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Structure, Magnetic, and Electric Properties of Bismuth Niobates Doped with *d*-Elements: IX.[1] State of Nickel in the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ Solid Solutions with Layered Perovskite-Like Structure

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Abstract—The study of magnetic susceptibility of the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions has shown that paramagnetic nickel atoms are present in diluted solutions as exchange-bound dimers formed by Ni(III) atoms in the high-spin state and characterized by the exchange parameter J of 12 cm^{-1}. As the concentration of the solid solutions increases, clusters consisting of pairs of ferromagnetic Ni(III) dimers with antiferromagnetic exchange type and $J = -170$ cm^{-1} are formed.

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Nickel(III) atoms in oxide layered perovskite-like structures can be in low-spin and high-spin states [2, 3]. The realization of one or other spin state is affected by the structure, size, and degree of coordination polyhedron distortion [4]. An increase in the distortion of the oxygen octahedron in compounds with the layered structure (K_2NiF_4) favors the realization of the nickel(III) low-spin state [5]. The study of magnetic dilution in the $LaSrMO_4$ and $YCaMO_4$ showed that the spin state of transition element atoms is also affected by the atomic composition of the second coordination sphere. In this case a partial replacement of La, Sr, Y, and Ca atoms by atoms with a greater polarizing ability favors the realization of high-spin state in atoms of *d*-elements [6–8].

Atoms of Ni(II) and Ni(III) in the high-spin state were found in nickel-containing solid solutions of bismuth niobate, $Bi_5Nb_3O_{15}$, having a mixed layered perovskite-like structure with alternating niobium-oxygen layers of one and two octahedra in thickness [9]. A tendency to paramagnetic atom aggregation into dimer clusters within two layers of perovskite-like blocks was found on the basis of magnetochemical studies of the $Bi_2BaCr(Cu)_xNb_{2-x}O_{9-\delta}$ solid solutions with layered structure [10, 11].

In this work the state and distribution of paramagnetic nickel atoms in solid solutions of bismuth niobate $Bi_2BaNb_2O_9$ were studied. Bismuth niobate $Bi_2BaNb_2O_9$ belongs to layered perovskite-like oxides (Aurivillius phases analogs) in its crystal structure and is characterized by an ordered alternation of bismuth-oxygen layers $(Bi_2O_2)^{2+}$ and perovskite-like blocks of two layers of niobium-oxygen octahedra in thickness (Fig. 1).

According to the data of neutron diffraction analysis, the crystal structure of $Bi_2BaNb_2O_9$ is described by the $A2_1am$ space group with the unit cell parameters a = 5.567 and c = 25.634 Å [12]. The $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions were obtained over a wide concentration range $0.01 < x < 0.20$, which seems to result from the isomorphous substitution of nickel atoms in octahedral sites for niobium atoms close to them in size. The unit cell parameters correspond to the unit cell parameters of $Bi_2BaNb_2O_9$ and vary only slightly as the nickel fraction increases.

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[1] For communication VIII, see [1].

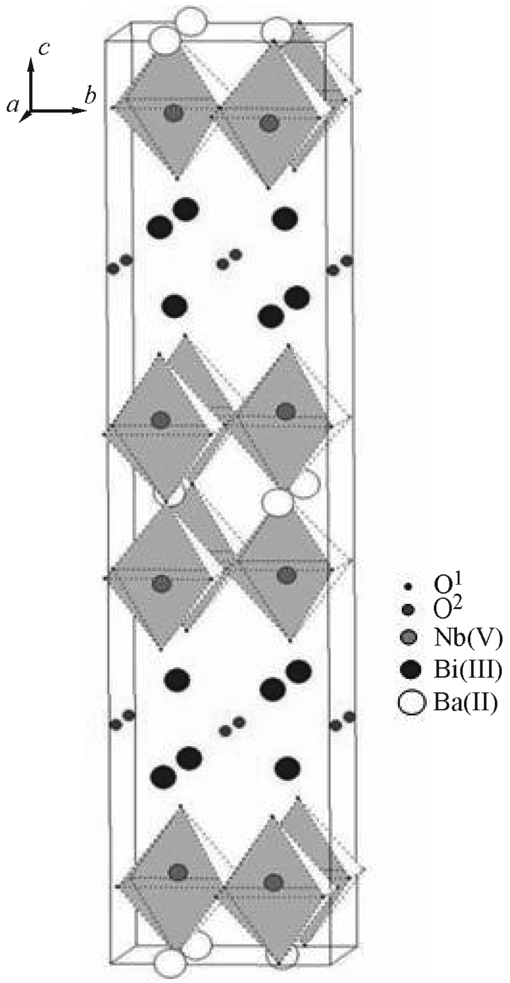

Fig. 1. Crystal structure of bismuth niobate $Bi_2BaNb_2O_9$.

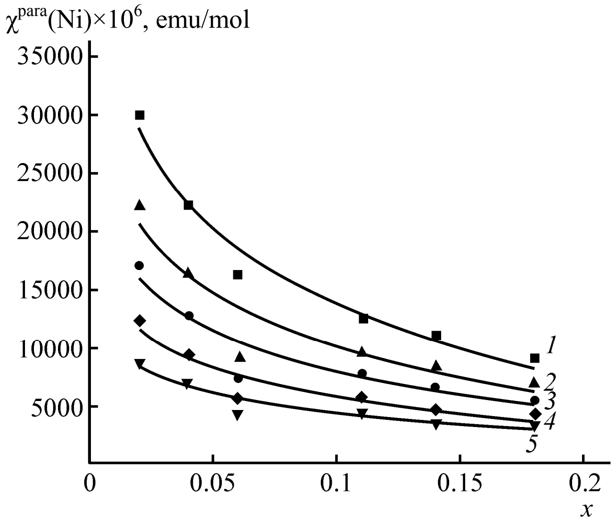

Fig. 2. Isotherms of paramagnetic components of magnetic susceptibility of nickel atoms in the solid solutions $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ at (*1*) 90, (*2*) 120, (*3*) 160, (*4*) 220, and (*5*) 293 K.

We have calculated paramagnetic components of magnetic susceptibilities [χ(Ni)] for the solid solutions and effective magnetic moments [μ_{eff}(Ni)] of nickel atoms at various temperatures and various concentrations of the solid solutions on the basis of magnetic susceptibility measurements. The diamagnetic corrections in the calculated paramagnetic component of magnetic susceptibility were introduced with respect to the susceptibility of $Bi_2BaNb_2O_9$ matrix measured within the same temperature range.

We have found that the temperature dependence of the inverse molar paramagnetic component of magnetic susceptibility of nickel atoms obeys Curie-Weiss law in the temperature range under study. The run of the isotherms of paramagnetic component of magnetic susceptibility [χ(Ni)] is typical for the dilution of antiferromagnets (Fig. 2). The extrapolation of the isotherms of paramagnetic component of magnetic susceptibility to zero concentration of paramagnetic atoms in the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions ($x\to0$) results in the effective magnetic moments depending on temperature and substantially exceeding the spin only values of high-spin nickel(III) atoms [μ_{eff}(Ni) = 3.87 BM].

T, K	90	120	160	220	293
μ, BM	5.15	5.30	5.36	5.61	5.46

The increase in the magnetic moment with increasing temperature points to the presence of nickel(III) atoms in the high-spin state ($^4T_{1g}$). To account for such variation of the magnetic characteristics, two assumptions can be suggested. First of all this is the oxidation of nickel atoms to Ni(IV) with the spin S = 2, which is improbable as tetravalent nickel is unstable and cannot be stabilized in air. In addition, tetravalent nickel must be in the low-spin state, since even trivalent nickel in the perovskite-like structures has a tendency to go into the low-spin configuration, and as the degree of oxidation increases, this tendency increases [9, 13].

Therefore we can suggest that even in the infinitely diluted solid solution no complete disaggregation of nickel atoms occurs, and clusters consisting of two or more high-spin nickel(III) atoms are preserved.

Theoretical calculation of experimental dependences of χ^{para}(Ni) on the concentration of solid solutions was carried out within the framework of the diluted solution model and Heizenberg–Dirack-van-

Vleck model [14]. The foundation of the proposed model is the concept that paramagnetic atoms in our solid solutions can exist as dimers of high-spin nickel(III) atoms with ferromagnetic type of exchange and as their aggregates (tetramers) with the total antiferromagnetic type of exchange (Table 1). With regard to the aforesaid the magnetic susceptibility is a sum of contributions of clusters and can be described by formula (1).

$$\chi(\mathrm{Ni})_{\mathrm{calc}} = a^{\mathrm{dim}}\,\chi^{\mathrm{dim}} + (1 - a^{\mathrm{dim}})\,\chi^{\mathrm{tetr}}. \qquad (1)$$

Here (a^{dim}) is the fraction of dimers of high-spin nickel(III) atoms, (χ^{dim} and χ^{tetr}) are paramagnetic components of magnetic susceptibility of tetramers and dimers.

Table 1. Distribution of nickel atoms in the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions[a]

x	$a_{\mathrm{Ni(III)–Ni(III)}}^{\mathrm{dim}}$	$a_{\mathrm{Ni(III)}}^{\mathrm{tetr}}$
$x\to0$	0.95	0.05
0.02	0.74	0.26
0.04	0.56	0.44
0.11	0.30	0.70
0.14	0.27	0.73
0.18	0.22	0.78

[a] [$a_{\mathrm{Ni(III)–Ni(III)}}^{\mathrm{dim}}$] is the fraction of Ni(III)–O–Ni(III) dimers, [$a_{\mathrm{Ni(III)}}^{\mathrm{tetr}}$] the fraction of tetramers of Ni(III) high-spin atoms.

The Heizenberg–Dirack-van-Vleck model is not applicable in the general case to Ni(III) high-spin atoms ($S = 3/2$) having the ground term $^4T_{1g}$, since we must take into account the splitting of the term both due to exchange interactions and spin-orbit coupling. However, it was shown in [8, 15] that the exchange interactions in dimers may be described with regard to the temperature dependence of g-factor of nickel atoms with the spin 3/2 within the framework of HDVV model of isotropic exchange. According to this model, the susceptibility of a dimer and its magnetic moment are determined by formulas (2) and (3), respectively.

$$\chi_{\mathrm{dim}} = \frac{1}{2}\,\frac{\sum\limits_{S'} g^2(S')S'(S'+1)(2S'+1)e^{-E(J,S')/kT}}{3kT\sum\limits_{S'}(2S'+1)e^{-E(J,S')/kT}}, \qquad (2)$$

$$\mu^2_{\mathrm{dim}} = \frac{g^2\sum\limits_{S'} S'(S'+1)(2S'+1)e^{-E(J,S')/kT}}{2\sum\limits_{S'}(2S'+1)e^{-E(J,S')/kT}}, \qquad (3)$$

$$E(J,S') = -J[S'(S'+1) - S_a(S_a+1) - S_b(S_b+1)],$$

$$S' = S_a + S_b,\ S_a + S_{b-1},\ \ldots,\ |S_a - S_b|,$$

$$g(S') = \frac{g_a + g_b}{2} + \frac{g_a - g_b}{2}\cdot\frac{S_a(S_a+1) - S_b(S_b+1)}{S(S+1)}.$$

Here (S_a, S_b) are spins of atoms constituting a dimer. In our case $S_a = S_b = S(\mathrm{Ni^{III}}) = 3/2$; ($g_a$, g_b) are g-factors of atoms forming a dimer, (J) is an exchange parameter, and (T) is an absolute temperature.

Temperature variation of $\mathrm{Ni(III)}_{S=3/2}$ g-factor can be estimated as follows. For low-spin state of Ni(III) g-factor ($g = 2.08$) is independent of temperature and can be found from Eq. (4) with account of the effective magnetic moment μ_{eff} 1.80 BM, which was estimated in [16].

$$\mu = g\sqrt{S(S+1)}. \qquad (4)$$

The equation $g = 2(1 - 2\lambda/10Dq)$ is valid for E-term without accounting for the splitting of excited levels, therefore, taking into consideration the value $10Dq = 17000\ \mathrm{cm}^{-1}$ [3], we can estimate the spin-orbit coupling constant as $\lambda_1 = -510\ \mathrm{cm}^{-1}$.

Since the single-electron spin-orbit coupling constant $\xi = \lambda_i 2S_i$ scarcely changes as the ground state term changes, the spin-orbit coupling constant for the state of Ni with $S = 3/2$ is $\lambda_2 = -170\ \mathrm{cm}^{-1}$. Then, neglecting the interaction of the split terms in the tetragonal field, we can calculate the effective magnetic moment of nickel(III) atoms in the high-spin $^4T_{1g}$ state by formula (5) and estimate the temperature changes in g-factor: $g(90\ \mathrm{K}) = 2.47$, $g(160\ \mathrm{K}) = 2.65$.

$$\mu^2_{\mathrm{Ni(III)}} = \frac{3[3.15x + 3.92 + (2.84x + 2.13)\exp(-15x/4) + (4.7x - 6.05)\exp(-6x)]}{x[3 + 2\exp(-15x/4) + \exp(-6x)]}, \qquad (5)$$

$x = \lambda_2/kT$ and k is Boltzmann's constant.

Table 2. Experimental and calculated magnetic susceptibilities χ(Ni) in relation to concentration of the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions

x	χ_{exp}/χ_{calc}, emu/mol				
	90 K	120 K	160 K	220 K	293 K
0.02	0.0299/0.0291	0.0223/0.227	0.0172/0.0176	0.0136/0.0132	0.0098/0.0100
0.04	0.0222/0.0221	0.0166/0.0172	0.0129/0.0135	0.0105/0.0103	0.0078/0.0079
0.11	0.0126/0.0119	0.0099/0.0094	0.0079/0.0075	0.0062/0.0060	0.0048/0.0048
0.14	0.0113/0.0107	0.0086/0.0085	0.0068/0.0068	0.0052/0.0055	0.0040/0.0045
0.18	0.0092/0.0087	0.0071/0.0070	0.0057/0.0057	0.0045/0.0046	0.0036/0.0039

With account of all the parameters Eq. (3) for calculating the squared magnetic moment of dimers of high-spin nickel(III) atoms transforms into Eq. (6).

$$\mu^2_{\mathrm{dim}(3/2\text{–}3/2)} = \frac{g^2[84e^{(4.5J/kT)} + 30e^{(-1.5J/kT)} + 6e^{(-5.5J/kT)}]}{2[7e^{(4.5J/kT)} + 5e^{(-1.5J/kT)} + 3e^{(-5.5J/kT)} + e^{(-7.5J/kT)}]}. \quad (6)$$

We considered the magnetic susceptibility of a tetramer as the susceptibility of a pair of dimers of high-spin nickel atoms with the total spin $S = 3$ and calculated the square of magnetic moment of such dimers by Eq. (7).

$$\mu^2_{\mathrm{dim}(3\text{–}3)} = \frac{g^2[546e^{(18J/kT)} + 330e^{(6J/kT)} + 180e^{(-4J/kT)} + 84e^{(-12J/kT)} + 30e^{(-18J/kT)} + 6e^{(-22J/kT)}]}{2[13e^{(18J/kT)} + 11e^{(6J/kT)} + 9e^{(-4J/kT)} + 7e^{(-12J/kT)} + 5e^{(-18J/kT)} + 3e^{(-22J/kT)} + e^{(-24J/kT)}]}. \quad (7)$$

Exchange interactions within a tetramer are antiferromagnetic, which can be inferred by the shape of magnetic susceptibility isotherms and temperature dependences of effective magnetic moments of paramagnetic atoms in the solid solutions at $x \to 0$ (Fig. 3).

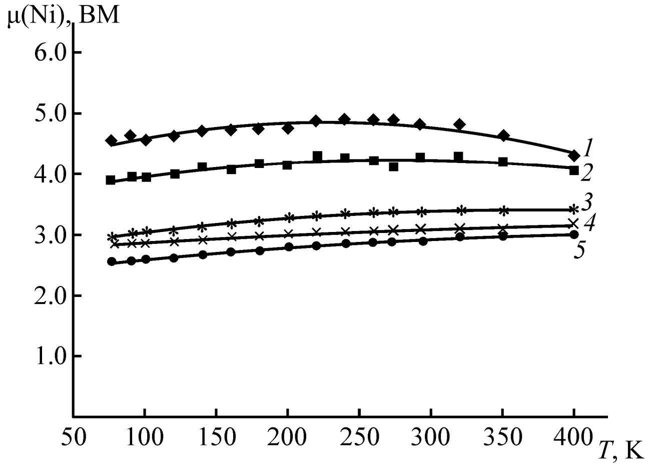

Fig. 3. Temperature dependence of nickel magnetic moment in $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions at x = 0.02 (*1*), 0.04 (*2*), 0.11 (*3*), 0.14 (*4*), and 0.18 (*5*).

The agreement between calculated and experimental values is achieved upon minimizing the $\sum_i\sum_j(\chi_{ij}^{\mathrm{calc}} - \chi_{ij}^{\mathrm{exp}})$, function, where $\sum_i$ is summing over all the concentrations, $\sum_j$ is summing over all the temperatures; $\chi_{ij}^{\mathrm{calc}}$, χ_{ij}^{exp} are calculated and experimental paramagnetic components of magnetic susceptibilities. The experimental and calculated magnetic susceptibilities of the $Bi_2BaNi_xNb_{2-x}O_{9-\delta}$ solid solutions are compared in Table 2.

As follows from the data presented, a sufficiently good agreement is observed between experimental and calculated paramagnetic components of nickel magnetic susceptibility, which allows us to conclude that a fraction of nickel(III) atoms exists in the solid solutions as dimers with ferromagnetic exchange (J = 12 cm^{-1}) and as their tetramers with the total antiferromagnetic exchange (J = –170 cm^{-1}), the fraction of those latter increasing as the concentration of the solid solutions increases.

It is believed that, when the crystal structure is retained, the heterovalent substitution of nickel atoms for niobium produces oxygen vacancies in oxygen blocks, and the location of nickel atoms in the vicinity of such a vacancy results in the fact that the paramagnetic atom has five nearest neighbors instead of six in the oxygen surrounding. The presence of such vacancies results in the distortion of the octahedra and in a decrease in the NiONi bond angle. The last gives rise to the appearance of a ferromagnetic component in the exchange interactions resulting from overlapping of perpendicularly oriented orbitals of nickel atoms $d_{z^2}|p_z{\perp}p_x|d_{x^2-y^2}$ and $d_{z^2}|p_z{\perp}p_y|_{xy}$ located along a perovskite-like layer. Further increase in the nickel content results in the appearance of greater clusters consisting of pairs of ferromagnetically bound dimers with antiferromagnetic exchange between them along the $d_{z^2}\|p_z\|d_{z^2}$ channel within two perovskite-like layers.

EXPERIMENTAL

The solid solutions were synthesized by the standard ceramic procedure from ultra-pure grade oxides of bismuth(III), niobium(V), barium, and chemically-pure grade nickel oxide. The synthesis duration was 10 h at 650°C and 50 h at 1050°C. We controlled the phase composition of the samples under study by the X-ray analysis (DRON-4-13, CuK_α-emission). We calculated the unit cell parameters of the solid solutions using the CSD program package [17].

We determined the quantitative content of nickel in the samples of solid solutions by the method of atomic emission spectroscopy (a SPECTRO CIROS spectrometer with inductively bound plasma). The accuracy of the analysis is 5% of x in the solid solution formula.

We measured the magnetic susceptibility of the solid solutions by the Faraday method in the temperature range of 77–400 K at 16 fixed temperatures. The accuracy of the relative measurements was 2%.

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