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State of Chromium in Solid Solutions of Multicomponent Bismuth Niobates with Pyrochlore Structure

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Abstract—Magnetic susceptibility of solid solutions of multicomponent bismuth niobates with pyrochlore structure containing chromium atoms was studied. The parameters determining the state of chromium atoms and the exchange coupling between the paramagnetic atoms were calculated. The best agreement between the experimental and theoretically calculated magnetic moments of the chromium atoms is observed on the condition that all the chromium atoms in the $Bi_2MgNb_2O_9$ structure are in the form of ferromagnetic exchange-coupled dimers with an exchange parameter J 18 cm^{-1}.

In the past decade, multicomponent bismuth niobates have attracted growing attention of researchers working in solid-state chemistry and physics owing to the possibility of varying the electrical and magnetic properties of the compounds over a wide range by varying their qualitative and quantitative composition. Multicomponent bismuth niobates with pyrochlore structure are stable over a wide range of molar ratios between atoms of bismuth, niobium, and a metal substituting niobium [1]. The study of specific features of the magnetic behavior of such systems will make it possible to find nanosize formations in the structure and to reveal their effect on the physicochemical properties of the compounds.

In this work we studied the behavior of chromium atoms in the matrix of a diamagnetic multicomponent bismuth niobate with the pyrochlore structure, $Bi_2MgNb_2O_9$ (Fig. 1). Solid solutions of $Bi_2Mg_{1-x}Cr_xNb_2O_9$ (x = 0.02–0.1) were synthesized by the ceramic technique. According to the X-ray analysis data, the sample of $Bi_2Mg_{0.9}Cr_{0.1}Nb_2O_9$ is a single-phase solid solution with the cubic pyrochlore structure and the unit cell parameter a 10.545(5) Å. Samples with lower content of chromium were found to crystallize in this structural type also, to give solid solutions. The unit cell parameter of pure $Bi_2MgNb_2O_9$ solvent is a 10.557(6) Å. Smaller chromium atoms (0.615 Å) substitute the magnesium (0.72 Å) or niobium (0.64 Å) atoms [2] in their crystallographic positions, which results in compression of the lattice and, correspondingly, in a decrease in its parameter.

We measured the magnetic susceptibility of the $Bi_2Mg_{1-x}Cr_xNb_2O_9$ solid solutions in the range 77–400 K. From the results obtained, we calculated the paramagnetic components of magnetic susceptibility (χ_{Cr}) and effective magnetic moments (μ_{eff}) of chromium atoms in the solid solutions. The temperature dependence of the reciprocal paramagnetic component of susceptibility of all the solid solutions obeys the Curie–Weiss law over the whole temperature range under study.

The χ_{Cr}–x isotherms for the $Bi_2Mg_{1-x}Cr_xNb_2O_9$ solutions are shown in Fig. 2. The concentration dependences of χ_{Cr} for the solid solutions of bismuth

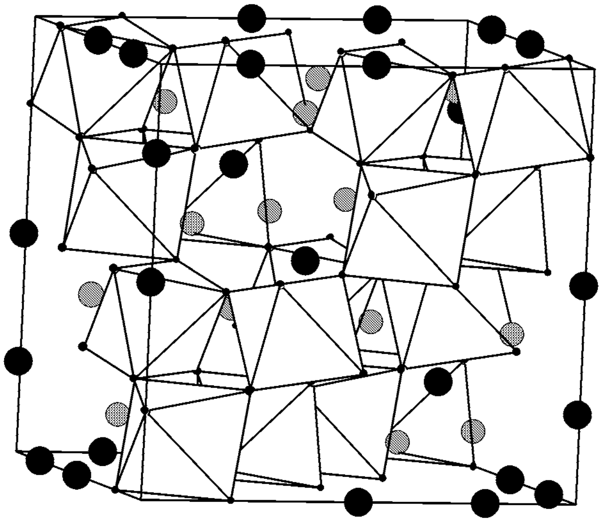

Fig. 1. Pyrochlore structure. Combination of octahedra containing Nb(V), Mg(II), and Cr(III) atoms. Black circles denote oxygen atoms in various crystallographic sites, and gray circles, Bi(III).

niobates containing magnesium and chromium substantially differ in shape at low and high temperatures, suggesting complex character of exchange coupling. At low temperatures (lower than room temperature), the exchange coupling is essentially antiferromagnetic, and at higher temperatures χ_{Cr} increases as the content of the paramagnetic element in the solid solution increases. The extrapolation of the concentration dependences of the paramagnetic component of the magnetic susceptibility to infinite dilution allowed us to calculate the effective magnetic moments in the solid solutions (at $x \to 0$) at various temperatures. These values are given in the table.

The effective magnetic moment calculated by the extrapolation of the concentration dependences of χ_{Cr} to the infinite dilution in the $Bi_2Mg_{1-x}Cr_xNb_2O_9$ solid solutions appears to be essentially higher than the purely spin value of μ_{eff} for atoms with the d^3 electronic configuration ($^4A_{2g}$ term). It smoothly decreases as the temperature grows. To account for such changes in the magnetic characteristics, we can put forward two assumptions. First, it can be the reduction of Cr(III) to Cr(II) (^5E_g) with the spin of 2. This assumption appears to be improbable for the following reasons: bivalent chromium is unstable and cannot be stabilized in air. Moreover, μ_{eff} for the ^5E_g ground state is independent of temperature, whereas we observe a substantial decrease in μ_{eff} as the temperature increases. Such a μ_{eff}–T dependence is typical for clusters of paramagnetic atoms with ferromagnetic exchange. Thus, we should suggest that even at infinite dilution the chromium atoms are not fully disaggregated in the solid solution. There remain some clusters, probably consisting of two atoms, linked by the ferromagnetic exchange coupling. With this assumption, we calculated the temperature dependence of the magnetic moment for dimer particles with the spin $S_1 = S_2 = 3/2$ within the framework of the Heisenberg–Dirac–van Vleck model [3]. We determined the magnetic moments for various exchange parameters J. The best agreement with the experiment is observed at J 18 cm^{-1}. The experimental and calculated effective magnetic moments are given in the table.

The positive exchange parameter is indicative of the ferromagnetic coupling between the chromium atoms in the dimer. As the temperature increases, the effective magnetic moment of the dimer decreases owing to the thermal motion and approaches the mean value of the magnetic moments of the separate atoms making the dimer.

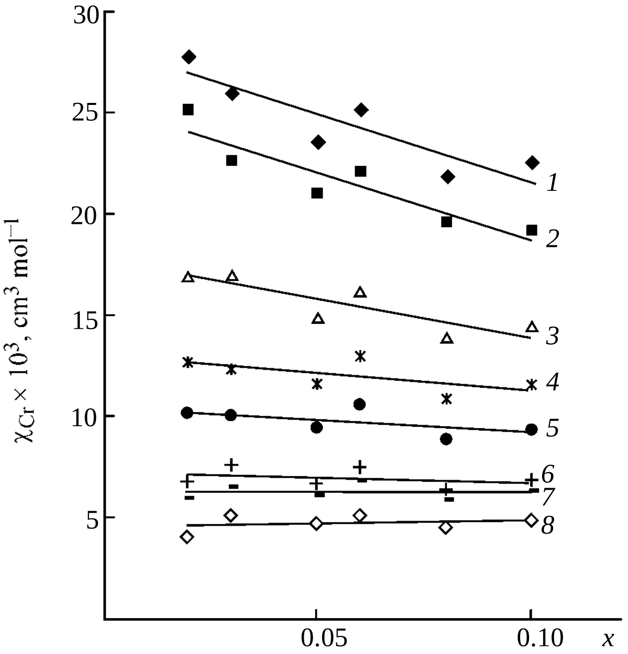

Fig. 2. Plot of paramagnetic component of magnetic susceptibility (χ_{Cr}) of the solid solutions vs. chromium concentration at (*1*) 90, (*2*) 100, (*3*) 140, (*4*) 180, (*5*) 220, (*6*) 293, (*7*) 320, and (*8*) 400 K.

The problem is that, in the context of the exchange channel theory, the superexchange between the chromium atoms via oxygen atom at an angle of 180° must be antiferromagnetic, since in such a system the main contribution to the exchange coupling is made by the channels $d_{xy} \parallel p_y \parallel d_{xy}$, $J < 0$, and $d_{xz} \parallel p_z \parallel d_{xz}$, $J < 0$. Comparatively small absolute values of J obtained earlier for perovskite-like structures [4] seem to be associated with the effect of ferromagnetic $d_{xy} \parallel p_y \perp p_z \parallel d_{xz}$ exchange channels. We suggest that in this case the specific features of the pyrochlore structure (Fig. 1), namely, the mode of combination of the oxygen octahedra, determine the ferromagnetic ex-

Effective magnetic moments of chromium atoms at infinite dilution (μ_{eff}^{exp}) and effective magnetic moments calculated theoretically for dimers (J cm^{-1}) (μ_{eff}^{theor})

T, K	$\chi_{Cr} \times 10^6$ ($x \to 0$), cm^3 mol^{-1}	μ_{eff}^{exp}, BM	μ_{eff}^{theor}, BM
90	30 300	4.69	4.72
100	25 400	4.52	4.60
140	17 700	4.47	4.52
160	15 100	4.42	4.48
180	13 000	4.34	4.43
220	10 400	4.30	4.31
320	6900	4.21	4.23
350	6400	4.24	4.25

change in the cluster. The reason is that antiferromagnetic exchange is connected with orbital overlapping: the greater the overlap integral, the greater the antiferromagnetic exchange. This effect was monitored in detail in perovskite-like structures [5]. In the pyrochlore structure, the octahedra are linked via apices, forming a three-dimensional chain framework. However, the M–O–M angle within the chains appears to be less than 180° (~135°), which substantially decreases the $p\pi$–$d\pi$ overlapping at least in one of the antiferromagnetic exchange channels ($d_{xy} \parallel p_y \parallel d_{xy}$). If we take into account the fact that, owing to the introduction of chromium atoms, additional local distortions are possible within the chain in the plain perpendicular to the axis connecting the two atoms via oxygen (“buckling” of the octahedra), the contribution of the second antiferromagnetic exchange channel can also decrease substantially. In such a case the ferromagnetic exchange channels appear to dominate, just what we observe in our case. However, it is obvious that the preservation of clusters at infinite dilution of the solid solutions is not determined by ferromagnetic exchange coupling only. As was shown in [6], such clusters must have a bond energy of about 75 kJ mol^{-1}. This means that the cluster formation should be accounted for by specific features of the chemical bonding in the pyrochlore structure, rather than in the magnetic exchange coupling. This is, however, the subject of a separate study.

The plot of χ_{Cr} vs. x is characterized at low temperatures by a decrease in the paramagnetic component as x increases and by its small increase at $T >$ 320 K, indicating that the exchange between the dimers is predominantly antiferromagnetic. At high temperatures, both effects become compensated, and the ferromagnetic contribution in the dimers can cause a certain increase in χ_{Cr} as the chromium concentration increases.

EXPERIMENTAL

The $Bi_2Mg_{1-x}Cr_xNb_2O_9$ solid solutions (x = 0.02–0.1) were prepared by the ceramic technique. A mixture of oxides of the corresponding elements was thoroughly ground, pelletized, and calcined in air at 600°C (10 h) and then at 1100°C (20 h). The X-ray diffraction analysis of the samples was performed with a DRON-4-07 diffractometer (CuK_α). The chromium content in the solid solutions was determined by the photometry of colored complexes. The error of quantitative determination of x in $Bi_2Mg_{1-x} \cdot Cr_xNb_2O_9$ did not exceed 5%. The magnetic susceptibility of the solid solutions was measured by the Faraday method in the range 77–400 K. The accuracy of relative measurements was 2%.

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