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Structure, Magnetic, and Electric Properties of Bismuth Niobates Doped with *d*-Elements: VII.[1] State of Copper in the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ Solid Solutions

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Abstract—Magnetic susceptibility of the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solutions ($0.01 < x < 0.20$) with the layered perovskite-like structure was studied. In dilute solid solutions, copper atoms are in the form of Cu(II) monomers. As the concentration increases, the fraction of monomers decreases and the fraction of exchange-bonded aggregates (dimers) of Cu(II) with antiferromagnetic exchange increases. The antiferromagnetic exchange parameter in the copper dimers was estimated at –300 cm^{-1}.

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The interest of researchers in bismuth-containing perovskite-like oxides belonging to Aurivillius phases is defined by the fact that this class of compounds shows ferrielectric properties [2, 3]. This is the reason for the active search of new representatives of this class [4, 5]. Synthesis and structural features of such compounds are of special interest [7, 8], and research into the influence of the nature and concentration of alloying atoms on the physical properties of the compounds is also in progress [9, 10].

We previously studied the state and distribution of paramagnetic chromium atoms in the niobium sublattice in the chromium-containing $Bi_2BaCr_xNb_{2-x}O_{9-\delta}$ solid solutions [11] and revealed a tendency of the paramagnetic atoms to aggregate into dimer clusters with the antiferromagnetic exchange parameter J –45 cm^{-1} within two layers of perovskite-like blocks.

This work is a continuation of the research into of the state and distribution of paramagnetic atoms, copper in this case, in the $Bi_2BaNb_2O_9$ solid solutions with the bismuth niobate structure.

The crystal structure of bismuth niobate belongs to Aurivillius-type layered perovskite-like oxides. It is characterized by an ordered alternation of bismuth–oxygen layers $(Bi_2O_2)^{2+}$ and perovskite-like blocks two layers of niobium–oxygen octahedra in thickness (Fig. 1). According to the neutron diffraction analysis, the crystal structure of $Bi_2BaNb_2O_9$ is described by the space group $A2_1am$ with the unit cell parameters a 5.567 Å and c 25.634 Å [12].

The $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solutions were obtained in a wide range of concentrations, $0.01 < x < 0.20$, which is associated with isomorphous substitution of octahedral sites in perovskite layers occupied by niobium atoms close in size to copper atoms. The X-ray diffraction study of the synthesized single-phase solid solutions in the concentration range under study showed that their structure corresponds to $Bi_2BaNb_2O_9$. The unit cell parameters, which are close to the cell parameters of $Bi_2BaNb_2O_9$, remain almost unchanged as the copper content increases.

From the measured magnetic susceptibilities of the solid solutions we calculated the paramagnetic susceptibilities $[\chi^{para}(Cu)]$ and effective magnetic moments $[\mu_{eff}(Cu)]$ of copper atoms at various temperatures and for various concentrations of the solid solutions. The paramagnetic susceptibilities were corrected for diamagnetism with regard to the susceptibility of the $Bi_2BaNb_2O_9$ matrix measured over the same temperature range.

The temperature dependence of the reciprocal molar paramagnetic susceptibility of copper on tem-

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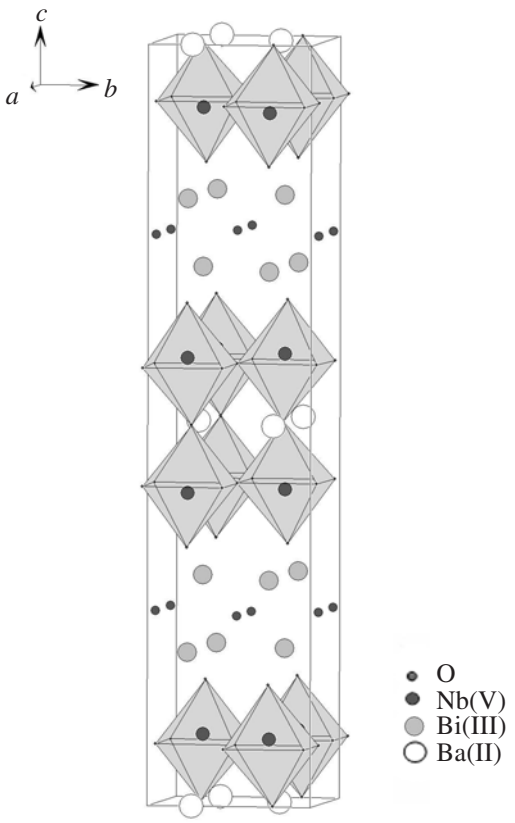

Fig. 1. Crystal structure of bismuth niobate $Bi_2BaNb_2O_9$.

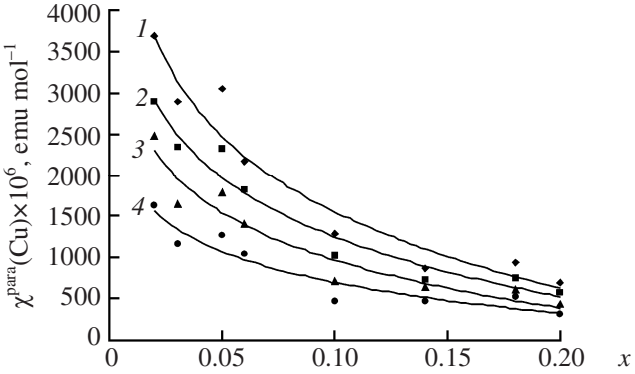

Fig. 2. Isotherms of the paramagnetic susceptibility of copper in the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solutions. *T*, K: (*1*) 90, (*2*) 120, (*3*) 160, and (*4*) 220.

perature was found to obey the Curie–Weiss law in the temperature range under study for all the solid solutions. As seen from the paramagnetic susceptibility isotherms (Fig. 2), χ^{para}(Cu) decrease with increasing copper content of the solid solutions.

The extrapolation of the isotherms of paramagnetic susceptibility to zero concentration of the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solution ($x \to 0$) gave us the paramagnetic susceptibility and the effective magnetic moments for a single paramagnetic atom.

T, K	90	120	160	220	300
μ, BM	1.725	1.763	1.843	1.738	1.699

As can be seen from these data, the effective magnetic moments of copper atom μ_{eff}(Cu) is independent of temperature and comprises an average of 1.75 BM. This value is close to the only spin value for the magnetic moment for one unpaired electron (1.73 BM), which points to the presence of copper monomers [Cu(II)] in an infinitely dilute solid solution.

The theoretical calculation of the experimental dependencies of χ^{para}(Cu) on the concentration of the solid solutions and on the temperature was carried out in the framework of the dilute solid solution model and of the Heizenberg–Dirack–van Vleck (HDVV) model [13]. The dilute solid solution model is based on the assumption that a solid solution of isomorphous substitution paramagnetic atoms can exist both as monomers and as exchange-bonded aggregates of two and more paramagnetic atoms in. As shown in [14], in sufficiently dilute solutions formation of aggregates containing more than two paramagnetic atoms, i.e. larger than dimers, is hardly probable and can be neglected. In view of the aforesaid, the magnetic susceptibility of paramagnetic atoms (copper) is the sum of the magnetic susceptibilities of monomers and dimers and can be described by formula (1).

$$\chi^{para}_{calc}(\mathrm{Cu}) = a^{mon}\chi^{mon} + a^{dim}\chi^{dim}. \quad (1)$$

Here a^{dim} and a^{mon} are the fractions of dimers and single atoms; and χ^{mon} and χ^{dim}, their magnetic susceptibilities. The magnetic susceptibility of dimers was calculated by the HDVV model. The *g*-factor of Cu(II) atoms was 2.025. Formula (1) contains two independent parameters: the fraction of single Cu(II) atoms (monomers) and the antiferromagnetic exchange parameter of between copper(II) atoms $J_{Cu(II)-Cu(II)}$ implicitly included into the formula.

The conclusion that the exchange between copper atoms in dimers is antiferromagnetic in nature was derived from the temperature dependence of the magnetic moment of copper atoms (Fig. 3).

Fitting calculated to experimental values is made by minimizing the $\sum_i\sum_j(\chi_{ij}^{calc} - \chi_{ij}^{exp})$ function, where $\sum_i$ is

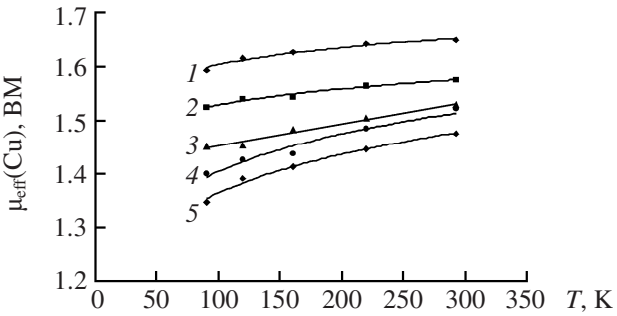

Fig. 3. Temperature dependence of the magnetic moment of copper in the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solutions. *x*: (*1*) 0.02, (*2*) 0.03, (*3*) 0.04, (*4*) 0.05, and (*5*) 0.06.

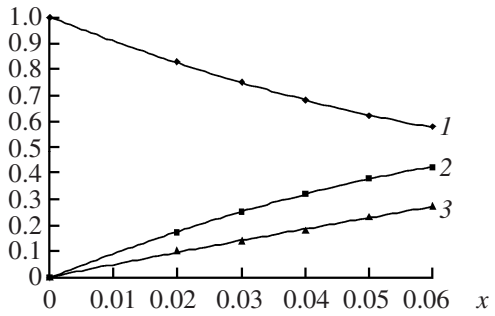

Fig. 4. Plots of the monomer and dimer fractions for the $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ solid solutions vs. concentration: (*1*) $a^{mon}_{Cu(II)}$, (*2*) $a^{dim}_{Cu(II)-Cu(II)}$, and (*3*) a^{dim}_{salt}.

summing up over all the concentrations; Σ, summing up over all the temperatures; and χ^{calc}_{ij} and χ^{exp}_{ij}, experimental and calculated paramagnetic susceptibilities.

The calculations gave data on the distribution of copper atoms in the solid solutions. The antiferromagnetic exchange parameter $J_{Cu(II)-Cu(II)}$ was estimated at –300 cm^{-1}. This value points to a strong antiferromagnetic exchange between copper atoms, which for Cu(II) atoms must occur over the $d^2_z\|p_z\|d^2_z$ channel.

The fractions of copper dimers in the solid solutions for various concentrations, calculated by the suggested model and for the statistical distribution of paramagnetic atoms are given in Table 1 (Fig. 4). The statistical distribution of copper dimers as a function of solid solution concentration was calculated in the assumption of five nearest paramagnetic copper atoms to take part in the exchange interactions [15]. The experimental and calculated magnetic susceptibilities of the solid solutions are compared in Table 2.

As follows from the presented data, these is a fairly good fit of the calculated paramagnetic susceptibility to experiment. This result suggests that a fraction of copper atoms exists as dimers with antiferromagnetic type of exchange, and this fraction increases with increasing concentration of the solid solutions. Presumably, the formation of exchange-bonded aggregates of copper atoms in amounts essentially exceeding the statistical fraction favors structural stabilization of the solid solutions. We are dealing here with the possibility for aggregates to localize in the vicinity of oxygen vacancies resulting from heterovalent substitution of Cu(II) atoms for Nb(V) and with the ability of the resulting "dimer–vacancy (hole)" complex to bind "holes" in its composition, thus stabilizing the crystal structure as a whole.

Noteworthy is the fact that the exchange parameters in bismuth niobates containing barium appear to be much larger in absolute value than those in other bismuth niobates containing the same paramagnetic atoms (chromium and copper) but free of barium [17, 18]. An examination of the structure of the niobates under study shows that their special feature is that barium atoms are localized between two adjacent perovskite layers. Owing to their size, barium atoms form the most ionic bond with oxygen among all alkaline-earth elements. This inevitably results in the most covalent transition metal–oxygen bond, enhanced overlap between metal *d* orbitals and oxygen *p* orbitals, and enhanced antiferromagnetic exchange. It is this circumstance which allows us to contend that the exchange-bonded dimers are formed along the *c* axis of the perovskite-like structure.

EXPERIMENTAL

The solid solutions were prepared by sintering stoichiometric amounts of corresponding metal oxides

Table 1. Distribution of copper atoms in $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$ [a]

x	a^{dim}_{sat}	$a^{dim}_{Cu(II)-Cu(II)}$	$a^{mon}_{Cu(II)}$
$x\to0$	0	0	1
0.02	0.10	0.17	0.83
0.03	0.14	0.25	0.75
0.04	0.18	0.32	0.68
0.05	0.23	0.38	0.62
0.06	0.27	0.42	0.58

[a] ($a^{mon}_{Cu(II)}$) Fraction of Cu(II) monomers; ($a^{dim}_{Cu(II)-Cu(II)}$) fraction of Cu(II)–O–Cu(II) dimers; and (a^{dim}_{salt}) statistical fraction of dimers.

Table 2. Experimental and calculated magnetic susceptibilities $\chi^{para}(Cu)$ at varied concentration of $Bi_2BaCu_xNb_{2-x}O_{9-\delta}$

x	$\chi_{exp(calc)} \times 10^6$, emu mol^{-1}				
	90 K	120 K	160 K	220 K	300 K
0.02	3500(3516)	2700(2639)	2050(1985)	1520(1460)	1150(1120)
0.03	3200(3177)	2450(2385)	1850(1798)	1380(1332)	1050(1035)
0.05	2700(2627)	2100(1973)	1600(1494)	1240(1124)	980(896)
0.06	2500(2457)	2000(1847)	1550(1400)	1180(1059)	920(854)

at 1220 K for 30 h with preliminary calcination of the oxide mixture at 850 K.

The phase composition of the solid solutions was controlled by X-ray phase analysis (DRON-4-13, CuK_α). The unit cell parameters were calculated using the CSD program package [16]. The copper contents of the synthesized samples were determined by photocolorimetry with an accuracy of ~5% x in the solid solution formula.

The magnetic susceptibilities of the solid solutions were measured by the Faraday method in the temperature range 77–320 K with a relative accuracy of 2%.

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