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States of Atoms and Interatomic Interactions in Complex Perovskite-like Oxides: XXIII.[1] Magnetic Dilution in the La(Sr)NiO_3–$LaGaO_3$ System

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Abstract—Magnetic susceptibility of dilute solid solutions of lanthanum gallates doped with nickel and also with nickel and strontium was studied. Calculations showed that the main contribution into the exchange interactions in gallates doped with nickel is made by dimers formed by low-spin nickel(III) (J –20 cm^{-1}), and in gallates doped with strontium and nickel the main contribution is due to dimers formed by high- and low-spin nickel (J 10 cm^{-1}). Electrical conductivity measurements showed that the samples under study are electron and ion conductors.

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Lanthanum gallates with the perovskite structure, doped with transition metals are extensively studied at present. The reason is that they can be used as cathodes in solid oxide fuel cells (SOFC). The cathodes in such fuel cells should have oxygen ion and electron conductivity simultaneously. They should also be stable at high temperatures at which they are commonly employed. Earlier lanthanum gallates doped with strontium and magnesium were offered as cathodes, but such cathodes appeared to be inefficient, since this structure is unstable. Doping strontium in lanthanum sites naturally produces oxygen vacancies and, consequently, ion conductivity. However, in the absence of transition metals, strontium destabilizes the structure. The role of 3*d* metals replacing gallium in octahedral sites is not completely clear. The assumption of Baker et al. [2] that the fraction of 3*d* atoms, equivalent to strontium, passes into the tetravalent state seems illogical, since in such a case we can obtain electron rather than ion conductivity. Moreover, our systematic magnetic susceptibility study showed that the state of chromium in the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ system is the same as in the $LaCr_xGa_{1-x}O_3$ solid solutions over a wide range of x, i.e. they are in the oxidation state +3 [3].

It should be noted lanthanum gallates doped simultaneously with strontium in lanthanum sites and a 3*d* metal (Mn, Fe, Co, or Ni [4]) in gallium sites are dilute isomorphous substitution solid solutions. Therefore, a systematic (over a wide range of concentrations) study of their magnetic properties can give us an opportunity to simulate their electronic structure and to elucidate the state of transition metals, their role in stabilizing vacancies in the oxygen sublattice of perovskite, and, hence, the mechanisms of ion conductivity. However, it is evident that we deal with a multicomponent system, which increases the number of independent parameters. Therefore, as the first step we were to study the state of the transition metal atoms and exchange interactions between them in the lattice of lanthanum gallate without strontium, and then we could draw certain conclusions about the influence of strontium on the properties of these systems. Such investigation was carried out for chromium-containing systems [5]. The aim of this work was to study the magnetic behavior of nickel atoms in lanthanum gallate, or, in other words, to obtain magnetic susceptibility and electrical conductivity data for the $LaNi_xGa_{1-x}O_3$ and $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ solid solutions. The Ni:Sr ratio should be kept constant in this case and, like in [3], it was selected to be 5 : 1.

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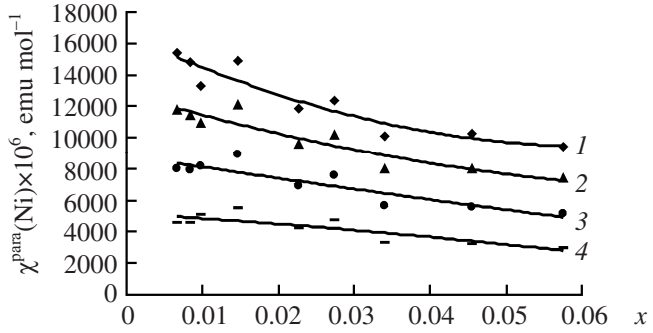

Fig. 1. Plot of the molar paramagnetic susceptibility $\chi^{para}(Ni)$ of nickel vs. nickel concentration for the $LaNi_xGa_{1-x}O_3$ solid solutions. *T*, K: (*1*) 90, (*2*) 120, (*3*) 189, and (*4*) 320.

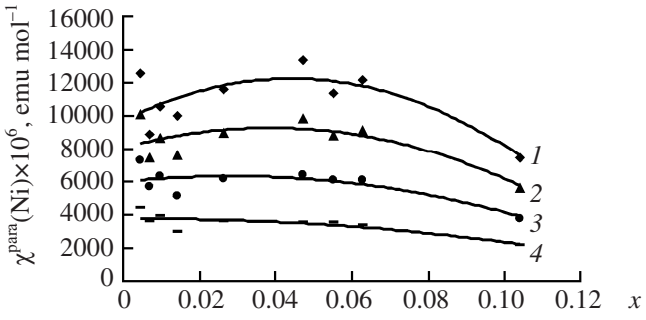

Fig. 2. Plot of the molar paramagnetic susceptibility $\chi^{para}(Ni)$ of nickel atoms vs. nickel concentration for the $La_{1-0.2x}Sr_{0.2x} \cdot Cr_xGa_{1-x}O_3$ solid solutions. *T*, K: (*1*) 90, (*2*) 120, (*3*) 189, and (*4*) 320.

We synthesized the $LaNi_xGa_{1-x}O_3$ and $La_{1-0.2x}Sr_{0.2x} \cdot Cr_xGa_{1-x}O_3$ solid solutions ($0.01 \le x \le 0.1$) with the perovskite structure. X-ray phase analysis showed that the samples all are monophase and have a cubic $LaGaO_3$ structure. X-ray fluorescent analysis for nickel and strontium showed that sintering affects in some way the nickel content, but the Ni : Sr ratio is almost preserved.

The magnetic susceptibility of all the solid solutions was studied. The experimental paramagnetic susceptibilities were used to plot χ_{Ni}–x isotherms. The shape of the χ_{Ni}–x plots for $LaNi_xGa_{1-x}O_3$ is typical of antiferromagnetic dilution (Fig. 1).

The dependences of the molar paramagnetic susceptibility of nickel on nickel content for strontium-doped solid solutions (Fig. 2) radically differ from those for the systems containing no strontium. The isotherms of strontium-containing samples have a maximum at $x \approx 0.05$.

The extrapolation of χ_{Ni} to infinite dilution of the $LaNi_xGa_{1-x}O_3$ solid solution ($x \to 0$) makes possible assessment of the state of single nickel atoms on the basis of the temperature dependence of effective magnetic moment.

T, K	90	100	120	140	160	180	200	220	320
μ_{eff}, BM	3.70	3.69	3.86	4.03	4.02	3.98	4.06	4.02	4.08

The μ_{eff} values and their temperature dependences point to the fact that, first, nickel is in the trivalent state in the solid solutions. This is supported by the ESR spectra at room temperature, which contain a single line with *g* 2.157. Second, nickel seems to be in the $^4T_{1g} \rightleftarrows {}^2E_g$ spin equilibrium. We calculated the μ_{eff}–*T* dependence by formula (1) under the assumption of spin equilibrium [6].

$$\mu_{eff} = \frac{12.675x + 49 + (8505x - 31.752)e^{-2x} + (7680x + 17.248)e^{3x/4} + 5400xe^{-(5/4 + E/\xi)x}}{900x[1 + 2e^{-3x/4} + 3e^{-2x} + 2e^{-(5/4 + E/\xi)x}]}. \quad (1)$$

Here $x = \xi/kT$, *k* is the Boltzmann constant; *T*, absolute temperature; ξ, one-electron spin–orbit coupling constant; and *E*, energy gap between the high- and low-spin states.

As a result, we obtained the crystal-field splitting $\Delta E \sim -940$ cm^{-1} with regard to the one-electron spin-orbit coupling constant ξ 390 cm^{-1}. In other words, the ground state for single Ni(III) atoms in $LaGaO_3$ is the low-spin ^2E_g state, and, as the temperature increases, the fraction of high-spin atoms increases.

To assess the nature and energy of exchange interactions in the solid solutions, we calculated paramagnetic susceptibilities in the *x* range 0.01–0.05 for all the measured temperatures in terms of the dilute solution model [7]. In this model, the magnetic susceptibility per 1 mole of a paramagnetic atom is an

additive value, e.g. is composed of the susceptibility of a monomer and of aggregates of n atoms with regard to their fraction in a particular solid solution (2).

$$\chi = \sum_{i=1} a_i \chi_i. \quad (2)$$

For a highly dilute solution ($x \leq 0.05$), the probability of the formation of aggregates with $n > 2$ is extremely low, and, therefore, for quantitative assessment of exchange interactions between nickel atoms we can use formulas (3) or (4), (5).

$$\chi_{Ni}^{para} = a_{mon}\chi_{mon} + a_{dim}\chi_{dim}, \quad (3)$$

$$\mu_{exp}^2 = (1 - a_{dim})\mu_{mon}^2 + a_{dim}\mu_{dim}^2, \quad (4)$$

$$\mu_{eff} = 2.84\sqrt{\chi_M T}\,. \quad (5)$$

The magnetic susceptibility of single nickel atoms χ_{mon} was determined on the basis of the magnetic susceptibility extrapolated to $x \to 0$; the susceptibility of a binuclear cluster χ_{dim} was determined by the Heizenberg–Dirack–van Vleck (HDVV) model [8].

According to this model, the spin-spin coupling Hamiltonian is determined by formula (6).

$$\hat{H}_{exch} = -2J\hat{S}\cdot\hat{S}\,. \quad (6)$$

Here J is the isotropic exchange parameter; and $\hat{S}$, operator of the total spin angular momentum. Then χ_{dim} is determined with by formulas (7) and (8).

$$\chi_{dim} = \frac{Ng^2}{6kT}\cdot\frac{\sum_{S'=0}^{2S} S'(S'+1)(2S'+1)\exp[-E(S')/kT]}{\sum_{S=0}^{2S}(2S'+1)\exp[-E(S')/kT]}\,, \quad (7)$$

$$E(S') = -J[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)], \quad (8)$$
$$S' = (S_1 + S_2), S_1 + S_2 - 1, \ldots, S_1 - S_2.$$

Here S is the atomic spin; g, g-factor; and T, absolute temperature.

The HDVV model is applicable to $Ni(III)_{ls}$ having the ^2E_g ground state, but not to $Ni(III)_{hs}$ ($^4T_{2g}$), since in the latter case splitting of the term both due to exchange interactions and spin–orbit coupling should be taken into account [8]. However, as shown in [9, 10], even in this case we still can use the GDVV model. To this end, we introduce a g-factor depending on temperature according to formula (9) into formula (7) for the $^4T_{2g}$ term.

$$\mu_{exp} = g/2\cdot\mu_{SO} \quad (9)$$

Here μ_{SO} is the spin only value of magnetic moment; and μ_{exp}, experimental magnetic moment at a given temperature.

Then $g(S)$ for the 3/2–1/2 dimers is calculated by formula (10).

$$g(S) = \frac{g_a + g_b}{2} + \frac{g_a - g_b}{2}\cdot\frac{S_a(S_a+1) - S_b(S_b+1)}{S(S+1)}. \quad (10)$$

Here S is the atomic spin; g, g-factor; and T, absolute temperature.

The magnetic susceptibility was calculated as a sum of the susceptibilities of monomers and of all the possible dimers (1/2–1/2, 1/2–3/2, 3/2–3/2). With a great number of experimental points, the fit of calculation to experiment was no worse than 5%. The calculation results for $LaNi_xGa_{1-x}O_3$ are given in Table 1. A rather large divergence of calculation from experiment was only observed for high concentrations, that is accounted for by the formation of larger aggregates than dimers.

The calculations showed (Fig. 3) that the main contribution into the exchange interactions between Ni(III) atoms in the $LaNi_xGa_{1-x}O_3$ solid solutions is introduced by $Ni_{1/2}$–O–$Ni_{1/2}$ dimers (J –20 cm^{-1}), whereas $Ni_{1/2}$–O–$Ni_{3/2}$ mixed dimers (J +10 cm^{-1}) contribute fairly little at low concentrations.

Now let us turn to the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ solutions. The isotherms for strontium-containing samples have a maximum at x ~0.05. The magnetic moments at infinite dilution for this system are much lower than those for strontium-containing samples μ_{eff} ($x \to 0$) 2.6–3.04 BM.

T, K	90	100	120	140	160	180	200	220	320
μ_{eff}, BM	2.6	2.64	2.62	2.65	2.4	2.75	2.81	2.83	3.04

The temperature trend of the magnetic moment at infinite dilution is roughly the same as for the $LaNi_xGa_{1-x}O_3$ solutions. This suggests that at infinite dilution a part of Ni^{III} remains, like in pure $LaGaO_3$, in spin equilibrium and a part, in the low-spin state. This probably relates to Ni^{III} located nearby strontium. Strontium(II) (r 1.44 A) slightly polarizes oxygen orbitals, thus increasing the crystal field in octahedra containing Ga and the transition metal, compared to the situation with La(III) (r 1.32 A), and this favors the transfer of nickel atoms into the low-spin state.

Table 1. Calculated and experimental paramagnetic susceptibilities of the $LaNi_xGa_{1-x}O_3$ system at 90–320 K

x	$\chi_{exp(calc)}\times10^6$, emu mol^{-1}					
	90 K	100 K	140 K	180 K	220 K	320 K
0.0067	14400(14700)	13100(13900)	10700(10300)	9100(8200)	7200(7200)	5000(5200)
0.0084	14100(14400)	12800(13500)	10500(10100)	8800(8000)	7000(7000)	4800(5100)
0.0098	13900(14100)	12600(13200)	10300(9800)	8600(7800)	6900(6800)	4700(4900)
0.0147	13100(13299)	12100(12415)	9800(9235)	8000(7345)	6500(6358)	4400(4580)
0.0226	12100(12000)	11100(11000)	8900(8100)	7000(6400)	5900(5500)	4000(4000)
0.0274	11600(11000)	10700(9900)	8500(7400)	6700(5900)	5700(5100)	3800(3500)
0.0340	10900(9700)	10000(9000)	7800(6700)	6100(5300)	5100(4500)	3600(3300)
0.0456	9900(7700)	9100(7100)	7000(5300)	5400(4200)	4300(3600)	3200(2600)
0.0576	9300(6400)	8600(5900)	6400(4400)	5000(3500)	3800(3000)	2900(2100)

Evidence for the coexistence of low-spin and spin-equilibrated nickel in $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ at infinite dilution was provided by the calculation by formula (11).

$$\mu^2_{exp} = a_{ls}\mu^2_{ls} + (1 - a_{ls})\mu^2_{av}. \quad (11)$$

T, K	90	100	120	140	160	180	200
$a_{ls}(Ni^{III})$	0.58	0.58	0.61	0.60	0.58	0.56	0.54

The fraction of low-spin nickel is ~0.58. As seen from Fig. 4, as the concentration increases, the high-spin nickel all fairly quickly passes into the $Ni_{1/2}$–$Ni_{3/2}$ dimers with ferromagnetic exchange (J 10 cm^{-1}). The fraction of such dimers increases up to the concentration of approximately 0.05. The fraction of dimers with antiferromagnetic exchange is so small that there is no sense to divide them into dimers formed separately by low- and high-spin nickel. The tendency of the fraction of dimers with antiferromagnetic exchange for increase becomes noticeable at $x > 0.047$ only. The same pattern is also observed in the isotherms of magnetic susceptibility (Fig. 2), where χ_{Ni} starts to decrease at $x > 0.05$. The calculated χ_{Ni} values are given in Table 2.

The measured electric conductivity of the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ and $LaNi_xGa_{1-x}O_3$ solid solutions showed (Figs. 5 and 6) that the systems possess a noticeable electron conductivity. This is evidently associated with the fact that Ni^{III} e_g has electrons on the e_g orbitals which are close in energy to the bottom of the $LaGaO_3$ conductivity band. With $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$, a

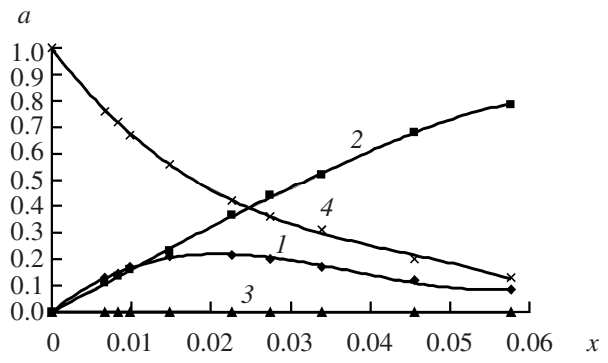

Fig. 3. Plot of the fractions of monomers and dimers vs. concentration of nickel in the $LaNi_xGa_{1-x}O_3$ solid solutions. Dimers: (*1*) 1/2–3/2, (*2*) 1/2–1/2, and (*3*) 3/2–3/2. (*4*) Monomers.

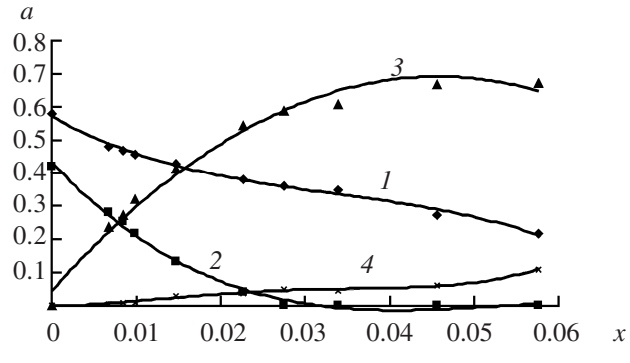

Fig. 4. Plot of the monomer and dimmer fractions vs. nickel concentration in the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ solid solutions. (*1*) Low-spin nickel, (*2*) spin-equilibrated nickel, (*3*) 1/2–3/2 dimers, (*4*) dimers with antiferromagnetic exchange (3/3–3/2 and 1/2–1/2).

Table 2. Calculated and experimental paramagnetic susceptibilities of the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ system at 90–320 K for $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$

x	$\chi_{exp(calc)}\times10^6$, emu mol^{-1}					
	90 K	100 K	140 K	180 K	220 K	320 K
0.0067	9900(10300)	9300(9300)	6800(7300)	5600(5900)	4800(4700)	3900(3300)
0.0084	10000(10500)	9400(9500)	6900(7500)	5700(5900)	4850(4800)	3950(3300)
0.0098	10200(10700)	9600(9700)	7000(7600)	5800(6000)	4900(4800)	3975(3300)
0.0147	10500(11100)	9900(10100)	7300(7800)	6000(6000)	5000(4900)	4000(3400)
0.0226	11300(11800)	10800(10800)	7800(8000)	6300(6200)	5150(5100)	4100(3500)
0.0340	11600(12200)	10100(11100)	8000(8200)	6400(6400)	5200(5300)	4100(3600)
0.0456	11900(13100)	11300(11900)	8200(8800)	6400(6900)	5200(5700)	3900(3900)
0.0576	11700(12104)	11060(10600)	8000(8281)	6200(6550)	5000(5466)	3700(3885)

contribution of ion conductivity was found, i.e. the solid solutions are electron and ion conductors. At low temperatures, the conductivity is mainly electron in nature, and at $T > 450$ K, ion conductivity contributes much.

Thus, the electrical conductivity data provide evidence for the assumption that the oxygen sublattice in strontium-containing samples contains vacancies, and the magnetic data show that the vacancies in lanthanum gallate are stabilized by the transition metal. The stabilization of the vacancies is associated, in some way, with the formation of exchange-bonded dimers of nickel atoms in different spin states.

EXPERIMENTAL

The $LaNi_xGa_{1-x}O_3$ and $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ solid solutions ($0.01 \le x \le 0.10$) were obtained by the ceramic procedure. Finely ground and pelleted mixtures of special purity grade La_2O_3, Ga_2O_3 obtained by dissolving metallic gallium in HNO_3 and subsequent thermolysis, NiO obtained by thermolysis of $Ni(NO_3)_2 \cdot 6H_2O$ (analytical grade, cobalt-free), and analytical grade $SrCO_3$ were annealed in air at 1450°C for 50 h. The homogeneity of the solid solutions was controlled by X-ray phase analysis (URS-50M diffractometer, CuK_α radiation) and by the constancy of the paramagnetic susceptibility at varied annealing

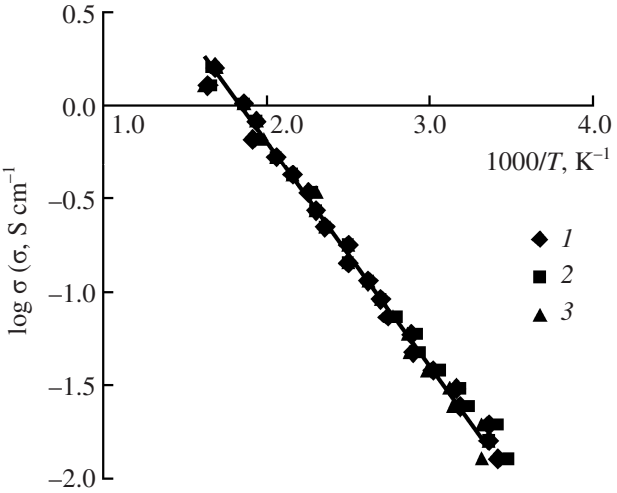

Fig. 5. Temperature dependence of specific conductivity for the $LaNi_xGa_{1-x}O_3$ solid solution, x 0.1 at ω (*1*) 1, (*2*) 10, and (*3*) 100 kHz .

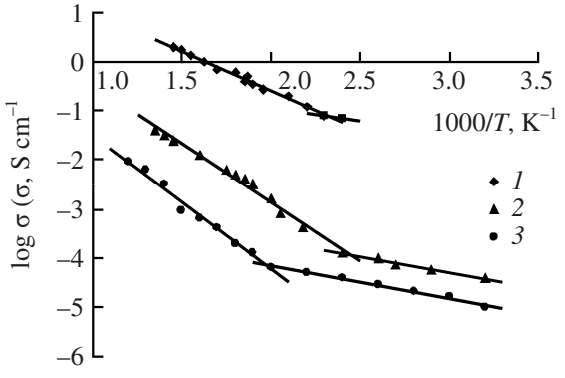

Fig. 6. Temperature dependence of specific conductivity for the $La_{1-0.2x}Sr_{0.2x}Cr_xGa_{1-x}O_3$ solid solutions. x (*1*) 0.10, (*2*) 0.08, and (*3*) 0.04 at ω 200 kHz.

time and composition of the gas phase (air and O_2). Nickel was determined by X-ray fluorescent analysis (REAN device with a rhodium tube) with an accuracy of no less than 2% *x* in the solid solution formula.

The magnetic susceptibilities were measured by the Faraday method on a device designed at the magnetochemistry laboratory, St. Petersburg State University. The measurements were carried out in the temperature range 77–400 K at 16 fixed temperatures. The accuracy of relative measurements was 2%. The molar paramagnetic susceptibilities of nickel atoms were corrected for the diamagnetic susceptibility of the $LaGaO_3$ matrix, measured over the same temperature range.

The electrical characteristics of the solid solutions were measured by the two-electrode method at alternating current. A silver paste was deposited on the end faces of the obtained tablets, and the samples were annealed at 400°C for 1h. The measurements were carried out at 1, 10, 100, and 200 kHz in the temperature range 300–1010 K in 10 deg increments in the heating–cooling mode.

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