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Atom State and Interatomic Interactions in Complex Perovskite-like Oxides: XXIX.[1] Influence of Strontium Concentration on Special Features of Magnetic Dilution in the La(Sr)CrO_3–$LaGaO_3$ System

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Abstract—Fractions of clusters and single chromium atoms were calculated for the series of solid solutions with various strontium content within the framework of diluted solution model using Heizenberg–Dirack–van-Vleck theory. A substantial influence of strontium concentration on the quantity of various clusters was found. For the systems with greater strontium contents the deviations from Curie–Weiss law are observed, which point to the presence of a noncompensated magnetic moment.

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A simultaneous doping of lanthanum gallate with alkaline-earth and transition metals makes it possible to obtain a wide spectrum of compounds that are electron-ionic conductors. An intensive search for the compositions providing a maximal ionic and (or) electron conductivity is going on from 1994, when an ionic conductivity was found in lanthanum gallate doped with calcium, strontium, and barium [2].

In spite of an extensive factual material on this subject, in the overwhelming majority of cases the studies are carried out empirically, and the obtained results have only a stating character. The absence of both systematic approach to the study of the properties of electron-ionic conductors and the examination of this problem in the united composition–structure–property key makes the interpretation of experimental results difficult and does not permit their generalization.

Lanthanum gallates containing less than 10 mol % of dopants are diluted solid solutions of isomorphous substitution. In this concentration range it is no use to expect relatively high conductivity in gallates, however only for diluted solutions containing magnetic atoms their electron structure (the character of interatomic interactions, valence and spin states of atoms, the occurrence or absence of clusters) can be precisely established using the methods of magnetic dilution and static magnetic susceptibility.

Solid solutions based on lanthanum gallate doped with chromium and also with chromium and strontium were studied previously, for each of the latest systems a particular Cr:Sr ratio being maintained: 5:1 and 2:1 [3–5] for $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and $La_{1-0.5x}Sr_{0.5x}\cdot Cr_xGa_{1-x}O_{3-\delta}$. It was found that chromium does not undergo the oxidation to the oxidation state four upon heterovalent doping with strontium, i.e. vacancies in the sublattice of oxygen atoms responsible for ionic (oxygen) conductivity are retained in the solid solution. For the system with Cr:Sr ratio 5:1 starting from $x = 0.02$ [4], the isotherms of magnetic susceptibility coincide with the isotherms for the system free from strontium, and for the solid solutions $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ [5] the isotherms of magnetic susceptibility lie essentially higher and at infinite dilution in no way can be ascribed to single chromium atoms in the solid solution, whatever valence state they were in. An assumption emerged naturally that strontium and vacancies associated with it take part in

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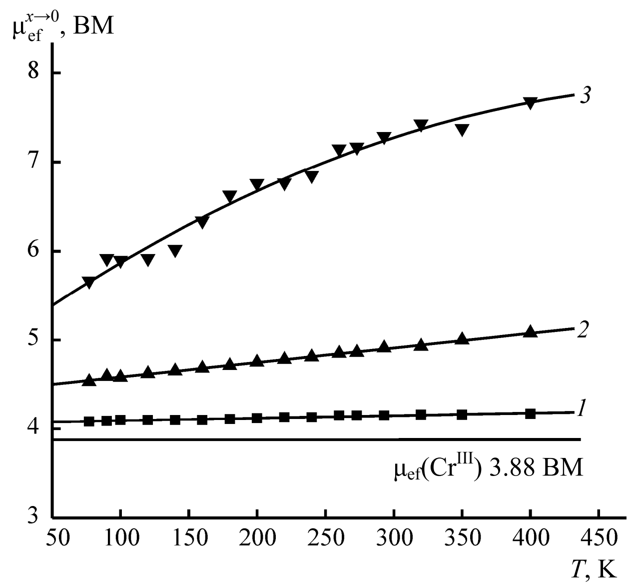

Fig. 1. Temperature dependences of effective magnetic moment at infinite dilution for (*1*) $LaCr_xGa_{1-x}O_3$, (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$, and (*3*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ systems.

clustering of the paramagnetic atoms in the solid solutions. In this case the clusters of special type appear to be so stable that they do not disintegrate at infinite dilution, as is usually observed in solid solutions of isomorphous substitution, in the $LaCr_x\cdot Ga_{1-x}O_3$ system in particular [3].

The aim of this work was to calculate the fractions of clusters and single chromium atoms in the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ ($0.01 \le x \le 0.1$) solid solutions and to examine the temperature dependence of susceptibility for the series of solid solutions with the Cr:Sr ratio 2:1.

We calculated the fractions of clusters and single atoms on the basis of the diluted solid solution model, whereby the experimental values of magnetic susceptibility [Eq. (1)] are determined as a sum of pair products of susceptibilities of each type of aggregates and single atoms (monomers) multiplied by their fraction in the solid solution (a_i). The fractions of clusters and single atoms are constant for each concentration of a solid solution and are interrelated by Eq. (2).

$$\chi = \sum_i a_i\chi_i, \qquad (1)$$

$$\sum_j a_j = 1. \qquad (2)$$

In $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}\cdot O_{3-\delta}$ we assume the presence of single chromium atoms, antiferromagnetic Cr(III)–Cr(III) dimers, antiferromagnetic linear trimers, and certain rather large clusters (no less than four paramagnetic atoms) with ferromagnetic type of exchange (clusters X) determining an unconventional temperature dependence of magnetic moment at infinite dilution (Fig. 1, curve *3*) [5]. The introduction of trimers in the calculation, which was not in use before, is determined by the fact that we consider a wider concentration interval, where the appearance of clusters with $n > 2$ is inevitable. We obtain resulting expression (3) for calculating theoretical susceptibilities from the model of diluted solution. For the effective magnetic moment we transform Eq. (3) to Eq. (4).

$$\chi_{Cr} = a_{clX}\chi_{clX} + a_{dim}\chi_{dim} + a_{trim}\chi_{trim} + (1 - a_{clX} - a_{dim} - a_{trim})\chi_{mono}, \qquad (3)$$

$$\mu^2_{exp} = a_{clX}\,\mu^2_{clX} + a_{dim}\mu^2_{dim} + a_{trim}\mu^2_{trim}, + (1 - a_{clX} - a_{dim} - a_{trim})\mu^2_{mono}. \qquad (4)$$

Here μ_{mono} is the spin only value of the moment of Cr(III). Values of μ_{dim} and μ_{trim} were calculated for each temperature by the Heizenberg–Dirack-van-Vleck model for two and three interacting spins. Generally the Hamiltonian of a system of interacting spins without taking Zeeman interaction into consideration is given by expression (5) [6].

$$\hat{H} = -2\sum_{i<j} J\hat{S}_i\hat{S}_j. \qquad (5)$$

Here J is the exchange parameter and $S_{i(j)}$ is spin of the $i(j)$ ion.

We can obtain either analytical or numerical solutions of the Hamiltonian as functions of the number of spins in a cluster and its geometry and find its eigenvalues, which are the energies of the spin levels. The energies are defined both by the total spin of the system (S) and by the spins of separate atoms (S_i), and for the dimers they are described by Eq. (6).

$$E_d(J_d,S) = -J_d[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]. \qquad (6)$$

The energy of the spin levels, $E(J, S)$ is connected with the effective magnetic moment calculated per 1 mol of metal atoms by Van-Vleck's Eq. (7) [6].

$$\mu^2_{ef} = \frac{g^2\sum_S S(S+1)(2S+1)e^{-[E(J,S)]/(kT)}}{n\sum_S (2S+1)e^{-[E(J,S)]/(kT)}}. \qquad (7)$$

Here (n) the number of paramagnetic atoms in a cluster, (k) Boltzmann constant, (T) absolute temperature, and (g) Lande factor.

Therefore for the $S_1 = S_2 = 3/2$ pair and $g_1 = g_2 = 2$ at $x = J_d/kT$ we obtain expression (8).

$$\mu^2_{\text{dim}} = \frac{g^2}{2} \cdot \frac{84e^{12x} + 30e^{6x} + 6e^{2x}}{7e^{12x} + 5e^{6x} + 3e^{2x} + 1}. \qquad (8)$$

The exchange parameter J_d of -12 cm^{-1} was selected according to the data of [3].

Let us dwell in more detail on the calculation of the susceptibility of a trimer. We consider a chain of 2–1–3 atoms (the figures are numbering the atoms) of $C_{\infty v}$ symmetry, since in our case for structural reasons a trimer may be either linear or orthogonal, and, as shown in [6], the susceptibilities of linear trimers and trimers with atoms located at 60° differ only slightly within the limits of the error of our calculations. Moreover, in a trimer, where the 2–1–3 angle is deflected from 180°, the distance between 2–3 atoms is ~5.2 Å for the structure of cubic lanthanum gallate, and oxygen atoms are absent from this diagonal. Consequently, we can argue that there is no exchange between these atoms.

For a homoneuclear Cr(III)–Cr(III)–Cr(III) trimer we have one exchange parameter, J_t. Spin-Hamiltonian and its eigenvalues, without taking Zeeman interaction into consideration, are found from Eqs. (9) and (10).

$$\hat{H} = -2J_t(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3), \qquad (9)$$

$$E_t(J_t,S) = -J_t[S(S + 1) - S_{23}(S_{23} + 1) - S_1(S_1 + 1)]. \qquad (10)$$

Here the rule of adding the moments gives the total (S) and intermediate (S_{23}) spins as $S = S_1 + S_{23}, S_1 + S_{23} - 1, \ldots, |S_1 - S_{23}|$ and $S_{23} = S_2 + S_3, S_2 + S_3 - 1, \ldots, |S_2 - S_3|$ respectively.

Using Van-Vleck's equation, it is easy to obtain final expression (11) for the magnetic moment of three exchange-bound atoms ($S_1 = S_2 = S_3 = 3/2$, $g_1 = g_2 = g_3 = 2$, $y = J_t/kT$).

$$\mu^2_{\text{trim}} = \frac{g^2}{3} \cdot \frac{247.5e^{21y} + 126e^{18y} + 52.5e^{15y} + 141e^{12y} + 52.5e^{11y} + 15e^{10y} + 1.5e^{7y} + 15e^{6y} + 52.5e^{5y} + 1.5e^{3y} + 15}{10e^{21y} + 8e^{18y} + 6e^{15y} + 12e^{12y} + 6e^{11y} + 4e^{10y} + 2e^{7y} + 4e^{6y} + 6e^{5y} + 2e^{3y} + 4}. \qquad (11)$$

The only distinction from the calculation of dimers is the fact that in the expression for the susceptibility we make summation by the intermediate spin to take into consideration the multiplicity of degeneracy of the spin multiplets with the same total spins.

From these calculations we determined the optimal exchange parameter for trimers, J_t –20 cm^{-1}.

Having neither the data on the structure of clusters X, nor the possibility to describe the $\mu^{x\to 0} = f(T)$ dependences (Figs. 1, 2, 3) with the help of Heizenberg–Dirack–van-Vleck model, when determining μ_{clX} we postulated that the effective magnetic moment at infinite dilution for the system with the ratio [Cr]:[Sr] = 2:1 is determined only by clusters X, i.e. their fraction is equal to 1. Then, as the calculation showed, the effective magnetic moments for the system with Cr–Sr (5:1) at infinite dilution are a superposition of 20% of clusters X and 80% of monomers, which is in complete agrement with the difference in the [Cr]:[Sr] ratio for the systems under study.

By the results of the calculations the difference between theoretical and experimental magnetic susceptibilities for the both systems is no more than 2% (Figs. 2a and 2b).

An attempt to exclude from the calculation some clusters: monomers, antiferromagnetic dimers, or trimers, resulted in an essential divergence between the data of theory and experiment (up to 7%). Therefore the advanced model of the structure of the solid solution is the most reliable.

The direct influence of strontium concentration on the quantity of various aggregates of chromium atoms can be traced by comparing concentration dependences of cluster fractions for the systems with various [Cr]:[Sr] ratio (Figs. 3a and 3b).

Some special features in the variations of aggregate fractions attract our attention. For the solutions $LaCr_xGa_{1-x}O_3$ containing no strontium we have a typical pattern of antiferromagnetic dilution: as the concentration of a paramagnetic component increases, the fraction of monomers monotonously decreases, and the fraction of antiferromagnetic dimers and trimers increases.

Upon introduction of strontium in the ratio of [Cr]:[Sr] = 5:1 aggregates (clusters X) appear with a competing antiferro- and ferromagnetic exchange, their quantity decreasing as the chromium concentration increases (like for monomers) (Fig. 3a).

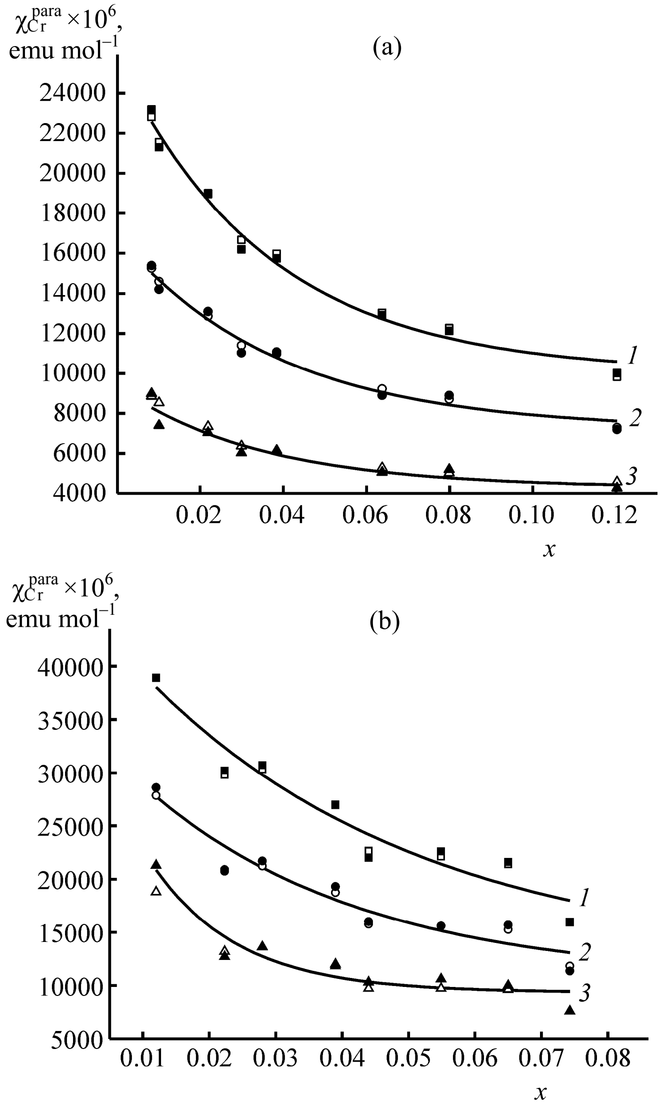

Fig. 2. Theoretical (open circles) and experimental (black circles) paramagnetic components of magnetic susceptibility calculated per 1 mol of chromium atoms: (a) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and (b) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ for three temperatures: (*1*) 100, (*2*) 160, and (*3*) 320 K.

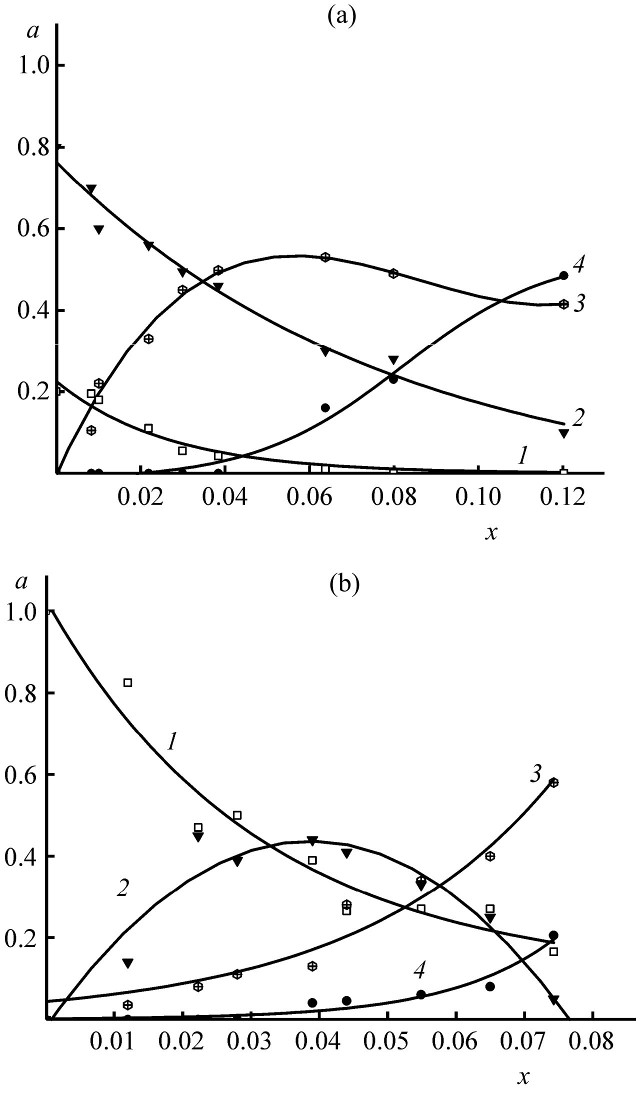

Fig. 3. Plot of the fractions of clusters and single atoms vs. chromium concentration for systems with various strontium contents: (a) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and (b) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$; (*1*) clusters X, (*2*) monomers, (*3*) dimers, and (*4*) trimers.

The increase in strontium concentration to the [Cr]:[Sr] ratio 2:1 results in a relative increase in the fraction of clusters X and in a nonmonotonous change in the fraction of monomers in the solid solution (a maximum at x ~0.045). As in two previous cases, the fractions of dimers and trimers increase as the chromium concentration increases. Such a tendency can be readily explained.

The interval $0 < x < 0.045$. If only ferromagnetic clusters are retained at infinite dilution ($x \rightarrow 0$) (Fig. 1), then, taking into account the ratio [Cr]:[Sr] = 2:1, strontium atoms will be deficient in such clusters for the formation of a real oxygen vacancy. Hence there remains a "half" of a vacancy in the site of oxygen, i.e. it is an electron ($SrO + La_{La}^{\times} + 1/2O_O^{\times} \rightarrow Sr_{La}^{\prime} + 1/2V_O^{\cdot\cdot} + 1/2La_2O_3$), which can either exist in a pair with a "hole" $h^+ \leftrightarrow \bar{e}$ by the type of the Vanier–Mott exciton (Fig. 4a) or pass to a nearest chromium(III) atom reducing it – $Cr(III) + e \rightarrow Cr(II)$ and favoring the emergence of ferromagnetic exchange between different-valence chromium atoms (Fig. 4b). As the quantity of strontium increases, the situation emerges when two strontium atoms are in the

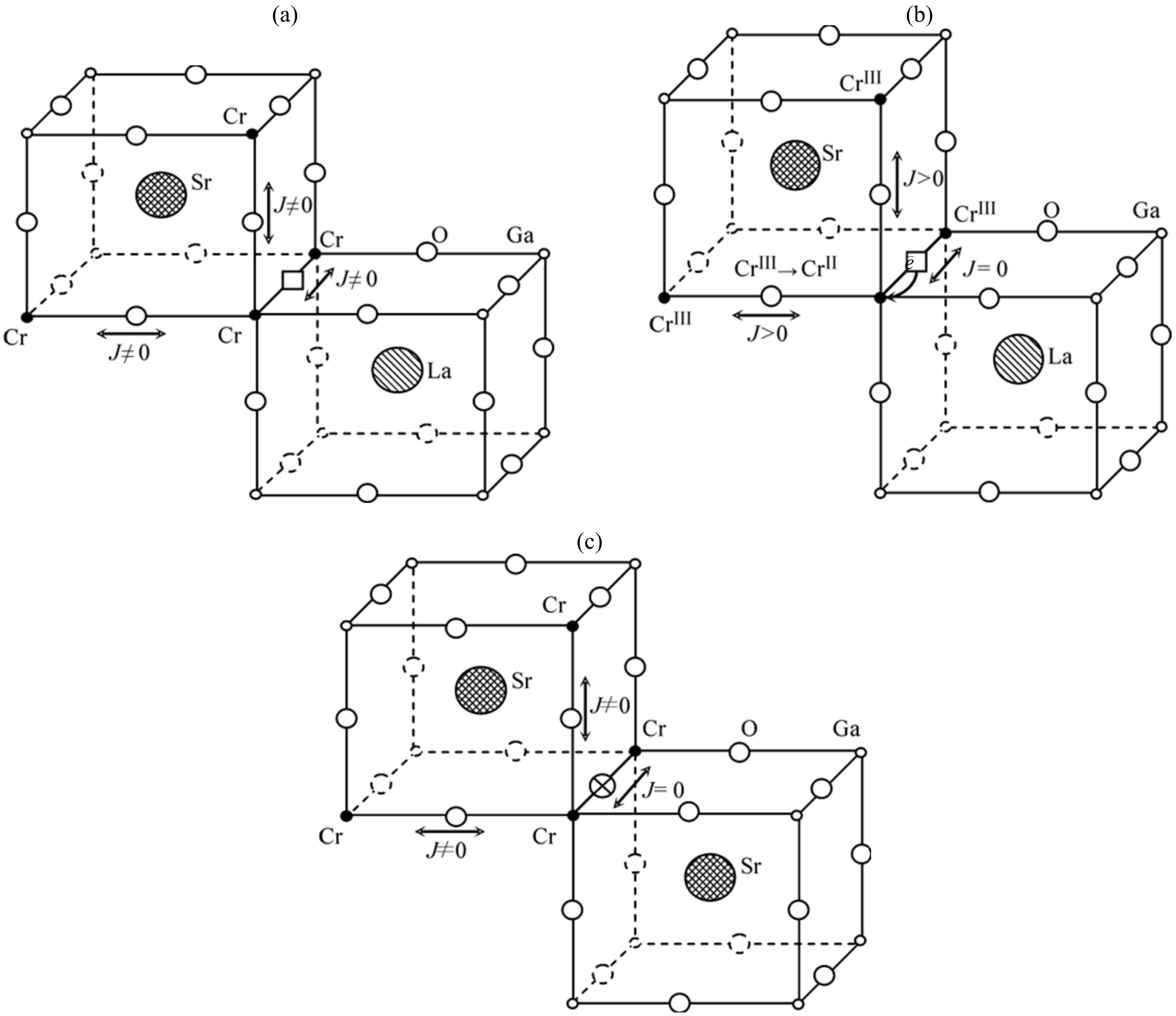

Fig. 4. Possible variants of interatomic interactions and location of clusters at infinite dilution (see comments in the text).

immediate vicinity, which gives an oxygen vacancy ($2\mathrm{SrO} + 2\mathrm{La}_{\mathrm{La}}^{\times} + \mathrm{O}_{\mathrm{O}}^{\times} \rightarrow 2\mathrm{Sr}'_{\mathrm{La}} + V_{\mathrm{O}}^{\bullet\bullet} + \mathrm{La_2O_3}$). A vacancy located between chromium atoms disrupts the integrity of the superexchange channel, which results in one of the chromium atoms ceasing to participate in the exchange and behaving as a monomer (Fig. 4c). At the same time this automatically decreases the number of clusters X. The fraction of dimers is minor in this case (~10% at x ~0.045).

The interval 0.045 < x < 0.075. When the fraction of monomers is maximal, as the critical concentration (x ~0.045) is attained, the conditions are created for their further aggregation not only to dimers but to trimers, their quantity monotonously increasing starting from x ~0.045. At this concentration the influence of strontium (by forming oxygen vacancies) is brought to a minimum, since the fraction of clusters is small and remains almost constant up to x 0.075. This results in an abrupt increase in the fractions of antiferromagnetic dimers and trimers as in the case of conventional antiferromagnetics.

The formation of clusters with a pronounced ferromagnetic exchange component can be accounted for by the double exchange in the clusters [7, 8] between heterovalent chromium atoms, Cr(III)–Cr(II). Introduction of strontium, as was shown earlier, can

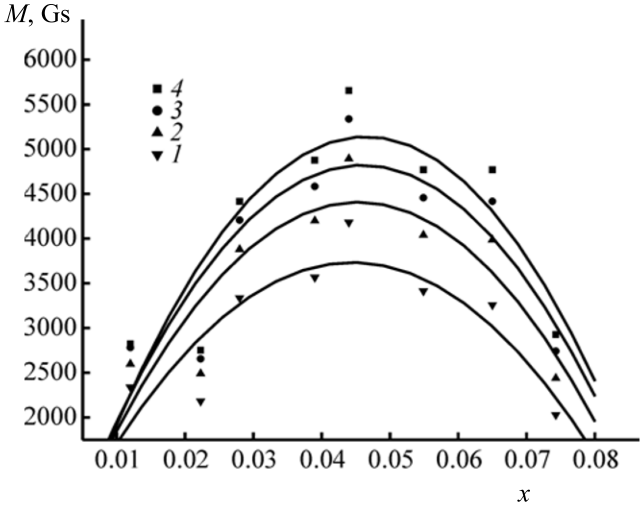

Fig. 5. Concentration dependence of $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ magnetization at various field intensities: (*1*) 3640, (*2*) 5230, (*3*) 6330, and (*4*) 7240 Oe.

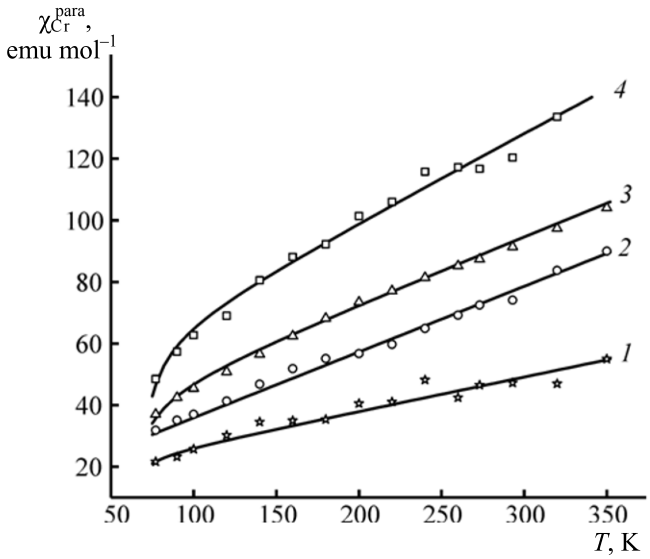

Fig. 6. Temperature dependence of inverse paramagnetic component of magnetic susceptibility of $La_{1-0.5x}Sr_{0.5x}Cr_x$· $Ga_{1-x}O_{3-\delta}$ for various chromium concentrations *x*: (*1*) 0.0120, (*2*) 0.0390, (*3*) 0.0440, (*4*) 0.0746. (Points) are experimental values, (lines) are calculation.

result not only in oxygen vacancies, but in “excess” electrons in the site of a vacancy. The migration of an electron from one paramagnetic center to another results in a strong ferromagnetism.

We must admit that the superexchange between heterovalent Cr(III)–Cr(IV) atoms also will be ferromagnetic, however, in the previous works [4, 5] the absence of chromium(IV) in the systems with strontium was proved.

Examining the concentration dependence of magnetization in various fields we can see a certain correlation between changes in the calculated fraction of monomers and the changes in the magnetization (Fig. 5).

The deviations from the Curie–Weiss law typical for ferrimagnetics are observed for the $La_{1-0.5x}Sr_{0.5x}$· $Cr_xGa_{1-x}O_{3-\delta}$ solid solutions. A bend in the dependence shows itself in the region of low temperatures and greatest (within the operating interval) chromium concentrations.

It can be assumed that in the region of low concentrations, when the number of clusters X is high, they interact with each other antiferromagnetically, the fractions of antiferromagnetic dimers and single atoms being small. As the chromium concentration increases, the fraction of clusters X abruptly decreases, which results in their presence in the matrix of lanthanum gallate as isolated particles with their own magnetic moment. The smooth decrease in the magnetic susceptibility with increasing chromium concentration testifies for the interactions of antiferromagnetic character as a whole.

We met for the first time such a phenomenon in the magnetically diluted systems, where by definition there must not be any magnetic ordering and effects associated with collective magnetism. Moreover, we realize that the deviation of the temperature dependence of magnetic susceptibility from Curie law can be connected both with special features of zero field splitting and with the spin orbit splitting. In this case a nonzero Weiss constant is not a proof of ferro-, ferri, or antiferromagnetism in a substance [6]. In our case the spin orbit coupling does not show itself, as it is not characteristic for Cr(III) (the ground state is a singlet). Therefore we tried to describe the run of the temperature dependence for a number of solutions using Eq. (12) for the susceptibility of a ferrimagnetic [9–11].

$$1/\chi_{Cr}^{para} = (T - \theta_a)/C - \sigma/(T - \theta). \qquad (12)$$

Here (C) is Curie temperature; (θ_a) is Weiss constant; (σ and θ) are constants depending on molecular parameters of each magnetic sublattices. Varying C, σ, and θ, we obtained the best agreement between theoretical and experimental values (Fig. 6) according to the Neel recommendations [11].

The origination of noncompensated state of an antiferromagnetic is connected with a special location of the magnetic atom spins determined by the type of magnetic symmetry of a substance. The absence of compensation shows itself when the vectors of magnetic moment are not fixed rigidly in antiparallel directions, but have a possibility to deviate from their original position at an angle determining a nonzero resulting magnetic moment.

Therefore, we observe the absence of compensation in an antiferromagnetic (a “weak ferromagnetism” of an antiferromagnetic) having the same type of magnetic atoms. Since the systems under study are magnetically diluted, the interaction between spins seems to occur at a short distance without ordering. Such a behavior for magnetically concentrated systems was found when studying manganese and cobalt carbonates [12].

For the systems with the ratio Cr:Sr = 5:1 Weiss constant decreases monotonously as chromium concentration increases and is negative everywhere. However such a tendency is not observed for Cr–Sr (2:1) systems, and in some cases we could recognize two Weiss temperatures, positive and negative.

All these facts are directly connected with the nonmonotony of changes in the fraction of single chromium atoms and relative increase in the fraction of ferromagnetic clusters X. This results in a change of the intensity and character of interatomic interactions leading to a magnetically noncompensated state of the solid solutions based on lanthanum gallate with [Cr]:[Sr] = 2:1.

Therefore, the calculations within the framework of the models of diluted solution and the Heizenberg–Dirac-van-Vleck model together with a comprehensive examination of magnetic characteristics show that the heterovalent doping of lanthanum gallate with strontium results in a certain clustering depending on the [Cr]:[Sr] ratio, vacancies in the oxygen sublattice playing a substantial role in clustering, and, consequently, so do strontium atoms adjacent to them.

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