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State of Atoms of Transition Elements in Dilute Solid Solutions Based on $LiMO_2$ (M = Sc, Ga, Al):
I. Magnetic Properties of $LiFe_xSc_{1-x}O_2$

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Abstract—Magnetic properties of solid solutions of the double oxide $LiFeO_2$ in a diamagnetic solvent $LiScO_2$ were studied. The observed anomalies in the magnetic parameters can be accounted for by the formation of nanoclusters of iron, oxygen, and lithium atoms.

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An increased interest in double oxides $LiMO_2$ (M is a 3*d* element) is caused by several factors. First, they are widely used as cathodic materials, but their properties strongly depend on the synthesis conditions, chemical composition, and structure. The extent of mutual influence of these factors has not been conclusively established until now, as the studies mostly deal with specific process features of the synthesis. Second, even within the limits of a single chemical composition, these oxides have a very broad spectrum of magnetic characteristics depending on the degree of structural order, which is associated with the unique possibility for lithium atoms to occupy the 3*d* element sites. The reasons for such a behavior are unclear. By now, a great body of experimental data on $LiMO_2$ properties have been accumulated, but they are incomplete and often contradictory. It became evident [1] that a systematic study of the chemistry of these oxides is necessary and, in particular, the study of oxide systems with a specified location of lithium and transition element atoms. For example, it seems appropriate to study physicochemical characteristics of oxide systems in which the location of lithium and 3*d* element atoms is known with certainty. The magnetic properties of the oxides are highly sensitive to variations in their chemical composition; hence, with the aim to obtain more accurate information about the state of atoms and of the local crystallographic parameters, we studied the magnetic susceptibility of dilute solid solutions of the double oxide $LiFeO_2$ in a diamagnetic solvent $LiScO_2$. The choice of this solvent was determined by the well-defined and stable location of lithium and scandium atoms. The solid solutions based on the diamagnetic solvent $LiScO_2$ have a tetragonal NaCl superstructure. It results from complete ordering of the lithium and scandium atoms. These atoms alternate in the crystallographic sites along two directions of the basic lattice: (110) and $(\bar{1}10)$. Such ordering results in the formation of a tetragonal body-centered unit cell with the doubled (with respect to NaCl) parameter *c*. This, in turn, results in the formation along the crystallographic *a*-axis of chains of oxygen octahedra elongated along the *c*-axis and sharing common apices. The chains of scandium and lithium atoms alternate.

The choice of the Fe atom as a 3*d* element is based on its stability in the oxidation state 3+. The single stable oxidation state decreases the number of factors affecting the magnetic characteristics.

We synthesized the $LiFe_xSc_{1-x}O_2$ solid solutions ($0.005 < x < 0.09$; in this region of transition element concentration, the state of paramagnetic atoms is not disguised by long-range interactions). We carried out their X-ray phase analysis, determined the content of the paramagnetic element by chemical analysis, and measured the magnetic susceptibility in the range from 77 to 400 K in 20 K steps.

The equilibrium distribution of paramagnetic atoms in the double oxides obtained was proved by the magnetic susceptibility measurements. The stability of the oxidation state of paramagnetic atoms was proved by the fact that the magnetic characteristics of the samples obtained in various gas media (air, nitrogen, and oxygen) do not change depending on the conditions of the synthesis and additional sintering. The oxidation state 3+ of iron atoms was proved by Mössbauer, ESR, and X-ray photoelectron spectros-

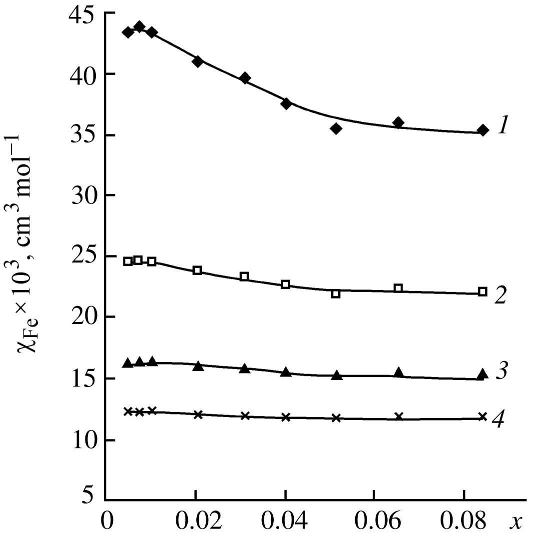

Fig. 1. Plot of χ_{Fe} vs. x for the $LiFe_xSc_{1-x}O_2$ system. T, K: (*1*) 90, (*2*) 160, (*3*) 240, and (*4*) 320.

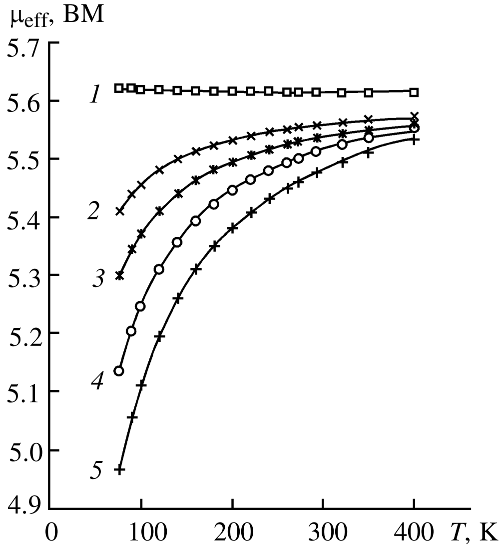

Fig. 2. Plot of μ_{eff} vs. T for the $LiFe_xSc_{1-x}O_2$ solid solutions. x: (1) 0.0075, (2) 0.0206, (3) 0.0310, (4) 0.0401, and (*5*) 0.0513.

copy and by magnetic susceptibility measurements [5].

From the results of analysis and of magnetic susceptibility measurements for the solid solutions and diamagnetic solvents, we calculated the paramagnetic components of magnetic susceptibility per mole of paramagnetic atoms and the effective magnetic moments.

As we showed previously, the plots of reciprocal paramagnetic component of the magnetic susceptibility vs. temperature are linear over the whole temperature range for all the solid solutions obtained, i.e., they obey the Curie–Weiss law [2]. The Curie–Weiss law is observed down to the temperature of liquid helium. The Weiss constants (θ) are negative for x greater than 0.005. The quantity θ is commonly considered in magnetochemistry as a characteristic of the exchange, and its negative values indicate that the superexchange interactions between the iron atoms via oxygen atoms must be antiferromagnetic. However, at the lowest iron content, the Weiss constant changes its sign and becomes positive. This fact indicates that interactions of the second type (ferromagnetic) are manifested at a large dilution of the paramagnetic oxide. The change in the character of interactions is possible only if the superexchange angle of paramagnetic atoms changes from 180° to 90°; hence, the above-noted change in the sign of θ is the first evidence of local distortions in the crystallographic surrounding of iron atoms. As the content of iron atoms in the solution increases, the surrounding of separate atoms becomes averaged, and the local effects are not recorded any more.

Let us consider the concentration and temperature dependences of the paramagnetic component of the magnetic susceptibility per mole of iron atoms (χ_{Fe}) and of the effective magnetic moment (μ_{eff}). These quantities decrease as the concentration of the solutions increases (Fig. 1), in agreement with the antiferromagnetic type of exchange. However, some anomalies are observed in the region of strongly dilute solutions, starting from x 0.01, in which the susceptibility ceases to depend on the concentration. Since a change in the state of iron atoms is unlikely, the observed effect can be attributed to a competition of two contributions to the magnetic susceptibility, ferro- and antiferromagnetic.

The temperature dependences of the magnetic moments of all the solutions (Fig. 2) confirm the occurrence of ferromagnetic interactions, which are recorded in the most dilute solutions and, consequently, are realized within the limits of a small number of atoms. As seen from Fig. 2, the magnetic moment increases with temperature down to x 0.01; this trend becomes less pronounced with increasing dilution, and at x 0.0075 the magnetic moment is almost independent of temperature. The independence of the magnetic moment from temperature is due to closeness of the contributions of different-sign interactions to the magnetic susceptibility, ferro- and antiferromagnetic. Consequently, these dependences are indicatve of strong local distortions of the nearest surrounding of the metal atom.

The temperature dependences of the magnetic moment at infinite dilution ($\mu^{x \to 0}$) of the $LiFe_xSc_{1-x}O_2$ solid solutions were obtained by extrapolating 16 experimental isotherms of the paramagnetic component of the magnetic susceptibility and of the effective magnetic moment to the zero concentration.

T, K	77	90	100	120	140	160	180	200	220	240	260	273	293	320	350	400
$\mu^{x \to 0}$, BM	5.57	5.58	5.58	5.59	5.60	5.60	5.60	5.61	5.61	5.61	5.61	5.61	5.61	5.61	5.62	5.62

In the general case, extrapolation of magnetic parameters to the infinite dilution at magnetic dilution of antiferromagnetics gives characteristics of the state of a single atom of a paramagnetic element.

It is seen from the above data that $\mu^{x \to 0}$ does not depend on temperature. The ^6A term is not split by the spin–orbital coupling, and the magnetic moment of a single Fe(III) atom, indeed, should not depend on temperature. Its value is 5.5–5.6 BM, which is somewhat less than the spin-only value of μ_{eff} for a single Fe(III) atom ($3d^5$, $t_{2g}^3 e_g^2$, S 5/2) in the high-spin state. The underestimation of μ_{eff} can be associated with the occurrence of a fraction of Fe(III) in the low-spin state ($t_{2g}^4 e_g^1$, $^2T_2$, S 1/2). The high-spin state is stable, the distortion of the octahedron does not strongly affect its stability, but when the degree of distortion is high and the crystal field splitting increases, the low-spin state can be realized [3]. The Fe(III) atom (S 5/2) must have μ_{eff} 5.92 BM. In the temperature range under study, the effective magnetic moment for the low-spin configuration varies from 2.2 to 2.5 BM [4]. Therefore, a fraction of low-spin Fe(III) can decrease the effective magnetic moment, but cannot result in a substantial increase in μ_{eff} with temperature. Strong local distortions of oxygen surrounding of iron atoms are confirmed by the results of studying the solid solutions by NMR, Mössbauer, and ESR spectroscopy [5]. An anisotropy of the local surrounding results not only in the realization of the low-spin state for a fraction of iron atoms, but in a change in the exchange angle between them and in the appearance of competing contributions to the magnetic susceptibility. If the magnetic susceptibility of the infinitely diluted solution is considered as an additive sum of the susceptibilities of noninteracting low- and high-spin iron atoms, expression (1) is valid.

$$a_2 = a_1\mu^2(Fe_{1/2}) + a_2\mu^2(Fe_{5/2}), \qquad (1)$$

If $\mu(Fe_{1/2})$ is 1.8 BM and $\mu(Fe_{5/2})$ is 5.95 BM, then a_1 is 0.09, i.e., the fraction of low-spin atoms does not exceed 10%. The magnetic susceptibility at infinite dilution can be represented as the sum of not only single iron atoms in the low- and high-spin states, but also of the dimers of these atoms. The anisotropy of the local surrounding results not only in the realization of the low-spin state for a fraction of iron atoms, but in a change in the exchange angle between them and in the appearance of competing contributions to magnetic susceptibility. The most probable ferromagnetic exchange at infinite dilution is within small clusters (dimers) of iron atoms, rather than between individual atoms. In the most general case, even at random distribution in the solid solution, at any $x > 0$ there is already a certain number of clusters and single atoms (monomers). Their fraction is determined by the coordination number of the metal atom sublattice. The results of calculating the fraction of dimers for octahedral surrounding (Z 6) in comparison with the total fraction of dimers calculated from experimental magnetic susceptibilities for the $LiFe_xSc_{1-x}O_2$ system are given below.

x	a_2 stat.	Σa_2 exp.
0.01	0.055	0.1
0.02	0.105	0.3
0.04	0.221	0.5
0.06	0.302	0.8

Examination of the temperature dependences of the magnetic moment for all the possible spin states of single iron atoms and also for their combinations shows that the experimental dependences obtained cannot be described unequivocally assuming the existence of only single noninteracting atoms in such a solution in the crystallographic octahedral surrounding preset by the diamagnetic matrix. The shape of the magnetic susceptibility isotherms is determined by the relationship between the fractions of single paramagnetic atoms in various spin states and the clusters of these atoms, and also by the value and sign of the exchange parameter. We must consider several alternative compositions of the clusters and, possibly, also their coexistence in the solution. The alternatives of the dimers with ferromagnetic exchange type are the following: $Fe_{1/2}$–O–$Fe_{5/2}$, $Fe_{5/2}$–O–$Fe_{5/2}$, and $Fe_{1/2}$–O–

$Fe_{1/2}$. For the sake of simplicity of calculations, it seems logical to assume that the probability of formation of the $Fe_{1/2}$–O–$Fe_{1/2}$ cluster is very low, because the fraction of iron atoms in the low-spin state does not exceed 10%, as has been shown before. The magnetic susceptibility of various clusters can be estimated assuming the additivity of contributions of monomers (single atoms) and various clusters, according to the theory of dilute solutions, and using the Heisenberg–Dirac–van Vleck (HDVV) model, with taking into account the effective *g*-factor for calculating the susceptibility of clusters [6, 7]. In the concentration range of a dilute solution under study, the formation of clusters containing more than two atoms (dimers) is unlikely.

The HDVV model can be rigorously used only for *A* ground terms, when the orbital moment is completely frozen, in particular, for Fe(III). According to the HDVV model, the Hamiltonian of the spin–spin interaction is of form (2).

$$\hat{H}_{\text{exch}} = -2J\hat{S}_a\hat{S}_b. \tag{2}$$

Here J is the exchange parameter, and $\hat{S}_a$ and $\hat{S}_b$, operators of complete angular spin moment.

Then the magnetic susceptibility of a dimer can be determined with Eq. (3).

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

Here S is the spin of an atom; g, g-factor; T, absolute temperature; and

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

The susceptibility of a monomer is the paramagnetic component of the magnetic susceptibility of the solid solution at infinite dilution. The dimers are the minimal clusters of the composition Fe(III)–O–Fe(III), their size (0.7 nm) being in the nanoregion.

The shape of the dependence of the magnetic susceptibility on the iron concentration for the $LiFe_xSc_{1-x}O_2$ system is completely described with the only assumption that every point in the smooth curve should be considered as an additive sum of the magnetic susceptibility of single Fe(III) atoms and of three types of dimers (J_1 –40 cm^{-1}, J_2 +10 cm^{-1}, and J_3 +2 cm^{-1}). The fraction of each contribution varies depending on the total iron content in the solid solution, except for the fraction of dimers with J +2 cm^{-1}. Such a situation can be described by formula (4).

$$[\mu(x)]^2 = a_1\mu^2(Fe_{5/2}) + a_2\mu^2(Fe_{5/2}\text{–}Fe_{5/2})_{J-40}$$
$$+\ a_3\mu^2(Fe_{5/2}\text{–}Fe_{5/2})_{J+10} + a_4\mu^2(Fe_{5/2}\text{–}Fe_{5/2})_{J+2}. \tag{4}$$

The total fraction of all the dimers calculated from the experimental data is given above. The dimer fraction is substantially higher than that corresponding to the random distribution.

Thus, summing up the results obtained, we come to the following conclusion. All the specific features of the magnetic characteristics are accounted for by the presence of nanosize clusters consisting of iron and oxygen atoms. Using a set of magnetic methods, we revealed a strong anisotropy in the surrounding of both lithium and 3*d* element atoms, i.e., the local distortions of the oxygen coordination polyhedra of the lithium 3*d* element atoms are observed simultaneously. Simultaneous strong distortions of the lithium and transition element sites should be undoubtedly interrelated, because in a magnetically dilute system they cannot extend far over the sites of lithium and 3*d* element. The most probable assumption with regard to the results of magnetic susceptibility measurements is the coexistence of lithium and 3*d* metal in a single cluster. Based on the structural data, we can determine the empirical formula of the cluster as $[Fe_2Li_1O_{14}]^{21-}$.

The possible character of distortions can be found from the sign of exchange spin–spin interactions between the 3*d* element atoms. Superexchange interactions via oxygen atoms (angle 180°) should be antiferromagnetic, with the exchange parameter $J < 0$. If the angle is 90°, the exchange is ferromagnetic, $J > 0$. According to the results obtained, the ferromagnetic contribution to the exchange interactions is determined by the intracluster exchange, and the interaction between clusters is antiferromagnetic. The lithium(I) atom having no unpaired electrons is a “hole,” which can interact with unpaired electrons of the iron atom. An additional electrostatic interaction increases the stability of the clusters and results in substantial distortions of the magnetic and structural order. Recently this phenomenon, found in magnetically concentrated oxides, was conventionally termed the magnetic and geometric frustrations.

EXPERIMENTAL

Dilute solid solutions of $LiFeO_2$ in a diamagnetic solvent $LiScO_2$ were prepared by the ceramic technique from a stoichiometric mixture of the components: Li_2CO_3, Fe_2O_3, and Sc_2O_3, which were checked for the absence of ferromagnetic impurities distorting the results of the measurements. Because of the high volatility, lithium carbonate was taken in 15% excess. Previous studies showed that this amount is necessary and sufficient for preserving the stoichiometric composition of the mixture during the synthesis [2]. The optimal conditions of the synthesis were chosen on the basis of the X-ray analysis data and magnetic susceptibility measurements. The diamagnetic solvent $LiScO_2$ was prepared by sintering at 1073 K for 40 h.

Powder X-ray patterns were recorded on a DRON-3 diffractometer using CuK_α radiation. The powder patterns were identified with the aid of Powder Diffraction File [8]. The magnetic susceptibility was measured by the Faraday method in the temperature range 77–400 K. The unit cell parameters determined from the X-ray data agree with the published data [2]. The optimal time of the synthesis of homogeneous $LiFe_xSc_{1-x}O_2$ solid solutions was 40 h at 1273 K. According to the X-ray data, we obtained homogeneous solid solutions with the preset structure and the unit cell parameters corresponding to the structure of the solvent.

Ten solid solutions thus obtained with a set of 3*d* element concentrations in the range from 0.5 to 9 mol% were analyzed by the atomic absorption spectroscopy for the content of the paramagnetic component.

We measured the magnetic susceptibility of the samples under study by the Faraday method. We carried out the measurements of the susceptibility of each sample at 16 fixed temperatures from 77 to 400 K. The error of the relative measurements was 1–2%. The diamagnetic corrections to the paramagnetic component of the magnetic susceptibility, calculated per mole of paramagnetic atoms (χ_M), were introduced with regard to the susceptibility of the diamagnetic matrices. The selected procedures of the extrapolation of magnetic characteristics to infinite dilution provided the error no higher than 3%.

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