Short-range charge ordering in Ho$_{0.1}$Sr$_{0.9}$CoO$_{3-x}$ (0.15 $\leq x \leq$ 0.49)

S. Streule,$^{1,*}$ M. Medarde,$^{1,2}$ A. Podlesnyak,$^1$ E. Pomjakushina,$^{1,2}$ K. Conder,$^2$ S. Kazakov,$^3$ J. Karpinski,$^3$ and J. Mesot$^1$

$^1$Laboratory for Neutron Scattering, ETH Zürich & Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^2$Laboratory for Developments and Methods, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^3$Laboratory for Solid State Physics, ETH Hönggerberg, CH-8093 Zürich, Switzerland

(Received 14 September 2005; revised manuscript received 28 November 2005; published 26 January 2006)

We report the observation of Co$^{3+}$/Co$^{4+}$ short-range charge ordering in 10% Ho-doped SrCoO$_{3-x}$ by means of high resolution neutron powder diffraction. The associated one-dimensional commensurate modulation, which can be described with the propagation vector $q_{CO}=(0 0 1/2)$ with respect to the cubic perovskite cell $Pm$
bmrm 3m, occurs for compositions close to $x=0.20$, corresponding to a 1:1 Co$^{3+}$/Co$^{4+}$ ratio and extends over clusters of finite size ($D \approx 250$ Å). The bond valence sums for the Co$^{3+}$ and Co$^{4+}$ sites are +3.07(7) and +3.95(11) ($x=0.19$), very close to their nominal values +3 and +4. We attribute this astonishing observation to the one-dimensional (1D) character of the associated distortion pattern, whose elastic stabilization is eased with respect to the 3D arrays reported for other charge-ordered perovskite oxides.

DOI: 10.1103/PhysRevB.73.024423
PACS number(s): 61.12.Ld, 31.15.Rh

I. INTRODUCTION

Structural modulations involving the real-space ordering of ions having different nominal charges have been the subject of intensive investigations during the last two decades. These phenomena, usually denoted by the generic name of charge ordering (CO), appear for some particular compositions, generally corresponding to integer concentration ratios of the involved charge-ordered species. Although the stabilization of a charge-ordered state frequently gives rise to abrupt changes in either the transport or the magnetic properties of the material, the structural modifications associated to the spacial rearrangement of the ions are in most cases unexpectedly weak. Perhaps the most remarkable example illustrating this problem is provided by the half-doped manganites R$_{1/2}$A$_{1/2}$MnO$_3$ ($R$: trivalent ion, A: Ca or Sr), which contain nominally equal amounts of Mn$^{3+}$ and Mn$^{4+}$. The existence of a Mn$^{3+}$/Mn$^{4+}$ CO pattern, which was proposed by Goodenough$^1$ in order to explain the unusual magnetic character of the associated distortion pattern, whose elastic stabilization is eased by means of showing charge-order phenomena, we decided to study the SrCoO$_{3-x}$ system ($0 \leq x \leq 0.5$). In this series, the nominal oxidation state of Co varies continuously from 4+ ($x=0$) to 3+ ($x=0.5$). Early work on SrCoO$_3$ and their reduced forms showed the existence of a multitude of superstructures$^{14,15}$ Most of them were observed by means of electron microscopy and attributed to the ordering of the oxygen vacancies, but only very few of them have been to date properly characterized. The lack of structural and, more precisely, neutron diffraction studies, may be partially attributed to the difficulties associated with the synthesis procedure, which requires the use of nonstandard equipment (high oxygen pressure) for the preparation of the most oxidized samples. Due to the limitations of our high oxygen pressure equipment ($p_{max}$...
We decided to include 10% Ho at the place of Sr, which, as demonstrated by James et al., eases the stabilization of the most oxidized SrCoO$_3$-x phases.

In this study we report room temperature structural data on the cobaltite series Ho$_{0.1}$Sr$_{0.9}$CoO$_{3−x}$ (0.15 ≤ x ≤ 0.49) that clearly show the existence of a nearly complete Co$^{3+}$/Co$^{4+}$ charge ordering for compositions close to x=0.23. The charge-ordering pattern is characterized by a structural modulation which can be described by the propagation vector q$_{Co}$=(0 0 1/2). The signature of the charge-ordered state is observed within a broad compositional range (0.19 ≤ x ≤ 0.31), although the apparent size$^{17}$ of the charge-ordered clusters decreases from 250 Å (x=0.27) to 50 Å (x =0.15, 0.31). The extremely simple one-dimensional deformation pattern displayed by these compounds is believed to be at the origin of this unusually well-established charge order. The nonexistence of a long-range charge-ordered state in this system is attributed to the competition between the ordering of the oxygen vacancies and that of the Co$^{3+}$/Co$^{4+}$ species, which, due to the Ho doping, are expected to happen at different oxygen vacancy concentrations (x=0.25 and x =0.20, respectively).

II. EXPERIMENT

The starting material was prepared by a conventional solid state reaction using Ho$_2$O$_3$, SrCO$_3$, and Co$_3$O$_4$ of a minimum purity of 99.99%. The as-prepared material had an oxygen deficiency x=0.25, as determined by thermogravimetric hydrogen reduction. The starting sample was then annealed at 500 K and 800 bar of oxygen for 24 h and slowly cooled down with 1 K/h. The resulting material with oxygen deficiency x=0.15, was then separated into portions of 1 g, which were individually reduced by annealing at 773 K in 20–50 bar of oxygen pressure (samples with x=0.18, 0.19, 0.22, 0.24, 0.37), or by annealing in evacuated quartz ampoules together with an appropriate amount of metallic copper getter (samples with x=0.15, 0.27, 0.31, 0.42, 0.49). The experimental uncertainty in the oxygen deficiency, as determined by reduction in the flow of 5% H$_2$+95% He at T=1273 K, was about 1%.

In order to precisely compare the lattice parameters of the different samples, room temperature (RT) x-ray diffraction (XRD) patterns of powders mixed with Si as an internal standard were collected on a Siemens D500 diffractometer using Cu Kα radiation. The patterns were measured within 4° < 2θ < 120° using a step size of 0.02°. For some representative compositions (x=0.15, 0.27, 0.31, 0.42, 0.49), neutron powder diffraction (NPD) data were collected on the high-resolution powder diffractometer HRPT$^{19}$ at SINQ (PSI, Switzerland) at RT. The data were acquired in the range 5° < 2θ < 165° using a step of 0.05° and λ = 1.494 Å. Additional RT NPD measurements (for x=0.19) were performed at D2B at the ILL, France, within 5° < 2θ < 160° and with λ=1.60 Å. The Rietveld program FullProf$^{20}$ was used to refine both the crystallographic and microstructures.

III. RESULTS

A. 0.15 ≤ x ≤ 0.31: Short-range charge ordering

1. Structure

Figure 1 shows the RT x-ray diffraction patterns of Ho$_{0.1}$Sr$_{0.9}$CoO$_{3−x}$, for oxygen deficiencies x=0.15 and 0.27. For 0.15 ≤ x ≤ 0.31, the reflections could be properly indexed using the same cubic, perovskitelike structure (a=b=c=a$_p$, space group Pm3m) as for the fully oxidized compound SrCoO$_3$. However, close inspection of the background shows the presence of several extremely small reflections, about 150 times smaller than the most intense peak. These extra features, which are also observed in the neutron diffraction patterns, are much broader than the resolution limited, Pm3m-allowed reflections (see enlargements in Fig. 1 and 5), and could only be indexed by doubling the cubic unit cell along c. Interestingly, the half value of c exactly coincides with that of a$_p$ (c=2a$_p$), indicating that, in spite of its tetragonal symmetry, the unit cell of the Ho$_{0.1}$Sr$_{0.9}$CoO$_{3−x}$ system in the 0.15 ≤ x ≤ 0.31 range is metrically cubic. In other words, the Co ions form a rigid framework able to accommodate large amounts of oxygen vacancies. This finding is probably related with the high ionic conduction displayed by SrCoO$_{3−x}$ and related systems.

The refinement of the crystallographic structure was performed using the tetragonal space group P4/mmm (which is a subgroup of Pm3m), with the restrictions a=b=a$_p$, c =2a$_p$, for the structural parameters see Table I. As shown in

FIG. 1. Room temperature x-ray diffraction patterns for two chosen samples (x=0.15 and 0.27) of the Ho$_{0.1}$Sr$_{0.9}$CoO$_{3−x}$ series. The indexing corresponds to the Pm3m unit cell. The peaks marked with * are reflections from the Si internal standard.
TABLE I. Crystallographic parameters derived from the Ho$_0.1$Sr$_{0.9}$CoO$_{3-x}$ NPD data: The sites are (i) for the cubic Pm3m phase ($x=0.15$): Sr/Ho 1a (0 0 0); Co 1b (0.5 0.5 0.5); O 3c (0 0 0.5); (ii) for the tetragonal P4/mmm ($0.19\leq x \leq 0.31$): Sr/Ho 2h (0.5 0.5 z); Co1 1a (0 0 0); Co2 1b (0 0 0.5); O1 2f (0 0 0); O2 2e (0.5 0.5 0.5); O3 2g (0 0 z). $\chi^2$ and $R_{Bragg}$ are also shown.

<table>
<thead>
<tr>
<th></th>
<th>$x=0.15$</th>
<th>$x=0.19$</th>
<th>$x=0.27$</th>
<th>$x=0.31$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>B</td>
<td>Occ.</td>
<td>z</td>
</tr>
<tr>
<td>Sr/Ho</td>
<td>0.98(03)</td>
<td>1.19(03)</td>
<td>1.8/0.2</td>
<td>0.258(5)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.43(04)</td>
<td>0.61(05)</td>
<td>1.0</td>
<td>0.48(04)</td>
</tr>
<tr>
<td>Co(2)</td>
<td>0.61(05)</td>
<td>1.0</td>
<td>0.48(04)</td>
<td>1.0</td>
</tr>
<tr>
<td>O(1)</td>
<td>1.69(02)</td>
<td>0.76(07)</td>
<td>1.89(2)</td>
<td>0.96(06)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2.23(13)</td>
<td>1.50(2)</td>
<td>2.63(12)</td>
<td>1.52(2)</td>
</tr>
<tr>
<td>O(3)</td>
<td>3.39(15)</td>
<td>2.04(5)</td>
<td>0.2402(9)</td>
<td>2.84(15)</td>
</tr>
<tr>
<td>Oxygen cont.</td>
<td>2.80(1)</td>
<td>2.72(3)</td>
<td>2.71(3)</td>
<td>2.67(3)</td>
</tr>
<tr>
<td>$a_p$ (Å)</td>
<td>3.8351(4)</td>
<td>3.8367(4)</td>
<td>3.8411(4)</td>
<td>3.8477(5)</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>12.6</td>
<td>6.3</td>
<td>12.2</td>
<td>8.2</td>
</tr>
<tr>
<td>$R_{Bragg}$</td>
<td>4.1</td>
<td>4.8</td>
<td>5.1</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Fig. 2 and the caption of Table I, the Co sites exactly coincide with those of the cubic perovskite, whereas the apical oxygens O3 and the Sr/Ho atoms can now move away from the cubic positions (arrows in Fig. 2) along the crystallographic c axis.

The displacements of the apical oxygens, which, for the sake of clarity, have been exaggerated in Fig. 2, lead to the splitting up of the unique Co position of the cubic perovskite into two sites (Co1 and Co2) with distinct octahedral distortions. As shown in Table II, the Co1 and Co2 coordination polyhedra have the same in-plane Co-O distances, but the first are squeezed and the second stretched along the c axis. The structure can then be described as a series of elongated and/or compressed CoO$_6$ corner-sharing octahedra planes alternating along the c axis.

As it was previously mentioned, this particular structural modulation is observed for oxygen vacancy concentrations ranging from $x=0.15$ to $x=0.31$. Interestingly, the composition close to the center of the interval ($x=0.19$) displays a formal Co oxidation state of +3.52(10). This value almost coincides with +3.50, which corresponds to an ideal 1:1 Co$^{3+}$/Co$^{4+}$ ratio and an oxygen vacancy concentration of $x=0.20$. This fact, together with the anomalies observed in the cell parameters [inset in Fig. 3(a)] strongly suggest the existence of Co$^{3+}$/Co$^{4+}$ charge ordering for oxygen vacancy concentrations close to $x=0.20$. This question will be further addressed in the next section, where the results of the bond valence sums calculations will be presented.

Concerning the location of the oxygen vacancies, we observe a preference for one of the two equatorial oxygen positions. Oxygen is mainly lost from the basal planes of the elongated octahedra (O2 sites), which display occupancies of ~75% compared with values close to 100% at the other basal oxygen position O1 and the apical O3 sites (Table I). Since such an oxygen ordering pattern also displays $k=(0 0 1/2)$ periodicity, it could be argued that oxygen ordering alone is responsible for the observed superstructure peaks. Rietveld refinements showed, however, that the intensities of the new reflections could only be properly reproduced by allowing the apical oxygens and the Ho/Sr atoms to move away from the Pm3m perovskite positions.

This type of vacancy ordering is consistent with the behavior observed for the other members of the series with larger oxygen deficiencies. The compounds with $x>0.31$ display a closely related vacancy ordering pattern which, by approaching $x=0.50$, gives rise to the so-called brownmillerite-type structure. In the P4/mmm compounds, the ideally vacant ordered composition is $x=0.25$. Here 25% of the oxygens of every second basal plane have been lost, reducing the effective Co2 coordination from 6 to 5. Due to the absence of x and y components in the observed k vector ($k=0 0 1/2$), we conclude that the oxygen vacancies are randomly distributed inside the basal planes. In the brownmillerite-related compounds ($x\sim0.50$), each second CoO$_6$ octahedron along the c direction becomes a tetrahedron due to the loss and the subsequent ordering of 50% of its basal oxygens, see Fig. 4 and Chap. IIIB. The Co coordination is in this case reduced from 6 to 4 and the vacancy ordering is described by an enlarged unit cell with $a=\sqrt{2}a_p$, $b=4a_p$, $c=\sqrt{2}a_p$. 024423-3
TABLE II. Individual and average Co-O distances; effective, average, and normalized BVS; deviations $\delta$ of site BVS from average BVS and distortions $\Delta_d$ [$(d_{\text{apical}} - d_{\text{basal}}) \times 100$] based on NPD measurements. No. indicates the number of bonds of this kind.

<table>
<thead>
<tr>
<th>No.</th>
<th>$x=0.15$</th>
<th>$x=0.19$</th>
<th>$x=0.27$</th>
<th>$x=0.31$</th>
<th>$x=0.49$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{Co}(1)-\text{O}(1)}$</td>
<td>6</td>
<td>1.9175(01)</td>
<td>4</td>
<td>1.9183(01)</td>
<td>1.9205(01)</td>
</tr>
<tr>
<td>$d_{\text{Co}(1)-\text{O}(3)}$</td>
<td>2</td>
<td>1.8434(67)</td>
<td>1.8392(46)</td>
<td>1.8602(63)</td>
<td>2</td>
</tr>
<tr>
<td>$\langle d_{\text{Co}(1)-\text{O}} \rangle$</td>
<td>1.9175(01)</td>
<td>1.8933(16)</td>
<td>1.8934(08)</td>
<td>1.9026(15)</td>
<td>2</td>
</tr>
<tr>
<td>$d_{\text{Co}(2)-\text{O}(2)}$</td>
<td>4</td>
<td>1.9183(01)</td>
<td>1.9205(01)</td>
<td>1.9238(01)</td>
<td>2</td>
</tr>
<tr>
<td>$d_{\text{Co}(2)-\text{O}(3)}$</td>
<td>2</td>
<td>1.9933(67)</td>
<td>2.0019(46)</td>
<td>1.9874(63)</td>
<td>1</td>
</tr>
<tr>
<td>$\langle d_{\text{Co}(2)-\text{O}} \rangle$</td>
<td>1.9433(16)</td>
<td>1.9476(08)</td>
<td>1.9450(15)</td>
<td>1.8533(13)</td>
<td></td>
</tr>
<tr>
<td>BVS Co(1)</td>
<td>3.11(02)</td>
<td>3.48(11)</td>
<td>3.48(07)</td>
<td>3.33(09)</td>
<td>2.54(06)</td>
</tr>
<tr>
<td>BVS Co(2)</td>
<td>2.60(07)</td>
<td>2.54(05)</td>
<td>2.50(07)</td>
<td>2.61(06)</td>
<td></td>
</tr>
<tr>
<td>$\langle \text{BVS} \rangle$</td>
<td>3.11(02)</td>
<td>3.05(09)</td>
<td>3.00(06)</td>
<td>2.92(08)</td>
<td>2.58(06)</td>
</tr>
<tr>
<td>Nominal value</td>
<td>3.60</td>
<td>3.52</td>
<td>3.36</td>
<td>3.27</td>
<td>2.92</td>
</tr>
<tr>
<td>shifted BVS Co(1)</td>
<td>3.60(02)</td>
<td>3.95(11)</td>
<td>3.84(07)</td>
<td>3.68(09)</td>
<td>2.87(06)</td>
</tr>
<tr>
<td>shifted BVS Co(2)</td>
<td>3.07(07)</td>
<td>2.90(05)</td>
<td>2.85(07)</td>
<td>2.95(06)</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.51(2)</td>
<td>0.52(1)</td>
<td>0.47(1)</td>
<td>0.04(1)</td>
<td></td>
</tr>
<tr>
<td>$\Delta_d[\text{Co}(1)]$ (%)</td>
<td>$-7.49(7)$</td>
<td>$-8.13(5)$</td>
<td>$-6.36(7)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_d[\text{Co}(2)]$ (%)</td>
<td>$7.50(7)$</td>
<td>$8.14(5)$</td>
<td>$6.36(7)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Bond valence sums

To estimate the valence of Co from the observed Co-O bond lengths, we calculated the BVS according to the expression proposed by Altermatt and Brown:12

$$V_j = \sum_i \exp \left( \frac{R_0 - R_{ij}}{B} \right)$$

Here $B$ and $R_0$ are tabulated parameters13 ($R_0=1.692$, 1.70, and 1.75 Å for Co$^{2+}$, Co$^{3+}$, and Co$^{4+}$ at RT, respectively, $B=0.37$ Å) and $R_{ij}$ are the experimental Co-O bondlengths at RT. The results are displayed in Table II, together with the refined Co-O distances $d$, the average Co-O bondlengths $\langle d \rangle$, the deviation $\delta$ of the site BVS, from the average BVS, and the distortion of the CoO$_6$ octahedra $\Delta_d$ in the charge-ordered phase, defined as $\Delta_d=(d_{\text{apical}}-d_{\text{basal}}) \times 100$.

The refined lattice parameters from XRD are shown in Fig. 3(a). Their evolution with growing oxygen deficiency will be addressed later in this text. As shown in Fig. 3(b) the site-averaged BVS Co valences are found to be lower than the values calculated from the nominal stoichiometry of the samples. This is a rather common observation in solid solutions and nonstoichiometric materials. In the BVS formalism it means that the Co-O distances found experimentally are longer than expected. This is probably due to an imperfect description of the O and/or Ho/Sr distribution in the Rietveld refinements, which try to include into the Co-O bondlength the fluctuations coming from the disorder.

The BVS valences for the individual Co1 and Co2 sites calculated from the results of the neutron diffraction Rietveld refinements are also shown in Fig. 3(b). In the $P4/mmm$ phase the difference between the Co valence at the com-
pressed (Co1) and elongated (Co2) octahedral positions is remarkable. The largest disparity corresponds to \( x = 0.19 \), whose nominal oxidation state \((+3.52)\) almost matches the ideal 1:1 \( \text{Co}^{3+}/\text{Co}^{4+} \) ratio value. In the compressed octahedra, the smaller average Co-O distance leads to an effective charge of \(+3.48(11)\), 0.88 electrons smaller than in the elongated ones \([+2.60(7)]\). By shifting these results in order to match the BVS average valence with the nominal oxidation state, we obtain \(+3.95(11)\) and \(+3.07(7)\), which are very close to the ideal +4.00 and +3.00 values. Hence, we interpret these results as evidence of a \( \text{Co}^{3+}/\text{Co}^{4+} \) charge-ordered state in this material.

In spite of the large number of studies dealing with \( \text{SrCoO}_{3-x} \) and related systems, this is—as far as we know—the first experimental evidence supporting the existence of charge ordering in these compounds. Only James et al. have commented briefly on shorter average Co-O bonds compared to the Co2-O ones in \( R_{0.10}\text{Sr}_{0.90}\text{CoO}_{3-x} \) (Ref. 27) and suggest the possibility of charge order. These authors have reported the observation of a \( k = (0 0 1/2) \) type superstructure in both the electron and neutron diffraction patterns for the \( R_{x}\text{Sr}_{1-x}\text{CoO}_{3-x} \) system \((R = \text{rare earth and } 0.67 \leq x \leq 0.90, \ x \sim 0.20) \). In contrast to our results, they have attributed the superstructure reflections to the ordering of oxygen vacancies located at the apical positions. As it was previously mentioned, we find instead that the oxygen vacancies are concentrated in the basal planes of the elongated octahedra.

We would like now to address the reasons leading to the observation of a nearly complete charge ordering in the \( \text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x} \) system. In our opinion, a plausible explanation may be the extremely simple distortion pattern displayed by these compounds. When comparing it to the much more complex arrangement of charges observed in systems such as \( \text{R}_{1/2}\text{Ca}_{1/2}\text{MnO}_{3} \) or \( \text{YNiO}_{3} \), it is evident that the elastic energy necessary to accommodate the two \( \text{Co}^{3+} \) and \( \text{Co}^{4+} \) octahedra in a one-dimensional \( k = (0 0 1/2) \) distortion pattern should be necessarily smaller than those needed to accommodate the \( \text{Ni}^{2+} \) and \( \text{Ni}^{4+} \) octahedra of \( \text{YNiO}_{3} \) in the observed three-dimensional \((3D)\) \( k = (1/2 1/2 1/2) \) array. An even less favorable situation is found in manganese perovskites, where the difference between the distortions of the nearly perfect \( \text{Mn}^{4+} \) and the Jahn-Teller distorted \( \text{Mn}^{3+} \) octahedra are so large that a 3D arrangement of these motives is topologically impossible without "relaxing" the degree of charge ordering or, in other words, its associated distortions. For the particular case of half-doped manganites, an alternative mechanism has been proposed by van den Brink et al.\(^{26}\) in order to explain the experimentally observed Mn charges in these compounds. These authors attribute the stabilization of a fractional charge ordering to the strong Coulomb repulsion between the electrons on the same Mn, their formalism being able to reproduce the reported experimental values. Further calculations for the \( \text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x} \) system would be very useful in order to estimate the influence of this mechanism in the formation of the charge-ordered state.

3. Microstructure

As mentioned in the previous sections, the \( P4/mmm \) superstructure reflections display a pronounced broadening which is absent in the fundamental reflections of the \( Pm3m \) parentage. The difference between both sets can be seen in Fig. 1, where the \((0 0 1/2)\), \((1 0 5/2)\), and \((1 1 5/2)\) reflections of the samples with \( x = 0.15 \) and 0.27 are displayed. Two possible origins can be considered to explain this extra broadening: On one side, the fluctuations of the cell parameter \( c \) as a consequence of the partial ordering of the oxygen vacancies along this direction (strain effect). On the other, the stabilization of the \((0 0 1/2)\) distortions associated to the charge ordering over clusters of finite size (size effect). Since these two mechanisms imply completely different dependencies of the extra broadening \( \beta \) with the scattering angle, it is possible to distinguish between them by including the appropriated expressions in the analysis of the Rietveld profiles.

In the case of microstrain broadening, we have used the formalism developed by Rodríguez-Carvajal et al.\(^{29}\) The broadening due to the existence of a lattice parameter distribution appears as an additional term \( D^{2}_{\text{strain}}(hkl) \) in the usual Caglioti formula:

\[
FWHM^{2}_{\Theta} = \left[ U + D^{2}_{\text{strain}}(hkl) \right] \tan^{2} \Theta + V \tan \Theta + W
\]

which describes the \( 2\Theta \) dependence of the full width at half maximum of the Gaussian component of a particular Bragg reflection, assuming that the full Bragg profile can be described by a Voigt function. In the present case (fluctuations of the cell parameter \( c \)) \( D^{2}_{\text{strain}}(hkl) \) can be written as

\[
D^{2}_{\text{strain}}(hkl) = \tan \Theta \times \frac{4l^{2} \varepsilon_{c} \sqrt{2 \ln 2}}{h^{2}(ca)^{2} + k^{2}(cb)^{2} + l^{2}}.
\]

This expression, which is zero for reflections with \( l = 0 \) (no extra broadening), introduces just one additional parameter in the Rietveld refinements \((\varepsilon_{c} = \sigma_{c} / c)\), whose refined value gives information about the standard deviation \( \sigma_{c} \) of the \( c \) parameter distribution.
To describe the size broadening effects, which we assumed to be isotropic (=spherical diffraction domains), we used the well-known Scherrer formula

$$\beta(hkl) = \frac{\lambda}{D \cos \Theta}.$$ 

Here $\beta(hkl)$ is the contribution to the integral breadth of the Lorentzian component of a particular reflection, $\lambda$ is the wavelength of the radiation used (neutrons or x ray), and the apparent size $D$ is the volume average of the diffraction domain perpendicular to the (hkl) plane. As in the strain case, this formalism introduces a single additional parameter $D$ in the Rietveld refinements.

The results obtained using both models are shown in Fig. 5. The better agreement of the size model is evident, especially at low angles, where the different 20 dependences of the strain and size corrections (tan $\Theta$ and sec $\Theta$, respectively) are most marked. Hence, we conclude that the origin of the extra broadening is the development of a Co$^{3+}$/Co$^{4+}$ charge-ordering state over clusters of finite size. The refined values of $D$, which range between 50 and 250 Å, are displayed in Fig. 3(c). A clear maximum is observed for $x=0.23$, close to the ideal 1:1 Co$^{3+}$/Co$^{4+}$ concentration $x=0.20$. It also coincides with the anomaly in the cell parameters and the distortion parameter of the CO$_6$, confirming the charge-ordering origin of the broadening.

Since, as mentioned in previous sections, the Co$^{3+}$/Co$^{4+}$ charge ordering in these materials is nearly perfect, the non-observation of a long-range charge-ordered state seems paradoxal. A possible explanation may be the competition between the ordering of the oxygen vacancies and that of the Co$^{3+}$/Co$^{4+}$ species, which, due to the Ho doping, are expected to occur at different oxygen vacancy concentrations ($x=0.25$ and $x=0.20$, respectively). As shown in Fig. 3(b), the maximum size of the charge-ordered domains is not found for $x=0.20$ but for $x=0.23$, that is, a composition in between 0.20 and 0.25. Further investigations on compounds without Ho would be necessary in order to confirm this hypothesis.

**B. 0.31 < x ≤ 0.49: Long-range oxygen vacancy ordering**

Close inspection of the neutron and x-ray diffraction patterns of Ho$_{0.1}$Sr$_{0.9}$CoO$_3-x$ with $x=0.37$ and 0.42 revealed that these samples were not single phase. The RT data could only be reasonably refined by assuming the existence of two phases: One (majority) with tetragonal $P4/mmm$ symmetry as in the materials discussed in the previous sections, and a second one (minority) with orthorhombic, brownmillerite-type $Imma$ symmetry, which, as it will be shown later, is displayed by the most oxygen-defective material studied in this work ($x=0.49$). The weight ratio of the tetragonal to the orthorhombic phase is estimated to be about 5:1 for $x=0.42$.

Due to the strong correlations between the structural parameters of both phases, we were forced to fix the values of the atomic coordinates, the occupancies, and the Debye-Waller factors of all atoms to those found in the neighboring single-phase compounds ($x=0.31$ and $x=0.49$). The lattice parameters could then be reasonably fitted. The refined values of the pseudocubic lattice parameters are displayed in Fig. 3(a).

The $x=0.49$ compound displays much more complex x-ray and neutron powder diffraction patterns than those of the $P4/mmm$ samples (see Fig. 6). The new reflections could be indexed with a $\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$ supercell (see Fig. 2), which corresponds to the brownmillerite-type structure (note the different orientations of the crystallographic axes with respect to the $P4/mmm$ unit cell). Since two different orientations of the tetrahedra are possible, a long polemic concerning the best way to describe the average structure was conducted. Following Greaves et al., we chose the centrosymmetric space group $Imma$. As shown in Table III, it describes the two possible orientations using a single Wyckoff position (8i) with only half the occupation. Using this
space group, an excellent fit between the $\text{Ho}_0.1\text{Sr}_{0.9}\text{CoO}_{2.51}$ NPD data and the calculated profile was achieved (see Fig. 6 and Table III).

By increasing $x$, a continuous decrease of the difference between the BVS valences at the two $P4/mmm$ Co ion sites is observed, indicating a progressive melting of the charge-ordered state. At $x=0.49$, both Co sites display almost identical oxidation states (2.88 and 2.96, see Table II), in spite of their different coordinations (octahedral and tetrahedral), in agreement with previous studies on $\text{Sr}_2\text{Co}_2\text{O}_5$.$^{14}$

### IV. SUMMARY AND CONCLUSIONS

We have studied the oxygen defective $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ cobaltite series within a broad compositional range (0.15 $\leq x \leq 0.49$). The cubic $Pm3m$ and orthorhombic $Imma$ structures of the parent materials $\text{SrCoO}_3$ and $\text{Sr}_2\text{Co}_2\text{O}_5$ are observed up to $x=0.15$ ($Pm3m$) and for $x \geq 0.42$ ($Imma$). Additionally, our high resolution neutron diffraction data clearly show the existence of a short-range $\text{Co}^{3+}/\text{Co}^{4+}$ charge ordering for oxygen vacancy concentrations close to $x=0.20$. The associated structural modulation can be described by the propagation vector $q_{\text{CO}}=(0 \ 0 \ 1/2)$, and the normalized bond valence sums values for the $\text{Co}^{3+}/\text{Co}^{4+}$ sites are very close to their nominal values (+3.07 and +3.95, for $x=0.19$). The signature of the charge-ordered state is observed within a broad compositional range, with the apparent size of the charge-ordered clusters decreasing from 250 Å ($x=0.27$) to 50 Å ($x=0.15, 0.31$). The noncoincidence of the 1:1 $\text{Co}^{3+}/\text{Co}^{4+}$ composition $x=0.20$ with the ideal vacancy ordered composition $x=0.25$ is thought to prevent long-range charge order in this system. The deformation pattern associated to the charge modulation can be described as an array of elongated and compressed $\text{CoO}_6$ corner-sharing octahedra planes alternating along the $c$ axis. This simple one-dimensional pattern is believed to be at the origin of the unusually well-established charge order.

### ACKNOWLEDGMENTS

We are grateful to D. Sheptyakov, A. Daoud-Aladine, and J. Rodríguez-Carvajal for helpful discussions concerning the Rietveld analysis as well as to the SINQ and ILL neutron facilities for the allocation of beam time. Financial support from the Swiss National Science Foundation through Grants SCOPES (No. IB7320-110859/1) and Marie Heim-Voegtlin (No. PMPD2-102504), as well as the NCCR MaNEP projects is also gratefully acknowledged.

---

*Electronic address: Sabine.Streule@psi.ch


5 As calculated using the bond valence sum method (Refs. 11–13), see Chapter IIIA2.


17 The apparent size is defined as the volume average of the domain in the direction perpendicular to a (hkl) plane (Ref. 18) see Chapter IIIA3.