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

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We report the observation of $\text{Co}^{3+}/\text{Co}^{4+}$ 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 $\mathbf{q}_{\text{CO}} = (0\ 0\ 1/2)$ with respect to the cubic perovskite cell $Pm\bar{3}m$, occurs for compositions close to $x=0.20$, corresponding to a 1:1 $\text{Co}^{3+}/\text{Co}^{4+}$ ratio and extends over clusters of finite size ($D \sim 250$ 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.

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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 $R_{1/2}A_{1/2}\text{MnO}_3$ (R : trivalent ion, A : Ca or Sr), which contain nominally equal amounts of Mn^{3+} and Mn^{4+} . The existence of a $\text{Mn}^{3+}/\text{Mn}^{4+}$ CO pattern, which was proposed by Goodenough¹ in order to explain the unusual magnetic structure displayed by these compounds, was one of the major contributions leading to the setting up of the Goodenough-Kanamori-Anderson superexchange rules. Further powder^{2,3} and single-crystal⁴ neutron diffraction experiments confirmed the presence of superstructure peaks, which were refined using distortion patterns involving two or more Mn sites. However, the very similar average Mn-O distances associated to all of them gave rise to extremely close bond valence sums (+3.53 and +3.50),⁵ far from the expected +4 and +3 values. Fractional charges have been also obtained from the analysis of single-crystal x-ray resonant scattering data,^{6,7} suggesting a distinct, much weaker charge redistribution than that predicted by Goodenough.

A similar situation has been described for other perovskite-related systems containing nominally equal amounts of $\text{Fe}^{3+}/\text{Fe}^{5+}$ (CaFeO_3),⁸ $\text{Co}^{2+}/\text{Co}^{3+}$ (YBaCo_2O_5),⁹ and $\text{Ni}^{2+}/\text{Ni}^{4+}$ (YNiO_3).¹⁰ Even if the stabilization of the CO state is accompanied in all cases by a sudden increase of the electrical resistivity (a metal-insulator transition in the case of CaFeO_3 and YNiO_3), the expected charge redistribution at

T_{CO} has been found to be always partial. Hence, the reported bond valence sums^{11–13} for the aforementioned compounds are $\text{Fe}^{4\pm\delta}$, $\text{Co}^{2.5\pm\delta}$, and $\text{Ni}^{3\pm\delta}$, with $\delta \sim 0.5$, 0.3, and 0.3, respectively, considerably smaller than the ideal values $\delta=1$, 0.5, and 1 values.

Although estimations of the ionic charges can be obtained from other techniques such as single-crystal x-ray diffraction (through electron density maps), Mössbauer or x-ray spectroscopies, the results of the high resolution neutron powder diffraction analysis combined with the bond valence method^{11–13} usually provide a good starting point to approach the problem. This is particularly true in the case of compounds with highly electronegative anions (as oxides and fluorides), as well as for systems exhibiting enough degrees of freedom in their crystallographic structure. Moreover, the relationship between the interatomic distances and the bond valences, while extremely simple, has the advantage of providing a fast, straightforward, and (very often) extremely useful picture, which contrasts with extensive computing work necessary in the case of single-crystal x-ray diffraction (especially in the case of twinned crystals) and with theoretical difficulties due to the interpretation of x-ray spectroscopies results.

In order to test the conclusions of the bond valence sum (BVS) analysis in other perovskite systems with possibilities 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}

=800 bar), we decided to include 10% Ho at the place of Sr, which, as demonstrated by James *et al.*,¹⁶ eases the stabilization of the most oxidized SrCoO_{3-x} phases.

In this study we report room temperature structural data on the cobaltite series $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ ($0.15 \leq x \leq 0.49$) that clearly show the existence of a nearly complete $\text{Co}^{3+}/\text{Co}^{4+}$ 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 $\mathbf{q}_{\text{CO}}=(0\ 0\ 1/2)$. The signature of the charge-ordered state is observed within a broad compositional range ($0.19 \leq x \leq 0.31$), although the apparent size¹⁷ 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 $\text{Co}^{3+}/\text{Co}^{4+}$ 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_2O_3 , SrCO_3 , and Co_3O_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% $\text{H}_2+95\%$ 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 $\text{Cu } K\alpha$ radiation. The patterns were measured within $4^\circ < 2\theta < 120^\circ$ 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 HRPT¹⁹ at SINQ (PSI, Switzerland) at RT. The data were acquired in the range $5^\circ < 2\theta < 165^\circ$ using a step of 0.05° and $\lambda=1.494$ Å. Additional RT NPD measurements (for $x=0.19$) were performed at D2B at the ILL, France, within $5^\circ < 2\theta < 160^\circ$ and with $\lambda=1.60$ Å. The Rietveld program FullProf²⁰ was used to refine both the crystallographic and microstructures.

FIG. 1. Room temperature x-ray diffraction patterns for two chosen samples ($x=0.15$ and 0.27) of the $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ series. The indexing corresponds to the $Pm3m$ unit cell. The peaks marked with * are reflections from the Si internal standard.

III. RESULTS

A. $0.15 \leq x \leq 0.31$: Short-range charge ordering

1. Structure

Figure 1 shows the RT x-ray diffraction patterns of $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ for oxygen deficiencies $x=0.15$ and 0.27 . For $0.15 \leq x \leq 0.31$, 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 .^{21,22} 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 $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ system in the $0.15 \leq x \leq 0.31$ 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.^{23–26}

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

TABLE I. Crystallographic parameters derived from the $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ NPD data: The sites are (i) for the cubic $Pm\bar{3}m$ 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 (0.5 0 0); O2 2e (0.5 0 0.5); O3 2g (0 0 z). χ^2 and R_{Bragg} are also shown.

	$x=0.15$		$x=0.19$		$x=0.27$			$x=0.31$		
	B	B	Occ.	z	B	Occ.	z	B	Occ.	z
Sr/Ho	0.98(03)	1.19(03)	1.8/0.2	0.2582(5)	1.16(03)	1.8/0.2	0.2574(4)	1.32(03)	1.8/0.2	0.2565(5)
Co(1)	0.43(04)	0.61(05)	1.0		0.48(04)	1.0		0.65(03)	1.0	
Co(2)		0.61(05)	1.0		0.48(04)	1.0		0.65(03)	1.0	
O(1)	1.69(02)	0.76(07)	1.89(2)		0.96(06)	1.94(2)		1.25(06)	1.92(2)	
O(2)		2.23(13)	1.50(2)		2.63(12)	1.52(2)		2.50(11)	1.49(2)	
O(3)		3.39(15)	2.04(5)	0.2402(9)	2.84(15)	1.95(5)	0.2394(6)	3.55(13)	1.92(5)	0.2417(8)
Oxygen cont.	2.80(1)		2.72(3)			2.71(3)			2.67(3)	
a_p (Å)	3.8351(4)		3.8367(4)			3.8411(4)			3.8477(5)	
χ^2	12.6		6.3			12.2			8.2	
R_{Bragg}	4.1		4.8			5.1			5.6	

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 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 $\text{Co}^{3+}/\text{Co}^{4+}$ 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 $\text{Co}^{3+}/\text{Co}^{4+}$ 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 $\sim 75\%$ 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 $\mathbf{k}=(0\ 0\ 1/2)$ 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 $Pm\bar{3}m$ 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 vacancy 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 ($\mathbf{k}=0\ 0\ 1/2$), we conclude that the oxygen vacancies are randomly distributed inside the basal planes. In the brownmillerite-related compounds ($x \sim 0.50$), 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 $a=\sqrt{2}a_p$, $b=4a_p$, $c=\sqrt{2}a_p$.

FIG. 2. Schematic representation of the elongated and/or compressed octahedra due to shifts of the oxygen ions from their ideal position in the cubic cell. Note that the Co ions do not move away from their original position, forming a rigid lattice. The Ho ions move in the opposite direction of the oxygen ions. The direction of the shifts is indicated by arrows.

TABLE II. Individual and average Co-O distances; effective, average, and normalized BVS; deviations δ of site BVS from average BVS and distortions Δ_d [$\Delta_d = (d_{\text{apical}} - d_{\text{basal}}) \times 100$] based on NPD measurements. No. indicates the number of bonds of this kind.

	No.	$x=0.15$	No.	$x=0.19$	$x=0.27$	$x=0.31$	No.	$x=0.49$
$d_{\text{Co(1)-O(1)}}$	6	1.9175(01)	4	1.9183(01)	1.9205(01)	1.9238(1)	4	1.9406(01)
$d_{\text{Co(1)-O(3)}}$			2	1.8434(67)	1.8392(46)	1.8602(63)	2	2.2491(14)
$\langle d_{\text{Co(1)-O}} \rangle$		1.9175(01)		1.8933(16)	1.8934(08)	1.9026(15)		2.0434(02)
$d_{\text{Co(2)-O(2)}}$			4	1.9183(01)	1.9205(01)	1.9238(01)	2	1.8045(19)
$d_{\text{Co(2)-O(3)}}$			2	1.9933(67)	2.0019(46)	1.9874(63)	1	1.8638(50)
$d_{\text{Co(2)-O(3)}}$							1	1.9403(50)
$\langle d_{\text{Co(1)-O}} \rangle$				1.9433(16)	1.9476(08)	1.9450(15)		1.8533(13)
BVS Co(1)		3.11(02)		3.48(11)	3.48(07)	3.33(09)		2.54(06)
BVS Co(2)				2.60(07)	2.54(05)	2.50(07)		2.61(06)
$\langle \text{BVS} \rangle$		3.11(02)		3.05(09)	3.00(06)	2.92(08)		2.58(06)
Nominal value		3.60		3.52	3.36	3.27		2.92
shifted BVS Co(1)		3.60(02)		3.95(11)	3.84(07)	3.68(09)		2.87(06)
shifted BVS Co(2)				3.07(07)	2.90(05)	2.85(07)		2.95(06)
δ				0.51(2)	0.52(1)	0.47(1)		0.04(1)
$\Delta_d[\text{Co(1)}]$ (%)				-7.49(7)	-8.13(5)	-6.36(7)		
$\Delta_d[\text{Co(2)}]$ (%)				7.50(7)	8.14(5)	6.36(7)

FIG. 3. Oxygen deficiency dependence of (a) the pseudocubic lattice parameters (where $a = a_{\text{brown}}/\sqrt{2}$, $b = b_{\text{brown}}/4$, $c = c_{\text{brown}}/\sqrt{2}$) (from XRD); (b) the BVS for the Co1 and Co2 sites, the BVS site average, and the nominal oxidation state (from NPD); (c) the apparent size of the charge-ordered clusters (from XRD). Lines are a guide to the eye. The vertical lines indicate the structural phase boundaries and the shaded area shows the region of phase coexistence.

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 δ of the site BVS, from the average BVS, and the distortion of the CoO_6 octahedra Δ_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-

FIG. 4. Schematic representation of the three crystallographic structures displayed by $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ as a function of the oxygen content. Oxygen loss only takes place in the basal planes.

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 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 Co1-O bonds compared to the Co2-O ones in $\text{R}_{0.10}\text{Sr}_{0.90}\text{CoO}_{3-x}$ (Ref. 27) and suggest the possibility of charge order. These authors^{16,27} have reported the observation of a $\mathbf{k}=(0\ 0\ 1/2)$ type superstructure in both the electron and neutron diffraction patterns for the $\text{R}_y\text{Sr}_{1-y}\text{CoO}_{3-x}$ 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 YNiO_3 , it is evident that the elastic energy necessary to accommodate the two Co^{3+} and Co^{4+} octahedra in a one-dimensional $\mathbf{k}=(0\ 0\ 1/2)$ distortion pattern should be necessarily smaller than those needed to ar-

range the Ni^{2+} and Ni^{4+} octahedra of YNiO_3 in the observed three-dimensional (3D) $\mathbf{k}=(1/2\ 1/2\ 1/2)$ array. An even less favorable situation is found in manganese perovskites, where the difference between the distortions of the nearly perfect Mn^{4+} and the Jahn-Teller distorted 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.*²⁸ 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 $Pm\bar{3}m$ 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 β 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 $D_{\text{strain}}^2(hkl)$ in the usual Cagliotti formula:

$$FWHM_G^2 = [U + D_{\text{strain}}^2(hkl)] \tan^2 \Theta + V \tan \Theta + W$$

which describes the 2Θ 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) $D_{\text{strain}}^2(hkl)$ can be written as

$$D_{\text{strain}}^2(hkl) = \tan \Theta \times \frac{4l^2 \epsilon_c \sqrt{2 \ln 2}}{h^2(c/a)^2 + k^2(c/b)^2 + l^2}.$$

This expression, which is zero for reflections with $l=0$ (no extra broadening), introduces just one additional parameter in the Rietveld refinements ($\epsilon_c = \sigma_c/c$), whose refined value gives information about the standard deviation σ_c of the c parameter distribution.

FIG. 5. Neutron powder diffraction patterns for $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ ($x=0.27$) fit with different models. Top: Using just the resolution function. Middle: Fit obtained using the strain model. Bottom: Using the size effect model.

To describe the size broadening effects, which we assumed to be isotropic ($\equiv$ 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, λ 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.¹⁸ 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 2Θ 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 $\text{Co}^{3+}/\text{Co}^{4+}$ charge-ordered 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 $\text{Co}^{3+}/\text{Co}^{4+}$ concentration $x=0.20$. It also coincides with the anomaly in the cell parameters and the distortion parameter of the CoO_6 , confirming the charge-ordering origin of the broadening.

Since, as mentioned in previous sections, the $\text{Co}^{3+}/\text{Co}^{4+}$ charge ordering in these materials is nearly perfect, the non-observation of a long-range charge-ordered state seems paradoxical. A possible explanation may be the competition between the ordering of the oxygen vacancies and that of the $\text{Co}^{3+}/\text{Co}^{4+}$ species, which, due to the Ho doping, are ex-

FIG. 6. Room temperature neutron powder diffraction pattern for the $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{2.51}$ compound.

pected 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. $0.31 < x \leq 0.49$: Long-range oxygen vacancy ordering

Close inspection of the neutron and x-ray diffraction patterns of $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ 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 (majoritary) with tetragonal $P4/mmm$ symmetry as in the materials discussed in the previous sections, and a second one (minoritary) 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.^{30–32} Following Greaves *et al.*,³³ we chose the centrosymmetric space group $Imma$. As shown in Table III, it describes the two possible orientations using a single Wyck-off position (8i) with only half the occupation. Using this

TABLE III. Crystallographic parameters derived from the $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-x}$ NPD data: For the orthorhombic *Imma* ($x=0.49$) the sites are Sr/Ho 8h (0.5 y z); Co1 4a (0 0 0); Co2 8i (x 0.25 z); O1 8g (0.25 y 0.25); O2 8h (0 y z); O3 8i (x 0.25 z). χ^2 and R_{Bragg} are also shown.

	<i>B</i>	Occ	$x=0.49$		
			<i>x</i>	<i>y</i>	<i>z</i>
Sr/Ho	0.82(2)	7.2/0.8		0.1102(1)	0.0103(3)
Co(1)	1.09(6)	4.0			
Co(2)	1.09(6)	4.0	0.9597(9)		0.9423(7)
O(1)	0.96(2)	8.0		0.9935(1)	
O(2)	1.36(2)	8.0		0.1419(1)	0.0423(3)
O(3)	1.25(5)	4.1(2)	0.6244(5)		0.8688(5)
Oxygen cont.			2.51(1)		
a_p (Å)			3.8331(4)	3.9390(5)	3.9146(4)
χ^2			6.31		
R_{Bragg}			4.89		

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 SrCoO_3 and $\text{Sr}_2\text{Co}_2\text{O}_5$ are observed up to $x=0.15$ ($Pm3m$) and for $x>0.42$ (*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 $\mathbf{q}_{\text{CO}}=(0\ 0\ 1/2)$, 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 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.

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