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Concentration dependence of the spin gap in solid solutions

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ABSTRACT

The temperature dependence of the static magnetization of polycrystalline rare-earth cobaltites $\text{La}_{1-x}\text{Gd}_x\text{CoO}_{3-\delta}$ ($x=0.2, 0.5, 1$) was measured in a wide temperature range up to 900 K. The contribution from Co^{3+} ions at high temperatures to the magnetic susceptibility was obtained. The Birch–Murnaghan equation and the magnetic data were used to determine the spin gap Δ_S as the difference between the energies of high-spin and low-spin states in these compounds.

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1. Introduction

The last few decades the cobaltites have been studied extensively both by theorists and experimentalists due to their magnetic and electrical properties [1], but the nature and the degree of stability of electronic states in cobalt oxide compounds are under discussion up to now. LnCoO_3 with the valence formula $\text{Ln}^{3+}\text{Co}^{3+}\text{O}_{3-\delta}$, where $\text{Ln}=\text{La}$ or rare earths can be considered as model materials for studying the role of strong electron correlations, hybridization, and also charge, orbital, and spin ordering in the formation of electronic states. In these oxides, the cobalt ion has no certain multiplicity and can have various spin states: low spin (LS, $S=0$), intermediate spin (IS, $S=1$), or high spin (HS, $S=2$) states [1]. The competition between these states leads to specific features of the magnetic, electrical, and structural properties of the cobaltites. At the present time, it is reliably established that cobalt ions in LaCoO_3 are in a low spin nonmagnetic ground state at a zero temperature [2]. This state is separated from the magnetic HS state by a narrow spin gap of ~ 150 K. The LS ground state can be stabilized by decreasing the Co–O bond length that can be achieved not only by a decrease in temperature, by external pressure [3–6], and also by replacing of lanthanum by other rare-earth element with a smaller ionic radius [7]. This exactly takes

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place in GdCoO_3 , where Co^{3+} has $S=0$ at low temperatures and the spin gap is much larger, about 2000 K [8]. Detailed study of the spin state of the Co^{3+} ions behavior, structural, magnetic and electronic properties of GdCoO_3 in the wide temperature range is given in [9,10].

In this paper we discuss the possibility to control the spin gap value by continuous change of the unit cell volume that can be achieved in the solid solution compounds $\text{La}_{1-x}\text{Gd}_x\text{CoO}_{3-\delta}$ ($0 < x < 1$). We have measured the temperature dependence of the magnetization in a wide temperature range up to 900 K and found the Co^{3+} contribution. High temperature measurements are essential here for a reliable determination of the Co magnetization due to the high value of the spin gap in GdCoO_3 . From the magnetic data we have obtained the spin gap value which is in a good agreement with linear extrapolation between LaCoO_3 and GdCoO_3 values.

2. Samples preparation and experimental methods

Polycrystalline $\text{La}_{1-x}\text{Gd}_x\text{CoO}_{3-\delta}$ ($x=0.2, 0.5, 1$) samples were prepared by standard ceramic technique. The starting materials La_2O_3 (precalcined in the air at 750 °C), Gd_2O_3 and Co_3O_4 , all 99.9% purity, were thoroughly mixed in stoichiometric amounts and fired at 1100 °C for 24 h. Then the mixture was reground and fired at just the same conditions twice. Then pellets was pressed and sintered at 1100 °C for 24 h.

The oxygen content and non-stoichiometry index δ were calculated using the value of mass loss (Δm , %) measured by the thermogravimetric reduction [11], assuming that all cobalt was reduced to the metallic state. The reduction was performed on a NETZSCH STA 449C analyzer equipped with an Aeolos QMS 403C mass spectrometer. The experiment has been done in a stream of argon with 5% H₂, heating the samples up to 900 °C with a rate of 10 °C min⁻¹. The reduction process was carried out in Al₂O₃ crucibles with percolated lid, a sample mass of 35 mg. The measurements were carried out with correction for the buoyancy force, i.e. blank experiments (base line) have been performed at the same conditions with empty crucibles. According to the results of the thermogravimetric reduction the composition of lanthanum–gadolinium cobaltite is close to the stoichiometry, $\delta \sim 0.01$.

The temperature dependence of static magnetization in the temperature range from room temperature to 900 K was measured in a magnetic field 5 kOe. The measurements were performed with a vibrating sample magnetometer VSM 7407 (Lake Shore Cryotronics). The relative measurement error was smaller than the linewidth in the experimental curves of the magnetic susceptibility.

3. Experimental data

Temperature dependence of La_{1-x}Gd_xCoO₃ ($x=0.2, 0.5, 1$) reciprocal magnetic susceptibility measured in a wide temperature range is shown in Fig. 1 (dark circles). The low-temperature region of GdCoO₃ has been studied previously [12,13] and the inverse susceptibility beautifully fits the antiferromagnetic Curie–Weiss

law

$$\chi_{Gd} = \frac{g_{Gd}^2 \mu_B^2 S(S+1)N}{3k_B(T-\theta)}, \quad (1)$$

where N is the number of Gd³⁺ ions per unit volume, $S=7/2$, and $g_{Gd}=2$, with the asymptotic Curie temperature $\theta \approx -5.3$ K, effective magnetic moment $\mu_{eff} \approx 7.91 \mu_B$ that is very close to the Gd³⁺ free ion $\mu_{eff}=7.94 \mu_B$. The Neel temperature of the antiferromagnetic Gd³⁺ spin ordering is equal to $T_N=3.3$ K. Using the mean field expression for the Neel temperature in the Heisenberg model, we can estimate the Gd–Gd exchange interaction parameter $J_{Gd-Gd} = -0.11$ K. Subtracting the Gd Curie–Weiss magnetic susceptibility from the measured one, we have obtained the Co³⁺ susceptibility. As expected, it is zero at low temperatures and increases at heating with a maximum at 100 K for LaCoO₃ and shift to 800 K for GdCoO₃.

4. Analysis of the magnetic susceptibility

The total magnetization of the La_{1-x}Gd_xCoO₃ substitutional solid solution can be presented as the sum of two terms: $M_{La_{1-x}Gd_xCoO_3} = M_{Gd} + M_{Co}$, where M_{Gd} and M_{Co} are the magnetizations of gadolinium and cobalt ions, respectively. To describe the contribution of Co³⁺ ions to the total magnetization of La_{1-x}Gd_xCoO₃, we consider the energy levels of Co³⁺ ions in the crystal field. The ground term is represented by low-spin singlet ¹A₁ separated from high-spin state ⁵T_{2g} by spin gap Δ_S . At $\Delta_S=150$ K and $x=0$, the term positions correspond to the data

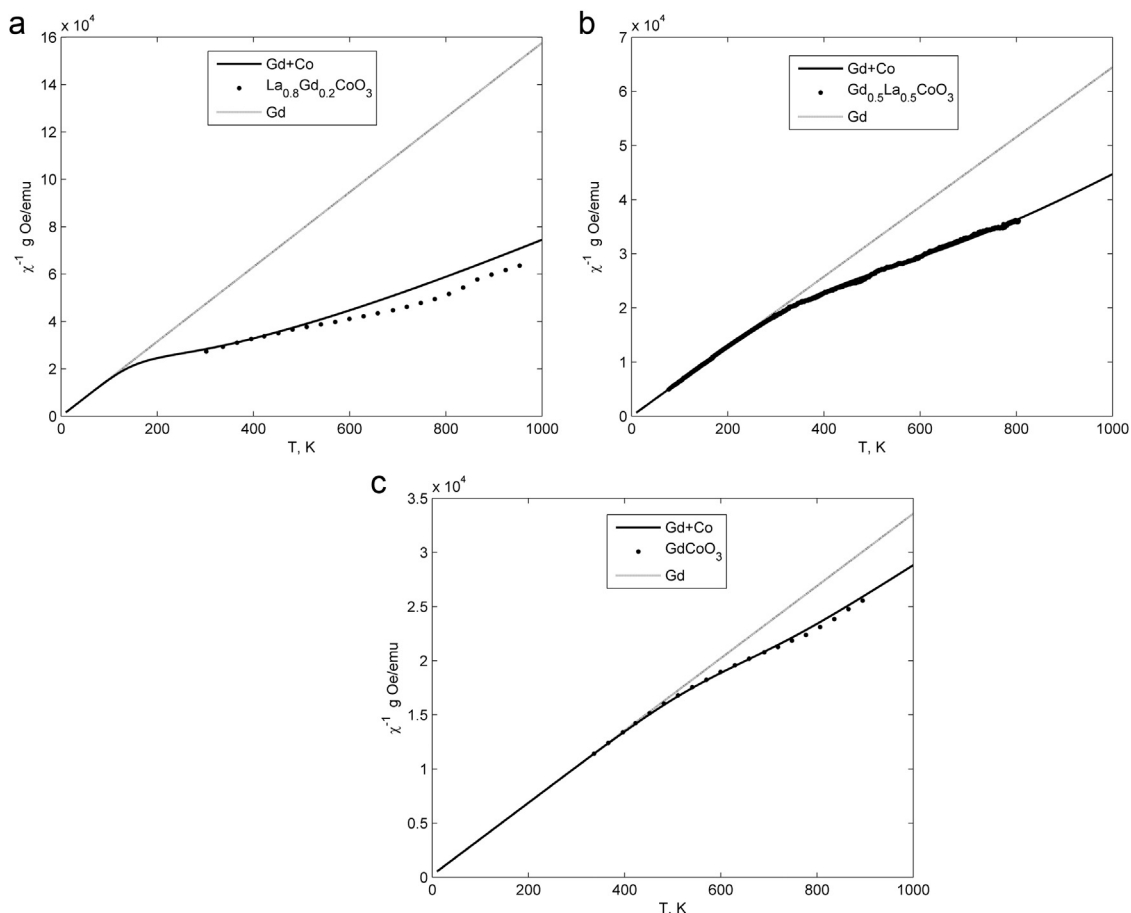


Fig. 1. Temperature dependence of La_{1-x}Gd_xCoO₃ $x=0.2$ (a); 0.5 (b); 1 (c) inverse magnetic susceptibility measured in a field 5 kOe (dark circles). Calculated $\chi_{La_{1-x}Gd_xCoO_3}^{-1}$ susceptibility (solid line) with the temperature dependent effective Co³⁺ magnetic moment [see Eq. (2)].

obtained for LaCoO_3 in Refs. [2,14,15]. The substitution of a certain rare-earth ion with a smaller ionic radius for lanthanum leads to the chemical pressure, which is equivalent to an external pressure. This substitution results in additional stabilization of a low-spin state, in other words, in an increase of the spin gap.

The expression for the molar magnetic susceptibility of cobalt may be obtained in the Curie–Weiss form with the effective Curie “constant” and temperature [9]

$$\chi_{\text{Co}} = N_A \frac{C_{\text{eff}}}{3k_B(T - \theta_{\text{eff}})} \quad (2)$$

$C_{\text{eff}} = g^2 \mu_B^2 S(S+1) n_{\text{HS}}$ is the effective Curie constant, depending on the population of high-spin state

$$n_{\text{HS}} = \frac{g_{\text{HS}} \exp(-\Delta_S/k_B T)}{1 + g_{\text{HS}} \exp(-\Delta_S/k_B T)}, \quad (3)$$

where $g_{\text{HS}}=15$ is the degree of degeneracy of the $^5T_{2g}$ term. The effective Curie temperature is equal to

$$\theta_{\text{eff}} = \frac{J_{\text{Co-Co}} z S(S+1)}{3k_B} n_{\text{HS}}.$$

Antiferromagnetic interaction $J_{\text{Co-Co}}$ between Co ions have previously been introduced in model calculations for the magnetic susceptibility of LaCoO_3 [15,16], and we adopt the similar approach for GdCoO_3 . According to Ref. [15], $J_{\text{Co-Co}} = -27.5$ K. We also have included the Gd–Co exchange interaction in the fitting procedure of the high- T magnetic susceptibility. The parameter $J_{\text{Gd-Co}}$ for GdCoO_3 was estimated to be less than 0.1 K. For high- T Co susceptibility, its contribution is negligibly small. For solid solutions $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ we have not reliable data for estimation $J_{\text{Co-Co}}$, $J_{\text{Gd-Gd}}$ and $J_{\text{Co-Gd}}$, that is why we take all $J=0$ for simplicity. As can be seen from these expressions, the effective magnetic moment of cobalt and the Curie temperature depends on temperature because the excited magnetic state HS is separated from the non-magnetic LS by the energy Δ_S . The temperature-dependent spin gap determines the Co^{3+} magnetic susceptibility. At low T , the concentration n_{HS} goes to zero and the magnetic susceptibility tends to zero also.

A prominent feature of the rare-earth cobaltites is their anomalous thermal expansion. According to Ref. [17], the temperature dependencies of the thermal expansion coefficient for LnCoO_3 with $\text{Ln}=\text{La, Dy, Sm, Pr, Y, Gd, and Nd}$ are not monotonic and have a maximum whose position correlates with features in the magnetic susceptibility and conductivity. The thermal expansion of the sample leads to an increase in Co–O bond length, and hence to a reduction of the spin gap Δ_S since the latter is determined by the crystal field $10Dq$. The analytic expression for the temperature dependence of the spin gap was proposed for a number of rare-earth cobaltites [17]. The energy $\Delta_S(T)$ was fitted by a power function

$$\Delta_S(T) = \Delta_0 \left[1 - \left(\frac{T}{T_S} \right)^n \right], \quad (4)$$

where Δ_0 is the spin gap at $T=0$ K, T_S is the spin crossover temperature where $\Delta_S(T_S) = 0$. T_S and n are the fitting parameters. According to Ref. [17] for GdCoO_3 $\Delta_0 = 2260$ K, $T_S = 717$ K, $n = 3.39$. Our recent estimation of the spin gap for GdCoO_3 at low temperatures using the Birch–Murnaghan equation [10] results in $\Delta_0 \approx 2000$ K, which agrees qualitatively with the data [17]. The solid lines in Fig. 1 show the results of calculating $\chi_{\text{La}_{1-x}\text{Gd}_x\text{CoO}_3}^{-1}$ with temperature dependent spin gap (4). Gd^{3+} contribution is shown by dashed curve. Temperature dependence of calculating χ_{Co} in $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ solid solutions using Eq. (2) and spin gap (4) is shown in Fig. 2. As it is seen the susceptibility maximum is shifted

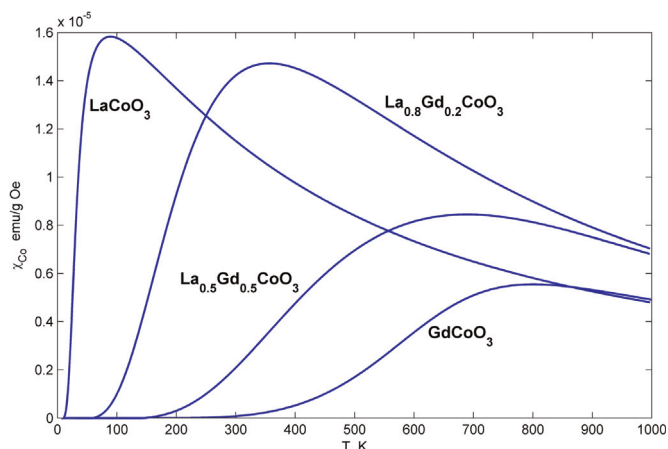


Fig. 2. Magnetic susceptibility of Co^{3+} ions in solid solutions $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$. Calculated Co^{3+} susceptibility obeys the Curie–Weiss law with the temperature-dependent effective magnetic moment [see Eq. (2)]. The susceptibility maximum is shifted to higher temperatures during the substitution of lanthanum by gadolinium with larger ionic radius.

Table 1

The parameters of the $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ magnetic susceptibility fit (see Eq. (4) for description of the parameters) for $x=0.2, 0.5, 1$.

	Δ_0 (K)	T_S (K)	n
$\text{La}_{0.8}\text{Gd}_{0.2}\text{CoO}_3$	600	600	3.5
$\text{La}_{0.5}\text{Gd}_{0.5}\text{CoO}_3$	1300	750	4
GdCoO_3	2300	800	4

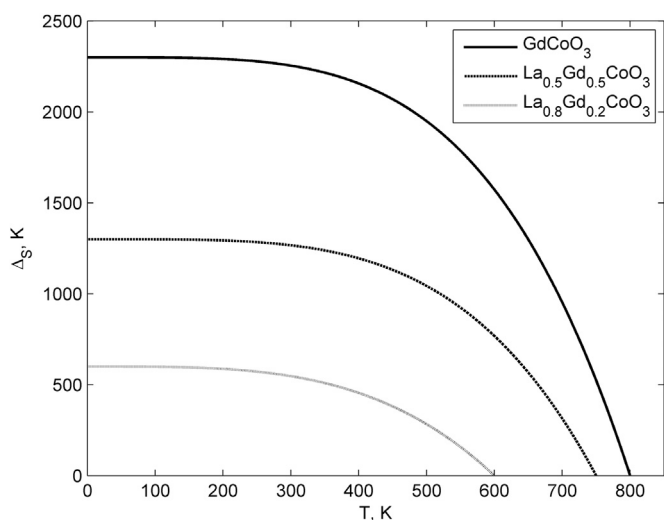


Fig. 3. Temperature dependence of the spin-gap Δ_S , obtained by fitting experimental magnetic susceptibility of $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ ($x=0.2, 0.5, 1$) with Eq. (4).

to higher temperatures during the substitution of lanthanum by gadolinium with larger ionic radius. The parameters of the susceptibility fit are summarized in Table 1. Fig. 3 shows the change of the spin gap with increasing temperature for these values. Parameters Δ_0 , T_S , and n for GdCoO_3 have been found by fitting the temperature-dependent Co^{3+} susceptibility both in Ref. [17] and here. Qualitatively, they are similar. The quantitative difference results from different assumptions for the excited magnetic state. In our paper, it is the HS state with degeneracy $g_{\text{HS}}=15$, while the LS state with $S=1$ was assumed in the model [17]. Using the Birch–Murnaghan equation of state we have estimated the value of chemical pressure and spin gap Δ_0 for the

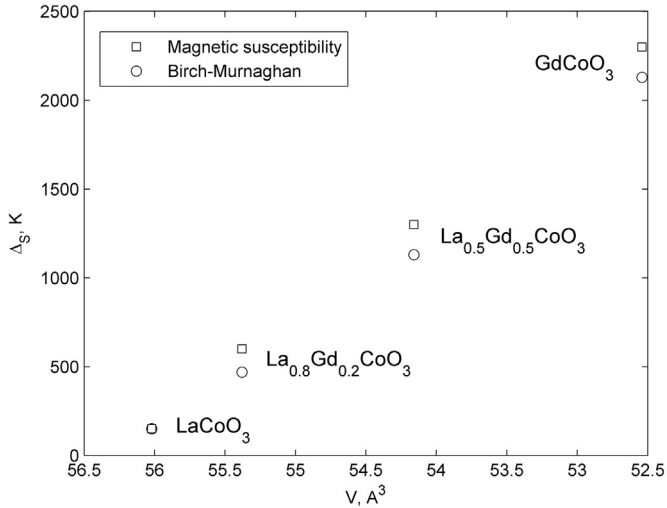


Fig. 4. Unit cell volume and the spin-gap Δ_0 of $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$.

considered concentration values of x in accordance with the experimentally measured unit cell volume of $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ (circles in Fig. 4). For comparison, by squares the figure shows the values obtained from magnetic measurements.

Spin gap Δ_0 is determined as the difference between the energies of high-spin (HS, $S=2$, $t_{2g}^4 e_g^2$) and low-spin (LS, $S=0$, $t_{2g}^6 e_g^0$) states, which can be represented in terms of the intraionic Racah (Coulomb interaction) parameters and crystal field $\Delta = 10 Dq$ ($E_{HS} = E_{HS}(at) - 4 Dq$, $E_{LS} = E_{LS}(at) - 24 Dq$). The Racah parameters for Co^{3+} for all $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ are assumed to be the same. Then, the dependence of Δ_0 on the interatomic distance is 2Δ

$$\Delta_0 = E_{HS} - E_{LS} = \Delta_{at} + 2\Delta, \quad (5)$$

where $E_{HS}(at)$, $E_{LS}(at)$ and $\Delta_{at} = E_{HS}(at) - E_{LS}(at)$ are given by the intraionic Coulomb energy. As a result of lanthanide compression, parameter Δ is different for various x in $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ and we can write

$$\Delta_0(\text{La}_{1-x}\text{Gd}_x\text{CoO}_3) = \Delta_0(\text{La}) + 2(\Delta(\text{La}_{1-x}\text{Gd}_x\text{CoO}_3) - \Delta(\text{La})). \quad (6)$$

Additional chemical pressure P induced by lanthanide compression can be determined from the Birch–Murnaghan equation [18,19]

$$P = \frac{3}{2}B_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4}(4 - B'_0) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}, \quad (7)$$

where B_0 and B'_0 are the empirical parameters having the meaning of the isothermal modulus of dilatation and its first pressure derivative (for LaCoO_3 , $B_0 = 150$ GPa, $B'_0 = 4$ [3]), respectively; V_0 is the unit cell volume of LaCoO_3 , and V is the unit cell volume for a given x in $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$. For LaCoO_3 we have $V_0 = 222.83 \text{ \AA}^3$, for GdCoO_3 $V = 210.2 \text{ \AA}^3$, therefore, $P = 9.81$ GPa. Lattice compression increases the crystal field, which can be represented as

$$\Delta(P) = \Delta(0) + \alpha_\Delta P. \quad (8)$$

The baric derivative α_Δ can be considered as an empirical parameter. This parameter has been determined by studying the spin crossover (transition from a high-spin into a low-spin state) in the ferroborate FeBO_3 , which has a similar type of chemical bond and a similar electronic structure formation mechanism [20].

For estimation, we assume that α_Δ for $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ is the same, i.e., $\alpha_\Delta = 0.018$ eV/GPa. Then, the spin gap in GdCoO_3 is $\Delta_0 \approx 2000$ K. The spin gap was estimated for other solid solutions $\text{La}_{1-x}\text{Gd}_x\text{CoO}_3$ from their unit cell volumes just the same procedure.

5. Conclusion

The magnetic investigation of the solid solution compounds $\text{La}_{1-x}\text{Gd}_x\text{CoO}_{3-\delta}$ have shown that there is a possibility to control the spin gap value by continuous change of the unit cell volume. From the magnetic data and Birch–Murnaghan equation we have obtained the spin gap value which is in a good agreement with non-linear interpolation between LaCoO_3 and GdCoO_3 values. The analytic expression for the temperature dependence of the spin gap has the same form as for a number of rare-earth cobaltites and their solid solution compounds.

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