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Neutron diffraction studies of $La_{1-x}Sr_xCoO_3$ magnetic structure at $x=0.15$ and 0.3

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Abstract

Neutron powder diffraction and zero-fields μSR studies of $La_{1-x}Sr_xCoO_3$ with $x = 0.15$ and 0.3 has been performed. Only compound with Sr concentration $x = 0.3$ shows ferromagnetically ordered state at low temperature. Values of Co magnetic moments have been refined.

Keywords: Cobaltites; Neutron diffraction; μSR; Ferromagnetism

The discovery of colossal magnetoresistance effect (CMR) in the manganites with perovskite structure stimulated the interest to the new perovskite-type compounds other, than $LaMnO_3$. A large magnetoresistance was obtained in $La_{1-x}Sr_xCoO_3$ with $0.15<x<0.2$ [1]. However, ferromagnetic ordering in $La_{1-x}Sr_xCoO_3$ does not lead to a metal–insulator transition like in CMR materials [2,3]. In addition, these compounds are of industrial interest because of their catalytic properties and possibilities to use them as electrode material in solid-oxide fuel cell and as a membrane in oxygen separation processes [4]. However, magnetic structure dependence on Sr doping level is still not clear (compare, for example, [3,5]). Undoped $LaCoO_3$ does not contain Co^{4+} and is paramagnetic. Magnetic moment appears when strontium substituted for lanthanum and converts Co^{3+} to Co^{4+}. According to Goodenough model [7,9] tetravalent cobalt ions polarize neighbouring Co^{3+} ion through the intermediate oxygen ion to the high spin state, Co^{3+}–O^{2-}–Co^{4+}. This interaction induces ferromagnetism of $La_{1-x}Sr_xCoO_3$. Authors of Ref. [10] predicted appearance of spin glass at $x<0.18$ due to competition between Co^{3+}–Co^{4+} double exchange and long range RKKY mechanisms. In this work we studied the magnetic structure of $La_{1-x}Sr_xCoO_3$ at $x = 0.15$ and 0.3.

Solutions of strontium and cobalt nitrates were prepared by dissolving of the corresponding nitrates in distilled water. Solution of lanthanum nitrate was prepared by dissolving of lanthanum oxide in nitric acid. The obtained solutions were characterized by EDTA titration. Obtained solutions were mixed together with the cation ratio corresponding to the stoichiometry of the $La_{1-x}Sr_xCoO_3$, $x = 0$, 0.15, 0.3. Solutions were frozen by spraying through a pneumatic nozzle into liquid nitrogen. After evaporation of nitrogen the metal trays with the frozen granules were transferred onto the shelves of an SMH-15 freeze-drier (Usifroid) precooled to 200 K. Freeze-drying was carried out at $p = 4\times10^{-2}$ mbar for 48 h while the temperature of the heating shelves was raised from –50°C to +50°C. The obtained powder was decomposed in air at 250°C. The product was re-grinned, pressed into pellets and annealed at 500°C in air followed by final treatment at 1000°C for 24 h. The samples were stoichiometric. There were no any impurities according to the X-ray analysis.

X-ray powder diffraction (XRD) patterns of all specimens were recorded with an FR-552 focusing camera using $CuK\alpha_1$ radiation with germanium as an internal standard ($a = 5.6574$ Å). Neutron diffraction experiments were carried out on DMC spectrometer of the SINQ neutron source in Paul Scherrer Institute.

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Table 1
Structural parameters for $La_{1-x}Sr_xCoO_3$ at $x = 0.15$ and 0.3 obtained at different temperatures with the DMC diffractometer

	$T = 15$ K		$T = 60$ K		$T = 110$ K		$T = 260$ K	
	0.15	0.3	0.15	0.3	0.15	0.3	0.15	0.3
a (Å)	5.446(4)	5.429(2)	5.449(3)	5.430(2)	5.444(4)	5.431(2)	5.449(3)	5.440(2)
c (Å)	13.094(6)	13.131(2)	13.097(2)	13.136(2)	13.111(6)	13.146(2)	13.139(3)	13.179(3)
Oxygen x	0.452(1)	0.459(1)	0.451(1)	0.459(1)	0.452(1)	0.462(1)	0.453(1)	0.459(1)
μ (μ_B)	—	3.3(1)	—	0.6(1)	—	0.3(1)	—	—

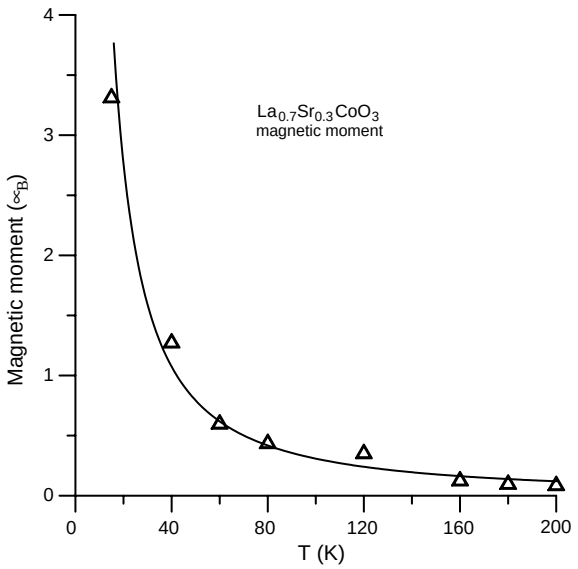

Fig. 1. Temperature dependence of the magnetic moment in $La_{0.7}Sr_{0.3}CoO_3$.

Incident neutron wavelength was $\lambda = 2.56$ Å, data were collected in the temperature range from 15 to 280 K.

Structural analysis of diffraction patterns was performed with FullProf Rietveld analysis program [6]. All peaks for both samples can be indexed in the hexagonal R–3c space group. Co occupies 6(b) site (0 0 0), La(Sr) is in 6(a) site (0 0 $\frac{1}{4}$), O is in 18(e) site (x 0 $\frac{1}{4}$). All refined parameters are listed in Table 1.

A ferromagnetic ordered Co magnetic moments present only in the sample with Sr concentration $x = 0.3$. Fig. 1 shows values of magnetic moment for different temperatures. The data for $La_{0.7}Sr_{0.3}CoO_3$ sample is in a good agreement with magnetic measurements performed in Ref. [7]. According to them the Curie temperature is equal to $\sim$240 K, and [Co^{4+}] concentration is approximately equal to 0.25. However, there is no magnetic ordering in $La_{0.85}Sr_{0.15}CoO_3$. It can be connected with the oxygen nonstoichiometry. The formation of oxygen deficiency can lead to the interruption in formation of ferromagnetic chains [7,10]. Compounds with low values of Sr concentration are especially sensitive to oxygen content [10].

In addition the μSR experiment was performed at GPD spectrometer in PSI in zero external magnetic field and the temperature range from 7 to 200 K. Muon spin precession has not been observed. This can be interpreted by presence of the local structural heterogeneities and fluctuations connected with heterogeneous distribution of oxygen, which mentioned in series of works [3,7,8].

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