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Magnetic Susceptibility and EPR Study of $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$

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Abstract. Magnetic susceptibility, microstructure and EPR of cobalt-containing solid solutions with layered perovskite-like structure $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ have been studied. Solid solutions of $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ ($x \leq 0.005$) can be crystallized in tetragonal syngony (sp. gr. P4/mmm), as cobalt content increases, monoclinic distortion of the unit cell emerges at $0.005 < x \leq 0.04$ (sp. gr. P2/m). The formation of exchange-bound aggregates of Co(III) and Co(II) atoms predominantly with antiferromagnetic exchange types has been found in the solid solutions. EPR indirectly confirms that cobalt ions are in octahedral positions of substitution of Nb(V) ions.

Keywords: ceramics, magnetic properties, EPR spectroscopy.

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The majority of bismuth-containing compounds with layered perovskite-like structure, analogues of the so called Aurivillius phases, are of practical and theoretical interest owing to their ferroelectric properties [1]. The composition of such compounds is described by the general formula $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$, where the bismuth-oxygen layers Bi_2O_2 consist of BiO_4 pyramids bound to each other by base edges and $\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$ are perovskite-like fragments consisting of BO_6 octahedra bound by vertices. The large cations A are located in the cubic octahedral sites between them [2, 3]. The coefficient n in the formula corresponds to the number of BO_6 octahedra forming the thickness of the perovskite-like fragment. Alongside with the layered compounds which contain the uniform perovskite-like fragments, there are the so-called mixed

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or hybrid layered compounds $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}) \dots (\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$ [4–6]. Their structure consists of alternating perovskite-like fragments of various widths. Bismuth niobate $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ belongs to the group of mixed layered compounds. Its structure is characterized by the ordered alternating of fragments formed by one and two niobium-oxygen octahedra. Therefore, its structure can be described as $(\text{Bi}_2\text{O}_2)(\text{NbO}_4)(\text{Bi}_2\text{O}_2)(\text{BiNb}_2\text{O}_7)$, with $n = 1$ and $m = 3$. Oxygen-niobium octahedra are bound by side vertices and are arranged in the a-b plane of the crystal, the Nb-O-Nb bond angle is 180° . The layers of the octahedra are separated by the bismuth-oxygen layers Bi_2O_2 formed by the BiO_4 pyramids and joined by the base edges (Fig. 1). The present work discusses the results of the EPR-spectroscopy and static magnetic susceptibility measurements of electron state and the nature of exchange interactions between cobalt atoms in the solid solutions of bismuth niobate $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ with layered perovskite-like structure, which were obtained by heterovalent substitution of niobium (V) with cobalt atoms (II).

1. Experimental

The synthesis of the solid solutions was carried out by the standard ceramic procedure from special-purity grade bismuth(III), niobium(V), and cobalt(II) oxides at 650, 850, 950 and 1050 °C. Phase composition of the products was determined by means of electron scanning microscopy (using a Tescan MIRA 3LM electron scanning microscope and a X-ACT energy-dispersive spectrometer) and X-ray diffraction analysis using a DRON-4-13 diffractometer ($\text{CuK}\alpha$ radiation). The cell unit parameters of solid solutions were calculated using the CSD software package [7]. The quantitative measurement of the composition of the solid solution samples was performed by atom-emission spectrometry (a SPECTRO CIROS ISP spectrometer). The magnetic susceptibility of the samples of the solid solutions was measured by the Faraday method in the temperature range of 77 – 350 K at 15 fixed temperatures and at the magnetic field strength of 724, 633, 523, and 364 mT. The semicommercial installation created in the laboratory of magnetochemistry of St. Petersburg State University and consisting of an electromagnet, an electronic balance, and cryostate was used for the magnetic susceptibility measurements. The accuracy of relative measurements was 5%. EPR measurements of finely crushed ceramic samples of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ solid solutions were carried out in the X-band RadioPAN SE/X 2547 spectrometer (IG Komi SC UB RAS) with 100 kHz field modulation at room temperature. The amplitude of the modulation was 0.25 mT, the microwave field power was 35 mW. A sample (near to 100 mg) was put into a thin-walled quartz test tube (internal diameter of 2.5 mm) together with the reference sample (anthracite, singlet line $g_0 = 2.003$, peak to peak distance $\Delta B_{PP} = 0.5$ mT) in an ampoule. For each sample, the spectrum in the magnetic field range of 0 – 700 mT and the reference line $g_0 = 2.003$ in the scan range of 5 mT were separately recorded. The intensity of the reference line served as a measure of the gain of the instrument and, when processing spectra, was used to accurately remove background signals from the test tube and ampoule. The spectra were normalized to the reference line intensity and then to 100 mg of the sample.

2. Results and discussion

The cobalt-containing solid solutions $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ have been studied with $0.005 \leq x \leq 0.04$. The single-phase nature of the samples was proved by the methods of scanning electron microscopy and X-ray analyses. Solid solutions of $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ ($x \leq 0.005$) can be crystallized in tetragonal syngony (sp. gr. P4/mmm), unit cell parameters with $x = 0.005$ are: $a = 0.5464$, $c = 2.093$ nm ($\text{Bi}_5\text{Nb}_3\text{O}_{15}$, sp. gr. P4/mmm, $a = 0.547$, $c = 2.097$ nm [6]); as cobalt content increases, monoclinic distortion of the unit cell emerges at $0.005 < x \leq 0.04$ (Fig. 1).

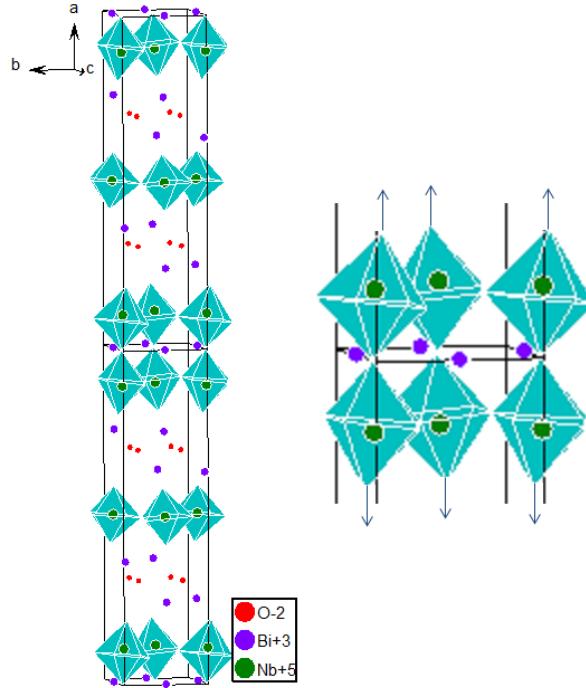


Fig. 1. The unit cell of $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ and a possible type of distortion of the polyhedron of cobalt (II) atoms

Fig. 1 shows the ($\text{Bi}_5\text{Nb}_3\text{O}_{15}$ unit cell, a possible type of distortion of the polyhedron of cobalt (II) atoms is seen to the right of the crystal lattice, given the fact that it represents Jahn-Teller ions. Monoclinic distortion of the tetragonal cell of the solid solutions $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ was established in previous works [6, 8] 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 P 2/m [6]. The unit cell parameters with $x = 0.04$ are: $a = 0.5463 \text{ nm}$, $c = 2.084 \text{ nm}$, $b = 0.5454 \text{ nm}$, the α angle changes from 90° to 90.7° . Fig. 2 shows the surface of samples of $\text{Bi}_5\text{Nb}_{3-x}\text{Co}_{3x}\text{O}_{15-\delta}$ ($x = 0.01, 0.02, 0.04$) obtained as secondary or elastically reflected electrons.

Based on the scanning electron microscopy data, the samples are porous compacts with merged melted fine grains $1\text{--}3 \mu\text{m}$. Using the measured magnetic susceptibility of the solid solutions, we calculated the paramagnetic components of the magnetic susceptibility and effective magnetic moments of cobalt atoms at various temperatures and concentrations of the solid solutions. The isotherms of paramagnetic component of magnetic susceptibility of cobalt atoms in $\text{Bi}_5\text{Nb}_{3-x}\text{Co}_{3x}\text{O}_{15-\delta}$ are typical for antiferromagnets, their comparison is shown in Fig. 3a.

The effective magnetic moments of single cobalt atoms calculated by extrapolating concentration dependencies of $[\chi^{\text{Para}}(\text{Co})]$ to infinite dilution of the solid solutions exceed pure-spin values and increase as the temperature increases from $6.18 \mu_B$ (90 K) to $6.69 \mu_B$ (320 K). The magnitude of the magnetic moment exceeds the pure spin values of high-spin cobalt atoms Co(II) ($\mu_{eff} = 3.89 \mu_B$) and Co(III) ($\mu_{eff} = 4.92 \mu_B$, therm ${}^5\text{E}_g$), which may indicate the formation of exchange-coupled aggregates with the antiferromagnetic type of exchange out of cobalt atoms in infinitely dilute solid solutions. The formation of aggregates out of paramagnetic atoms in highly dilute solutions did not turn out to be unexpected, it was previously observed in solid solutions of $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ containing manganese or iron [8] atoms and is displayed in case of distorted coordination polyhedron caused by heterovalent substitution. Monoclinic distortion of

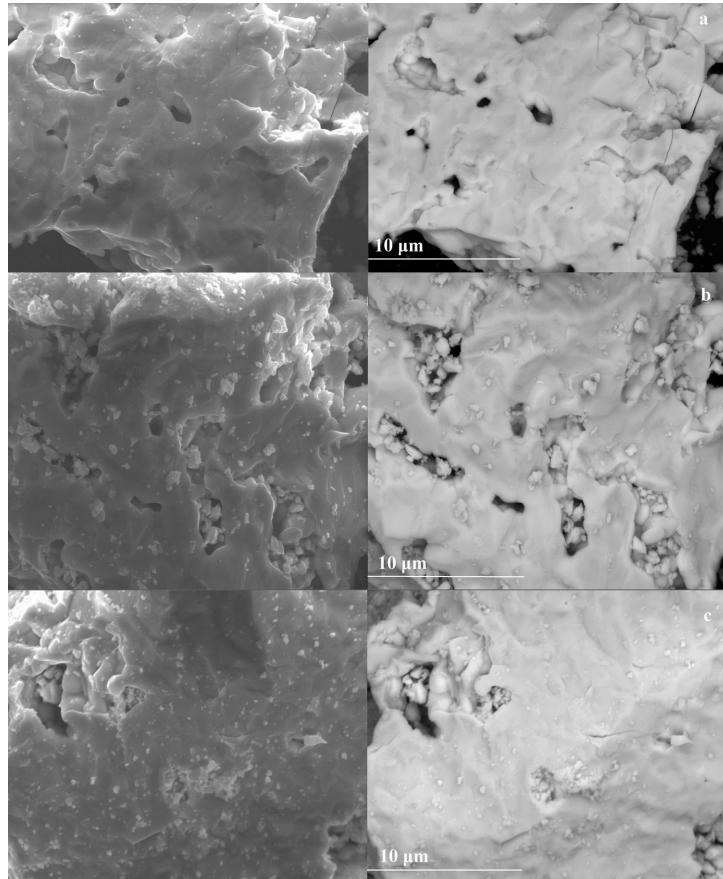


Fig. 2. Surface photomicrographs of the sample $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ at $x=0.01$ (a), 0.02 (b), 0.04 (c) in the mode of secondary and elastic backscattered electrons

the tetragonal structure of the solid solutions of bismuth niobate associated with the incline of the crystallographic axis c to the plane of perovskite layers indirectly indicates such distortions. Apparently, the formation of aggregates of paramagnetic atoms near the oxygen vacancies results in stabilization of the structure of the solid solutions.

The decrease of the paramagnetic component of magnetic susceptibility of the atoms with increasing concentrations of solid solutions may be also associated with low-spin atoms of Co(III) ($\mu_{eff} = 0 \mu_B$, $^1\text{A}_{1g}$) and increase of the portion of cobalt clusters with antiferromagnetic type of exchange between atoms [9]. Reduced magnitude of the magnetic moment in more concentrated solid solutions testifies in favour of the suggestion on the described clustering. Growing with higher temperatures dependence of the effective magnetic moment on cobalt atoms in solid solutions of various concentrations indicates the antiferromagnetic type of exchange between atoms (Fig. 3b). The antiferromagnetic type of exchange is supported by cobalt atom electrons in 3d-orbitals and layered perovskite structure of bismuth niobate ensuring indirect exchange between atoms at the angle of 180° and accessibility of exchange channels $d_{xz} \parallel p_z \parallel d_{xz}$, $d_{x^2-y^2} \parallel p_y \parallel d_{x^2-y^2}$ and between the layers through the channel – $d_{z2} \parallel p_z \parallel d_{z2}$. Earlier, the validity of this suggestion was shown at the example of iron-containing solid solutions with layered perovskite structure [8]. The suggestion on diamagnetic cobalt (III) atoms in concentrated solutions can be explained by a number of reasons. The oxidized state of cobalt is likely to

decrease the destabilizing effect of oxygen vacancies on the structure of solid solutions; cobalt (III) atoms in the high-spin state, with their significant magnetic moment, cannot ensure such a sharp reduction of magnetic susceptibility of solid solutions, and, what is more, the accumulated distortions of oxyden polyhedra caused by heterovalent substitution of Nb(V) atoms by cobalt atoms contribute to higher tension of the crystal field of paramagnetic atoms and stabilized low-spin state of cobalt atoms.

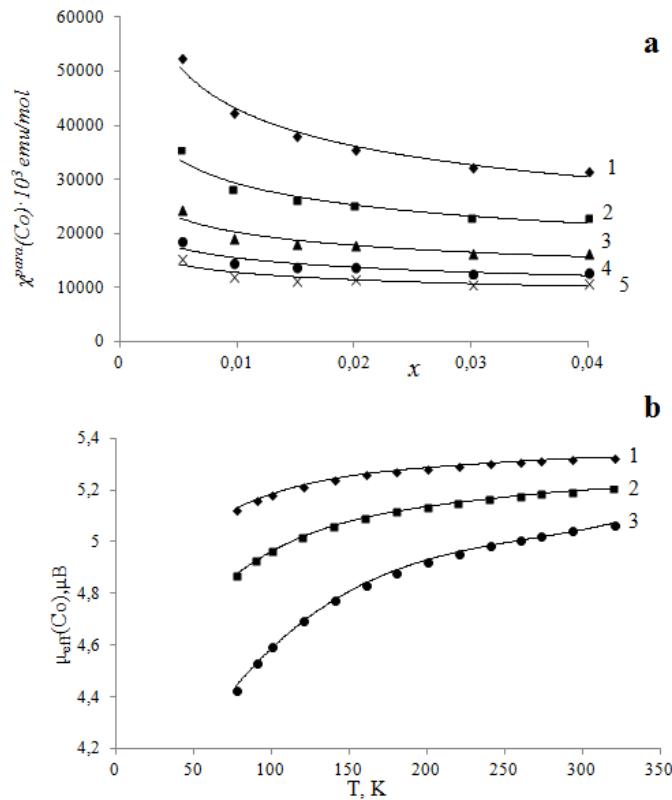


Fig. 3. **a** — Isotherms of paramagnetic component of magnetic susceptibility of the cobalt-containing solid solutions $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ at 77 K (1), 120 K (2), 180 K (3), 240 K (4) and 293 K (5); **b** — Temperature dependencies of the effective magnetic moment of cobalt in the $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ at $x = 0.010$ (1), 0.015 (2) and 0.04 (3)

At the top of Fig. 4 shows the EPR spectra of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ solid solutions for $x = 0.005, 0.02, 0.04$, and 0.06 , reduced to standard registration options. Only one component is reliably established in all spectra. This is an asymmetric narrow line with the value of $\Delta B_{PP} = 17-19 \text{ mT}$ and a g-factor of about 4.3. The integral intensity of this line monotonously decreases almost twice as x increases from 0.005 to 0.06. For a nominally pure compound, this signal could be attributed to the high-spin state ($S = 3/2$) of Co^{2+} ions in a weak, slightly distorted octahedral crystal field at Nb^{5+} substitution positions. In the limit of a weak crystal field of an ideal octahedral coordination, Co^{2+} ions in the EPR spectra give an isotropic line with $g = 4.33$ and the magnitude of hyperfine splitting on ^{59}Co nuclei around 300 MHz, the spin-orbit interaction depending on the strength of the crystal field decreases these values [10, 11]. The asymmetry of line 4.3 can be explained by small distortions of the octahedral coordination, and its width corresponds to the unresolved hyperfine structure from ^{59}Co . However, due to the pe-

culiarities of the splitting of the energy levels of the octahedral Co^{2+} complexes in a weak crystal field, their EPR line 4.33 can be observed in the EPR spectra only at very low temperatures. At room temperature, the spectra of Co^{2+} ions are observed for low-spin states ($S = 1.2$) in a strong or strongly distorted crystal field, and the EPR lines are grouped in the g-factor region 2.0, rather than 4.3.

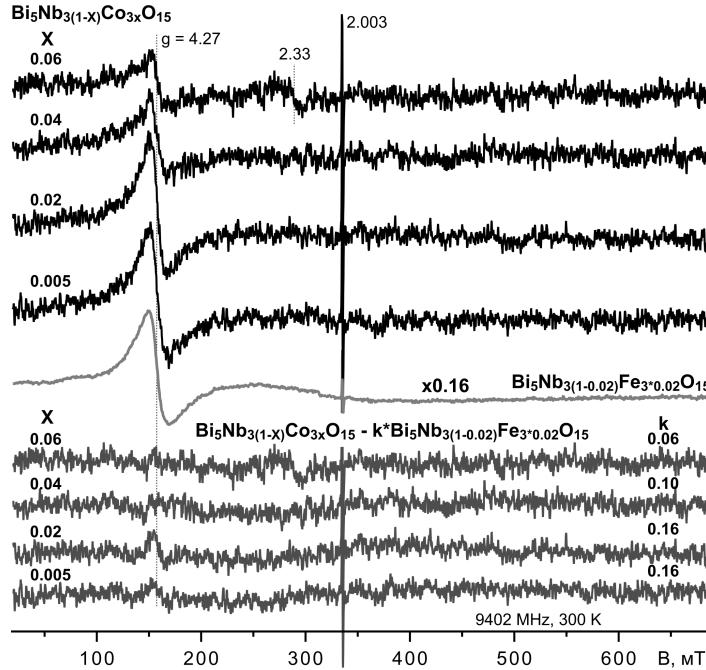


Fig. 4. EPR spectra of solid solutions $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ for $x = 0.005 - 0.06$ in comparison with the Fe^{3+} spectrum of the compounds $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ from [8]. The residues of subtraction from the $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ spectra of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ spectrum with a weight coefficient k are shown in the bottom. The narrow line with $g = 2.003$ is the signal of the reference sample

A more adequate explanation of the EPR 4.3 signal in the spectra of cobalt ceramics of the $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ follows from our results of the EPR studies of a similar compound doped with Fe^{3+} ions [8]. In the EPR spectra of $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ at small x , the asymmetric line 4.3 with $\Delta B_{PP} = 20 - 22$ mT dominates. This is typical EPR signal for a strongly rhombic distorted octahedral oxygen environment Fe^{3+} ions. We relate it to the NbO_6 octahedra of the compound. At high concentrations, the Fe^{3+} ions in the EPR spectra increase the intensity of a wide band with $g = 2.0$ from the clusters of these ions. With an increase in the concentration of Fe^{3+} ions, a wide band $g = 2.0$ of their clusters develops. A comparison of the EPR spectra of ceramics shows that the spectrum of $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ is identical to the spectrum of Fe^{3+} c g = 4.3 of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ ceramics with a low iron content (Fig. 4, bottom). The difference in the shape of the line is reduced only to a slightly larger line width of 4.3 in the ceramics $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$. Since the line width 4.3 increases with an increase in the Fe^{3+} content in the compound, we can assume that $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ ceramics contain uncontrolled traces of Fe^{3+} ions causing weak 4.3 signals in the EPR spectra. The marked decrease in the integrated intensity of the line $g = 4.3$ of the minor content Fe^{3+} in cobalt ceramics with an increase in the cobalt content is explained by the competing occurrence of both iron and cobalt ions in one structural position of the $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ compound, namely NbO_6 . Here is a Fig. 5

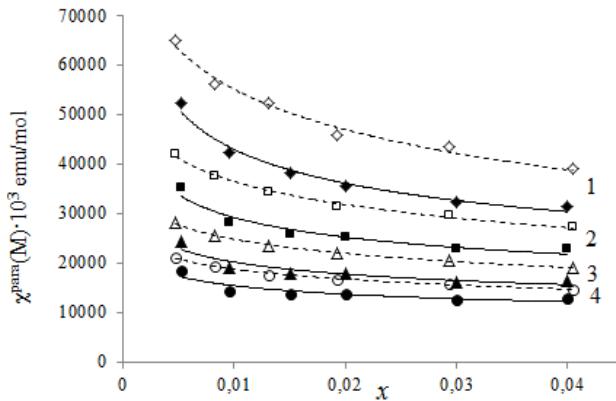


Fig. 5. Isotherms of the paramagnetic component of the magnetic susceptibility of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ [8] and $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ solid solutions at 77 K (1), 120 K (2), 180 K (3), 240 K (4) (the solid line is $\chi^{\text{para}}(\text{Co})$, the dashed line is $\chi^{\text{para}}(\text{Fe})$)

obtained by applying isotherms of the paramagnetic component of the magnetic susceptibility of the $\text{Bi}_5\text{Nb}_{3-3x}\text{Fe}_{3x}\text{O}_{15-\delta}$ [8] and $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ solid solutions at 77 K (1), 120 K (2), 180 K (3), 240 K (4) (the solid line is $\chi^{\text{para}}(\text{Co})$, the dashed line is $\chi^{\text{para}}(\text{Fe})$). Comparison of magnetic susceptibilities of both series of solid solutions shows 0.815 to 1 correlation between the susceptibility values of cobalt- and iron-containing solid solutions. Assuming that the magnetic susceptibility of $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}(\text{Fe})_{3x}\text{O}_{15-\delta}$ is mainly caused by the presence of impurity iron atoms, for any x the proportion of iron atoms should be approximately $4/5x$, which can hardly be seen as an impurity. It remains to admit that the absorption band in the EPR spectrum ($g = 4.27$) can belong to $\text{Co}(\text{II})_{s=3/2}$ ions.

Conclusions

Thus, it was shown that the magnetic behavior of cobalt doping bismuth niobate solid solutions with perovskite-like layered structure is generally similar and is determined mainly by the crystal structure of the solid solutions, the symmetry, and the strength of the crystal field formed by ligands. The cobalt (III), (II) atoms in solid solutions of heterovalent substitution aggregate forming strong clusters of cobalt atoms predominantly with the antiferromagnetic type of exchange, which not disintegrate even at infinite dilution. EPR indirectly confirms that cobalt ions are in octahedral positions of substitution of $\text{Nb}(\text{V})$ ions.

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Исследование магнитной восприимчивости и ЭПР $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$

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Аннотация. Исследованы магнитная восприимчивость, микроструктура и ЭПР кобальтодержащих твердых растворов $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ со слоистой первоскитоподобной структурой. Твердые растворы $\text{Bi}_5\text{Nb}_{3-3x}\text{Co}_{3x}\text{O}_{15-\delta}$ ($x \leq 0.005$) кристаллизуются в тетрагональной сингонии (пр. гр. $P4/mmm$), с увеличением содержания кобальта возникает моноклинное искажение элементарной ячейки при $0.005 < x \leq 0.04$ (пр. гр. $P2/m$). В твердых растворах обнаружено образование обменно-связанных кластеров из атомов Co(III) и Co(II) преимущественно с антиферромагнитным типом обмена. ЭПР косвенно подтверждает, что ионы кобальта замещают октаэдрические позиции ионов Nb (V).

Ключевые слова: керамика, магнитные свойства, ЭПР.