

# Powder Neutron and X-Ray Diffraction Study of $\text{La}_4\text{Co}_3\text{O}_{10.00}$ \*

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The crystal structure of stoichiometric  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  is of the Ruddlesden—Popper type and contains slabs of triple perovskite-type layers separated by rock salt layers, the composition corresponding to  $n = 3$  in the  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  series. On heating, the slightly orthorhombically deformed structure converts into a tetragonal one at around 840 K. Antiferromagnetic ordering occurs below  $T_N \approx 10$  K. Crystal structure data from powder neutron diffraction are presented. Slight line broadening of some X-ray reflections and a few, weak additional neutron reflections indicates that the true symmetry is lower than  $Fmmm$ .

The 4:3:10 phases like  $\text{La}_4\text{Co}_3\text{O}_{10}$  belong to the so-called Ruddlesden—Popper type phases [1]. The 4:3:10 phases are members of the  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  series ( $n = 3$ ), and structurally they are closely related to the 3:2:7 ( $n = 2$ ), 2:1:4 ( $n = 1$ ,  $\text{K}_2\text{NiF}_4$ -type), and  $\text{ABO}_3$  ( $n = \infty$ , perovskite-type) phases. Such phases are found for several transition metals both in the bulk and/or as intergrowth segments in other stable phases of the  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  series. Examples of the  $n = 3$  members of the series are:  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$  with four-valent titanium [1, 2],  $\text{La}_4\text{Co}_3\text{O}_{10}$  [3],  $\text{La}_4\text{Ni}_3\text{O}_{10}$  [4], and  $\text{La}_4\text{Cu}_3\text{O}_{10}$  [5, 6] where Co, Ni, and Cu have an average oxidation state of 2.67, and  $\text{La}_{1.5}\text{Sr}_{2.5}\text{Mn}_3\text{O}_{10}$  with an average oxidation state of 3.5 of Mn [7].

The effect of nonstoichiometry on the crystal structure and physical properties is of major interest for the wide range of perovskite-type related phases. For  $\text{La}_4\text{Co}_3\text{O}_{10\pm\delta}$ , the maximum oxygen content obtainable in air corresponds to  $\delta = 0.30$ , however, a lower limit for the oxygen content of 9.00 can be obtained *via* low-temperature reduction [8]. It is therefore of great interest to extract crystal structure data for  $\text{La}_4\text{Co}_3\text{O}_{10\pm\delta}$  and consider structure—property relations. So far the assumption of a Ruddlesden—Popper type atomic arrangement for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  is based on qualitative comparisons of X-ray powder diffraction patterns [3]. The present work reports on Rietveld refinements of powder neutron diffraction data for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ .

## EXPERIMENTAL

$\text{La}_4\text{Co}_3\text{O}_{10.00}$  was synthesized first by dissolving

$\text{La}_2\text{O}_3$  (99.99 % Molycorp; heated to 1273 K for removal of carbonate and water) in concentrated  $\text{HNO}_3$ . Thereafter citric acid monohydrate (> 99.8 %, Riedel-Häen) was added, and finally also  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (> 99 %, Fluka) along with distilled water. The citrate solution was dehydrated at 450 K, carbonaceous species were removed by incineration at 720 K and the final product was obtained after annealing pressed pellets at 1300 K for 110 h under flowing nitrogen ( $p(\text{O}_2) = 10$  Pa). The sample was then slowly cooled while the oxygen partial pressure was kept constant. The oxygen content was evaluated thermogravimetrically by subsequent heating of the phase-pure product in pure oxygen to 1300 K whereby the sample transformed completely into  $\text{La}_2\text{O}_3$  and  $\text{LaCoO}_3$ .

Unit cell dimensions were determined from powder X-ray diffraction data at 298 K (Guiner Hägg cameras,  $\text{CuK}\alpha_1$  and  $\text{CrK}\alpha_1$  radiation, Si as internal standard). Powder X-ray diffraction showed that all samples were single phase  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  (detection limit for impurities is *ca.* 0.3 mass % using  $\text{CrK}\alpha_1$  radiation [9]). High-temperature X-ray diffraction data were collected as a function of temperature upon heating by a Guinier Simon camera (Enraf Nonius),  $\text{CuK}\alpha_1$  radiation.

Powder neutron diffraction (PND) data were collected using the OPUS IV two-axis diffractometer at the JEEP II reactor, Kjeller, at and below room temperature. Cylindrical sample holders were used. Monochromatized neutrons of wavelength 182.5 pm were obtained by reflection from  $\text{Ge}(111)$ . The diffraction patterns were measured by means of five  $^3\text{He}$  detectors, positioned ten degrees apart. Intensity data were collected from  $2\theta = 10$  to  $100^\circ$  in steps of  $\Delta 2\theta$

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= 0.05° Temperatures between 10 K and 300 K were obtained by means of a Displex cooling system. A Lake Shore DRC 82C controller was used, and the temperature was measured and controlled by means of a silicon diode. A second set of PND data was collected at 1.7 K with the D1A instrument at Institut Laue Langevin (ILL), Grenoble, wavelength 190.9 pm for studies of magnetic scattering. An ILL orange cryostat was used for obtaining low temperatures.

Structural and instrumental parameters were obtained from profile refinements. The Hewat version [10] of the Rietveld program was used. The scattering amplitudes  $b_{\text{La}} = 8.24$  fm,  $b_{\text{Co}} = 2.49$  fm, and  $b_{\text{O}} = 5.805$  fm [11] were adopted.

Magnetic susceptibility data were measured by a Quantum Design SQUID-magnetometer (MPMS) ( $T = 2\text{--}300$  K) and according to the Faraday method ( $T = 300\text{--}1000$  K).

## RESULTS AND DISCUSSION

The powder X-ray diffraction data were indexed on an  $F$ -centred orthorhombic unit cell,  $a = 541.4$  (2) pm,  $b = 547.6$  (2) pm,  $c = 2777$  (1) pm,  $V = 823.4$  (6)  $\times 10^6$  pm<sup>3</sup> ( $Z = 4$ ),  $M(20) = 36.2$ . The degree of orthorhombic deformation in terms of the deviation of  $|1 - a/b|$  from zero is small, 0.012. Two further aspects should be noted; i) close inspection of the half-widths of the Bragg-reflections (Guiner films evaluated by means of an LS-18 film-scanner and the SCANPI program system) shows a systematic broadening of the ( $h0l$ ) reflections, which

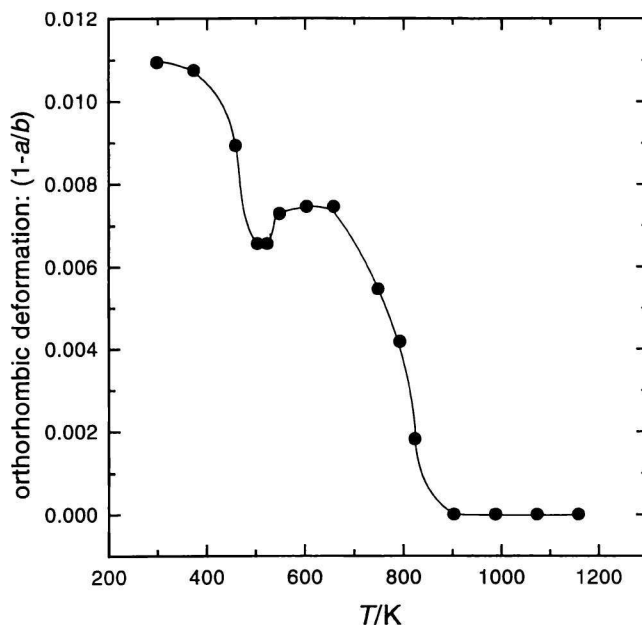


Fig. 1. Degree of orthorhombic deformation in terms of  $|1 - a/b|$  as a function of temperature.

is caused by a small and systematic splitting of the reflections as confirmed by high-resolution X-rays [12], indicating lower symmetry than orthorhombic, ii) on heating the degree of orthorhombic deformation diminishes and finally vanishes. The temperature variation of  $|1 - a/b|$  is shown in Fig. 1. At high temperatures,  $T > 840$  K,  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  is tetragonal ( $a_{\text{T}} = a_{\text{O}}/\sqrt{2}$ ,  $c_{\text{T}} = c_{\text{O}}$ ; space group

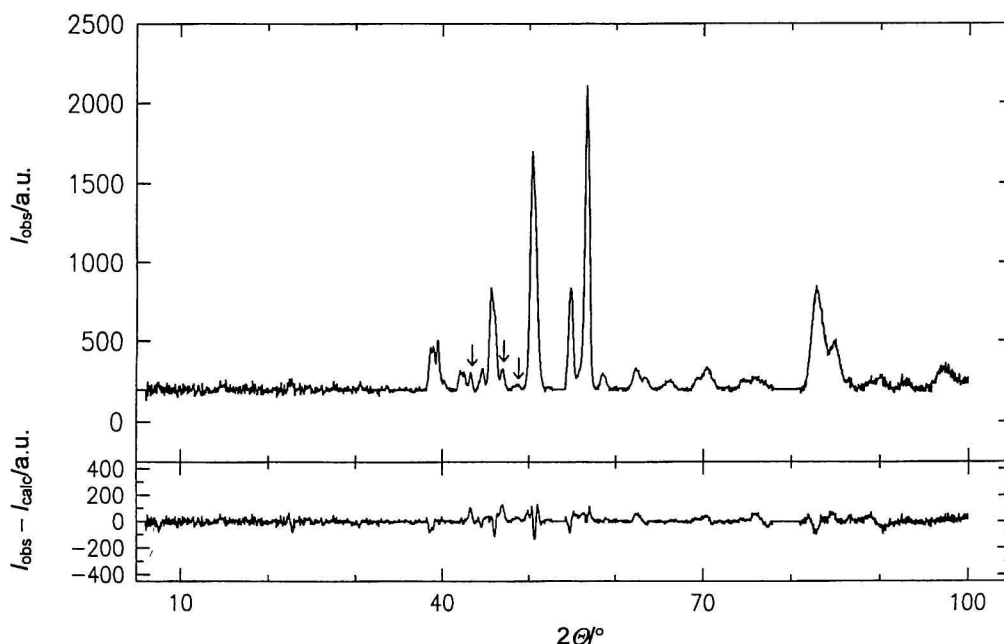


Fig. 2. Observed and difference powder neutron diffraction pattern for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ . Data collected with the OPUS IV instrument, Kjeller,  $\lambda = 182.5$  pm,  $T = 298$  K. Nuclear reflections not in accord with space group  $Fm\bar{3}m$  marked with arrows.

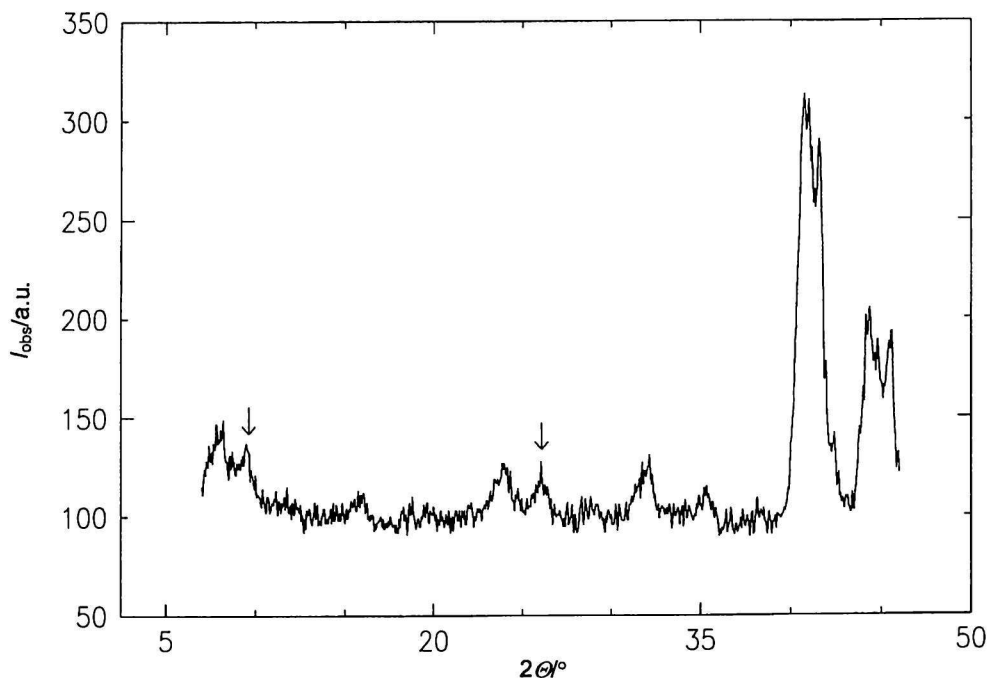


Fig. 3. Observed powder neutron diffraction pattern for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ , D1A, ILL,  $\lambda = 190.9$  pm,  $T = 1.7$  K. Magnetic reflections indicated by arrows.

$I4/mmm$ ). TGA data show that there is no compositional change at the orthorhombic-to-tetragonal phase transition. In that sense  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  is different from the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  high-temperature superconductor where the orthorhombic-to-tetragonal phase transition is connected with loss and randomization of oxygen [13].

The crystal structure described for  $\text{Sr}_4\text{Ti}_3\text{O}_{10}$  [1, 2] was taken as starting point for the Rietveld refinements of the PND data since the calculated PXD pattern with the LAZY PULVERIX program [14] corresponded well to the observed pattern.

A reasonable fit was obtained between the calculated and observed PND pattern for the Kjeller data (Fig. 2). However, some weak reflections around  $2\theta \approx 43^\circ$ ,  $47^\circ$ , and  $48^\circ$ , marked with arrows in Fig. 2, could not be accounted for. These reflections were not observed with X-rays, and since no known impurity phase in the La—Co—O system matched the observations, it is believed that they reflect details of the oxygen and/or defect ordering in  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ . The reflections can be indexed on a primitive cell, and together with the slight line broadening, this suggests that the correct Bravais-lattice is primitive monoclinic, although the structure must obviously be very close to  $F$ -centred orthorhombic. Probably the situation is rather similar to that observed for *e.g.* the 2:1:4 phase  $\text{La}_2\text{NiO}_{4+\delta}$ , where the structure for  $\delta = 0.25$  is described in space group  $C2$  and not in  $Fmmm$  [15]. To resolve the situation for  $\text{La}_4\text{Co}_3\text{O}_{10+\delta}$ , high-resolution powder X-ray (BM2, ESRF, Grenoble) and

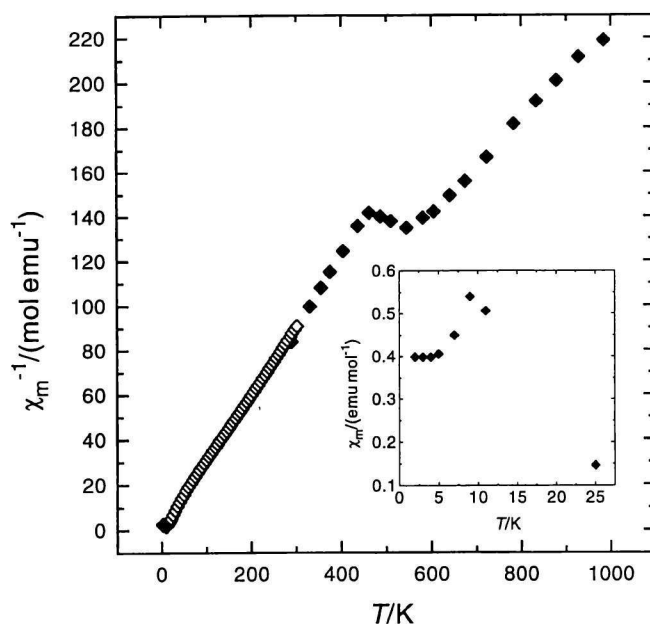


Fig. 4. Inverse magnetic susceptibility *vs.* temperature for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  between 1.7 and 1000 K. Insert shows magnetic susceptibility between 1.7 and 25 K.

neutron diffraction data (D2B, ILL, Grenoble) will be analyzed and presented [12].

The PND data at 1.7 K from D1A, ILL, showed the presence of a few, very weak additional reflections indicating long-range magnetic order (see reflections

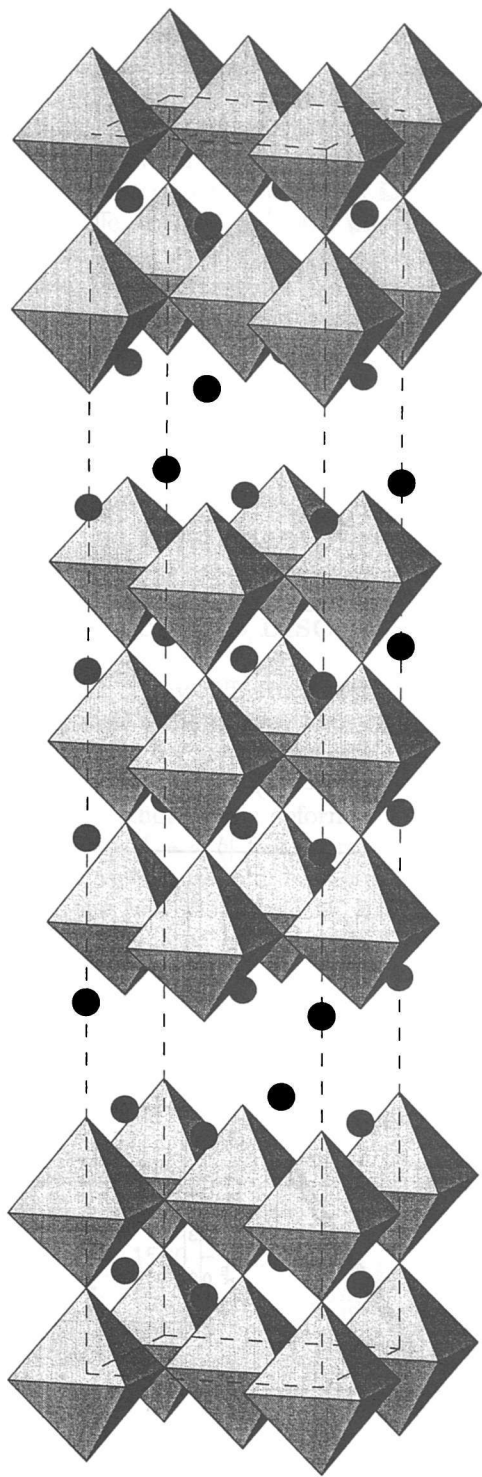


Fig. 5. Crystal structure of  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ . La-atoms (black circles) and  $\text{CoO}_6$ -octahedra are shown.

marked with arrows in Fig. 3). As seen from the inverse magnetic susceptibility curves in Fig. 4, an antiferromagnetic transition occurs around 10 K. Fig. 4 furthermore shows another magnetic (electronic) transition in the paramagnetic regime around 460 K. This transition influences the degree of orthorhombic

Table 1. Crystal Structure Data and Profile Refinement Parameters for  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ . Space Group  $Fm\bar{3}m$ . Co(1) in 4a (0,0,0); O(1) in 8e ( $1/4, 1/4, 0$ ); La(1), La(2), Co(2), O(2), and O(4) in 8i (0,0,z); O(3) in 16j ( $1/4, 1/4, z$ ). Calculated Standard Deviations in Parentheses

Parameter	Atomic position	10 K	298 K
$a/\text{pm}$		540.51(8)	541.88(8)
$b/\text{pm}$		547.02(9)	547.37(9)
$c/\text{pm}$		2776.67(44)	2782.42(44)
La(1)	8i; z	0.3011(2)	0.3009(2)
La(2)	8i; z	0.4335(2)	0.4347(2)
Co(1)	4a; (0,0,0)		
Co(2)	8i; z	0.1381(5)	0.1380(5)
O(1)	8e; ( $1/4, 1/4, 0$ )		
O(2)	8i; z	0.0671(4)	0.0689(4)
O(3)	16j; z	0.1415(2)	0.1411(2)
O(4)	8i; z	0.2140(3)	0.2138(4)
$R_p$		19.96	20.39
$R_{wp}$		16.33	16.58
$R_{exp}$		16.10	16.88

deformation of the structure (see the first minimum in Fig. 1). The electronic transition occurs below the temperature for the structural orthorhombic-to-tetragonal transition.

A perspective visualization of the crystal structure of  $\text{La}_4\text{Co}_3\text{O}_{10.00}$  is shown in Fig. 5 and the results of the Rietveld profile refinement of the PND data are given in Table 1. Due to the quality of the present PND data, it was necessary to fix the  $x$  and  $y$  coordinates for all atoms in order to limit the number of refined parameters. Between the two-dimensional slabs with perovskite-type atomic arrangement of  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ , La—O sheets with rocksalt arrangement exist. The cobalt atoms, which are the carriers of magnetic moments, are reasonably close within the two-dimensional slabs ( $ab$ -plane), but are rather far apart along the  $c$ -axis, *i.e.* at the distances 387 pm and 674 pm, respectively. In the related  $\text{LaCoO}_3$  perovskite-type phase, all Co(III) atoms have octahedral coordination. For this phase no cooperative magnetic order is found [16, 17] and cobalt is considered to be in a low-spin state ( $d^6$ ,  $S = 0$ ) at  $T < 100$  K. In that respect  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ , with two octahedral Co(III) and one octahedral Co(II), behaves significantly differently since the PND pattern at 1.7 K (Fig. 3) clearly shows a few, weak additional peaks of magnetic origin.

Among the  $\text{LaMO}_3$  oxides ( $M =$  transition element), different types of deformed perovskite-type structures prevail.  $\text{LaCoO}_3$  takes the rhombohedral  $\text{LaAlO}_3$ -type structure. Here the octahedra are tilted with a Co—O—Co angle of  $163.91^\circ$  [17]. However, in the orthorhombic structure of  $\text{La}_4\text{Co}_3\text{O}_{10.00}$ , there are no tilts of the octahedra in the two-dimensional perovskite-type slabs since the  $x$ ,  $y$  coordinates for the

special positions of space group  $Fm\bar{3}m$  are fixed. Fixing the atomic coordinates limits the accuracy of the interatomic distances, and thus prevents a further discussion on shape and tilt of the polyhedra.

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