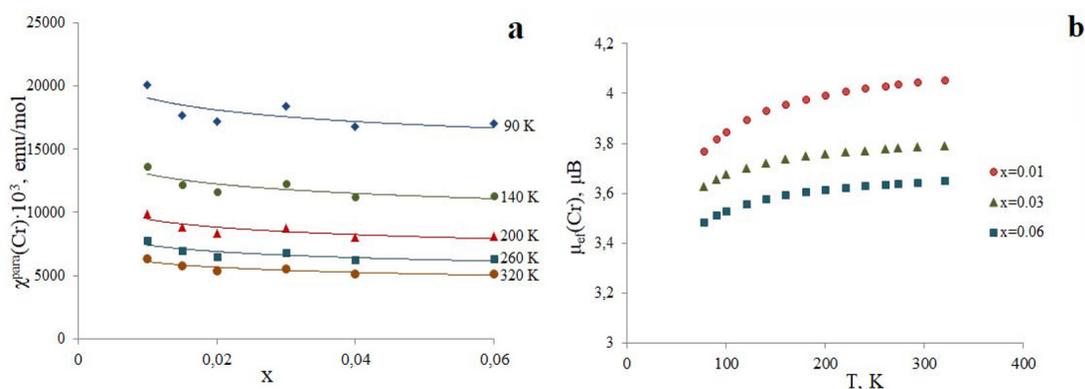


Fig. 5. a) Paramagnetic component isotherms of the magnetic susceptibility of chromium in the solid solutions of  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$ ; b) Temperature dependencies of the effective magnetic moment of chromium atoms in  $\text{Bi}_5\text{Nb}_{3-3x}\text{Cr}_{3x}\text{O}_{15-\delta}$  solid solutions at  $x=0.01, 0.03$  and  $0.06$

The isotherms of the paramagnetic component of the magnetic susceptibility of chromium in solid solutions  $[\chi^{para}(Cr)]$  are shown in Fig. 5a and have a form typical for diluted antiferromagnetics.

The value of the effective magnetic moment of chromium atoms calculated as a result of extrapolation of concentration dependencies of  $[\chi^{para}(Cr)]$  on infinite dilution of solid solutions increases with temperature from  $\mu_{eff}(Cr) = 3.75 \mu\text{B}$  (90 K) to  $4.00 \mu\text{B}$  (320 K) and slightly exceeds the purely spin value of the magnetic moment of chromium(III) atoms ( $3.87 \mu\text{B}$ ). The dependence of magnetic moment on temperature indicates the presence in an infinitely diluted solid solution of clusters, dimers, of chromium atoms with antiferro – and ferromagnetic type of exchange. With increasing concentration, the proportion of antiferromagnetically bound clusters increases, which can be judged by the temperature dependence of the magnetic moment of chromium atoms in the entire concentration range (Fig. 5b).

The appearance of indirect antiferromagnetic type of exchange between chromium atoms is beyond doubt. First, the angle of connection between chromium atoms, which are metabolically bound, located in oxygen octahedrons of perovskite-like layers, is 180 degrees, which favours the overlapping of atomic orbits of chromium and oxygen through exchange channels  $d_{xy}|p_y|d_{xy}$ ,  $d_{xz}|p_z|d_{xz}$ . The appearance of ferromagnetically bonded dimers from chromium atoms in an infinitely diluted solution is possible due to geometric distortions in the polyhedral environment of chromium atoms caused by oxygen vacancies due to heterogeneous substitution of niobium atoms with less valence – chromium atoms, then ferromagnetic exchange channels are activated, for example,  $d_{xy}||p_y \perp p_z||d_{xz}$ .

## Conclusion

Nickel and chromium-containing solid solutions of bismuth niobate in a narrow concentration range ( $x \leq 0.06$ ) were obtained by the solid phase method. According to the magnetic susceptibility study it was found that the infinitely diluted solid solutions are mainly high spin atoms of Ni(II) and Cr(III) and their aggregates with antiferromagnetic type of exchange, the proportion of which increases with increasing concentration of paramagnetic atoms. According to NEXAFS-spectroscopy data, nickel and chromium atoms in solid solutions occupy octahedral positions and have the charge state of Cr(III) and Ni(II).

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