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# Magnetic and magnetotransport properties of $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me=Cr, Fe) cobaltites

**Keywords:** magnetic interactions; magnetization; magnetoresistance; metal-insulator transition

## 1. Introduction

Perovskite oxides of transition metal ions are of particular interest due to unusual magnetic and transport properties. Cobaltites of $RCoO_3$ systems (R – rare earth ions) have attracted special attention because of additional degree of freedom provided by different spin configurations. The most known member of this family $LaCoO_3$ has been intensively studied for more than six decades [1-6].

Comparable influence of the intra-atomic Hund's exchange energy and the crystal field splitting causes a flexibility in spin-states of $Co^{3+}$ ions in $LaCoO_3$. There are three possible spin states of the cobalt ions with $3d^6$ configurations - low-spin state with $S=0$, an intermediate-spin state with $S=1$ and a high-spin state with $S=2$.

Besides the extra degree of freedom caused by spin-state flexibility, the substituted cobaltites $R_{1-x}A_xCoO_3$ (A – alkali earth ions) have attracted great attention due to other phenomena i.e. a competition between ferromagnetism, antiferromagnetism and cluster-glass ground state, giant magnetoresistance as well as phase separation [1-7]. The origin of the ferromagnetism in the metallic cobaltites remains the subject of discussions for a long time.

It is considered than ferromagnetic coupling between cobalt ions being in 3+ and 4+ oxidation states is coused by double exchange interaction [8]. However some compounds having only homovalent Co ions like $SrCoO_3$, $SrFe_{1-x}Co_xO_3$ and $LaCo_{1-x}Ni_xO_3$ show metallic behavior and ferromagnetism [9-12]. Epitaxially strained $LaCoO_3$ thin films also exhibit long-range ferromagnetic order below 85 K [13].

The available studies do not definitely solve the issue of the origin of magnetic interactions in cobaltites.

The substitution of Co ions can modify the magnetic ordering and facilitate understanding the origin of the ferromagnetic state as well as estimating the spin state of the Co ions. The effect of the substitution of Co ions by Cr ones in $La_{0.5}Ba_{0.5}Co_{1-x}Cr_xO_3$ system has been studied in Ref. [14] where an increase of the Curie point from 189 K (x = 0) up to 205 K (x = 0.1) has been reported. The change in the Curie point has been attributed to the double exchange interactions between cobalt and chromium ions. In the actual study we declare contrary effect caused by a substitution of cobalt ions by Cr, Fe ones in $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ system.

## 2. Experimental procedures

$La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me = Cr, Fe) ceramics and the parent compound $La_{0.5}Sr_{0.5}CoO_3$ were prepared by solid state reaction. High purity oxides $La_2O_3$, $Co_3O_4$, $Cr_2O_3$, $Fe_2O_3$ and carbonate $SrCO_3$ were taken in stoichiometric ratio and thoroughly mixed in planetary mill Retsch-PM100; the mixture were annealed in air at 1270 K for 10 h. After regrinding, the samples were annealed in air at 1470 – 1600 K for 10 h and slowly cooled at a rate of 15 C/h. Step-scanned powder X-ray diffraction data were recorded at room temperature using DRON-3M diffractometer with Cu-$K_\alpha$ radiation. The diffraction data were analysed by the Rietveld method using the Full Prof software package. The structural data testified a formation of the single phase compounds with perovskite-like structure. The magnetic and transport properties of the samples were investigated using PPMS set-up (Cryogenic Ltd) in magnetic fields up to 14 T and temperature range of 5 – 320 K. Resistivity measurements were carried out using standard four-probe technique.

## 3. Experimental results

The results of X-ray diffraction measurements indicate that all studied samples are characterized by single phase rhombohedral perovskite structure (space group R-3c). The estimated structure of the parent compound $La_{0.5}Sr_{0.5}CoO_3$ is in agreement with that declared in the earlier reports [15]. The chemical substitution by cobalt ions does not lead to significant modification of the unit cell parameters particularly the bond angle Co – O – Co and the bond length Co – O. Herein, the lattice degree of freedom can be ignored while considering the magnetic and electrical transport behavior for different Cr and Fe doped samples.

Figure 1 shows the magnetization as a function of temperature measured for parent compound and $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me = Cr, Fe) solid solutions in magnetic field of 0.01 T. The $La_{0.5}Sr_{0.5}CoO_3$ compound undergoes a paramagnetic to

ferromagnetic state transition at $T_C$ of 248 K. Chemical substitution leads to notable decrease of the Curie point. Less pronounced decrease of the Curie point is observed for $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ compound ($T_C$ = 215 K) while drastic reduction of the ferromagnetic state is detected in $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ compound (inflection of the magnetization curve is observed at T = 60 K).

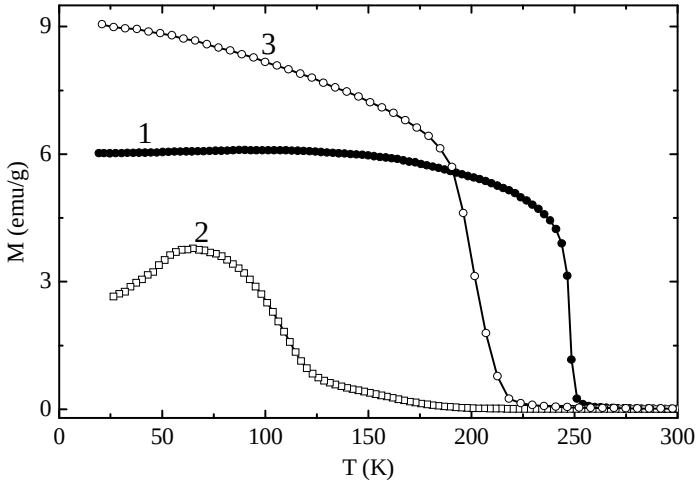


**Fig. 1.** Field-cooled magnetization of the $La_{0.5}Sr_{0.5}CoO_3$ (1) and $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ compounds (Me = Cr (2), Fe (3)) recorded in magnetic field of 0.01 T

The magnetic hysteresis loops measured at 30 K (Fig. 2) well correlate with the temperature dependencies of magnetization of $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me = Cr, Fe) solid solutions. The initial cobaltite and Fe-doped compound have very close spontaneous magnetization around 2 $\mu_B$ per formula unit. The spontaneous magnetization for the chromium doped composition is much lower and 0.45 $\mu_B$ per formula unit. The magnetization curves of the doped compounds are not saturated even in the magnetic fields up to 14 T thus indicating the presence of clusters with negative magnetic interactions.

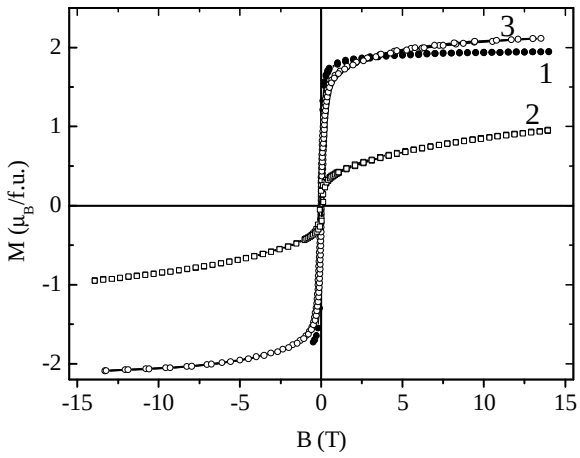


**Fig. 2.** Magnetic hysteresis loops of the $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ compounds (Me = Cr, Fe) obtained at T=10 K

Figure 3 shows the temperature dependencies of the resistivity of $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ compounds obtained in zero field and in magnetic fields of 13 – 14 T. The initial compound has metallic-type temperature dependence of resistivity while the value of resistivity is quite low (1-2*$10^{-4}$ Ohm*cm). The change in the slope of the resistivity curve is observed near the Curie temperature though the dependence remains to be metallic-type. Decrease of resistivity is probably caused by reduced spin-disorder scattering in the magnetically active phase. It is seen that substitution of the cobalt ions by chromium ones leads to drastic changes of magnetic and transport properties of the compound and the resistivity dependence of the $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ testifies semiconductor-type behavior.

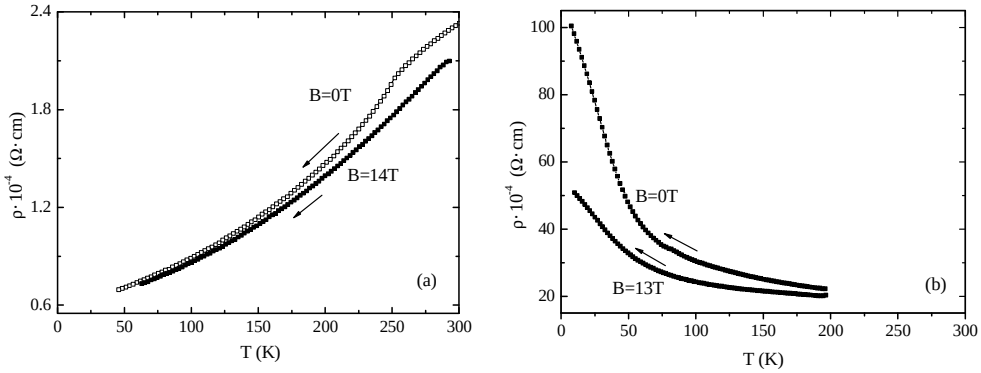


**Fig. 3**. Temperature dependencies of resistivity of the for $La_{0.5}Sr_{0.5}CoO_3$ (a) and $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ (b) compounds measured in zero-field and in magnetic field of 13-14 T.

Figure 4 shows the field dependence of magnetoresistance for $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ compound calculated in accordance with the following formula MR%=[R(H)-R(0)]/R(0)*100% where R(H) is the resistivity in magnetic field. One can see that maximal magnetoresistance is at low temperatures. It should be noted that even in the large magnetic fields there is no tendency to the saturation.

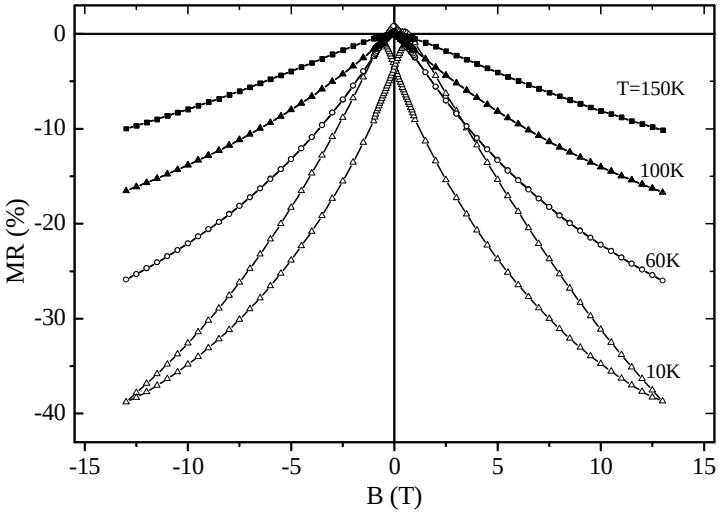


**Fig. 4.** Magnetoresistance dependencies of the $La_{0.5}Sr_{0.5}Co_{0.8}Cr_{0.2}O_3$ compounds measured at different temperatures

Moreover, a large magnetic hysteresis is observed at low temperature. Magnetoresistance and magnetic hysteresis strongly decrease with temperature growth. We suppose the large negative magnetoresistance at low temperatures (where intermediate spin state is destabilized) is associated with antiferromagnet–ferromagnet transition induced in antiferromanetic clusters by external magnetic field. This suggestion is in agreement with the magnetoresistance results published in the earlier works [15, 16]. According to Ref. [16] the antiferromagnetic phase in the perovskite-like cobaltites is characterized by significantly larger resistivity than that attributed to the ferromagnetic one. Apparently the ferromagnetic and antiferromagnetic phases contain cobalt ions in different spin states [15, 16].

The ferromagnetic character of coupling between iron and cobalt ions (Figs. 1 and 2) is most probably caused by specific electronic state of these ions. Mössbauer spectroscopy and magnetization measurements performed on the $La_{0.5}Sr_{0.5}Co_{0.978}{}^{57}Fe_{0.022}O_3$ compound [17] have testified that iron ions are formally in 4+ valent state with high-spin configuration. Such electronic configuration is associated with metallic conductivity and assumes partial delocalization of the $e_g$-electrons, e.g. $SrFe_{1-x}Co_xO_3$ compounds with $x > 0.3$ are metallic ferromagnets with Curie point above room temperature [11]. The small antiferromagnetic component

(Fig. 1 and 2) is most probably associated with $Fe^{3+}$-enriched clusters while the superexchange interactions between $Co^{3+}$ and $Fe^{3+}$ ions are strongly antiferromagnetic [18]. The magnetization and the Curie point of chromium doped sample are minimal among the considered compounds (Figs. 1 and 2). This is probably caused by strong antiferromagnetic coupling between chromium and cobalt ions. The antiferromagnetic type of the interactions between chromium and cobalt ions points on the dominance of superexchange interactions as the double exchange interaction lead to ferromagnetic coupling.

## 4. Summary

Magnetic and magnetotransport properties of $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me = Cr, Fe) perovskite-like cobaltites with stoichiometric compositions were studied. It is shown that the substitution with Fe ions does not strongly affect spontaneous magnetization and the Curie point. In contrast, chromium substitution leads to dramatic decrease of magnetization, Curie point and strongly modifies the temperature dependence of magnetization. The magnetization data are discussed assuming positive magnetic interactions between Co and Fe ions, while magnetic interactions between Co and Cr are considered to be negative. Substitution of Co by Cr ions strongly increases magnetoresistance at low temperature and causes metal-insulator transition. Drastic increase of magnetoresistance seems to be caused by antiferromagnet-ferromagnet transition induced by strong magnetic field.

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## Abstract

Magnetic and magnetotransport properties of $La_{0.5}Sr_{0.5}Co_{0.8}Me_{0.2}O_3$ (Me = Cr, Fe) stoichiometric cobaltites has been investigated in magnetic fields up to 14 T. It is shown that doping with Fe ions changes spontaneous magnetization only slightly herewith the Curie point significantly decreases. The chromium doping leads to dramatic decrease of magnetization and the Curie point and a strong increase in magnetoresistance at low temperature. The obtained results indicate that the magnetic interactions between Co and Fe are positive whereas those between Co and Cr ions are negative. Enhancement of magnetoresistance is attributed to the magnetic field induced transition from antiferromagnetic order to ferromagnetic one.

## Streszczenie

Właściwości magnetyczne i magnetotransportowe stoichiometrycznych kobaltytów zbadano w polach magnetycznych do 14T. Ustalono, że domieszkowanie przez jony Fe zmienia namagnesowanie spontaniczne bardzo słabo w tym czasie jak punkt Curie obniża się znacząco. Domieszkowanie przez atomy chromu powoduje dramatyczne zmniejszenie namagnesowania i obniżenie punktu Curie i mocny wzrost magneto rezystancji w niskich temperaturach. Otrzymane rezultaty wskazują oddziaływanie magnetyczne pomiędzy Co i Fe jest pozytywne w tym czasie jak pomiędzy Co a Cr jest negatywne.

Wzmocnienie magnetorezystancji przypisano do pola magnetycznego indukowanego przejściem z antyferromagnetycznego układu do ferromagnetycznego.

**Słowa kluczowe:** Oddziaływania magnetyczne; namagnesowanie; magnetorezystancja; przejście metal-izolator