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State of Atoms and Interatomic Interactions in Complex Perovskite-Like Oxides: XXX.[1] Influence of the Nature of Diamagnetic Substituents on the Dynamics of Clustering in Lanthanum Gallate Doped with Strontium, Chromium, and Magnesium

N. V. Chezhina and D. A. Korolev

St. Petersburg State University, Universitetskii pr. 25, St. Petersburg, 198504 Russia
e-mail: chemdim@mail.ru

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Abstract—The fractions of clusters and single chromium atoms were calculated by the diluted solution and Heisenberg-Dirac-van-Vleck models for a series of solid solutions containing chromium, strontium, and magnesium in the ratio 5:1:1, respectively. A principal genetic relationship was revealed between $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$, $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$, and $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ systems. Deviations from Curie-Weiss law are observed for the systems with the ratio [Cr]:[Sr]:[Mg]=5:1:1, which point to a noncompensated magnetic moment.

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A vigorous development of energy-saving technologies based on solid-oxide fuel cells poses one of the most important problems for the researchers: preparation of ceramic materials with controlled properties. When selecting materials for anodes, cathodes, and electrolytes for solid oxide fuel cells, the compounds of perovskite family are preferred in the great majority of cases [2]. This choice is not accidental: The perovskite structure is tolerant to substitution, which allows a qualitative and quantitative composition of the obtained materials and, consequently, their properties to be varied over widest limits. One of the perfect matrices is lanthanum gallate. Undoped $LaGaO_3$ belongs to diamagnetics and broad-band dielectrics with the energy gap ~4.5 eV [3]. Doped lanthanum gallate can be an ionic conductor or have a mixed type of conductivity depending on the nature of doping atoms. A high conductivity of doped lanthanum gallates favorably distinguish it from doped aluminates or indates [2].

The problems of valence (spin) state of the atoms of the transition element and of interatomic interactions in lanthanum gallate still remain open. The search for the answer to them is of utmost importance, since the interpretation of electrophysical properties (the explanation of one or another type of conductivity, the mechanisms of the charge transfer, etc.) cannot be unambiguous, clear, and understandable without the knowledge of electronic structure.

Electrophysical properties of lanthanum gallate doped with strontium, magnesium, and transition elements were considered in a number of works, and the conductivity was found to increase in the series: Cr < Mn < Fe < Co < Ni [4,5]. For example, it is noted in [5] that for the $La_{0.9}Sr_{0.1}Cr_{0.05}Ga_{0.95}O_{3-\delta}$ compound a decrease in the oxygen conductivity, as compared to $La_{0.9}Sr_{0.1}GaO_{3-\delta}$, may result from an increase in the energy of Coulomb Cr–O interaction owing to the partial oxidation of chromium to Cr(IV). In the case of magnetically concentrated $LaGa_{0.40}Mg_{0.20}M_{0.40}O_{3-\delta}$ systems (M = Cr, Co, Fe) a decreased ionic conductivity of chromium-containing gallates, as compared to cobalt- and iron-containing gallates, is also accounted for by the same reason [5]. It remains incomprehensible why chromium atoms can transform (even if partially) to the tetravalent state, and such a possibility is not considered for cobalt and iron.

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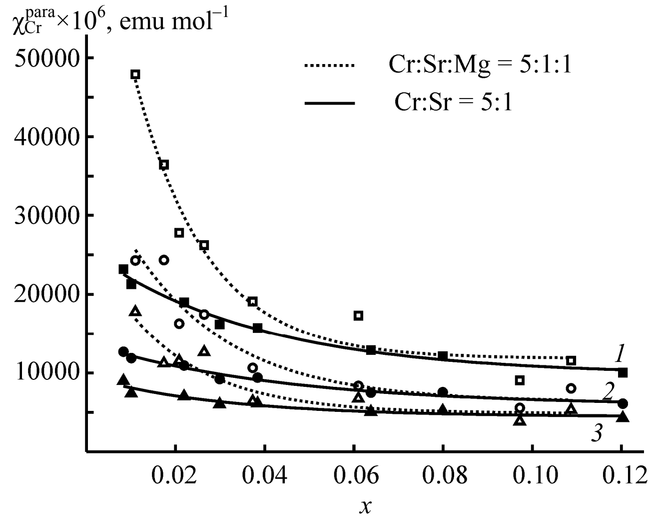

Fig. 1. Concentration dependence of paramagnetic component of magnetic susceptibility calculated per 1 mole of chromium atoms for the $\mathrm{La}_{1-0.2x}\mathrm{Sr}_{0.2x}\mathrm{Cr}_x\mathrm{Ga}_{1-x}\mathrm{O}_{3-\delta}$ and $\mathrm{La}_{1-0.2x}\mathrm{Sr}_{0.2x}\mathrm{Cr}_x\mathrm{Ga}_{1-1.2x}\mathrm{Mg}_{0.2x}\mathrm{O}_{3-\delta}$ systems at (*1*) 100, (*2*) 200, and (*3*) 320 K.

An increase in the activation energy for the transfer in the $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{Ga}_{0.80-y}\mathrm{Mg}_y\mathrm{M}_{0.20}\mathrm{O}_{3-\delta}$ systems (M is a transition element), as compared to $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{Ga}_{1-y}\cdot\mathrm{Mg}_y\mathrm{O}_{3-\delta}$, is again interpreted either as a consequence of the formation of stable M^{4+}–O–Mg^{2+} clusters, in which the mobility of oxygen ions is decreased owing to strong Coulomb interactions with metal cations, or due to a local ordering in the oxygen sublattice at the expense of vacancies association with bivalent cations (Sr^{2+}, Mg^{2+}, M^{2+}) [6].

If a decrease in the ionic transport in gallate is explained from the point of view of interactions between a vacancy and a bivalent cation, such an approach may be valid only in the case of the $\mathrm{Mg}'_{\mathrm{Ga}}|V_{\mathrm{O}}$ couple, where the energy is –0.90 kJ mol^{-1}, whereas the energy of the $\mathrm{Sr}'_{\mathrm{La}}|V_{\mathrm{O}}$ pair interaction is only –0.01 kJ mol^{-1} [7].

The reasons of the decrease in the oxygen transport can be revealed without using the hypotheses about the disproportionation of transition metal cations. Earlier we studied solid solutions based on lanthanum gallate doped with chromium and also with chromium and strontium in a particular [Cr]:[Sr] ratio: $\mathrm{La}_{1-0.2x}\cdot\mathrm{Sr}_{0.2x}\mathrm{Cr}_x\mathrm{Ga}_{1-x}\mathrm{O}_{3-\delta}$ (5:1) and $\mathrm{La}_{1-0.5x}\mathrm{Sr}_{0.5x}\mathrm{Cr}_x\mathrm{Ga}_{1-x}\mathrm{O}_{3-\delta}$ (2:1) [8–10]. We found that chromium was not oxidized to tetravalent state upon heterovalent doping with strontium, i.e. the vacancies in the oxygen sublattice were preserved in the solid solution. They are responsible for ionic (oxygen) conductivity. At the same time the introduction of strontium favors an aggregation of chromium atoms: the greater strontium amount is introduced, the more intensive is the clustering. In this case we distinctly trace not only the influence of strontium on clustering, but also the fact that these clusters necessarily include vacancies in the oxygen sublattice. One sublattice in the structure necessarily affects another sublattice (metal – oxygen). Therefore, vacancies and oxygen ions, being the integral part of a cluster, undoubtedly experience a greater impact from surrounding atoms compared with the case when clusters are absent and atoms foreign to the mother structure are randomly distributed.

A situation may arise, when, as the result of migration under the action of electric field, the oxygen ions entering the field of a cluster are located in the site of a vacancy. However the oxygen ion outlet for its further migration appears to be hampered by the effective cluster field, which results in a decreased ionic conductivity.

The aim of this work was to consider the influence of the nature of a diamagnetic substituent on the electronic structure of lanthanum gallate doped with chromium by simultaneous introducing strontium and magnesium in the ratio [Cr]:[Sr]:[Mg] = 5:1:1, and also to study the magnetic characteristics of the $\mathrm{La}_{1-0.2x}\mathrm{Sr}_{0.2x}\mathrm{Cr}_x\mathrm{Ga}_{1-1.2x}\mathrm{Mg}_{0.2x}\mathrm{O}_{3-\delta}$ solid solutions ($0.01 \le x \le 0.10$) and calculate the fractions of clusters and single chromium atoms.

The examination of isotherms of paramagnetic component of magnetic susceptibility allows us to reveal several special features of the $\mathrm{La}_{1-0.2x}\mathrm{Sr}_{0.2x}\cdot\mathrm{Cr}_x\mathrm{Ga}_{1-1.2x}\mathrm{Mg}_{0.2x}\mathrm{O}_{3-\delta}$ system. As can be clearly seen in Fig. 1, the isotherms of the systems with magnesium lie much higher than the isotherms of the system with the ratio [Cr]:[Sr]=5:1 up to $x \sim 0.06$. The isotherms of the two systems coincide for $x > 0.06$. A similar situation was also observed when comparing the systems with the ratios [Cr]:[Sr] = 5:1 and [Cr]:[Sr] = 2:1, however the isotherms of those latter were located higher within the whole concentration range [1].

The extrapolation of paramagnetic components of magnetic susceptibility and of effective magnetic moment to the infinite dilution of the solid solution ($x\to0$) results in $\mu_{\mathrm{eff}} \sim 8.0 - 9.5$ BM, μ_{eff} increasing as the temperature increases as was observed for the systems with the ratios [Cr]:[Sr] = 5:1 and [Cr]:[Sr] = 2:1. It is obvious that the introduction of magnesium together with strontium into the system abruptly increases the clustering, and the clusters of chromium atoms including also strontium and magnesium are preserved at the infinite dilution. In this case the clusters are principally different in the number of atoms and, perhaps, in their geometry compared to the clusters existing in the systems with strontium only (Fig. 2).

These aggregates, which we called Y clusters, with competing antiferro- and ferromagnetic exchange seem to be as strong as X clusters, which we discussed earlier when considering the systems with the ratios [Cr]:[Sr]=5:1 and 2:1 [1]. Moreover, magnesium as a heterovalent substituent favors a more intensive clustering as indicated by the immediate increase in both paramagnetic component of magnetic susceptibility and effective magnetic moment at infinite dilution. The enhancement of clustering seems to be associated with a weaker polarizing ability of magnesium compared to gallium. As a result the magnesium-oxygen bond has a more ionic character, and the chromium-oxygen bond becomes more covalent. This circumstance must favor the formation of stable aggregates of chromium atoms, which is experimentally observed.

We calculated the fractions of various clusters in the solid solutions on the basis of temperature and concentration dependences of the paramagnetic component of magnetic susceptibility. The method of calculating the fractions of cluster forms in the concentration range under study was the same as in the case of the system with the ratio [Cr]:[Sr] = 2:1 [1]. The difference consisted in the introduction of one more type of Y clusters into the calculation for the ratio [Cr]:[Sr]:[Mg] = 5:1:1. We determined the effective magnetic moment for these clusters at the infinite dilution. Therefore the calculation was based on the inclusion of monomers, antiferromagnetic dimers (J_d –12 cm^{-1}), linear trimers (J_t –20 cm^{-1}), and X and Y clusters.

An immediate influence of the nature of magnesium on the quantity of various aggregates of chromium atoms can be traced by comparing concentration dependences of cluster fractions for the systems with the ratios [Cr]:[Sr]:[Mg] = 5:1:1 and [Cr]:[Sr] = 5:1 (Figs. 3a and 3b).

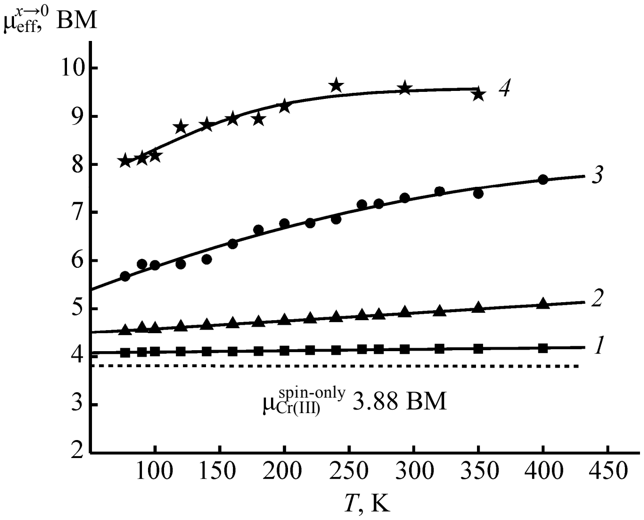

Fig. 2. Dependence of effective magnetic moments at infinite dilution on temperature for the systems: (*1*) $LaCr_xGa_{1-x}O_3$, (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$, (*3*) $La_{1-0.5x}Sr_{0.5x}\cdot Cr_xGa_{1-x}O_{3-\delta}$, and (*4*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$.

The dynamics of clustering in the systems containing simultaneously strontium and magnesium essentially differs from that in the system without magnesium ([Cr]:[Sr] = 5:1) in the concentration range $x < 0.06$. Therefore the influence of magnesium as a heterovalent diamagnetic substituent shows itself particularly at short distances, which is attested by a divergence of the isotherms of paramagnetic components of magnetic susceptibility in the concentration range $x < 0.06$ (Fig. 1). Since at $x > 0.06$ the isotherms of the systems with the ratios [Cr]:[Sr]:[Mg] = 5:1:1 and [Cr]:[Sr] = 5:1 coincide, this is a direct evidence of the similarity of the processes of evolution and degradation of the cluster forms in solutions as the concentration increases.

Let us dwell in more detail on the dependence of the fractions of clusters and single chromium atoms on the concentration for the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ system. In Fig. 3b we can distinguish four concentration regions differing by the composition of clusters.

Region I. If at infinite dilution ($x\to0$) only Y clusters with clearly prevailing ferromagnetic component of exchange are retained (Fig. 3, curve *5*), we conclude that, with respect to the ratio [Cr]:[Sr]:[Mg] = 5:1:1, such clusters will contain a sufficient number of heterovalent atoms for the formation of true oxygen vacancies in case when strontium and magnesium are located in the same unit cell in the immediate vicinity of each other (Fig. 4a).

$$2SrO + 2La_{La}^{\times} + MgO + 2Ga_{Ga}^{\times} + 2O_{O}^{\times} \rightarrow 2Sr'_{La} + 2Mg'_{Ga} + 2V_{O}^{\bullet\bullet} + La_2O_3 + Ga_2O_3.$$

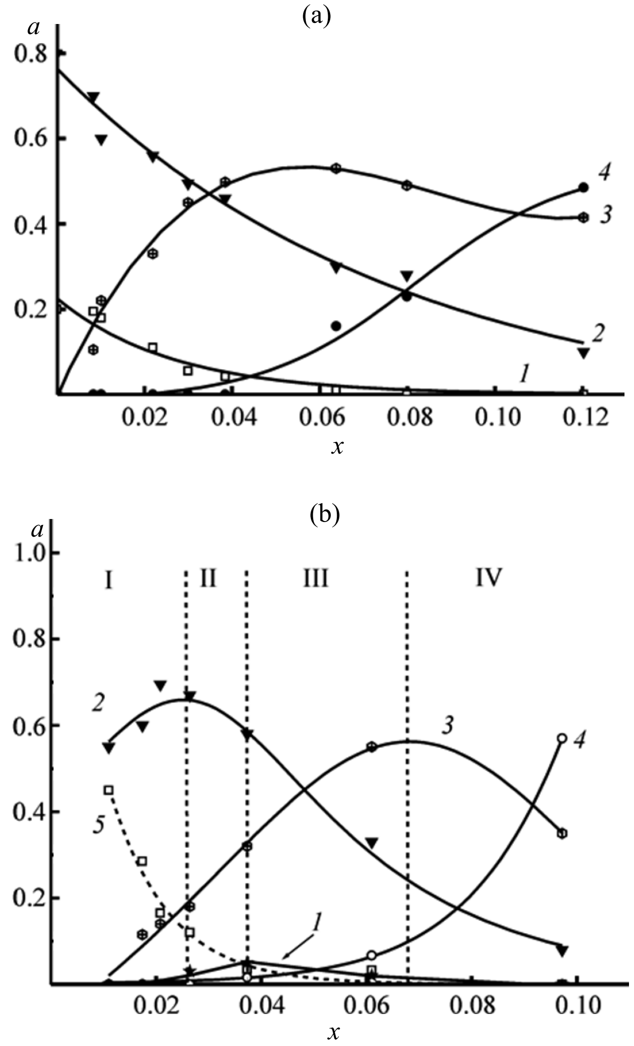

Fig. 3. Dependence of fractions of clusters and single chromium atoms on chromium concentration for (a) $\mathrm{La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}}$ and (b) $\mathrm{La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}}$. (*1*) X clusters, (*2*) monomers, (*3*) dimers, (*4*) trimers, and (*5*) Y clusters.

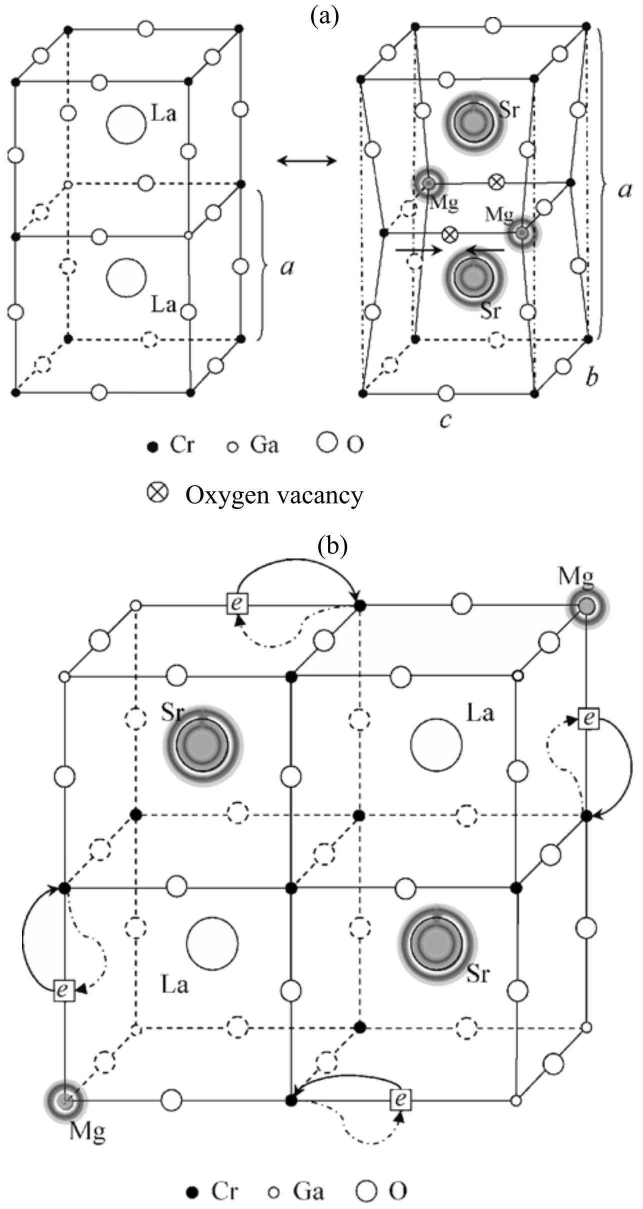

Fig. 4. Hypothetical version of (a) the structure of Y cluster and (b) versions of interatomic interactions in the structure of cubic lanthanum gallate.

In this case the origin of ferromagnetism can be accounted for only by local distortions in the structure, i.e. by a deviation of the exchange angle from 180°. In Fig. 4a a possible way of arising orthorhombic distortions is also shown, since in our case the structure, though being cubic, but orthorhombic distortions show themselves in the X-ray patterns at large scattering angles.

A dispersion of paramagnetic atoms and also strontium and magnesium atoms can include several unit cells, and strontium and magnesium can be located at a considerable distance from each other (two and more lattice spacings). Then they do not form a true vacancy, but give rise to “extra” electrons at the vacancy sites (separately for strontium and magnesium), as was supposed earlier [1].

$$\mathrm{SrO} + \mathrm{La}^{\times}_{\mathrm{La}} + 1/2\mathrm{O}^{\times}_{\mathrm{O}} \rightarrow \mathrm{Sr}'_{\mathrm{La}} + 1/2V^{\bullet\bullet}_{\mathrm{O}} + 1/2\mathrm{La_2O_3},$$

$$\mathrm{MgO} + \mathrm{Ga}^{\times}_{\mathrm{Ga}} + 1/2\mathrm{O}^{\times}_{\mathrm{O}} \rightarrow \mathrm{Mg}'_{\mathrm{Ga}} + 1/2V^{\bullet\bullet}_{\mathrm{O}} + 1/2\mathrm{Ga_2O_3},$$

$$1/2V^{\bullet\bullet}_{\mathrm{O}} \equiv e.$$

Such electrons can migrate between chromium atoms (Fig. 4b) to cause a non-typical temperature dependence of the cluster magnetic moment and a strong ferromagnetic exchange inside the aggregate owing to the double exchange [1].

As the concentration increases, monomers and dimers are generated in the solid solution. The reason for this behavior can be found in the scheme of Y cluster (Fig. 4b): The location of additional chromium atoms in the sites adjacent to magnesium atoms or to oxygen vacancy results in the fact that such atoms behave as monomers, and further increase in the concentration gives rise to the appearance of dimers separated from the cluster by a magnesium atom or a vacancy. Therefore the fraction of Y clusters seemingly decreases.

Region II. At the background of the total increase in chromium concentration (and also of strontium and magnesium concentrations) in the solution the fraction of Y clusters continues to decrease monotonically. Passing a local maximum, the fraction of monomers also decreases monotonically, which in its turn favors a regular increase in the fraction of dimers. This part of the diagram is remarkable by the fact that it is this concentration range where the X clusters are formed. Their fraction moderately increases at the interface of I and II regions and is about 0.05. The result of X cluster formation seems to be a partial destruction of Y clusters, which apparently have a greater nuclearity. The destruction may be determined both by the inserion of magnesium atoms into the sites of chromium (separate exchange channels are destroyed) and by mutual influence of strontium and magnesium atoms forming oxygen vacancies, which also destroy the integrity of the exchange channels in the line of Cr–O–Cr bonds between paramagnetic atoms. As a result, the effective magnetic moment of the cluster decreases (the magnetic moment of X cluster is much lower than the moment of Y cluster).

Region III. Further increase in the amount of doping additives results predominantly in dimers. The fraction of monomers decreases abruptly. In this part of the diagram the relative fraction of X clusters begins do decrease.

A characteristic feature of this concentration range is the appearance of antiferromagnetic trimers, the increase in their fraction occurring in parallel with the increase in the amount of dimers. The formation of dimers and trimers at the expense of partial destruction of X and (or) Y clusters does not seem too realistic, since their fraction is extremely small (<0.05%) and decreases moderately, whereas the fraction of dimers increases by 25% and of trimers, by 10%.

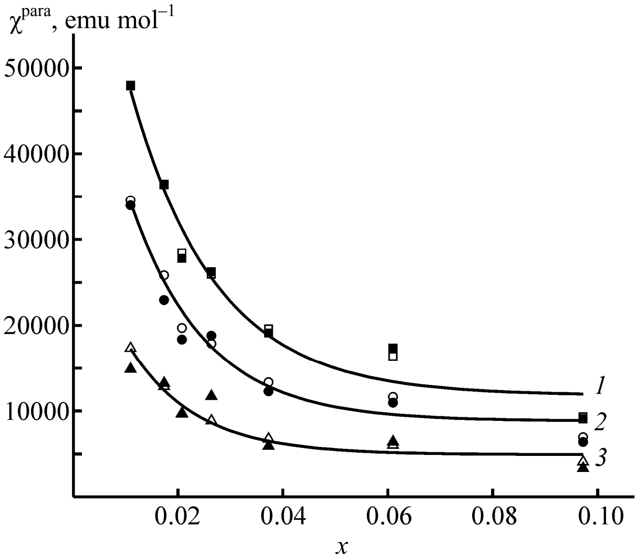

Fig. 5. Theoretical (open symbol) and experimental (black symbol) values of paramagnetic components of magnetic susceptibility calculated per 1 mole of chromium atoms at (*1*) 100, (*2*) 160, and (*3*) 320 K.

At the interface of regions III and IV at a certain critical concentration $x \sim 0.070$ the fraction of dimers is maximal: 55%.

Region IV. A defined maximum in the amount of dimers necessarily points to a further decrease in the fraction of this type of aggregates. The amount of monomers continues to decrease monotonically in this case. The fractions of X and Y clusters are zero. Therefore we may conclude that almost all chromium atoms are aggregated into trimers and they are the only cluster form favorable in the concentration range under study.

A sufficiently large number of the parameters of the model must result in a decrease in the accuracy of calculation. Hence we tried to reduce the number of independent variables as much as possible and consider the dynamics of clustering in such a manner that, first, the difference between calculated and experimental values of susceptibility was minimal (Fig. 5) and, second, the very model remained logically consistent.

Considering the concentration dependence of magnetization at various fields, we can see a certain correlation between the changes in the fractions of monomers, dimers, and trimers obtained from the calculation and the changes in magnetization (Fig. 6). The dependence

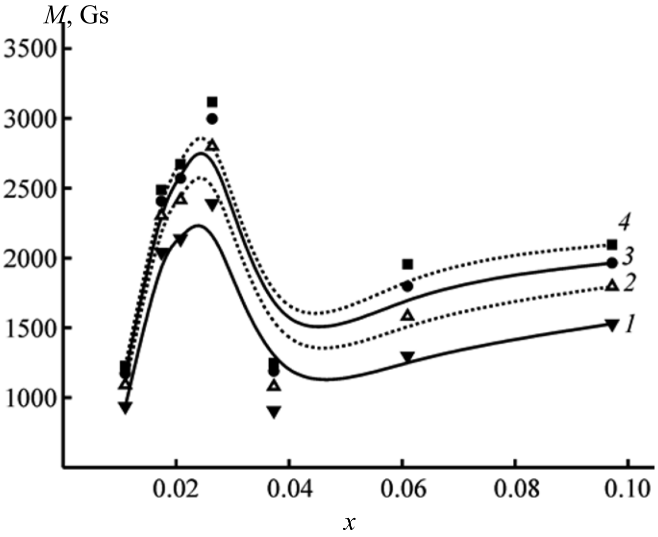

Fig. 6. Concentration dependence of magnetization of $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ at 320 K for various strengths of the field: (*1*) 3640, (*2*) 5230, (*3*) 6330, and (*4*) 7240 Oe.

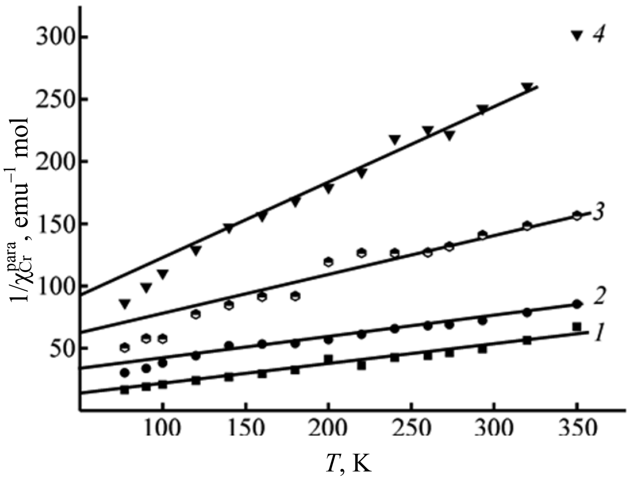

Fig. 7. Temperature dependence of the inverse paramagnetic component of magnetic susceptibility for various chromium concentrations: (*1*) x 0.0110, (*2*) 0.0264, (*3*) 0.0610, and (*4*) 0.0972.

of magnetic susceptibility on the strength of magnetic field shows itself for the series of $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ and $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ solid solutions.

For the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ solid solutions deviations from Curie–Weiss law typical for ferromagnetics are observed (Fig. 7). A similar trend was observed also for the ratio [Cr]:[Sr] = 2:1, where a bend in the dependence showed itself in the region of low temperatures and at small chromium concentrations. No deviations was found for the system with the ratio [Cr]:[Sr] = 5:1 .

The reasons for the deviations from Curie–Weiss law were discussed in detail earlier [1]. For the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ system under study they are accounted for by the clusters with a distinct ferromagnetic type of interaction (Fig. 7).

A detailed examination of magnetic characteristics and calculations within the framework of diluted solution model allowed us to show how substantially the dynamics of cluster formation and the character of interatomic interactions depend on the nature of the diamagnetic substituent. A simultaneous introduction of strontium and magnesium into lanthanum gallate results in an abrupt increase in clustering of chromium atoms. This undoubtedly points to the fact that magnesium and strontium, and also oxygen vacancies associated with them are the components of the clusters. All other factors being equal, the nature of heterovalent substituents, magnesium, to a greatest extent affects the clustering of chromium atoms, the reason for this being a low polarizing ability of magnesium atoms.

EXPERIMENTAL

The X-ray analysis was carried out on a URS-50 I diffractometer using CuK_α emission. We simultaneously determined quantitative contents of chromium, strontium, and magnesium in the samples by the method of atomic emission. The accuracy of the analysis was 2% of x in the solid solution formula.

The magnetic susceptibility of the solid solutions was measured by Faraday method in the temperature range 77–400 K. The accuracy of relative measurements of specific magnetic susceptibility was 1%. We introduced the diamagnetic corrections with respect to the susceptibility of lanthanum gallate matrix measured over the same temperature range as the samples under study.

The $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ solid solutions ($0.01 \leq x \leq 0.1$) were obtained by the sol–gel method. In the synthesis we used the following reagents: extra pure grade lanthanum and gallium oxides, analytically pure grade strontium carbonate. We obtained chromium oxide by the reduction of a stoichiometric amount of analytically pure grade ammonium bichromate with hydrogen peroxide in acid medium. To obtain the gel, we dissolved the stoichiometric amounts of the starting components in nitric acid on heating. We cooled the obtained solution and neutralized it with ammonium hydroxide to pH ~7. The acidity of the medium was controlled by litmus paper. After neutralization we added citric acid and ethylene glycol [12] to the solution. We ground the highly dispersed powder obtained by the decomposition of citrate gel in an agate mortar, then pressed the oxide mixture into pellets, and sintered them in air for 50 h at 1450°C. The time of sintering for obtaining single phase samples was determined by the data of the X-ray analysis. Solid solutions have the structure of orthorhombic lanthanum gallate. We found by the method of magnetic susceptibility that all the solutions are close to equilibrium state.

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