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State of Atoms of the Transition Group Elements in Dilute Solid Solutions Based on $LiMO_2$ (M = Sc, Ga, Al): IV.[1] Magnetic Susceptibility of the $LiM_xGa_{1-x}O_2$ Solid Solutions (M = Cr, Cu)

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Abstract—Magnetic dilution of $LiMO_2$ complex oxides (M = Cu, Cr) was studied. The results obtained were correlated to the physical and chemical properties of two-dimensional perovskite-like oxides containing copper and lithium. Various valence and spin states of copper and chromium were found, which are associated with essential anisotropy of the local surrounding of a transition element and with the influence of lithium atoms on the electron state of nanoclusters containing these elements.

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At present a large number of theoretical works are devoted to the study of transition element oxides, in which a strongly correlated behavior of electrons gives rise to a wide spectrum of magnetic and electric characteristics. Complex $LiMO_2$ oxides belong to them. For example, a dilution of spins or an introduction of doping elements is targeted for experimental studying the electron behavior [1, 2]. A competition of two kinds of exchange, ferro- and antiferromagnetic, in one compound is considered to be an indication of spin fluctuations. In this work we present the results of the study of complex $LiCuO_2$ and $LiCrO_2$ oxides, which form the basis for the experimental study of the spin fluctuations on diluting $LiCuO_2$ with the diamagnetic $LiGaO_2$ solvent.

We synthesized and studied the $LiM_xGa_{1-x}O_2$ solid solutions ($0.005 < x < 0.07$). Over this concentration range the solid solutions must have the structure of the solvent. A specified stabilization of the distribution of lithium and a transition element in the structure of diamagnetic solvent is possible while solid solutions of isomorphous substitution are formed. This allows changes in the spin states of a paramagnetic to be traced as its concentration in the solid solution gradually changes. Earlier, when studying iron-, cobalt-, and nickel-containing solid solutions with similar structures, we have found that lithium atoms substantially affect the electron structure of neighboring transition element atoms [1]. In all the solutions the atoms of a 3*d* element show a strong tendency to form nanoclusters. The electron structure of nanoclusters influences the realization of particular microstates of the whole system, which, in their turn, determine the character of long-order interactions. The clusters include not only transition element atoms, but also the atoms of its nearest surrounding (oxygen, lithium). Lithium atoms cause the strongest redistribution of the electron density within the cluster. The lithium-oxygen distances are changed, which results in the local distortions of the surrounding and in the changes in spin states.

According to the general formula, chromium and copper atoms in the solid solutions should have the oxidation state +3. Chromium atoms are stable in this state, for copper atoms it is considered to be unstable, and the both atoms can be in two spin states. Chromium atom is paramagnetic in either variant, the low spin state being extremely rare. Copper atom in the low spin state has no unpaired electrons and is diamagnetic; in the high spin state it has two unpaired electrons. In the solid solutions copper and chromium atoms are in the tetrahedral surrounding defined by the

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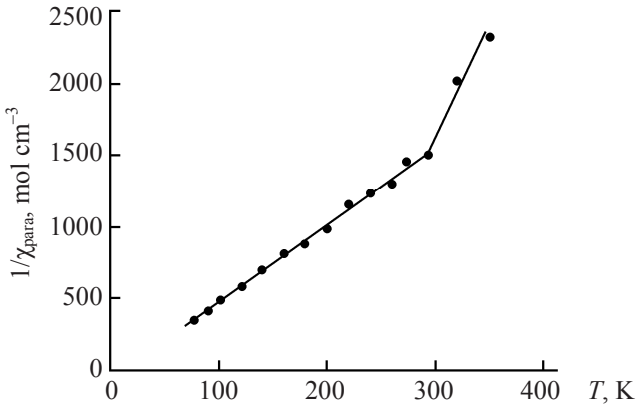

Fig. 1. Plot of the reciprocal of the paramagnetic component of magnetic susceptibility vs. temperature for the $x(LiCrO_2)$–$(1–x)LiGaO_2$ system.

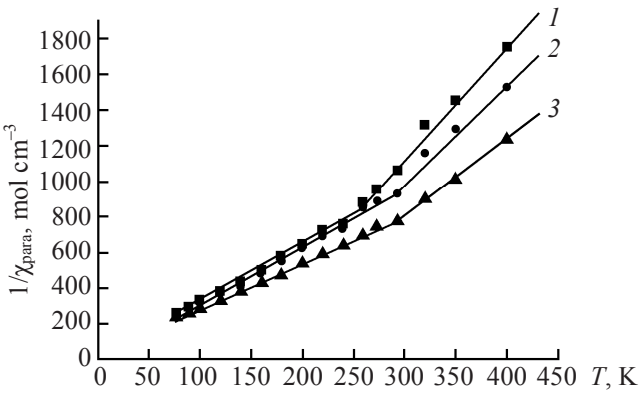

Fig. 2. Plot of the reciprocal of the paramagnetic component of magnetic susceptibility vs. temperature for the $x(LiCuO_2)$–$(1–x)LiGaO_2$ system at x: (*1*) 0.0150, (*2*) 0.0197, and (*3*) 0.0312.

diamagnetic matrix. The data obtained in this work suggest that oxygen tetrahedra containing metal atoms have strong local distortions. The interactions between the atoms are indirect.

The plot of magnetic susceptibility vs. temperature for $LiCr_xGa_{1–x}O_2$ is linear, i.e. it obeys Curie–Weiss law. However, at 290 K there is a break in the plot (Fig. 1) resulting in a decrease in the susceptibility and in an increase in the Weiss constant. For example, for a sample with x = 0.03 the low and high temperature values are –8 and 148 K, respectively. It points to the presence of ferro- and antiferromagnetic contributions to the magnetic susceptibility. The superexchange at an angle of 180° is antiferromagnetic and at an angle of 90° is ferromagnetic. The superexchange angle in the $LiGaO_2$ structure is 116°. The emergence of positive Weiss constants means that the superexchange angle changes, i.e. the nearest surrounding of chromium atoms becomes locally distorted. The temperature of antiferromagnetic ordering of magnetically concentrated $LiCrO_2$ is 300 K, no ferromagnetic contribution being reported [3]. It shows itself only in magnetically diluted samples, i.e. corresponds to the short-order interactions.

The magnetic susceptibility and the effective magnetic moment of the solid solutions remain almost constant as the chromium concentration changes up to x = 0.03, whereas on further dilution their decrease is observed. For example, μ_{eff} varies within 0.8–1.2 BM at 100 K. This is substantially less than for Cr(III) atoms in the high spin state ($3d^3$ S 3/2; ^4T). The extrapolation of μ_{eff}–x isotherms to infinite dilution results in magnetic moments 0.9–0.4 BM at infinite dilution. If only single chromium atoms in the high spin state remain at infinite dilution, their magnetic moment must increase from 1.9 to 2.8 BM. If the low spin state (S 1/2, ^2E) is realized in the distorted surrounding, the magnetic moment does not depend on temperature. Therefore, a superposition of two spin states also will not result in a decrease in the observed magnetic moment at infinite dilution. Since the experimental data do not fit the presence of only single chromium atoms in the solution, the only explanation of the magnetic parameter behavior is the presence of clusters consisting of at least two chromium atoms. The character of superexchange via oxygen atoms within the clusters is antiferromagnetic, its value being about 500 cm^{-1}. The emergence of a ferromagnetic contribution can result from magnetic frustrations of the structure (deviation from strictly antiparallel location of the spins) owing to strong local distortions.

Anomalies of magnetic characteristics were found also in the $LiCu_xGa_{1–x}O_2$ solid solutions.

The experimental dependence of $1/\chi_{Cu}^{para}$–T (Fig. 2) can be represented as two sites, a high temperature (HT) and a low temperature (LT), obeying Curie-Weiss law [$\chi_{Cu}^{para} = C/(T – \theta)$], but with different Weiss constants θ. Weiss constants as functions of concentration for the $LiCu_xGa_{1–x}O_2$ system are given below.

x	0.0044	0.0075	0.0102	0.015	0.0197	0.0312
θ_{LT}, K	65	15	0	0	0	0
θ_{HT}, K	220	210	240	240	240	240

The dependence of χ_{Cu}^{para}–x for the system under study has a shape not typical for the dilution of antiferromagnetics, though $LiCuO_2$ is an antiferromagnetic; the paramagnetic component of the magnetic susceptibility abruptly increases as the copper atom concentration increases, whereas in the region of $0.015 < x < 0.03$ it remains almost unchanged. The dependence of effective magnetic moment on the composition of the solution has the same shape. The effective magnetic moment decreases as the temperature increases for almost all concentrations. Only for solid solutions with the copper content $x > 0.02$ μ_{eff} remains almost unchanged as the temperature increases. Such a character of the changes in χ_{Cu}^{para} and μ_{eff} points to a ferromagnetic contribution to the magnetic susceptibility.

Experimental values of μ_{eff} decrease at infinite dilution from 0.5 to 0 BM. In the region of low temperatures $\mu_{eff}^{x\to 0}$ does not depend on temperature, whereas at $T > 180$ K its value begins to decrease. Therefore, even at infinite dilution the effective magnetic moment does not fit any of single copper atom states. Moreover, an essential special feature of the dilution is the fact that χ_{Cu}^{para} and μ_{eff} obviously tend to zero, which points to the presence of Cu(III) atoms in the diamagnetic state.

We can consider also the presence of a paramagnetic copper atom, $Cu(II)_{S1/2}$. In the tetrahedral crystal field μ_{eff} for such an atom increases from 1.7 up to 2.5 BM, and this state can be recorded in the EPR spectra at 293 K. In a sample with $x < 0.03$ no signal in the EPR spectrum was observed. The experimental magnetic moments can be adequately accounted for only by the presence of clusters of two paramagnetic copper atoms and oxygen atoms with antiferromagnetic character of superexchange. As well as in the case of chromium atoms the exchange parameter must be no less than 500 cm^{-1}. On the basis of the solution structure the cluster composition may be described by the formula $[M_2Li_1O_{10}]$[13].

Therefore, for the $LiM_xGa_{1-x}O_2$ solid solutions (M = Cr, Cu) a competition of two kinds of exchange, ferro- and antiferromagnetic, and a strong tendency to clustering were found. For all the solutions a strong anisotropy of the surrounding was also found, both of lithium atoms and of transition element atoms, i.e. temperature-dependent local distortions of lithium coordination polyhedra and of 3*d* element coordination polyhedra are observed. Simultaneous strong distortions of lithium and transition element sites undoubtedly must be interrelated, since in a magnetically diluted system they cannot extend far over the lithium and a paramagnetic atom sites. The most advantageous variant of realizing such distortions is the presence of lithium and transition element atoms in the same cluster. As stated above, lithium initiates a redistribution of the electron density within the cluster, which results in geometrical and magnetic frustrations of the structure and in the change in the spin states.

EXPERIMENTAL

The $LiCuO_2$ and $LiCrO_2$ solid solutions in the $LiGaO_2$ diamagnetic solvent were synthesized by the ceramic technique from stoichiometric mixture of corresponding components: Li_2CO_3, CuO, Cr_2O_3, Ga_2O_3, which were checked for the absence of ferromagnetic admixtures misrepresenting the results of the measurements. Owing to a high volatility of lithium carbonate we used it in a 15% excess. The optimal conditions of the synthesis were selected on the basis of the X-ray analysis and magnetic susceptibility measurements. The diamagnetic $LaGaO_3$ solvent was obtained by sintering for 20 h at 1073 K.

Powder diffraction patterns were recorded on a DRON-3 X-ray diffractometer using CuK_α emission and identified with the help of the Powder Diffraction File [4]. We measured the magnetic susceptibility by Faraday method in the temperature range 77–400 K. The optimal time of the synthesis of homogeneous $LiM_xGa_{1-x}O_2$ solid solutions was 30 h at 1173 K. According to the X-ray data, the homogeneous solid solutions with a predetermined structure and the unit cell parameters fitting the structure of the solvent were obtained.

A series of solid solutions with a set of 3*d*-element concentrations in the region from 0.5 to 7 mol% was synthesized. All the solid solutions were analyzed for the content of the paramagnetic component by the method of atomic absorption spectroscopy.

We measured the magnetic susceptibility of the samples under study by Faraday method. Magnetic susceptibility of each sample was measured at 16 fixed temperatures from 77 to 400 K. The error of relative measurements was 1–2%. To determine the paramagnetic component of magnetic susceptibility calculated per one mole of paramagnetic atom, we introduced diamagnetic corrections with regard to the experimental susceptibilities of diamagnetic matrices. The selected procedures of extrapolating magnetic

characteristics to the infinite dilution provided for an error of no more than 3%.

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