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State of Atoms of the Transition Group Elements in Dilute Solid Solutions Based on $LiMO_2$ (M = Sc, Ga, Al): III.[1] State of Iron and Lithium Atoms in the $LiFe_xSc_{1-x}O_2$ Solid Solutions

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Abstract—$LiFe_xc_{1-x}O_2$ solid solutions ($0.005 < x < 0.10$) were studied by the NMR and magnetic susceptibility methods. The anomalies of temperature and concentration dependences of magnetic susceptibility are accounted for by the contributions of single iron atoms and clusters containing iron, oxygen, and lithium atoms. According to the NMR spectroscopy data, lithium atoms also are in two states and enter the cluster composition.

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Complex $LiMO_2$ oxides (M = 3*d*-element) are extensively used as cathode materials, but their properties depend crucially on the synthesis conditions, chemical composition, and structure. Thus far, the degree of mutual influence of the indicated factors has not been conclusively established; the studies mostly concern technological features of the synthesis. As was shown earlier, the information about the local structure of complex oxides gives exhaustive information for the insight into their macroscopic physical and chemical properties [2].

A variant of such investigation can be the study of physical and chemical characteristics of the oxide systems, where the location of lithium and 3*d*-element atoms is known with certainty. The magnetic properties of the oxides are highly sensitive to the changes in the chemical composition of a compound. Therefore, with the aim of obtaining more accurate information about the state of atoms and the local crystallographic parameters we studied the magnetic susceptibility of diluted solid solutions of the complex $LiFeO_2$ oxide in the diamagnetic $LiScO_2$ solvent. The choice of this solvent is determined by a clear-cut and stable location of lithium and scandium atoms. The solid solutions based on $LiScO_2$ have a tetragonal superstructure of NaCl resulting from the total ordering of lithium and iron atoms. These atoms alternate between each other in the sites along two directions of the basic lattice: (110) and (–110). Such ordering results in tetragonal volume centered unit cell with the *c* parameter twice of that of NaCl (Fig. 1a).

The coordination polyhedron for lithium and iron atoms is a tetragon-distorted octahedron elongated along the *c* crystallographic axis. Chains of oxygen octahedra are formed along the *a* crystallographic axis. They are elongated along the *c* axis and joined by apexes. The chains of scandium and lithium atoms alternate. This, in its turn, results in zigzag structural motives alternating along the *c* axis and shifted along the *a* axis by a half of the unit cell parameter.

In such a structural motive the coordination octahedra of metal atoms are joined between themselves by apexes and edges, therewith by the apexes only they are located at short distances from the center, and by the edges only at the long distances.

The interactions between lithium atoms and also between iron atoms (substituting for scandium atoms) have an indirect character. A superexchange between

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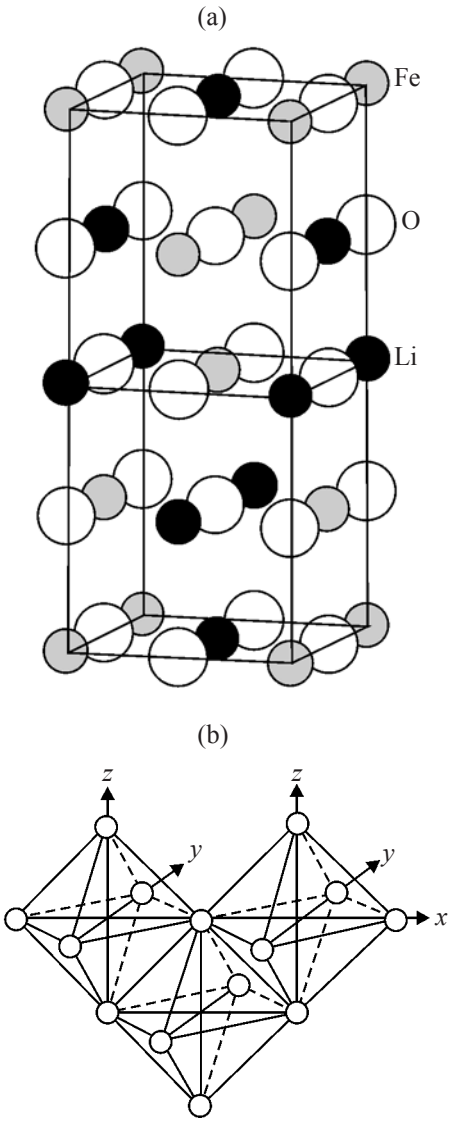

Fig. 1. (a) Structure of diamagnetic $LiScO_2$ solvent and of $LiFe_xSc_{1-x}O_2$ solid solutions and (b) structural motive.

neighboring metal atoms in the same layer via oxygen atoms can take place along two directions, at angles of 169° and 95.6°.

We synthesized the $LiFe_xSc_{1-x}O_2$ solid solutions ($0.005 < x < 0.10$), carried out their X-ray and chemical analysis for the paramagnetic element content, and measured the magnetic susceptibility in the range 77–400 K in steps of 20 K.

The examination of temperature and concentration dependences of magnetic susceptibility of the solid solutions and also of Mössbauer spectra allowed the following conclusions to be made.

(1) Iron atoms are in two spin states: $Fe(III)_{S5/2}$ and $Fe(III)_{S1/2}$. The fraction of those latter does not exceed 7%.

(2) Along with single Fe(III) atoms there are stable nanosize clusters in the solution including not only iron atoms but lithium atoms in their composition. Consequently, lithium atoms can also be single and take part in the interactions within the cluster.

(3) There is a strong anisotropy of the local surrounding both of lithium atoms and iron atoms. Simultaneous strong local distortions of lithium and iron sites undoubtedly must be interrelated, since in the magnetically diluted system they cannot extend far, especially over the sites of a paramagnetic atom. Hence the most probable suggestion is the coexistence of iron and lithium atoms in the same cluster. According to the structural characteristics, the minimal empirical formula of the cluster is $[Fe_2Li_1O_{14}]^{21-}$ [3].

The study of the $LiFe_xSc_{1-x}O_2$ solid solutions by the magnetic dilution method allowed us to draw a conclusion about the presence of nanoclusters (dimers) of iron and oxygen atoms in the diluted solid solution, their fraction being essentially higher than that corresponding to the statistical distribution of iron atoms over scandium sites in the diamagnetic $LiScO_2$ solvent.

The run of the plot of magnetic susceptibility vs. iron concentration for the $LiFe_xSc_{1-x}O_2$ system can be adequately described with an only assumption: it is necessary to consider every point of the temperature and concentration dependences of magnetic characteristics as a sum of magnetic susceptibilities of single Fe(III) atoms and of three types of dimers of these atoms (J_1 –40, J_2 10, J_3 2 cm^{-1}). The run of χ_{Fe}–x isotherms determined by the presence of clusters has been examined in detail in [3] (Fig. 2). The fraction of each contribution varies depending on the total content of iron in the solid solution, except for the fraction of the dimers with $J = 2$ cm^{-1} (a_4 0.07) and the fraction of $Fe_{S1/2}$ (a_5 0.09). Such a situation can be described by formula (1).

$$\chi(x) = a_1\chi(Fe_{S5/2}) + a_2\chi(Fe_{S5/2} - Fe_{S5/2})_{J-40} + a_3\chi(Fe_{S5/2} - Fe_{S5/2})_{J\,10} + a_4\chi(Fe_{S\,5/2} - Fe_{S5/2})_{J\,2} + a_5\chi(Fe_{S1/2}). \quad (1)$$

The magnetic susceptibility of a dimer can be determined from the HDVV model using Eq. (2).

$$\chi_{dim} = \frac{Ng^2\beta^2\sum_S S(S+1)(2S+1)e^{-E(J,S)/kT}}{3kT\sum_S (2S+1)e^{-E(J,S)/kT}}. \quad (2)$$

Here g is the g-factor ($g = 2$), T is absolute temperature;

$$E(J, S) = -J[S(S+1) - S_a(S_a+1) - S_b(S_b+1)],$$
$$S = S_a + S_b, S_a + S_b - 1, \ldots |S_a - S_b|,$$
$$g(S) = \frac{g_a + g_b}{2} + \frac{g_a - g_b}{2} \quad \frac{S_a(S_a+1) - S_b(S_b+1)}{S(S+1)}.$$

An increased resistance of these nanoclusters to dilution is connected with the inclusion of lithium atoms into their composition.

In this context it is clear that additional information about the state of lithium atoms in the solution is of great importance. Therefore we studied the solid solutions by the NMR method.

The ^{7}Li NMR spectrum of the diamagnetic $LiScO_2$ solvent presents a triplet typical for quadrupole nuclei with the nuclear spin $I = 3/2$. The quadruple splittings are ν_0 35.9 (303 K) and 39.4 kHz (133 K) (Fig. 3, spectrum *1*).

Substitution of Fe atoms for a fraction of Sc atoms upon the formation of the solid solutions results in a widening of the resonance line owing to the appearance of superfine interactions (SFI) on lithium nuclei resulted from the noncompensated spin of the 3*d* shell of iron atoms. As the concentration of iron increases the line becomes asymmetrical (Fig. 3, specta *2*). The resolution of the line with the help of "Simul" program showed that the spectrum of the $LiFe_xSc_{1-x}O_2$ solid solutions is a combination of two lines (lines *2a* and *2b*) with different isotropic shifts

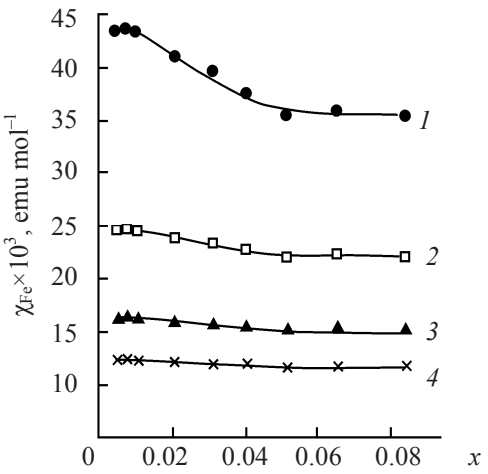

Fig. 2. Plots of χ_{Fe}–x for the $LiFe_x\ Sc_{1-x}O_2$ solid solutions: (*1*) 90; (*2*) 160; (*3*) 240; and (*4*) 320 K.

(K_{iso}). The dependences of K_{iso} and the line width (ΔH) on x are given in Figs. 4 and 5, respectively.

The emergence of two lines in the spectrum means that lithium atoms are in two different states. These could be lithium atoms in two different crystallographic sites, but it is impossible for structural reasons. Then different states of lithium are associated with special features of lithium nuclei interactions with their nearest surrounding.

As was noted earlier [3], there are clusters in the solution containing iron, lithium, and oxygen atoms. Therefore, in the ^{7}Li NMR spectrum we have the lines

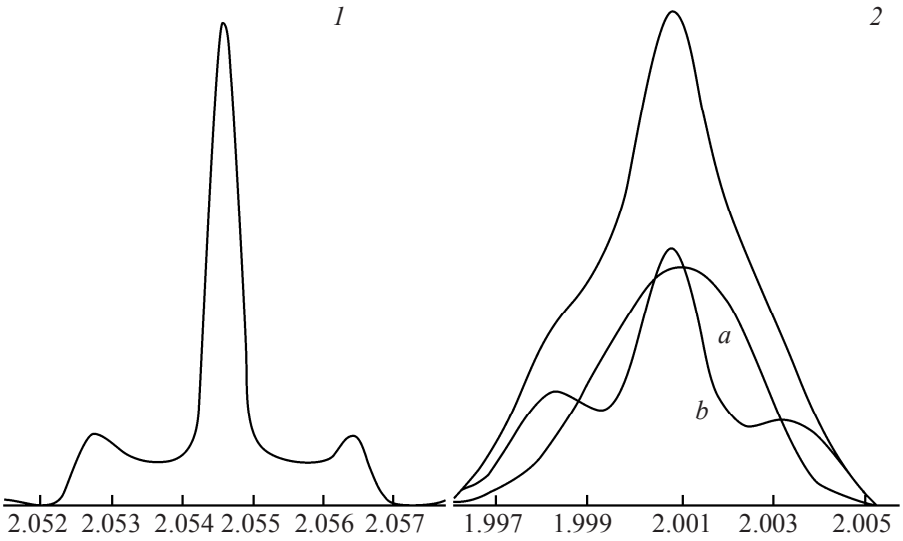

Fig. 3. ^{7}Li NMR spectra for (*1*) $LiScO_2$ solvent and (*2*) $LiFe_xSc_{1-x}O_2$ solid solution.

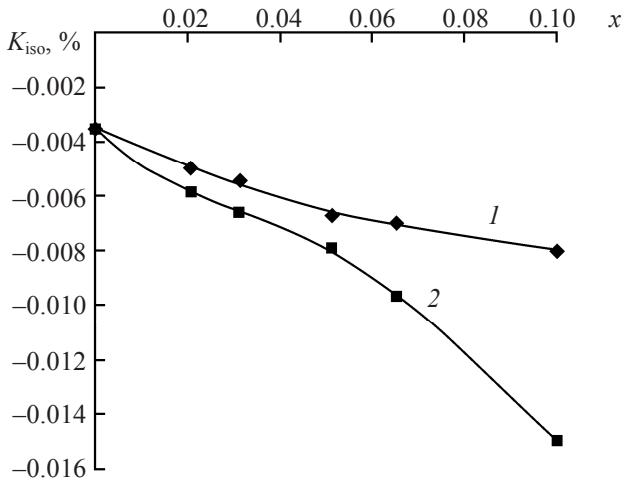

Fig. 4. Plots of K_{iso}–x for $LiFe_xSc_{1-x}O_2$ solid solutions; (*1*) line *2a* and (*2*) line *2b*, see Fig. 3.

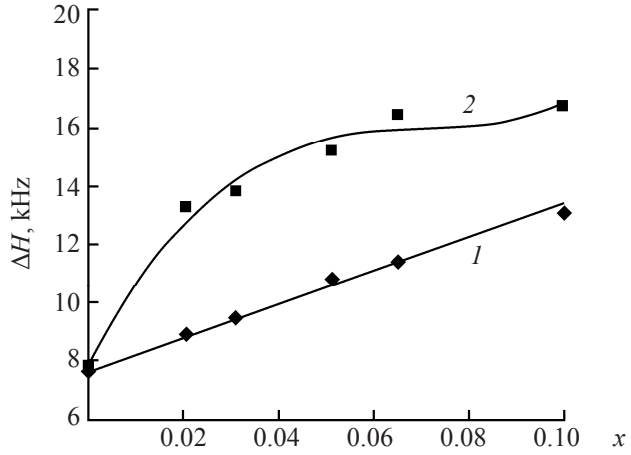

Fig. 5. Plots of ΔH–x for $LiFe_xSc_{1-x}O_2$ solid solutions; (*1*) line *2a* and (*2*) line *2b*, see Fig. 3.

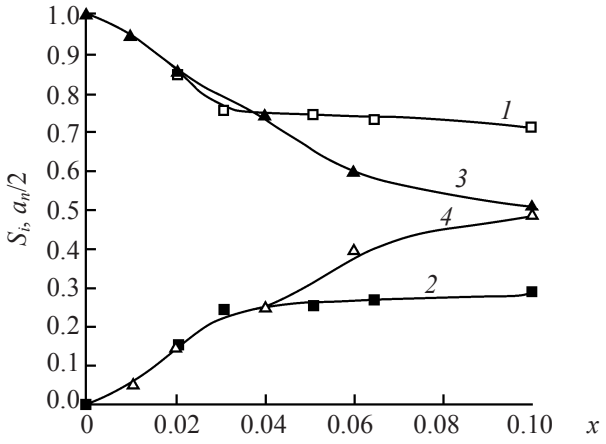

Fig. 6. Plots of S_i–x and $a_n/2$–x for $LiFe_xSc_{1-x}O_2$ solid solutions; (*1*) line *2a* and (*2*) line *2b*; (*3*) $a_{1.5}/2$; and (*4*) $a_{2\text{-}3}/2$.

from single lithium atoms and from lithium atoms included into the cluster.

As iron content in the solution increases the integral intensity (S) (Fig. 6) increases for line *2b* and decreases for line *2a* (Fig. 3, spectrum *2*). This coincides with the increase in the total fraction of clusters ($a_{2\text{–}4}$) in the solution following from the examination of magnetic susceptibility. Therefore, line *2b* may be attributed to the state of lithium atoms included into the cluster, and line *2a* to single lithium atoms.

The line width ΔH increases as the iron content in the solution increases, the broadening of line *2a* occurrs evenly, in contrast to line *2b* . Breaks at $x \sim 0.02$ and 0.06 correspond to the changes in the magnetic susceptibility as the concentration of iron in the solution increases. The change in K_{iso} with increasing concentration correlates with the run of the ΔH dependence.

The dependences of S_i on x completely coincide with the dependences of a_n on x with the proviso that in the region of $0 < x < 0.05$ the fraction of monomers and the total fraction of dimers must be exactly twice decreased. This also corroborates the conclusion made about the empirical formula of the nanocluster, namely, that a dimer cluster contains one lithium atom.

A divergence of $S_i(x)$ and $a_n(x)$ curves beginning from $x > 0.05$ is associated with the fact that starting from this concentration there is no more single iron atoms, and further enlarging of clusters and interaction between them begin.

Values of K_{iso} are different for lines *2a* and *2b*. This difference points to two variants of local magnetic fields of iron atoms acting on lithium atoms being in the cluster and out of it.

Consequently, the complex study of magnetic and resonance properties of the $LiFe_xSc_{1-x}O_2$ solid solutions confirms both the general formula of the nanoclusters of iron atoms advanced earlier and the presence of lithium atoms in them.

EXPERIMENTAL

We synthesized diluted solid solutions of $LiFeO_2$ in the diamagnetic $LiScO_2$ solvent by the ceramic technique from the stoichiometric mixture of corresponding components: Li_2CO_3, Fe_2O_3, Sc_2O_3. We used a 15% excess of lithium carbonate owing to its high volatility. The data of emission spectral analysis

and the measurements of magnetic susceptibility pointed to the absence of ferromagnetic admixtures in the starting components, which could misrepresent the results of the measurements. The concentration range of the paramagnetic component was from 0.5 to 10 mol %. In this range of transition element concentrations the state of paramagnetic atoms is not masked by long-order interactions. The optimal conditions for the synthesis were selected on the basis of the data of X-ray phase analysis and magnetic susceptibility measurements. The diamagnetic $LiScO_2$ solvent was obtained on sintering for 40 h at $T = 1073$ K.

The powder diffraction patterns were recorded on a DRON-3 diffractometer using CuK_α emission. We identified the powder diffraction patterns with the help of Powder Diffraction File [4]. We determined the unit cell parameters by the X-ray data. We found that the optimal time of synthesizing homogeneous $LiFe_xSc_{1-x}O_2$ solid solutions is 40 h at 1273 K. According to the X-ray results, we obtained homogeneous solid solutions with the predetermined structure. The equilibrium state of the obtained samples was proved by magnetic susceptibility measurements. The stability of the oxidation state of paramagnetic atoms is proved by the magnetic characteristics of the samples obtained in various gas media (air and oxygen), which are independent of the synthesis conditions and of additional sintering. The oxidation state of iron atoms is three, which was proved by Mössbauer, EPR, and Roentgen photoelectron spectroscopy data.

All the obtained solid solutions were analyzed for the content of the paramagnetic component by the method of atomic absorption spectroscopy. On the basis of these results and also on the data of measuring the specific magnetic susceptibility for the solid solution and diamagnetic solvent we calculated the paramagnetic component of magnetic susceptibility per one mole of paramagnetic atom and the effective magnetic moment.

The magnetic susceptibility of the samples under study was measured by Faraday method. We carried out the measurements of magnetic susceptibility of each sample at 16 fixed temperatures from 77 to 400 K. The error of relative measurements was 1–2%. The diamagnetic corrections for the determination of paramagnetic component calculated per one mole of paramagnetic atoms (χ_{Fe}) were introduced with regard to the experimental susceptibilities of diamagnetic matrices. The selected procedures of extrapolating the magnetic characteristics to the infinite dilution provided for the error not exceeding 3%.

The ^{7}Li NMR spectra were recorded on an upgraded TESLA BS-567A spectrometer at a frequency of 33 MHz using a LiCl aqueous solution as a reference for measuring the shifts. The measurements were carried out for the whole series of the obtained solid solutions in the temperature range 120–300 K.

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