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State of Atoms and Interatomic Interactions in Complex Perovskite-Like Oxides: XXXI.[1] Influence of Magnesium Concentration on Chromium Atoms State and Interatomic Interactions in Lanthanum Gallate Doped with Chromium and Magnesium

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Abstract—Magnetic susceptibility of $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ solid solutions with the ratios [Cr]:[Mg] = 5:1 and 2:1 was studied. Fractions of clusters and single chromium atoms were calculated for the series of solid solutions with [Cr]:[Mg] = 5:1. The relation of the systems with [Cr]:[Mg] = 5:1 and [Cr]:[Sr]:[Mg] = 5:1:1 was revealed. For the system with [Cr]:[Mg] = 2:1 a temperature dependence of effective magnetic moment was found, which suggests that the exchange parameter is temperature dependent.

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A simultaneous doping of lanthanum gallate with alkaline earth elements and magnesium allows a wide series of compounds to be obtained, which are ionic conductors. For the first time the ionic conductivity was found in lanthanum gallate doped with strontium, calcium, barium, and magnesium [2]. Since then an intensive search started for the compositions ensuring maximal conductivity. This is accounted for by a practical significance of materials based on doped lanthanum gallate in the technologies of solid oxide fuel cells (SOFC). It is necessary to pay attention to a serious problem arising when lanthanum gallate is doped with only alkaline earth metals and magnesium, the obtained samples do not consist of a single phase. The limit of strontium dissolving in $LaGaO_3$ is 10 mol % [2]. The introduction of sole magnesium does not result in foreign phases up to 20 mol % [3]. An excess of magnesium favors the release of $La_4Ga_2O_9$, $LaSrGaO_4$, and $LaSrGa_3O_7$. As a rule, the amount of foreign phases is small (no more than 5%). The reason of their appearance is the instability of doped lanthanum gallate, which has a thermodynamic explanation, i.e. the emergence of oxygen vacancies is unfavorable from the point of view of energy. Foreign phases, being nonconducting, lead to a substantial decrease in the conductivity and life time of the material. In some cases foreign compounds were not detected [4].

It was noted in some works [5, 6] that the effects of stabilizing the structure of lanthanum gallate doped with strontium and (or) magnesium appear on introduction of transition metal ions. In this case the stabilization means the possibility of a single phase formation without foreign compounds.

When studying systems with various fractions of strontium ([Cr]:[Sr] = 5:1, 2:1), e.g., $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$ and $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ [1, 7–10], we have found that chromium is not oxidized to the tetravalent state on heterovalent doping with strontium, i.e. the vacancies in the sublattice of oxygen atoms responsible for ionic conductivity are preserved in the

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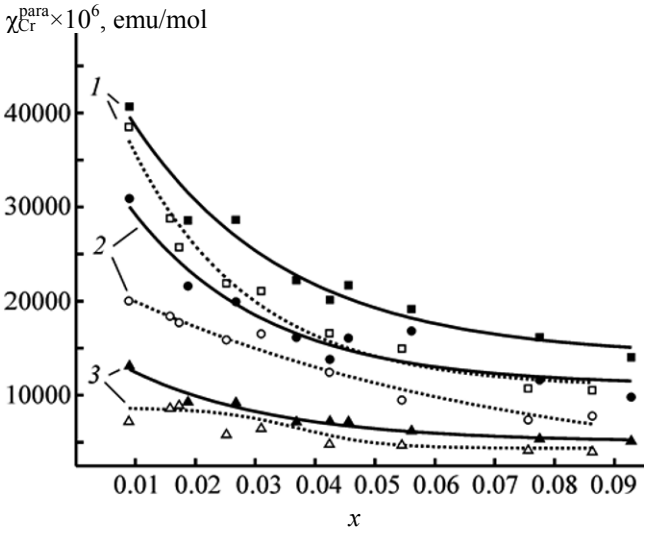

Fig. 1. Concentration dependence of paramagnetic component of magnetic susceptibility calculated per 1 mole of chromium atoms for $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ (black symbol) and $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ (open symbol) at (*1*) 90, (*2*) 140, and (*3*) 320 K.

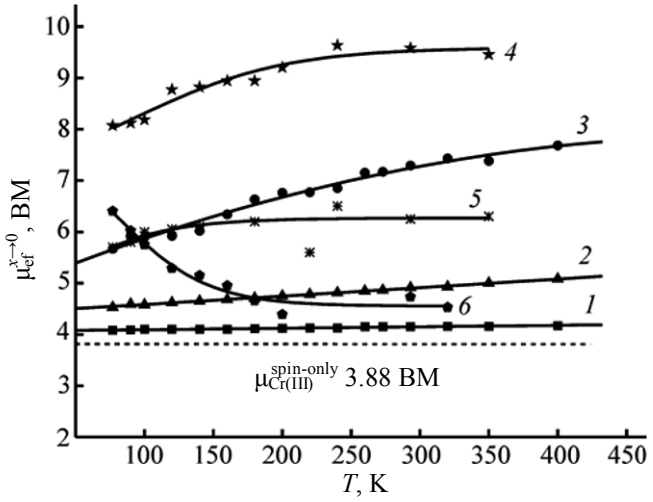

Fig. 2. Temperature dependence of effective magnetic moments at infinite dilution for the systems: (*1*) $LaCr_xGa_{1-x}O_3$, (*2*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_{3-\delta}$, ([Cr]:[Sr] = 5:1), (*3*) $La_{1-0.5x}Sr_{0.5x}Cr_xGa_{1-x}O_{3-\delta}$ ([Cr]:[Sr] = 2:1), (*4*) $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ ([Cr]:[Sr]:[Mg] = 5:1:1), (*5*) $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ ([Cr]:[Mg] = 5:1), and (*6*) $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ ([Cr]:[Mg] = 2:1).

solid solution. An increase in the amount of strontium results in an abrupt increase in clustering (an increase in the amount of high-nuclearity clusters).

This work considers the influence of magnesium concentration on the electronic structure of lanthanum gallate doped with chromium. The aim of this work was to study the magnetic susceptibility of a series of $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ solid solutions ($0.01 \le x \le 0.10$), to calculate the fractions of clusters and single chromium atoms, to examine the temperature dependence of inverse susceptibility and concentration dependence of magnetization for both systems.

As a result of the study we have obtained single phase samples for both systems ([Cr]:[Mg] = 5:1 and 2:1). All the solutions in the concentration range $0.01 \le x \le 0.10$ have the structure of cubic lanthanum gallate, and orthorhombic distortions show themselves at large scattering angles.

$LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ system. A comparison of the isotherms of paramagnetic component of magnetic susceptibility for $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and $LaCr_xGa_{1-x}O_3$ solutions [7, 8] points to the absence of chromium(IV) and to the presence of clusters of chromium atoms in the systems with magnesium: the isotherms for magnesium-containing systems lie higher over the whole concentration range. As the temperature changes, the character of the isotherms remains unchanged, and a monotonous decrease in the susceptibility is observed as chromium concentration increases (Fig. 1).

The extrapolation of the isotherms to the infinite dilution allows the temperature dependence of effective magnetic moment to be obtained. Thus obtained μ_{eff} values are much larger than μ_{eff} for the $LaCr_xGa_{1-x}O_3$ system, same as in the case of solutions containing strontium and chromium, that confirms once more the absence of Cr(IV). In the region of low temperatures (77–140 K) μ_{eff} is almost the same as for the [Cr]:[Sr] = 2:1 system. However, at higher temperatures it remains constant (~6.2 BM, Fig. 2). The character of the dependence $\mu_{eff} = f(T)$ has much in common with a similar dependence for the [Cr]:[Sr]:[Mg] system, for which we earlier postulated the presence of only clusters Y at infinite dilution [1]. The effective magnetic moments for the [Cr]:[Mg] = 5:1 system at infinite dilution can be represented as a superposition of magnetic moments of 35% of Y clusters and 65% of single chromium(III) atoms. This interesting special feature points to a stronger influence of magnesium and a weaker influence of strontium on clustering and interatomic interactions. This tendency has the following explanation.

The isotherms of magnetic susceptibility for the [Cr]:[Mg] = 5:1 and [Cr]:[Sr] = 5:1 systems allow a

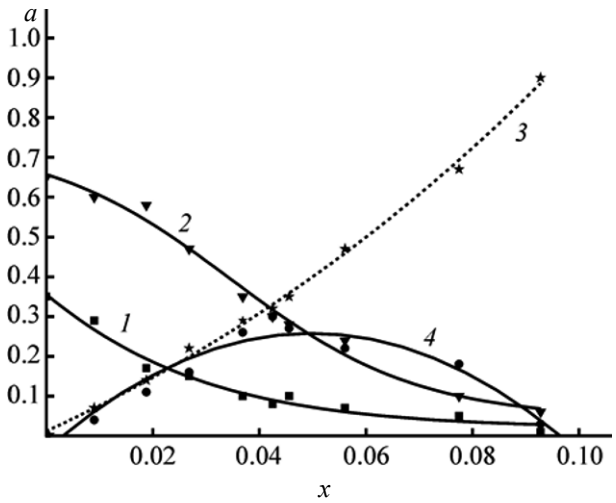

Fig. 3. Plot of cluster and single atom fractions vs. chromium concentration for $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$. (*1*) Y clusters, (*2*) monomers, (*3*) dimers, and (*4*) trimers.

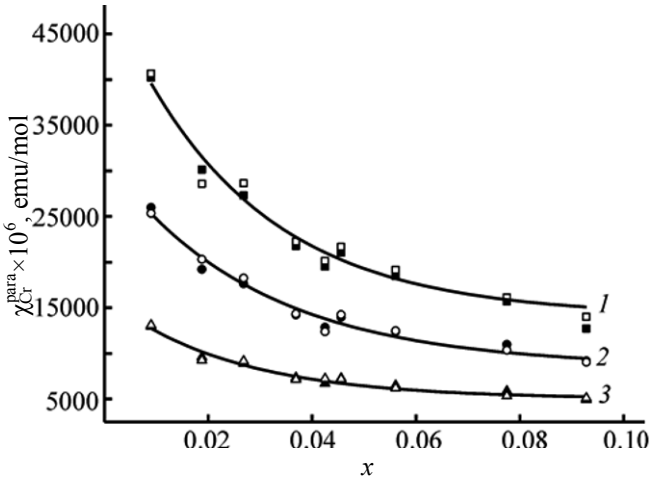

Fig. 4. Theoretical (black symbol) and experimental (open symbol) paramagnetic component of magnetic susceptibility for $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ at (*1*) 90, (*2*) 160, and (*3*) 350 K.

conclusion that in the magnesium-containing systems chromium atoms are clasterized stronger as a result of a weaker polarizing ability of magnesium compared to strontium. An increase in the ionicity of Mg–O bonds results in an increase in the degree of covalence of Cr–O bonds [1], which must favor the clustering of chromium atoms. The different behavior of strontium and magnesium as heterovalent substituents is also accounted for by their different crystallographic sites in the structure of lanthanum gallate: magnesium, like chromium, is in the same bond line with oxygen atoms when replacing gallium. In this manner a direct overlapping of orbitals is ensured, and the effects associated with orbital polarization become more distinct as opposed to strontium-containing analogs.

We were able to carry out a calculation for this system within the framework of the diluted solution model. The calculation was based on taking into account monomers, antiferromagnetic dimers (J_d –12 cm^{-1}), linear trimers (J_t –20 cm^{-1}), and Y clusters (Fig. 3) [1]. The difference between calculated and experimental susceptibilities does not exceed 5% (Fig. 4).

As the concentration of the solution increases, the fractions of Y clusters and monomers monotonically decrease, and the fraction of dimers monotonically increases. The changes in the fraction of trimers are non-monotonic. This special feature can be accounted for in the following manner: as the concentrations of chromium and magnesium in the solution increase, magnesium can be localized in one of the sites occupied by chromium atoms in a trimer, which results in its partial destruction with the formation of a dimer and a monomer (Fig. 5).

There is a certain correlation between the concentration dependences of the fraction of trimers and the change in magnetization (Fig. 6). It should be noticed that a similar situation has been already encountered in the case of [Cr]:[Sr] = 2:1, in which a non-monotonic run of the monomer fraction and also of magnetization was observed [10].

Therefore, the examination of magnetic characteristics of the [Cr]:[Mg] = 5:1 system and the relationship between this system and the [Cr]:[Sr]:[Mg] = 5:1:1 system point to a strong dependence of interatomic interactions and clustering on the nature of a diamagnetic element. Each of the elements (strontium and magnesium) increases the clustering of chromium atoms to a various degree (upon a simultaneous doping with strontium and magnesium the nuclearity of the clusters is the greatest). Magnesium has a greater impact owing to special features of its location in the structure, which in its turn favors a more distinct manifestation of polarizing effects.

$LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ system. As for the [Cr]:[Mg] = 5:1 system, the isotherms of magnetic susceptibility for the solutions with the ratio [Cr]:[Mg] = 2:1 lie much higher than for the $LaCr_xGa_{1-x}O_3$ system, which also points to the presence of clusters of chromium atoms and the absence of chromium(IV).

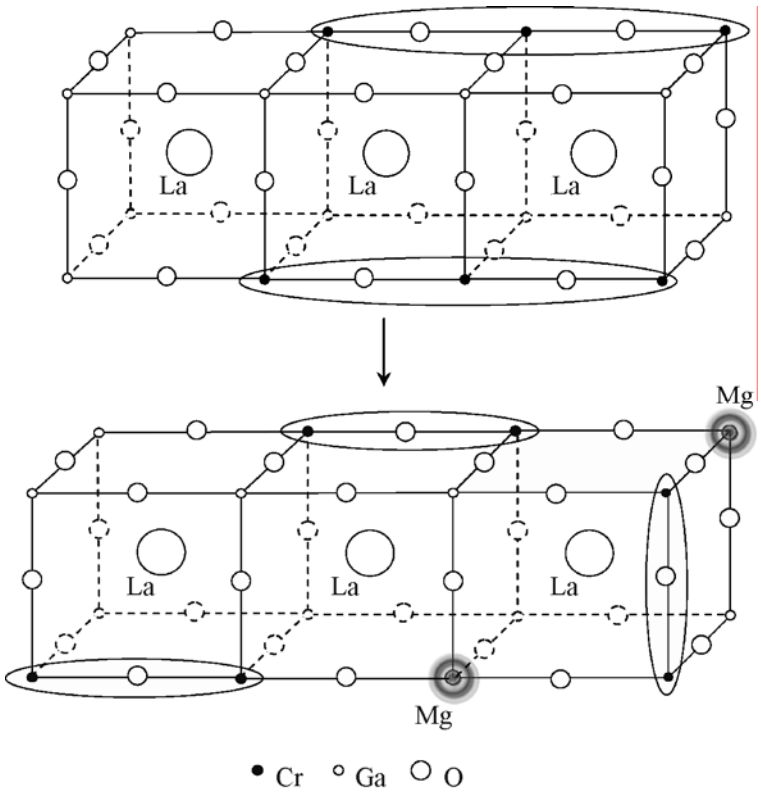

Fig. 5. Formation of dimers from trimers.

The most important special feature of this system is the changing character of the magnetic susceptibility isotherms in the temperature range 77–400 K (Fig. 7). At low temperatures the susceptibility decreases smoothly as the chromium concentration increases, whereas starting from 140 K the isotherm bends, and after 240 K a region of a plateau appears in the concentration range $0.01 < x < 0.03$. No such pattern was observed for any studied chromium-containing systems.

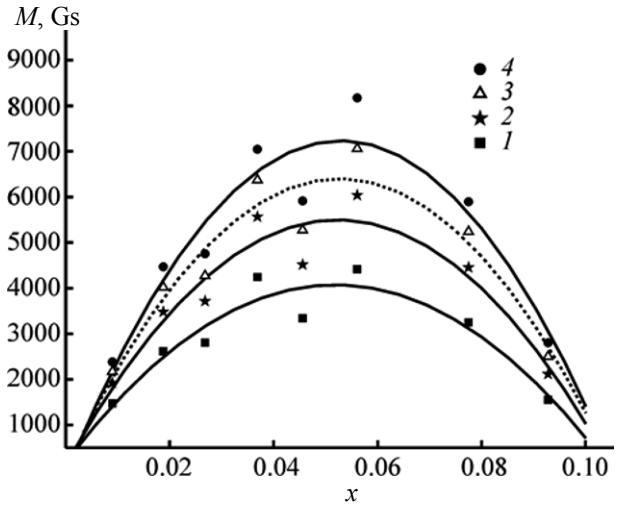

Fig. 6. Concentration dependence of magnetization of the $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ system at 77 K for various field strength: (*1*) 3640; (*2*) 5230; (*3*) 6330; and (*4*) 7240 Oe.

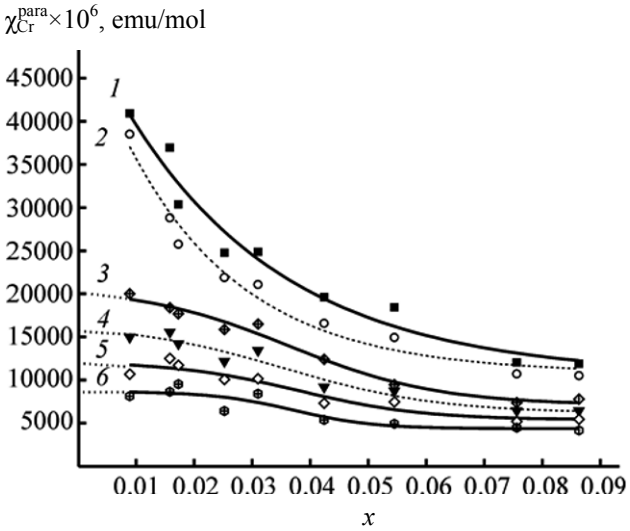

Fig. 7. Concentration dependence of paramagnetic component of magnetic susceptibility calculated per 1 mole of chromium atoms for the $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ system at (*1*) 77, (*2*) 90, (*3*) 140, (*4*) 180, (*5*) 240, and (*6*) 320 K.

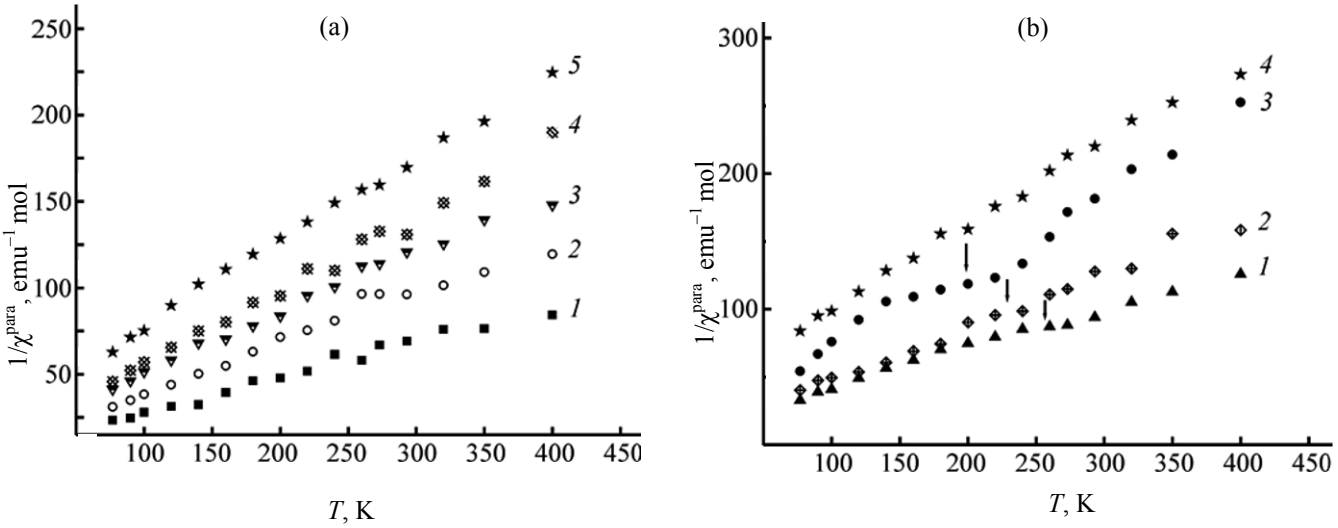

Fig. 8. Temperature dependence of inverse paramagnetic susceptibility for (a) $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and (b) $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ systems for various chromium concentrations. (a): (*1*) x 0.0090, (*2*) 0.0268, (*3*) 0.0456, (*4*) 0.0561, and (*5*) 0.0928; (b): (*1*) x 0.0173, (*2*) 0.0310, (*3*) 0.0545, and (*4*) 0.0863.

Temperature-dependent character of the isotherms can indicate a temperature-dependent exchange parameter in the clusters, which seems to be a result of structural distortions extremely sensitive to temperature variations. The distortions result in a change in the angle of orbital overlapping and, consequently, in the changes of the exchange parameter. The version of distortions is invoked by the reason that magnesium has an essentially larger ionic radius than gallium (0.72 and 0.62 Å, respectively [11]), and in this system with a high content of magnesium the local distortions of the structure are inevitable.

The extrapolation to the infinite dilution points to a fundamentally different character of the temperature dependence of effective magnetic moment at infinite dilution, as compared to the systems studied earlier, in particular, to the [Cr]:[Mg] = 5:1 system. From 77 to 200 K μ_{eff} decreases from ~6.5 to ~ 4.5 BM and does not change further. The value of μ_{eff} ~6.5 BM points to the presence of clusters with a strong ferromagnetic exchange, but such an abrupt (up to ~ 4.5 BM) decrease in the magnetic moment with rising temperature cannot be described within the limits of a constant exchange parameter. The structural distortions existing at low temperatures and resulting in a strong ferromagnetism seem to be partially removed as temperature increases, and the channels of antiferromagnetic exchange begin to play increasingly greater role in the exchange, as was observed on dilution of lanthanum manganites doped with alkaline earth elements [12]. In other words, as the concentration of magnesium increases, some new clusters are formed in the system.

The appearance of clusters with variable exchange parameter makes it impossible to carry out a correct calculation within the framework of diluted solution model including Heisenberg-Dirac-van Vleck model.

Common features and distinctions in the systems with the ratios [Cr]:[Mg] = 5:1 and [Cr]:[Mg] = 2:1. In both systems the presence of clusters of chromium atoms and the absence of chromium in a higher valence state are noted. In the [Cr]:[Mg] = 5:1 system at the infinite dilution there are 35% of Y clusters and 65% of monomers. In the [Cr]:[Mg] = 2:1 system there are Z clusters differing in their composition and structure. For both cluster types the observed temperature dependence of the effective magnetic moment is not typical, which results from competing antiferro- and ferromagnetic interactions. A possibility of double exchange is not excluded as is the case in strontium-containing analogues. Magnesium as well as strontium can give rise to full-value oxygen vacancies and electrons at the site of a vacancy.

$$MgO + Ga_{Ga}^{\times} + 1/2O_O^{\times} \rightarrow Mg'_{Ga} + 1/2V_O^{\cdot\cdot} + 1/2Ga_2O_3,$$

$$1/2V_O^{\cdot\cdot} \equiv e.$$

The migration of electrons from one paramagnetic center to another must result in a strong ferromagnetism, which is observed at the infinite dilution as judged from the absolute values of the magnetic moment.

Comparing magnesium- and strontium-containing analogs, we can make an important conclusion about the influence of the concentration of the heterovalent diamagnetic substituent on clustering of chromium atoms. An increase in strontium concentration in lanthanum gallate doped with chromium results in an increase in the amount of high-nuclearity clusters (X clusters). An increase in the amount of magnesium in lanthanum gallate doped with chromium results in the inverse tendency: in a partial disaggregation of chromium atoms and in the formation of clusters with lower nuclearity (Y and Z clusters).

Therefore, the influence of the nature and concentration of diamagnetic elements on the electronic structure of chromium-containing gallates is fundamental. Strontium and magnesium act as antagonists of clustering owing to special features of their electronic nature and, what is no less important, to their different location in the structure of lanthanum gallate.

The character of temperature dependence of the inverse paramagnetic susceptibility for both systems is of interest because in the systems with the ratio [Cr]:[Mg] = 2:1 distinct bends are observed in the $1/\chi_{Cr}$–T plots, which are shifted to the left as the paramagnetic concentration increases. It proves the fact that the character of interatomic interactions varies with temperature owing to a fine balance between structural distortions, a lattice deformation, and the degree of overlapping orbitals of interacting magnetic atoms (Fig. 8).

The fact of the appearance of high-nuclearity clusters with a distinct ferromagnetic component in the exchange is also doubtless. These clusters consist of not only chromium atoms, but contain heterovalent diamagnetic atoms, strontium and (or) magnesium, and also vacancies in the oxygen sublattice.

Special features of the subjects under study are directly connected with both qualitative and quantitative compositions. Varying only one parameter (concentration or the nature of a substituent) results in the irreversible changes in the whole system, which is the consequence of complex and multiform interactions between separate atoms and their aggregates.

EXPERIMENTAL

We carried out the X-ray analysis on a URS-50 I diffractometer using CuK_α radiation. The single-phase samples of the solid solutions have the orthorhombic structure of lanthanum gallate. We determined the quantitative content of chromium and magnesium simultaneously by the method of atom emission analysis with inductively bound plasma. The accuracy of analysis was 2% of x in the solid solution formula.

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

The $LaCr_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and $LaCr_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ solid solutions ($0.01 \le x \le 0.1$) were obtained by a ceramic procedure. We used extra pure grade lanthanum, gallium, magnesium, and chromium oxides. The stoichiometric mixture of oxides was ground in an agate mortar for 1 h, then pressed into pellets and sintered in air at 1450°C for 50 h. The time of sintering for obtaining single-phase samples was determined by the X-ray data. The constancy of the magnetic susceptibility after the second 10 h sintering testifies that all the solutions are close to equilibrium state.

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