Conclusions

A setup for combined X-ray diffraction and fluorescence analysis has been developed. The technique was tested on a microstructure of gold on silicon substrate and by measuring a meteoritic material. The presented technique can be used for investigations of samples with large area, specifically multilayer structures, thin surface layers, powders, ceramics, for depth profile analysis where the knowledge of the definite component is required. The usage of glass monocapillary allows to increase the integral intensity of the beam and to raise signal/background ratio. The technique proved its efficiency while investigating meteoritic material, during which a phase impurity of homogeneous composition, corresponding to pure iron, was detected.

Acknowledgements

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NEUTRON DIFFRACTION STUDY OF $La_{0.6}Sr_{1.4}CoO_4$ AT HIGH PRESSURE UP TO 4.3 GPa

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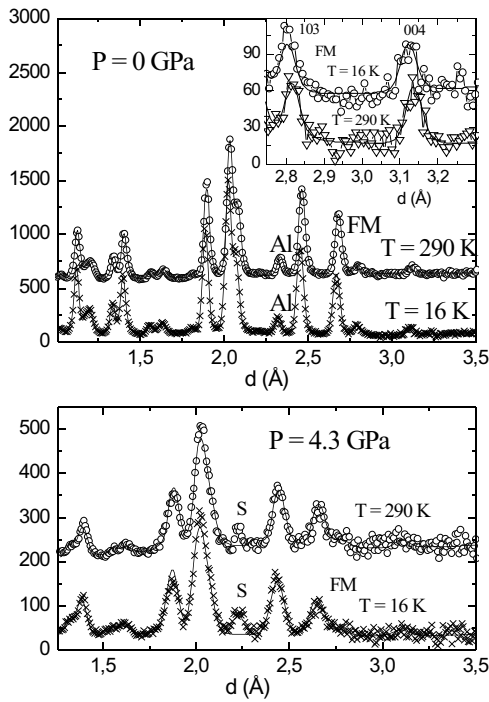
Keywords:

neutron diffraction, high pressure, mixed-valent cobalt oxides, structural and magnetic properties

Abstract

The structural and magnetic properties of the layered cobaltite $La_{0.6}Sr_{1.4}CoO_4$ have been studied by the neutron diffraction at the temperature range 16-290 K and high-pressure up to 4.3 GPa. The observed spectra of $La_{0.6}Sr_{1.4}CoO_4$ at 16 K have not shown any new line that could be a signature of an antiferromagnetic order. The ferromagnetic contribution to some diffraction peaks reveals that the magnetic moments are oriented perpendicular to the CoO_6 octahedral layers and their magnitude are increase from 0.7 $_B$ at ambient pressure to 0.9 $_B$ at 4.3GPa. The calculation of the linear compressibilities ($k_i = -(1/a_{i0})(da_i/dP)_T$) shows that the lattice compressibility is lower along c, i.e., between the perovskite layers.
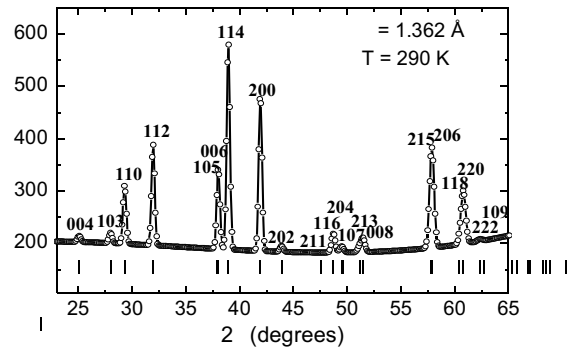
Introduction

The mixed-valent cobalt oxides $La_{1-x}Sr_xCoO_4$ with the layered perovskite structure [1] is a recent subject of great interest, because of the strong correlation between electronic, magnetic, transport and structural properties [2-7]. In the $La_{2-x}Sr_xCoO_4$ system, the valence of Co can be varied over large range, hypothetically from Co^{2+} for x = 0 to Co^{4+} for x = 2. Extensive data are available for the $Co^{2+/3+}$ region x = 0–1. La_2CoO_4 (x = 0, Co^{2+}) is an antiferromagnetic insulator with T_N = 275 K [3, 4]. The mixed $Co^{2+/3+}$ valency in the 0 < x < 1 region brings about magnetic disorder, and spin-glass behavior is found below 100 K for these systems. The electric conduction remains of an activation character. The absolute resistivity steeply decreases with increasing Co^{3+} content. The magnetic and electronic data suggest that Co^{2+} ions are in HS state while Co^{3+} ions gradually change with x from HS to IS state [4-6]. On the other hand, there are less reports concerning the $Co^{3+/4+}$ region of $La_{2-x}Sr_xCoO_4$ in a composition range x > 1.0. Very recently, a systematic low-temperature investigation in the range *x* = 1.0–1.5 was published by Shimada et al. [7]. The magnetic measurements revealed a formation of the ferro-

a)

b)

Figure 1. Neutron diffraction patterns of $La_{0.6}Sr_{1.4}CoO_4$. (a) – measured on DN-12 diffractometer at T = 290 and 16K at ambient pressure (upper panel) and 4.3GPa (lower panel). (b) – measured on KSN-2 diffractometer at T = 290K and at ambient pressure.

magnetic state for higher rates of Co^{4+}. Of special interest is to investigate effects of high pressures on the structural and magnetic properties of these ferromagnetic compounds. The aim of the present work is a neutron diffraction study of the mixed-valent $Co^{3+/4+}$ oxide $La_{0.6}Sr_{1.4}CoO_4$ at high pressure.

Experimental

The samples $La_{0.6}Sr_{1.4}CoO_4$ was prepared by standard sol-gel method. The X-Ray diffracti on analysis (Bruker D8, CuK , SOL-X energy dispersive detector) detected the single n = 1 Ruddlesden-Popper phase (K_2NiF_4 type). Lattice parameters and atomic coordinates within the *I4/mmm* space group symmetry were determined at room temperature by x-ray powder analyses using the FULLPROF program. The neutron diffraction experiment has been performed at room temperature on the diffractometer KSN-2 [8] at research reactor LWR-15 (Řež, Czech Republic) [9]. The study was completed down to low temperatures, both at normal pressure and up to 4.3

Table 1. Structural parameters of $La_{0.6}Sr_{1.4}CoO_4$ at selected pressures and ambient temperature. The atomic positions are La/Sr and O2 – 4(e) (0, 0, z), Co – 2(a) (0, 0, 0) and O1 – 4(c) (0.5, 0, 0) of the space group I4/*mmm*. Values of Co-O1 and Co-O2 bond lengths and the Co magnetic moments are also presented. (Data from KSN-2 are added in the first column.)

P, GPa	0 (KSN-2)	0	2	4.3			
T, K	290	290	16	290	12	290	10
a, Å	3.7983(3)	3.798(4)	3.790(4)	3.778(5)	3.770(5)	3.768(5)	3.756(5)
c, Å	12.514(8)	12.516(7)	12.488(7)	12.476(9)	12.461(9)	12.441(9)	12.425(9)
La/Sr (z)	0.3589(4)	0.3585(6)	0.3586(6)	0.358(2)	0.358(2)	0.361(2)	0.358(2)
O2 (z)	0.1604(4)	0.1606(7)	0.1593(7)	0.155(3)	0.157(3)	0.155(3)	0.156(3)
Co-O1, Å (4x)	1.899(1)	1.899(2)	1.895(2)	1.889(3)	1.885(3)	1.884(3)	1.878(3)
Co-O2, Å (2x)	2.007(5)	2.010(4)	1.989(4)	1.93(1)	1.95(1)	1.93(1)	1.94(1)
La/Sr-O1, Å (4x)	2.593(7)	2.597(6)	2.590(6)	2.59(1)	2.59(1)	2.56(1)	2.58(1)
La/Sr-O2, Å (4x)	2.686(2)	2.686(3)	2.680(3)	2.671(4)	2.666(4)	2.664(4)	2.656(4)
La/Sr-O2, Å (1x)	2.484(9)	2.477(8)	2.489(8)	2.53(2)	2.51(2)	2.56(2)	2.51(2)
, $_B$			0.7(1)		0.8(1)		0.9(1)
R_p, %	2.58	6.63	4.27	7.16	10.10	7.84	8.29
R_{wp}, %	2.44	4.34	3.13	6.34	8.11	7.80	7.96

GPa, on the high pressure diffractometer DN-12 [10] at pulsed reactor IBR-2 (Dubna, Russia) [11]. The experimental data were analyzed by the Rietveld method using the MRIA and FULLPROF programs.

Results and discussion

The powder diffraction patterns of $La_{0.6}Sr_{1.4}CoO_4$ taken on time-of-flight diffractometer DN-12 (at P = 0 and 4.3 GPa, T = 290, 16, and 10 K) and constant wavelength diffractometer KSN-2 (at P = 0 GPa, T = 300 K) are shown in Figures 1(a) and 1(b), respectively. At ambient pressure, the low-temperature spectra (T = 16K) do not show any new diffraction line that could be ascribed to an antiferromagnetic order. On the other hand, existence of a long-range ferromagnetic order is evidenced by an intensity contribution to some fundamental diffraction lines. This is illustrated in more detail in the inset of Figure 1(a) (upper panel) where observed intensity at line (103) exceeds significantly the calculated intensity for nuclear scattering while no additional intensity is observed at line (004). This observation determines that the spontaneously ordered cobalt moments are oriented along the c axis of the $I4/mmm$ structure, i.e., perpendicular to the layers. Their calculated magnitudes amount to 0.7 $_B$/Co atom, which is in agreement with the magnetization in Ref. [12].

A low value of spontaneous moments suggests that the ferromagnetic transition remains incomplete, leading to a ferromagnetic-paramagnetic phase segregation. Since the magnetic interactions are associated with electron transfer, either real (double exchange) or virtual (superexchange), they are extremely sensitive to the transition metal $3d$-oxygen $2p$ orbital overlap. It appears that the overlap integrals and, consequently, the double exchange vary with the metal-oxygen bond lengths approximately according to a power dependence $\sim l^{-3.5}$ while the superexchange may vary even much more steeply [13]. Therefore, one would expect enhancement of the magnetic interactions on lattice contraction, forced by high pressures. The possibility to induce more ferromagnetic phase was a primary motivation for a high-pressure neutron diffraction study of $La_{0.6}Sr_{1.4}CoO_4$. The analysis of observed spectra showed, however, only a modest increase of ferromagnetically ordered cobalt moments from 0.7 $_B$ at ambient pressure to 0.9 B at 4.3 GPa.

Complete results obtained by the neutron diffraction studies of $La_{0.6}Sr_{1.4}CoO_4$ are summarized in Table 1. The room temperature data at different pressures allow us to calculate linear compressibilities $k_i = -(1/a_{i0})(da_i/dP)_T$ both for the lattice parameters ($k_a = 0.0011 GPa^{-1}$, $k_c = 0.0007 GPa^{-1}$) and the equatorial and apical Co-O bond lengths ($k_{Co-O1} = 0.0011 GPa^{-1}$, $k_{Co-O2} = 0.004(1) GPa^{-1}$). Similar values are observed at low temperatures, $k_a = 0.0011 GPa^{-1}$, $k_c = 0.0006 GPa^{-1}$, $k_{Co-O1} = 0.0011 GPa^{-1}$, $k_{Co-O2} = 0.003(1) GPa^{-1}$. This shows that the lattice compressibility is lower along c, i.e., between the perovskite layers. Despite this, there is an unexpectedly high compressibility of the Co-O2 (apical) bond, which is compensated by expansion under an external field of the shortest La/Sr-O2 (apical) bond length. This seemingly anomalous effect can be attributed to the opposite stresses in the CoO_2 and (La, Sr)O layers as mentioned with the X-Ray diffraction results.

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