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Magnetic and structural properties of $La_{1-x}Gd_xCoO_3$ compounds

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Abstract

We present a study of magnetic and structural properties of $La_{1-x}Gd_xCoO_3$ compounds with $x = 0$, 0.2, 0.5 and 1. The Gd term in magnetic susceptibility obeys the Curie-Weiss law with antiferromagnetic interaction between the magnetic moments of Gd^{3+} ions. The value of the paramagnetic Curie temperature Θ is proportional to Gd content and for $GdCoO_3$ it reaches $\Theta \simeq -5.5$ K. The Co contribution, $\chi_{Co}(T)$, derived by subtracting the Gd term from the total susceptibility, shows a non-monotonous behavior which is originated by the temperature induced transition of Co^{3+} ions from the ground low spin state to a higher spin state separated by an energy Δ. The revealed strong increase in Δ with increasing Gd content is presumably due to the manifestation of a chemical pressure upon replacing La with Gd having a smaller ionic size.

Key words: $La_{1-x}Gd_xCoO_3$ compounds; Magnetic susceptibility; Spin states crossover; Chemical pressure effect

1. Introduction

Among the perovskite oxides of cobalt with the general formula $RCoO_3$ (R = La, Y, rare-earths) the $LaCoO_3$ compound stands out for the most pronounced anomalies in its physical properties due to the manifestation of the spin crossover phenomenon - a change in the spin state of Co^{3+} ions under the influence of external factors such as temperature, pressure, magnetic field, etc. (see [1–3] and references therein). The energies, corresponding to different spin states of Co^{3+} ions, depend on the balance of the crystal field splitting between the t_{2g} and e_g states of $3d^6$ Co^{3+} ions configuration and the Hund's rule coupling. As

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a result, the difference between energies of different spin states turns out to be small and very sensitive to the external factors. This makes it difficult to determine the type of spin transition, which is the subject of persistent ongoing debate. On the way to solving this problem, more light needs to be shed on the origin of the cobalt spin states through further theoretical and experimental researches.

One of the effective methods for studying a phenomenon of the spin crossover of Co^{3+} ions in $RCoO_3$ cobaltites is to explore the dependence of the Co^{3+} ions contribution to total magnetic susceptibility on temperature and the unit cell volume. Such studies for $LaCoO_3$ [4–7] and for a number of $RCoO_3$ compounds (R= Pr, Nd, Sm and Eu) [6] have revealed a strong increase under pressure of the energy difference Δ between the ground and excited states of these compounds, which correspond to the non-magnetic low spin state (LS, $S = 0$) and the magnetic state with either intermediate (IS, $S = 1$) or high (HS, $S = 2$) spin value of the Co^{3+} ions. The magnetic susceptibility studies for $La_{1-x}R_xCoO_3$ compounds (where R= Pr [8, 9], Nd [10], Sm [11], Eu [12, 13]) have provided some information on behavior of the Co^{3+} spin state under chemical pressure, which corresponds to decrease in the unit cell volume when replacing La^{3+} ions with smaller R^{3+} ones. The main qualitative result of these studies is the observation of a shift of the characteristic maximum in the temperature dependence of the Co^{3+} ions magnetic susceptibility, $\chi_{Co}(T)$, towards higher temperatures and a simultaneous decrease in its height. However, a quantitative estimation of χ_{Co} in $La_{1-x}R_xCoO_3$ systems is somewhat complicated by a noticeable background magnetism of R^{3+} ions, which has to be carefully evaluated.

One of the suitable system for further study of the chemical pressure effects on the spin state of Co^{3+} ions in $La_{1-x}R_xCoO_3$ cobaltites are the $La_{1-x}Gd_xCoO_3$ compounds. Here the Gd^{3+} ion has the smallest ionic radius in the above mentioned R-series and its substitution for La^{3+} ion effectively reduces the lattice volume. In addition, the background magnetism of Gd^{3+} ions can be properly described by the Curie-Weiss law, which favors the reliable extraction of the Co^{3+} ions magnetism from the total magnetization. At the moment, the available experimental information on the magnetic properties of $La_{1-x}Gd_xCoO_3$ system [14, 15] turns out to be rather ambiguous. Thus, the more preferable data on magnetic susceptibility from Ref. [14] seem to significantly exceed their predicted estimates for compounds with low Gd content.

In this work, in order to refine the magnetic properties of $La_{1-x}Gd_xCoO_3$ compounds the measurements of their magnetic susceptibility have been carried out using the samples with detailed attested structural parameters. The aim of the work was to explore dependence of the Co^{3+} spin state in these compounds on temperature and chemical pressure. The results of analysis of the obtained experimental data in the framework of the two-level model are used to clarify a type of the spin state transition of Co^{3+} ions in $La_{1-x}Gd_xCoO_3$ compounds with different gadolinium content.

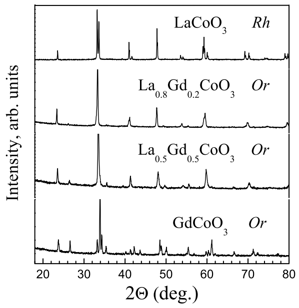

Figure 1: XRD patterns of $La_{1-x}Gd_xCoO_3$ compounds (Cu K_α radiation) with rhombohedral (*Rh*) and orthorhombic (*Or*) perovskite structures.

2. Experimental details and results

A set of precursor powders with the nominal composition $La_{1-x}Gd_xCoO_3$ ($x = 0$, 0.2, 0.5 and 1) was prepared by solid-state route starting from La_2O_3 (Sigma Aldrich, 99.9%), Gd_2O_3 (Sigma Aldrich, 99.9%) and Co_3O_4 (Sigma Aldrich, 99.5%) high-purity powders. Before mixing in stoichiometric proportion with other components, lanthanum and gadolinium oxides were annealed at 973 K for 2 h in air atmosphere to remove moisture and absorbed CO_2. The powdered precursors were calcined at 1173–1323 K, followed by intermediate regrinding after each step. The obtained powders were uniaxially compacted and sintered at 1373 K for 30 h.

Phase composition of the $La_{1-x}Gd_xCoO_3$ materials was studied using Rigaku D/Max-B powder diffractometer (Cu K_α radiation, $\lambda = 1.54185$ Å). Examination of XRD patterns (Fig. 1) revealed pure rhombohedral perovskite structure for $LaCoO_3$ compound and the orthorhombic one for $GdCoO_3$ and $La_{1-x}Gd_xCoO_3$ samples with $x = 0.2$, 0.5 and 1. In order to evaluate precise values of the lattice parameters, atomic coordinates and displacement parameters of atoms in the $La_{1-x}Gd_xCoO_3$ materials studied, full profile Rietveld refinement of corresponding structures was performed by using WinCSD program package [16]. For this purpose XRD patterns of the samples were collected in a broad 2Θ range of 15-150^o on the modernized DRON-3M diffractometer applying Co K_α radiation ($\lambda = 1.79026$ Å). The last X-ray wavelength was chosen in order to avoid undesirable fluorescence of the Co- and Gd-rich $La_{1-x}Gd_xCoO_3$ samples under X-ray radiation from a copper target. In all cases the Rietveld refinement procedure led to a good fit between calculated and experimental diffraction profiles; exemplary graphical results for $La_{0.8}Gd_{0.2}CoO_3$ structure are presented in Fig. 2. Refined structural parameters for all materials studied and corresponding residuals are collected in Table 1.

Obtained structural parameters agree well with the literature data for the

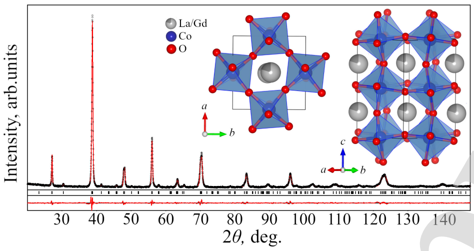

Figure 2: Graphical results of Rietveld refinement of $La_{0.8}Gd_{0.2}CoO_3$ structure. Experimental XRD pattern (Co K_α radiation) is shown in comparison with calculated pattern (black dots and red line, respectively). The difference between measured and calculated profiles is shown as the red curve below the diagrams. Short vertical bars indicate positions of Bragg's maxima in space group *Pbnm*. Inset shows octahedral representation of the structure in two different projections.

Table 1: Unit cell dimensions, atomic coordinates and displacement parameters of atoms in $La_{1-x}Gd_xCoO_3$ structures.

Atoms, sites	Parameters, residuals	Sample, space group			
		$LaCoO_3$ $R\bar{3}c$	$La_{0.8}Gd_{0.2}CoO_3$ *Pbnm*	$La_{0.5}Gd_{0.5}CoO_3$ *Pbnm*	$GdCoO_3$ *Pbnm*
	a, Å	5.4434(3)	5.4135(3)	5.3375(5)	5.2269(5)
	b, Å	-	5.3692(3)	5.3597(4)	5.3958(5)
	c, Å	13.0939(9)	7.6073(4)	7.5912(6)	7.4571(7)
	V, Å^3	336.00(6)	221.11(3)	217.16(5)	210.31(6)
La/Gd:	x	0	-0.0048(3)	-0.0015(11)	-0.0157(10)
6*a* in $R\bar{3}c$;	y	0	0.0211(2)	0.0356(2)	0.0589(5)
4*c* in *Pbnm*	z	1/4	1/4	1/4	1/4
	B_{iso}, Å^2	1.02(2)	0.86(2)	1.03(3)	0.78(11)
Co:	x	0	0	0	0
6*b* in $R\bar{3}c$	y	0	1/2	1/2	1/2
4*b* in *Pbnm*	z	0	0	0	0
	B_{iso}, Å^2	0.7(3)	0.73(4)	0.64(5)	0.7(2)
O1:	x	0.537(5)	0.069(3)	0.035(5)	0.071(6)
18*e* in $R\bar{3}c$	y	0	0.506(2)	0.509(2)	0.476(5)
4*c* in *Pbnm*	z	1/4	1/4	1/4	1/4
	B_{iso}, Å^2	1.6(6)	1.9(5)	1.6(7)	1.0(6)
O2:	x	-	-0.271(2)	-0.266(3)	-0.294(5)
8*d* in *Pbnm*	y	-	0.276(2)	0.271(2)	0.295(5)
	z	-	0.032(1)	0.052(2)	0.047(3)
	B_{iso}, Å^2	-	1.5(3)	0.8(4)	1.0(3)
	R_I	0.067	0.031	0.035	0.047
	R_P	0.171	0.128	0.158	0.191

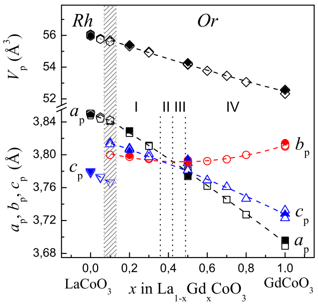

Figure 3: Concentration dependence of the perovskite unit cell dimensions in the $La_{1-x}Co_xO_3$ system. Lattice parameters and unit cell volumes of rhombohedral (*Rh*) and orthorhombic (*Or*) structures are normalized to perovskite (*P*) ones as follow: $a_p = a_{rh}/\sqrt{2}, c_p = c_{rh}/\sqrt{12}, V_p = V_{rh}/6; a_p = a_{or}/\sqrt{2}, b_p = b_{or}/\sqrt{2}, c_p = c_{or}/2, V_p = V_{or}/4$. The dashed lines are guides for the eye and the dotted lines demarcate areas I-IV with different ratios between a_p, b_p and c_p parameters of the orthorhombic phase (see text for details). The hatched area shows two-phase perovskite (phase separation) region. Solid symbols correspond to the data from present study. Open symbols represent the literature data for $La_{1-x}Gd_xCoO_3$ materials taken from Refs. [17] (x=0, 0.05, 0.1, 0.2, 0.5, 1), [15] (x=0.05, 0.3, 0.5, 0.7), [18] (x=0.05, 0.6, 0.8) and [19] (x=0, 0.2, 0.3, 0.5, 1).

”pure” $LaCoO_3$ and $GdCoO_3$ compounds, as well as for already known mixed lanthanum-gadolinium cobaltites (Fig. 3). Lattice parameters and unit cell volume of $La_{1-x}Gd_xCoO_3$ materials studied (full symbols) in comparison with corresponding data for similar materials reported by diverse research groups [15, 17–19] are presented in Fig. 3. As it is evidenced from Fig. 3, two kinds of solid solutions with rhombohedral and orthorhombic perovskite structure with an immiscibility gap between them are formed in the $La_{1-x}Gd_xCoO_3$ system. Morphotropic phase transition in $La_{1-x}Gd_xCoO_3$ system occurs at $x \sim 0.1$, where coexistence of both perovskite phases is observed. Unit cell volume of $La_{1-x}Gd_xCoO_3$ series decreases practically linearly with increasing gadolinium content, in accordance with Vegard’s rule. Peculiarity of $La_{1-x}Gd_xCoO_3$ solid solution with orthorhombic perovskite structure is pronounced anisotropy in concentration dependence of the lattice parameters: significant decrease of the *a*- and *c*-parameters is accompanied with gradual increase of *b*-parameter (Fig. 3). As a result, lattice crossovers in $La_{1-x}Gd_xCoO_3$ series occur at the certain compositions. In accordance, four concentration ranges with different relations between perovskite-like cell parameters are observed in the orthorhombic $La_{1-x}Gd_xCoO_3$ solid solution, namely range I with $a_p > c_p > b_p$, range II with $a_p > b_p > c_p$, range III with $b_p > a_p > c_p$ and range IV with $b_p > c_p > a_p$ (Fig. 3). Similar structural behavior is inherent for the related system $La_{1-x}Eu_xCoO_3$ [13, 18]. Earlier the lattice parameters crossover phenomena were observed among the related mixed rare earth aluminates $La_{1-x}R_xAlO_3$ (R=Sm, Eu, Gd,

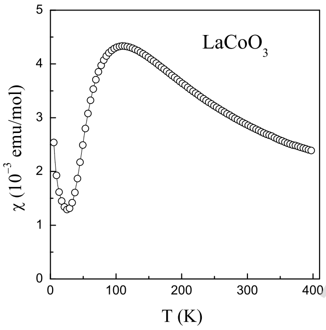

Figure 4: Temperature dependence of LaCoO$_3$ magnetic susceptibility.

Tb) and gallates La$_{1-x}$R$_x$GaO$_3$ (R=Pr, Nd, Sm, Eu, Gd) [20–22].

For prepared samples of La$_{1-x}$Gd$_x$CoO$_3$ compounds, the temperature dependence of magnetic susceptibility, $\chi(T)$, was measured in the temperature range of 5–400 K in a magnetic field of 1 T using a Quantum Design SQUID magnetometer. The obtained data are presented in Figs. 4 and 5. As seen in Fig. 4, the $\chi(T)$ dependence for LaCoO$_3$ shows a pronounced maximum at $T \simeq 110$ K, the position and magnitude of which are consistent with the literature data. At low temperatures, the Curie-like contribution was observed, $\chi_{\mathrm{CW}} = C/T + \chi_0$, with $C \simeq 10 \cdot 10^{-3}$ K·emu/mol and $\chi_0 \sim 1.0 \cdot 10^{-3}$ emu/mol. Here C/T term implies a presence of paramagnetic impurities and χ_0 is the temperature-independent host background. For compounds containing gadolinium, the temperature dependence of magnetic susceptibility is determined mainly by the Gd^{3+} ions (Fig, 5). At low temperatures it follows the Curie-Weiss law, $\chi(T) = C/(T - \Theta)$, with effective magnetic moment of about 8 μ_B per Gd ion and negative paramagnetic Curie temperature Θ indicating an antiferromagnetic coupling between Gd moments.

3. Discussion

The temperature dependence of magnetic susceptibility of La$_{1-x}$Gd$_x$CoO$_3$ compounds (Figs. 4 and 5) is assumed to be determined by two main terms related to the subsystems of Gd and Co ions, $\chi(T) \simeq \chi_{\mathrm{Gd}}(T) + \chi_{\mathrm{Co}}(T)$. The gadolinium term obeys the Curie-Weiss law

$$\chi_{\mathrm{Gd}}(T) = \frac{C}{T - \Theta}. \tag{1}$$

The resulted from low temperature data estimates of the effective magnetic moment of Gd ions, μ_{eff}, and the paramagnetic Curie temperature, Θ, are shown in Fig. 6 as a function of gadolinium content. The value $\mu_{\mathrm{eff}} \simeq 8\ \mu_{\mathrm{B}}$ is close

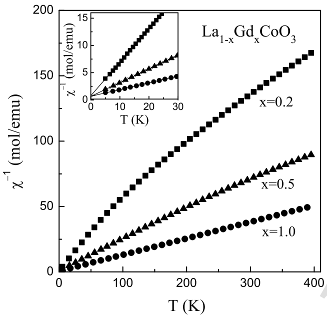

Figure 5: Temperature dependencies of the reciprocal magnetic susceptibility of $La_{1-x}Gd_xCoO_3$ compounds. In insert: the low temperature data on an expanded scale.

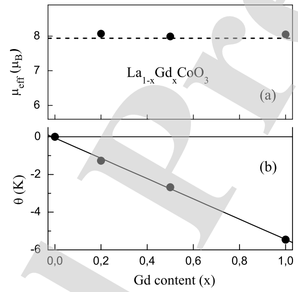

Figure 6: Values of the effective magnetic moment, μ_{eff}, of Gd^{3+} ions (a) (the dotted line indicates the value of μ_{eff} for the free Gd^{3+} ion) and the paramagnetic Curie temperature, Θ, (b) in $La_{1-x}Gd_xCoO_3$ compounds.

to that for the free Gd^{3+} ion. The magnitude of Θ increases linearly with increase of Gd content, being negative in sign. For $GdCoO_3$, the obtained value of $\Theta \simeq -5.5$ K agrees reasonably with available literature data, $\Theta \simeq= 5,3$ K [23] and -6.4 K [24]. The smallness of Θ and its proportionality to Gd content are in favor of a dipolar mechanism of antiferromagnetic interaction between Gd^{3+} magnetic moments in $La_{1-x}Gd_xCoO_3$ compounds.

Now we discuss the magnetism of the Co^{3+} ions subsystem, $\chi_{\text{Co}}(T)$, which is the main interest of this work. The $\chi_{\text{Co}}(T)$ value is extracted from the measured susceptibility $\chi(T)$ by subtracting the Gd^{3+} ions term and the host background value χ_0:

$$\chi_{\text{Co}}(T) = \chi(T) - \chi_{\text{Gd}}(T) - \chi_0. \qquad (2)$$

Here we neglect the contribution of paramagnetic impurities assuming its small-

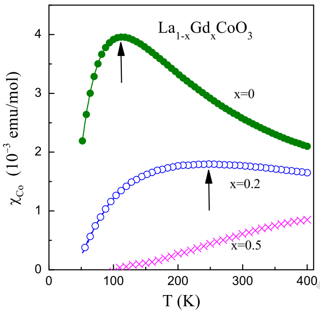

Figure 7: Temperature dependencies of the Co^{3+} ions magnetic susceptibility, χ_{Co}, in $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds.

ness at rather high temperatures considered in analysis below. The magnetic susceptibility of Gd^{3+} ions is described by Eq. 1 using the Curie-Weiss parameters $C = xN_\mathrm{A}\mu^2_\mathrm{eff}(x)/3k_\mathrm{B}$ and $\Theta(x)$ shown in Fig. 6, where N_A is the Avogadro number and k_B the Boltzmann constant. As to the value of χ_0, it is usually determined when analyzing the low-temperature contribution of paramagnetic impurities in the base LaCoO_3 compound. There is a rather large scatter in the literature data on the value of this parameter, which is assumed to be due to the manifestation of magnetically ordered foreign phases at T below about 85 K [9]. It is generally believed that the χ_0 quantity is originated from the Van Vleck paramagnetism of Co^{3+} ions, theoretical estimate of which is about $0.2\cdot10^{-3}$ emu/mol [25], being close to the experimental values of χ_0 in the most perfect crystals of LaCoO_3 [5, 12]. Thus in Eq. 2, we have accepted the value $\chi_0 \simeq 0.2\cdot10^{-3}$ emu/mol to be valid for all compounds under study.

The temperature dependencies of the Co^{3+} ions magnetic susceptibility, $\chi_{\mathrm{Co}}(T)$, in $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds, resulted from Eq. 2 with the accepted values of its parameters, are shown in Fig. 7 for compositions with $x = 0$, 0.2 and 0.5 (for GdCoO_3 ($x = 1$), the magnetism of Co^{3+} ions arises at $T \geq 400$ K [23], being outside the temperature range used by us). When comparing the data shown in Fig. 7 with available literature data, we would like to point out a noticeable difference between our data on $\chi_{\mathrm{Co}}(T)$ for $x = 0.2$ and 0.5 and analogous data of Ref. [14]. At the moment, we cannot comment on this fact, but we would like to note that, as can be seen from the discussion below, our data are in agreement with the general trends in the behavior of Co^{3+} ions magnetism in the studied $\mathrm{La}_{1-x}\mathrm{R}_x\mathrm{CoO}_3$ systems (see Table 2).

The observed specific maximum of $\chi_{\mathrm{Co}}(T)$ dependence in $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds (Fig. 7) is typical for RCoO_3 family. It is commonly believed to be due to a temperature driven transition of the Co^{3+} ions from the non-magnetic low spin state (LS) to the magnetic state with either intermediate (IS) or high

(HS) spin number. In this case, the Co^{3+} ions magnetic susceptibility can be reasonably described by the expression for the two-level system with the energy difference Δ between these levels [12, 26, 27]:

$$\chi_{\mathrm{Co}}(T) = \frac{N_{\mathrm{A}} g^2 \mu_{\mathrm{B}}^2 S(S+1)}{3k_{\mathrm{B}}T} w(T) \equiv \frac{C}{T} w(T). \tag{3}$$

Here the factor C/T describes the Curie susceptibility of the excited state assuming a negligible interaction between the Co^{3+} magnetic moments; g and S are the Lande factor and the spin number, respectively, $w(T)$ is the population of the excited state expressed by

$$w(T) = \frac{\nu(2S+1)\mathrm{e}^{-\Delta/T}}{1+\nu(2S+1)\mathrm{e}^{-\Delta/T}}, \tag{4}$$

where $2S+1$ and ν are the spin and orbital degeneracy of the excited state, respectively, and the energy difference between the excited and ground states, Δ, is in units of T. According to Eqs. 3 and 4 the behaviour of $\chi_{\mathrm{Co}}(T)$ can be properly described by the single parameter Δ and its variation with temperature given by relation

$$\Delta(T) = T \ln\left[\nu(2S+1)\frac{1-w(T)}{w(T)}\right]. \tag{5}$$

As was shown in Refs. [12, 26], the above approach provides a reasonable description of the $\chi_{\mathrm{Co}}(T)$ dependence in $\mathrm{LaCoO_3}$ at least up to room temperatures when choosing the LS→IS scenario of the spin states transition. For this scenario [12, 26, 27], the model parameters are: $g = 2$, $S = 1$ and $\nu = 1$ (the latter assumes that orbital degeneracy of IS state is lifted due to local distortions of the crystal lattice).

Substituting $\chi_{\mathrm{Co}}(T)$ data presented in Fig. 7 into Eq. 3 we have determined temperature dependence of the excited state population, $w(T)$. In turn, the use of this quantity in Eq. 8 has allowed to evaluate temperature dependencies of the excited state energy $\Delta(T)$ for $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds with $x = 0$, 0.2 and 0.5, which are shown in Fig. 8. As can be seen, the most complete data were obtained for $\mathrm{LaCoO_3}$ compound, while for compounds with $x = 0.2$ and 0.5, a reliable determination of $\Delta(T)$ with a decrease in temperature below about 200 K is complicated by a gradual increase in the error in the determination of $\chi_{\mathrm{Co}}(T)$ (and $\Delta(T)$) due to its small magnitude compared to $\chi_{\mathrm{Gd}}(T)$ and an increasing manifestation of the parasitic phases contribution.

For $\mathrm{LaCoO_3}$, there is a noticeable decrease in $\Delta(T)$ with increasing temperature. For example, the value of $\Delta \simeq 165$ K at $T = 0$ K falls down to $\Delta \simeq 0$ at $T \simeq 270$ K, being close in magnitude and temperature dependence to the available literature data [27]. It should be also noted a strong growth of Δ at fixed temperature with increasing x. According to data in Fig. 5, the value of $\partial\Delta/\partial x$ at $T \simeq 270$ K is about 1500 ± 100 K. Assuming this effect to be due to a decrease in the unit cell volume upon increasing the Gd content, we have

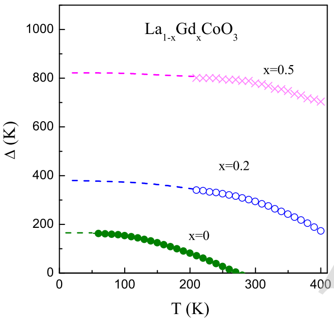

Figure 8: Temperature dependencies of the excited energy Δ in $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds.

estimated the chemical pressure effect on Δ,

$$\frac{\partial\Delta}{\partial P} = -\frac{\partial\Delta}{\partial x}\left(B\frac{\partial\ln V}{\partial x}\right)^{-1} = (15 \pm 1)\ \mathrm{K/kbar}, \tag{6}$$

by using data on the volume change with x at room temperature from Table 1, $\partial\ln V/\partial x \simeq -0.066$, and the bulk modulus value of LaCoO$_3$, $B \simeq 1.5$ Mbar [28]. The obtained value of $\mathrm{d}\Delta/\mathrm{d}P$ is close to analogous value of the chemical pressure effect on Δ observed in $\mathrm{La}_{1-x}\mathrm{Pr}_x\mathrm{CoO}_3$ compounds [8, 9].

In addition, it should be noted that a useful information on the spin state of Co^{3+} ions can be resulted from the analysis of the experimental magnitude of maximum in the $\chi_{\mathrm{Co}}(T)$ dependence, $\chi_{\mathrm{Co}}^{\max}$, and the value of temperature, $T_{\max}$, at which it occurs. The values of $\chi_{\mathrm{Co}}^{\max}$ and $T_{\max}$ given in Table 2 for $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{CoO}_3$ compounds and relevant $\mathrm{La}_{1-x}\mathrm{R}_x\mathrm{CoO}_3$ systems reveal some common feature of the product of these values, $\xi = \chi_{\mathrm{Co}}^{\max} \cdot T_{\max}$, depending on the composition x.

For all considered compounds with $x \leq 0.3$, the value of ξ turns out to be approximately the same and equal to about 0.45, whereas for compounds with $x = 1$ the value of this parameter is approximately 1.3. Based on the results of analysis of the magnetic properties of systems under consideration [5, 6, 8, 9, 12, 14, 23, 26] we can conclude that values $\xi = 0.45$ and 1.3 correspond to LS→IS and LS→HS scenarios of spin crossover, respectively. According to Eq. 3 of the two-level model the ξ value is determined as

$$\xi = C \cdot w(T_{\max}), \quad \text{where} \quad C = \frac{N_{\mathrm{A}} g^2 \mu_{\mathrm{B}}^2 S(S+1)}{3k_{\mathrm{B}}}. \tag{7}$$

It can be reasonably assumed that the value of $w(T_{\max})$ in Eq. 7 is approximately the same for both scenarios of the spin transition. Then the quantitative difference in the values of ξ is determined by the difference in the Curie constant

Table 2: Values of magnetic susceptibility of the Co^{3+} ions, $\chi_{\mathrm{Co}}^{\max}$, at $T = T_{\max}$ and parameters $\xi = \chi_{\mathrm{Co}}^{\max} \cdot T_{\max}$ for $La_{1-x}Gd_xCoO_3$, $La_{1-x}Pr_xCoO_3$ and $La_{1-x}Eu_xCoO_3$ compounds. Data in brackets are rough estimates.

x	$\chi_{\mathrm{Co}}^{\max}$, 10^{-3} emu/mol	$T_{\max}$, K	$\xi = \chi_{\mathrm{Co}}^{\max} \cdot T_{\max}$, K· emu/mol
		$La_{1-x}Gd_xCoO_3$	
0,0	3.98	112	0.45
0,2	1.80	250	0.44
0,5	(0.9)	(500)	(0.45)
1.0[a]	1.7	800	1.36
		$La_{1-x}Pr_xCoO_3$	
0,0[b]	4,04	111	0.45
0,1[b]	3.28	138	0.45
0,2[b]	2.70	162	0.44
0,3[b]	2.27	197	0.45
1.0[c]	$\sim$ 1.8	$\sim$ 700	$\sim$ 1.25
		$La_{1-x}Eu_xCoO_3$[d]	
0.00	4.04	122	0.49
0.10	2.63	150	0.40
0.15	2.21	180	0.40
0.20	1.9	240	0.46
0.25	1.65	305	0.50
0.50	1.5	690	1.0
0.75	1.4	810	1.13
1.00	(1.35)	(970)	(1.3)

[a,b,c] From data of Refs. [23], [9] and [8], respectively.

[d] From data of Ref. [12].

values, $C = 1$ and 3 (in units of K·emu/mol), corresponding to the IS ($S = 1$) and HS ($S = 2$) spin states of Co^{3+} ions, respectively.

We also note close values of $T_{\max}$ in $La_{1-x}R_xCoO_3$ compounds with $x = 1$ (see Table 2), in which the LS→HS spin state transition is realized. This fact indicates the absence of a clear and univocal effect of chemical pressure on the LS→HS excited energy and presumably suggests a weak volume dependence of the corresponding parameter Δ.

4. Conclusion

In summary, we present the results of experimental studies of the structural and magnetic properties of $La_{1-x}Gd_xCoO_3$ compounds with x=0, 0.2, 0.5 and 1.

The obtained refined data on the crystal structure for all materials studied are in good agreement with the available literature data, complementing noticeably the list of the structural properties of $LaCoO_3$-$GdCoO_3$ system.

The measured magnetic susceptibility of $La_{1-x}Gd_xCoO_3$ is implied to be the sum of two main contributions, $\chi_{\mathrm{Gd}}(T,x)$ and $\chi_{\mathrm{Co}}(T,x)$, related to Gd^{3+} and Co^{3+} ions, respectively. The $\chi_{\mathrm{Gd}}(T,x)$ dependence obeys the Curie-Weiss law with linear growth of Θ with x. Such behavior of $\Theta(x)$ indicates a dipole-dipole mechanism of antiferromagnetic interaction between the magnetic moments of Gd^{3+} ions.

New refined data were obtained for the $\chi_{\mathrm{Co}}(T,x)$ contribution to magnetism of $La_{1-x}Gd_xCoO_3$ compounds with $x = 0.2$ and 0.5. The results of analysis of experimental data in the framework of the two-level model are in favor of the LS→IS scenario for spin state transition of Co^{3+} ions in $La_{1-x}Gd_xCoO_3$ compounds with $x = 0$ and 0.2 (and presumably with $x = 0.5$). The observed strong dependence of the excitation energy Δ on Gd content is due to manifestation of a chemical pressure effect. It was estimated to be of $\mathrm{d}\Delta/\mathrm{d}P \simeq 15$ K/kbar in reasonable agreement with effects of directly applied pressure, $\mathrm{d}\Delta/\mathrm{d}P = 12 \div 14$ K/kbar [5, 9]. Such similarity indicates a strong correlation of the Co^{3+} spin state with the lattice volume.

In addition, summarizing our data and the reported in literature data on the spin crossover in relevant $La_{1-x}R_xCoO_3$ compounds, we have proposed a phenomenological criterion for classification of the crossover types by using some magnetic parameters of the cobaltites under study.

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Research Highlights

Highlights

- Structural and magnetic properties of $La_{1-x}Gd_xCoO_3$ compounds were studied
- Antiferromagnetic interaction between magnetic moments of Gd ions is revealed
- Co magnetic state excitation energy grows strongly in $La_{1-x}Gd_xCoO_3$ with Gd content
- LS to IS transition of Co spin state with temperature is expected for low Gd content
- Criterion is proposed for spin crossover type of Co ions in $La_{1-x}R_xCoO_3$ compounds

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Declaration of interests

+ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: