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Calcium-induced cation ordering and large resistivity decrease in $Pr_{0.3}CoO_2$

Petr Brázda [a,*], Lukáš Palatinus [a], Jan Drahokoupil [a], Karel Knížek [a], Josef Buršík [b]

[a] Institute of Physics AS CR, v.v.i., Na Slovance 1999/2, 182 21 Prague 8, Czech Republic
[b] Institute of Inorganic Chemistry AS CR, v.v.i., Husinec-Řež 1001, 25068 Řež, Czech Republic

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ABSTRACT

Structure of layered cobaltates $Pr_{0.3}CoO_2$ and $(PrCa)_{0.3}CoO_2$ were investigated by electron diffraction tomography and powder X-ray diffraction. The effect of the calcium substitution on thermoelectric properties was evaluated. The structure consists of hexagonal sheets of edge-sharing CoO_6 octahedra interleaved by cationic monolayers. The cations form a 2-dimensional $a\sqrt{3} \times a\sqrt{3}$ superstructure in the a–b plane. While $Pr_{0.3}CoO_2$ showed no layer order in the [001] direction, introduction of calcium resulted in the formation of a superstructure spanning over six cationic layers along the [001]. This superstructure model appears to be valid also for the description of the superstructures of Ca_xCoO_2 and Sr_xCoO_2 with x about 1/3. Thanks to the increased number of charge carriers, the substitution of Ca^{2+} for Pr^{3+} significantly lowers the electric resistivity, while keeping quite high thermopower around 100 μV K^{-1}, though the character of resistivity remained semiconducting.

1. Introduction

Layered cobaltates with mixed-valent $Co^{3+/4+}$ atoms are a group of materials with large thermoelectric power [1]. Our group successfully prepared $Ln_{0.3}CoO_2$ (Ln=La, Pr, and Nd) by solid state ion exchange reaction from γ-Na_xCoO_2 ($P6_3/mmc$ symmetry) [2] and showed that these materials possess large Seebeck coefficient reaching 175 μV K^{-1} and are thermally stable up to 800 K [3–5]. Application of $Ln_{0.3}CoO_2$ materials for thermoelectric conversion is limited by their high electrical resistivity. The partial substitution of Ca^{2+} for Ln^{3+} may increase Co valency and thus the charge-carrier concentration. This could eventually lead to a decrease of electrical resistivity and possibly to a change of the semiconducting behaviour of $Ln_{0.3}CoO_2$ to metallic. The substitution of Ca^{2+} for Pr^{3+} was selected because of the similar ionic radii of these cations.

Intercalated cations in $Me_{1/3}CoO_2$ (Me=Ca, Sr, Ba, La, Pr, and Nd) form the $a\sqrt{3} \times a\sqrt{3}$ superstructure (Fig. 1) [3,4,6–9]. The cationic arrangement in the a–b plane is well developed for this superstructure and therefore frequently discussed in the literature. To the best of our knowledge, the order along [001] direction for the $a\sqrt{3} \times a\sqrt{3}$ superstructure has not been discussed in the literature except for our recent works dealing with $La_{0.3}CoO_2$, where we used powder X-ray (PXRD) and neutron diffraction [5] and electron diffraction tomography (EDT) [10]. In the latter work we theoretically deduced some limitations of the layer stacking sequences with respect to the cationic site occupancy ($P1$ and $P2$, Fig. 1) [10]. The obtained experimental results for $La_{0.3}CoO_2$ show that there is no order of the cationic layers along the [001] direction in this material. This contrasts with the calcium and strontium analogues, where the maxima of diffracted intensity proving the existence of the order along c may be observed in both PXRD [7,11,12] and selected area electron diffraction (SAED) [6,7,13]. All the published SAEDs are similar and may be interpreted as a result of an R-centred arrangement of cations with periodicity either equal to three CoO_2 layers (indicating that the cations would have to occupy the $P1$ site, which is in disagreement with powder XRD data) [7] or equal to six CoO_2 layers assuming presence of a symmetry operation of the structure, which leads to the systematic absences for diffractions with $l=2n+1$ (in this case occupancy of the $P2$ site would be allowed).

In this article, we investigate the cationic arrangement in $Pr_{0.3}CoO_2$ and $(PrCa)_{0.3}CoO_2$ (the ratio Pr:Ca is about 1:1). We show that while the stacking of layers in $Pr_{0.3}CoO_2$ is completely random along [001] in analogy to its lanthanum analogue, substitution of calcium for praseodymium in the structure induces ordering of the cations along the [001] direction. We also show that the published powder X-ray diffractogram of $Sr_{0.35}CoO_2$ [7] can be explained with the same structural model for the stacking order. Further, measurement of conductivity of the $Pr_{0.3}CoO_2$ and $(PrCa)_{0.3}CoO_2$ materials showed that introduction of Ca into the system leads to a significant decrease of resistivity of $(PrCa)_{0.3}CoO_2$

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[*] Corresponding author.
E-mail address: brazda@fzu.cz (P. Brázda).

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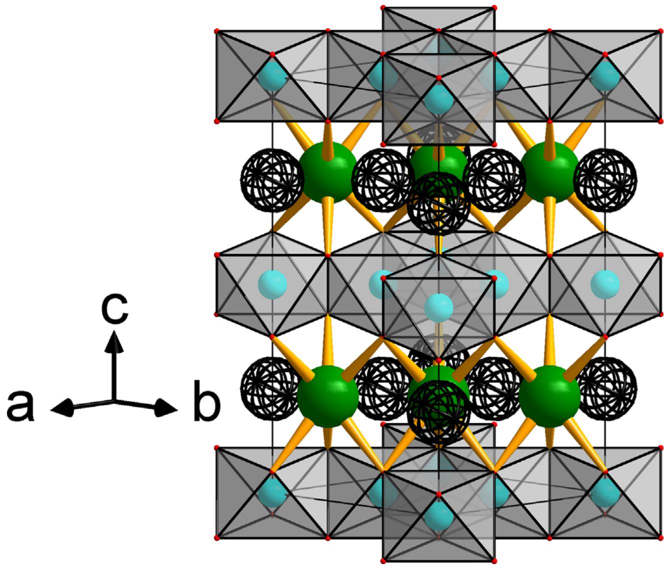

Fig. 1. Basic building block of the $a\sqrt{3}\times a\sqrt{3}$ superstructure. It is a three times expanded unit cell of γ-$NaCoO_2$ ($P6_3/mmc$ symmetry). The superstructure in $Me_{1/3}CoO_2$ (only 1/3 of the $P2$ (green) cation sites in a layer are occupied) is caused by ordering of the vacancies. The $P1$ sites (sites between Co atoms) are shown as black hollow spheres. Cobalt atoms are shown with their coordination polyhedron. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in comparison to $Pr_{0.3}CoO_2$.

2. Experimental

The materials were prepared by an ionic exchange between sodium cobaltate and Ca and Pr nitrates (γ-$Na_{0.77}CoO_2$, $a=2.841(1)$ Å, $c=10.802(5)$ Å [14]) was mixed with anhydrous $Pr(NO_3)_3$ or with a mixture of anhydrous $Pr(NO_3)_3$ and $Ca(NO_3)_2$ in a dry-box. The molar ratios $Na_{0.77}CoO_2$:$Pr(NO_3)_3$:$Ca(NO_3)_2$ were 1:0.5:0 ($Pr_{0.3}CoO_2$) and 1:0.7:0.3 ($(PrCa)_{0.3}CoO_2$). Preliminary experiments revealed, that the rate of the ionic exchange of Ca is higher than that of Pr, therefore in order to achieve Pr:Ca=1:1 stoichiometry in $(PrCa)_{0.3}CoO_2$, the excess of Ca over Pr should be used. The final annealing was done for two days at 340 °C for $Pr_{0.3}CoO_2$ and at 310 °C for $(PrCa)_{0.3}CoO_2$. The unreacted nitrates were washed out repeatedly with large amount of water using an ultrasonic treatment. The products were isolated by sedimentation in water and then dried at 120 °C for 16 h. For the transport measurement experiments, the materials were pressed into pellets and sintered at 300 °C for one day. The density (compactness) of the pellets is affected by the low sintering temperature and it was about 60–65%.

Powder X-ray diffraction was carried out with the Bruker D8 (Cu K_α radiation, $\lambda=1.5418$ Å, secondary monochromator, Bragg-Brentano geometry) and PANalytical X'Pert (Co K_α radiation, $\lambda=1.790$ Å, transmission geometry, Kapton sample support) diffractometers. Rietveld analyses of the PXRD data were performed with Fullprof software package [15]. Partial disorder of the cationic layer stacking was simulated by programme FAULTS [16].

Transmission electron microscopy (TEM) was conducted on a Philips CM120 transmission electron microscope with a LaB_6 cathode operating at 120 kV. The microscope is equipped with a CCD Camera Olympus SIS Veleta with 14 bit dynamical range and with an EDAX SSD detector Apollo XLTW for EDS analysis. The electron diffraction tomography [17] was measured in the range from $-50°$ to $+50°$ and with the tilt step of 0.7°. The samples were used as they were or only very gently ground and then they were transferred onto the Cu TEM grids. Selected area electron diffraction was simulated in the programme JEMS.

Electrical resistivity and thermoelectric power were measured using a four-probe method with a parallelepiped sample cut from the sintered pellet. The electrical current density varied depending on the sample resistivity between 10^{-1} A cm^{-2} (metallic state) and 10^{-7} A cm^{-2} (insulating state). The measurements were performed on sample cooling and warming using a close-cycle cryostat working down to 3 K, see Ref. [18] for details.

3. Results and discussion

3.1. Transmission electron microscopy

The $Pr_{0.3}CoO_2$ crystals show the $a\sqrt{3}\times a\sqrt{3}$ superstructure. The lack of order along [001] of the superstructure diffractions (Fig. 2) is in accord with PXRD data (see below). Intergrowths with Co_3O_4 were frequently observed (Fig. S1). The Co_3O_4 crystals are frequently twinned according to the spinel-law. The observed twinning was perpendicular to only one out of the four possible three-fold axes and this particular axis was parallel to the [001] direction of $Pr_{0.3}CoO_2$. For indexing purposes, it was therefore convenient to transform the cubic unit cell of Co_3O_4 to the hexagonal unit cell setting (H subscript), where the twinning three-fold axis becomes the c-axis. The transformation is then $\boldsymbol{a}_{\mathrm{H}}=\boldsymbol{a}/2-\boldsymbol{b}/2$, $\boldsymbol{b}_{\mathrm{H}}=\boldsymbol{b}/2-\boldsymbol{c}/2$ and $\boldsymbol{c}_{\mathrm{H}}=\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}$. This situation is completely analogous to the behaviour of the $Co_3O_4/La_{0.3}CoO_2$ system [10].

Introduction of calcium into the praseodymium cobaltate induced a change of the ordering of the structure. While the *a–b* superstructure did not change, an appearance of maxima within the rods of diffracted intensity due to cationic superstructure clearly indicate that the stacking sequence is no longer random, but exhibits long-range order, albeit not perfect. The appearance of the diffraction patterns is similar to those published in the literature [6,7,13]. Based on the analysis of the possible ordering with cations in the $P2$ site we constructed two possible sequences of the cationic layers. The resulting structures have a six-layer periodicity with two interpenetrating *R*-centred cationic substructures (one substructure is composed of the cations located in the odd layers and the other one in the even layers). These two *R*-centred substructures may be either both obverse (or both reverse) or they can have the obverse-reverse relationship. These structures are shown in Fig. 3. The symmetry of the obverse-obverse (O–O) structure is $C2/c$[1] and the symmetry of the obverse-reverse (O–R) structure is $P6_122$. The lattice vector transformations from the average ($P6_3/mmc$) unit cell is $\boldsymbol{a}_{\mathrm{O-O}}=3\boldsymbol{a}$, $\boldsymbol{b}_{\mathrm{O-O}}=\boldsymbol{a}+2\boldsymbol{b}$, $\boldsymbol{c}_{\mathrm{O-O}}=3\boldsymbol{c}$ for the O–O structure (dimensions of the cell are $3a\times a\sqrt{3}\times 3c$ with respect to the average structure unit cell) and $\boldsymbol{a}_{\mathrm{O-R}}=2\boldsymbol{a}+\boldsymbol{b}$, $\boldsymbol{b}_{\mathrm{O-R}}=-\boldsymbol{a}+\boldsymbol{b}$, $\boldsymbol{c}_{\mathrm{O-R}}=3\boldsymbol{c}$ ($a\sqrt{3}\times a\sqrt{3}\times 3c$) for the O–R structure. The simulations of the reciprocal space sections corresponding to *h*0*l*, –*h*–*hl*, and –*hhl* (O–O structure) and *h*0*l*, 0–*kl*, and –*hhl* (O–R structure) are shown in Fig. S2. All three sections are identical for the O–R structure ($P6_122$ symmetry) and the patterns look like the patterns of an obverse-reverse twin, which is an intrinsic feature of the structure. The six-layer periodicity may be directly observed in these sections. Due to the lower symmetry, only the –*h*–*hl* and –*hhl* sections of the O–O structure are identical and show the six-layer periodicity. The *h*0*l* section is different because the diffraction maxima with $l=2n+1$ are absent due to the presence of *c*-glide plane.

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[1] Further details of the crystal structure may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-430226.