

NEUTRON DIFFRACTION STUDY OF LAYERED PEROVSKITE $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ ¹M. Dlouhá^{2,*}, S. Vratislav^{*}, A. Chichev^{*}, Z. Jiráček[‡]^{*}Nuclear Sciences and Physical Engineering CTU, Břehová 7, 115 19 Prague 1, Czech Republic[‡]Institute of Physics of ASCR, Cukrovarnická 10, Prague 6, Czech Republic

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The layered cobaltite system $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ has been prepared in the range from $x = 0$ (pure Co^{3+}) up to $x = 0.4$ (40 % Co^{4+}). Analogously to the pseudocubic perovskites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, a ferromagnetic moment is induced with increasing x . Its presence is evidenced by neutron diffraction study performed on sample $x = 0.4$ at low temperatures. The relatively low magnitudes of cobalt moments ($0.7 - 0.8\mu_B$) suggest that the ferromagnetic ordering is not complete and significant part of the sample remains in a paramagnetic or spin-glass state.

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1 Introduction

The mixed-valent transition metal oxides of perovskite type are solids with an extreme diversity of structural, magnetic and electronic properties. As a typical example in the case of cobaltites can be taken the pseudocubic system $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. Upon the strontium doping, the non-magnetic and insulating phase of the $x = 0$ composition (pure Co^{3+} system) transforms first into an inhomogeneous state consisting of ferromagnetic clusters embedded in the diamagnetic matrix. When reaching $x \sim 0.25$ (formal concentration 25 % Co^{4+}), the system forms a bulk ferromagnetic state of metallic-like character [1]. The conductivity gradually increases and achieves maximum for about $x \sim 0.5$, which is the actual strontium solubility limit under normal conditions.

2 Experiment

In order to investigate the effects of lower dimensionality, we have prepared a related layered-type $\text{Co}^{3+}/\text{Co}^{4+}$ system $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ up to maximum possible composition $x = 0.4$ (see also [2, 3]) by the following method. La_2O_3 , SrCO_3 and Co_2O_3 were mixed with the proper molar ratios and the mixture was calcined at 600°C for 8 h. The resulting powder was ground and pressed into pellets and annealed at 1000°C for 108 h in an oxygen atmosphere.

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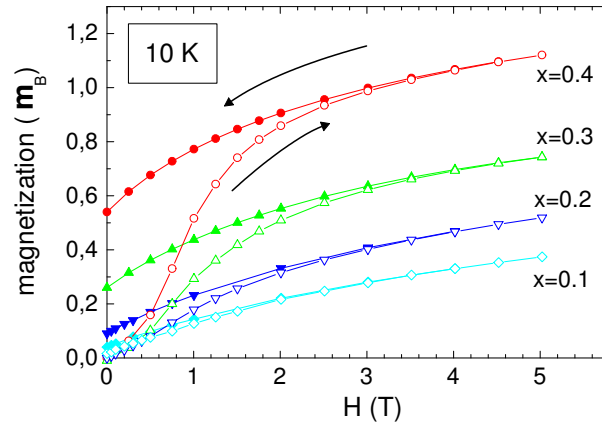


Fig. 1. Magnetization curves of $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$.

Magnetic measurements (Fig. 1) reveal a rapid increase of magnetic moments with increasing strontium content and suggest that for $x = 0.4$ (40 % Co^{4+}) the spontaneous magnetization makes about $0.8\mu_B$ per Co. The observed value is about twice as lower than expected for ferromagnetically ordered Co^{3+} ions in the intermediate spin state ($S = 1$) and Co^{4+} ions in the low spin state ($S = 0.5$) ions. This suggests a more complex, possibly non-uniform magnetic state, which led us to a neutron diffraction investigation of the $x = 0.4$ compound.

Power neutron diffraction study of the $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ sample was carried out at the room and 16 K temperatures on the DN-12 diffractometer at IBR-2 in LNF JINR, Dubna and on the diffractometer KSN-2 in LND of Faculty of Nuclear Sciences and Physical Engineering, TU, Prague. High-pressure study is planned for near future. The experimental data were analysed by the Rietveld-type MRIA and FullProf programs [4,5].

3 Results

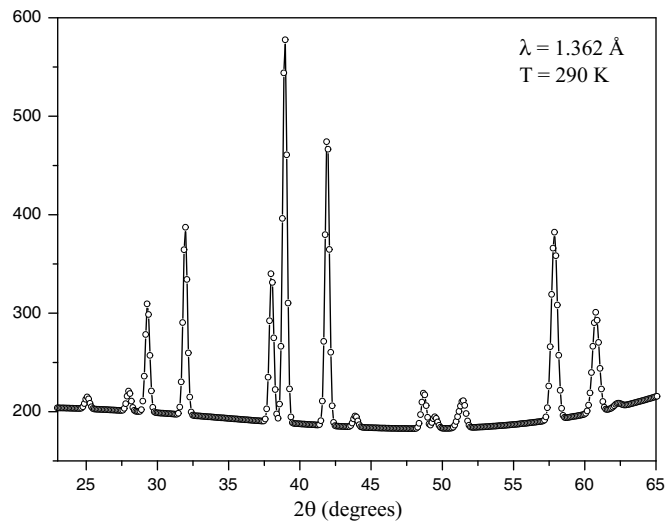
The system $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ has so-called Ruddlesden-Popper type of crystal structure. It can be viewed as a stacking of separated CoO_6 octahedral layers instead of the three dimensional network in common perovskites.

The neutron-diffraction pattern of $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ at room temperature is shown in Fig. 2. The time-of-flight spectra of the same compound are shown in Fig. 3. The refined structural parameters are given in Tab. 1.

The time-of-flight spectra of $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ at 16 K do not show any new line that could be ascribed to an antiferromagnetic order. However, a clear ferromagnetic contribution can be revealed by a closer inspection of Fig. 3 (d), where observed intensity at reflection position (103) exceeds markedly the calculated one. Absence of ferromagnetic contribution at the diffraction peak (004) reveals that the magnetic moments of cobalt ions are oriented perpendicular to the CoO_6 octahedral layers. Their calculated magnitudes amount to $0.7\mu_B$ per Co, which is in excellent agreement with the above mentioned magnetization data.

Tab. 1. The Structural parameters of $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ (space group I4/mmm).

T	T=290 K	T= 16 K
a [nm]	0.37893(3)	0.37837(3)
c [nm]	1.2514(13)	1.2456(15)
V [nm^3]	0.17969	0.17831
z (La/Sr)	0.3589(3)	0.3591(3)
z (O)	0.1604(3)	0.1601(3)
Rp [%]	2.58	2.73
Rb [%]	7.83	7.78
Rw [%]	2.44	2.69
Re [%]	2.69	3.16

Fig. 2. Neutron-diffraction pattern of $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ on the KSN-2 diffractometer at T= 290 K.

4 Conclusion

The neutron diffraction study evidences a presence of the long range ferromagnetic order in $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ at low temperatures. The relatively low magnitude of cobalt moment ($0.7 - 0.8\mu_B$) suggest that the magnetic state is in fact non-uniform. It consists of ferromagnetic regions aligned by strong $\text{Co}^{3+} - \text{O} - \text{Co}^{4+}$ double exchange interactions, which coexist with paramagnetic or spin-glass regions.

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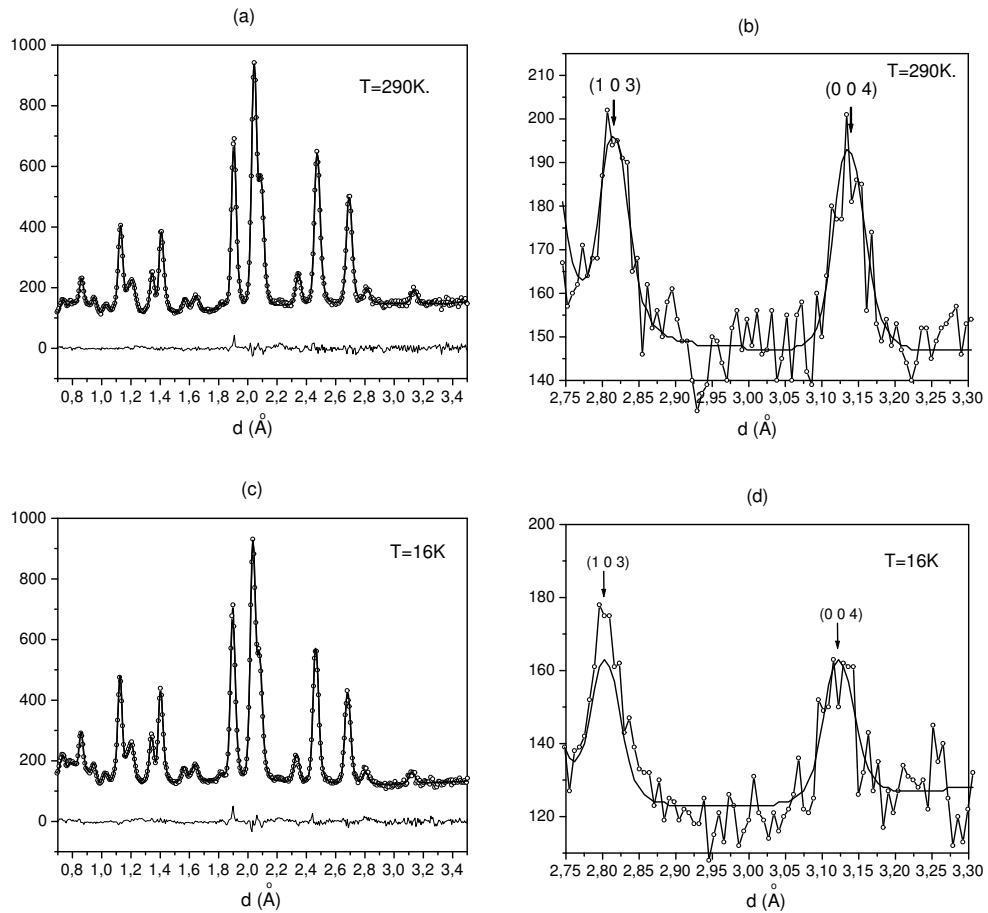


Fig. 3. The TOF neutron-diffraction pattern of $\text{La}_{0.6}\text{Sr}_{1.4}\text{CoO}_4$ measured on the diffractometer DN-12 at $T = 290\text{ K}$ (a), (b) and $T = 16\text{ K}$ (c), (d).

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