State of Atoms of the Transition Group Elements in Dilute Solid Solutions Based on LiMO$_2$ (M = Sc, Ga, Al): IV. Magnetic Susceptibility of the LiM$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$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
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\textsubscript{x}Ga\textsubscript{1-x}O\textsubscript{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\textsubscript{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\textsubscript{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, \( \mu_{\text{eff}} \) varies within 0.8–1.2 BM at 100 K. This is substantially less than for Cr(III) atoms in the high spin state (3\( d^3 \) S 3/2; 4\( T \)). The extrapolation of \( \mu_{\text{eff}} \) 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 (\( S = 1/2 \), 2\( E \)) 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\textsubscript{x}Ga\textsubscript{1-x}O\textsubscript{2} solid solutions. The experimental dependence of 1/\( \chi_{\text{para}} \)–\( T \) (Fig. 2) can be represented as two sites, a high temperature (HT) and a low temperature (LT), obeying Curie-Weiss law [\( \chi_{\text{para}} = C/(T - \theta) \)], but with different Weiss constants \( \theta \). Weiss constants as functions of concentration for the LiCu\textsubscript{x}Ga\textsubscript{1-x}O\textsubscript{2} system are given below.

<table>
<thead>
<tr>
<th>( x )</th>
<th>0.0044</th>
<th>0.0075</th>
<th>0.0102</th>
<th>0.015</th>
<th>0.0197</th>
<th>0.0312</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_{\text{LT}} ), K</td>
<td>65</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \theta_{\text{HT}} ), K</td>
<td>220</td>
<td>210</td>
<td>240</td>
<td>240</td>
<td>240</td>
<td>240</td>
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