Transport properties of cobaltites containing holmium

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Abstract. Dependences of electrical conductance of ceramic samples $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_3 – \delta$ and $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_3 – \delta$ on temperature and magnetic field are investigated in the interval from room to nitrogen temperatures and magnetic fields up to 7 kOe applied perpendicular to the dc current flow direction. Electrical conductivity of the samples has a character typical of a semiconductor while magnetoresistance shows a different sign varying from – 50% to + 120% in a narrow temperature interval at the same field. At low transport current, the resistance of the samples is nonlinear in the current. The magnitude of the resistance is highly sensitive to low magnetic field. Analysis of the data obtained suggests that under the condition of percolation conductivity, a magnetic contribution into the mechanism of correlation between electrons manifests itself, i.e., the states of $\text{Co}^{3+}$ ions with lowered ($S = 1$) spin, $t^2_2e^1_g$, or high ($S = 2$) spin, $t^2_2e^2_g$, exist. The corresponding activation energies are estimated.

Introduction

Wide researches on perovskite–like oxides of transition metals and compounds on their basis have shown that in these systems electron correlation is brightly shown, mainly defining their electronic properties. It has been established that such correlating factors as charge, spin, and orbital symmetry of the electrons in atoms of these materials lead to a big variety of states which depend on the character of magnetic and electrostatic interaction. Excepting HTSC, by present time the most widespread in a number of studied systems with correlating electrons are manganites (perovskites $\text{MnO}_3$) and cobaltites (perovskites $\text{CoO}_3$) doped by lantan, including those with partial replacement of lantan for rare earth metals Ba, Ca, and Sr. The attention to these systems is explained by their raised sensitivity to the factors coupling their magnetic and electronic states, and ability to manifest unique electronic properties such as giant or colossal magnetoresistance [1 – 3]. Here we have studied conductivity of cobaltites in which electronic orbitals of Ho and Sr act as factors capable to control spin state of ions $\text{Co}^{3+}$ from low–spin state (LS, $t^6_2e^0_g; S = 0$) up to high – spin state (HS, $t^2_2e^2_g; S = 2$), including intermediate – spin state (IS, $t^2_2e^1_g; S = 1$), subject to the type and concentration of rare earth dopants [4 – 7].

Results and discussion

Transport properties of ceramic samples $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_3 – \delta$ ($x = 0.45$ and 0.55) prepared by a standard technology of solid–phase synthesis [8] were investigated. Samples had the form of rectangular parallelepipeds, 0.25 × 0.55 × 2.5 cm$^3$ in size. Resistance measurements were performed by a four–probe method at dc current flow in a regime of stabilization and readout of temperature with a total error less than 10%.
a) **Conductivity in a zero magnetic field.**

In Fig. 1, dependence of the resistance typical for all the samples investigated on value of the transport current is shown. It clearly reveals a deviation from Ohm’s law at low currents. It is obvious that similar nonlinear effect which manifests itself as an increase in the resistance along a potential probes line while the current (electrical bias $eV$) is raised, is only possible under percolate character of transport in samples with cluster structure and tunnel conductivity of the branched chains of potential barriers between clusters, or under electronic phase stratification capable to result in macroscopic nonuniformities and in mixed conductivity of percolating type [9]. From the curve it can be seen that the region of ohmic conductivity is realized at the currents exceeding approximately 100 mcA which can be considered corresponding to a threshold of percolation in our materials.

Character of the temperature dependences of electric resistance of the samples, with values of $x$ investigated, in a zero magnetic field beyond a percolate threshold (at a dc current 10 mA) corresponds to the behaviour of the Arrenius function, i. e., in general is in line with an exponential semiconductor behaviour. However by detailed consideration of the dependences, important features which are convenient to analyze in logarithmic representation of curves (Fig. 2) were discovered. It is visible that in such representation the curves exhibit a nonlinearity, sensitivity to the concentration of doping elements and cannot be described by a single Arrenius function with an exponent $\sim T^{-1}$, as in case of ideal semiconductor systems with intrinsic conductivity. Attempts to describe conductivity of our compounds by universal exponential functions with exponents $\sim T^{-n}$ ($n < 1$) considering strong nonuniformity which causes effects of localization [10 – 12], also have appeared unsuccessful.

It means that we have not one channel of conductivity but at least two parallel channels, due to large–scale phase stratification of the system and percolate character of conductivity. In accordance with the model of two parallel channels, conductivity of a system $\sigma$ can be represented in the form of the sum of two independent contributions: first, considering the presence of HS states in a narrow hole band, $\sim F_1(T)$, and second, $\sim F_2(T)$, describing density of states in a conduction band of a semiconductor matrix [in proportion to $m$ and $(1 – m)$ taking into account that $\sigma \rightarrow \sigma_\infty$ for $T \rightarrow \infty$]. Then total resistance of the samples can be written as follows.

$$ R = R_\infty[mF_1 + (1 – m)F_2]^{-1}; \quad R_\infty = \sigma^{-1}_\infty(L/S) \quad (1) $$

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**Figure 1.** Typical dependence of resistance of prepared samples $Ho_{1-x}Sr_xCoO_{3-δ}$ vs. transport dc current.

**Figure 2.** Inverse temperature dependences of resistance of samples in logarithmic units. Points – experiment, solid lines – description of the experiment by expression (2) (for explanations see text).
(L and S are the length and cross section of the sample, respectively). As $F_1$, we have chosen a known expression for the conductivity proportional to the concentration of ions Co thermally excited to the HS state [5]:

$$F_1 = \nu / [\nu + \exp(\Delta_1/T)]$$

($\Delta_1$ – spin gap in a spectrum of LS and HS ionic states; $\nu = 15$ is a multiplicity of the HS state), and as $F_2$ – common Arrenius relation $F_2 = \exp(-\Delta_2/T)$ for conductivity of a zone semiconductor. In the Table we show the values of fitting parameters and their relative errors. The latters are such deviations of the quantities from the indicated ones which leave the position of curves calculated in accordance with Eq. (1) at any point in the limits of an experimental error.

| $x$ | $R_\infty, \Omega$ | $\Delta_1, K$ | $\Delta_2, K$ | $m$ |
|-----|---------------------|----------------|----------------|-----|
| 0.45 | 0.105 ± 2%          | 2500 ± 0.5%   | 844 ± 0.5%     | 0.005 |
| 0.55 | 0.95 ± 0.5%         | 2500 ± 0.5%   | 690 ± 0.7%     | 0.005 |

The value of $\Delta_1$ shows that at comparable concentrations of the second dopant, Sr, which activates HS ions Co$^{3+}$, in particular, ions Co$^{4+}$ ($t_{2g}^2 e_g^2$) [13], the density of hole states realized by double exchange interaction between the ions Co$^{3+}$ and Co$^{4+}$, cannot be large, because of significant activation energy of HS ionic states under wide $t_{2g} - e_g$ gap. Normalized number ($F_1$) of thermally excited ions Co$^{3+}$ varies for Ho$_{0.55}$Sr$_{0.45}$CoO$_{3-\delta}$ from $F_1 = 4 \cdot 10^{-8}$ (for Ho$_{0.45}$Sr$_{0.55}$CoO$_{3-\delta}$ – from $1 \cdot 10^{-5}$) at heating from temperature $T_c \approx 150$ K, accepted for the temperature of transition into a paramagnetic state and the beginning of double exchange interaction, up to $F_1 = 3.7 \cdot 10^{-2}$ at $T \sim 300$. Concentration $n_h$ of the holes participating in double exchange interaction, can be received from the expression [14]:

$$k_B T_c = n_h \xi \Delta_1$$

(2)

where $\xi$ is the number of the nearest oxygen ions. For Ho$_{0.55}$Sr$_{0.45}$CoO$_{3-\delta}$ $n_h = 0.98$ at. % and for Ho$_{0.45}$Sr$_{0.45}$CoO$_{3-\delta}$ it consists 1. 2 at. %.

**Figure 3.** Magnetoresistance of the sample Ho$_{0.45}$Sr$_{0.55}$CoO$_{3-\delta}$

**Figure 4.** Magnetoresistance of the sample Ho$_{0.55}$Sr$_{0.45}$CoO$_{3-\delta}$

b) Magnetoresistance

In an external magnetic field $H$, conductivity of ceramic samples Ho$_{1-x}$Sr$_x$CoO$_{3-\delta}$ with investigated concentrations of Sr reveals a specific behaviour appearing already in low fields. In Figs. 3 and 4, magnetoresistance (MR) of the samples is presented as a ratio $\Delta R/R_0 = [\rho(H) - \rho(0)]/\rho(0)$ depending on a magnetic field. It is seen that the most typical features of
MR, such as change of sign and great changes in the MR value, are basically shown in low fields (up to 1 kOe) and at high enough temperatures (not below, approximately, 150 K).

All this specifies that the electronic phase state of the studied chemical compounds essentially depends on their magnetic state which structure is defined by a character of spin ordering. The ordering is established, as an analysis of the system $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, for example, shows, under the action of a competition between antiferromagnetic (between localized $t_{2g}$ states) and ferromagnetic (of jump type, between $e_g$ states) interactions [15]. The most impressive are effects at a room temperature when applying a magnetic field of only 1 kOe leads to the occurrence of negative magnetoresistance, i. e., to excluding a certain mechanism of electron scattering from the magnetic (spin) disorder. This circumstance suggests that in our samples magnetic structure of ferromagnetic clusters is available, with magnetic moments (spins) randomly aligned in zero magnetic field. Ability of that spin structure to be reconstructed already in a low field testifies to its magnetic instability which fact is additionally confirmed by high sensitivity of the magnetic structure to charge ordering of the system. Namely, with decreasing the concentration of the dopant Sr by 10 %, negative MR at $T \approx 295$K changes by an order of magnitude, from $-3 \%$ (Fig. 3) up to $-50 \%$ (Fig. 4). When temperature is reduced by $20 \div 30$K magnetoresistance changes a sign, becoming positive and reaching $+120 \%$, and at $T = 78$K MR practically disappears (Fig. 4). The nature of this effect is not absolutely clear, and we hope that it will manage to be cleared at studying thermopower.

Conclusion
Dependences of electrical conductance of ceramic samples $\text{Ho}_{0.55}\text{Sr}_{0.45}\text{CoO}_3-\delta$ and $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_3-\delta$ on temperature and magnetic field are investigated in the interval from room to nitrogen temperatures and magnetic fields up to 7 kOe applied perpendicular to the dc current flow direction.

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