Refinement of the Crystal Structures of Strontium Cobalt Oxychlorides by Neutron Powder Diffraction

S. M. Loureiro,*,† C. Felser,†,‡ Q. Huang,§,|| and R. J. Cava†

Department of Chemistry and Princeton Materials Institute, Princeton University,
Princeton, New Jersey 08544, Institut für Anorg. und Anal. Chemie,
Johannes Guttenberg-Universität, MainzBecher Weg 24, D55099, Mainz, Germany,
NIST Center for Neutron Research, National Institutes of Standards and Technology
Gaithersburg, Maryland 20899, and Department of Materials and Nuclear Engineering,
University of Maryland, College Park, Maryland 20742

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The crystal structures of strontium cobalt oxychlorides of general formula Sr_2CoO_3Cl (Co-1L), $Sr_3Co_2O_5Cl_2$ (Co-2L), and $Sr_4Co_3O_{7.5}Cl_2$ (Co-3L) have been determined from neutron powder data. The compounds crystallize in tetragonal symmetry, space group *P*4/*nmm* (Co-1L) or *I*4/*mmm* (Co-2L and Co-3L). Their structures are analogous to the Ruddlesden−Popper phases of general formula $Sr_{n+1}M_nO_{2n+1}$. All three structures contain layers of highly distorted CoO_5Cl octahedron. The Co-3L structure, in addition, has a layer of regular CoO_6 octahedra. Because the in-plane oxygen position of the latter is partially occupied, some of the Co atoms adopt pyramidal coordination, with their basal planes parallel to the *c*-axis. The temperature dependence of the magnetic susceptibility is also reported. The moment per mole of Co atom decreases with increasing number of (CoO_2) layers.

Introduction

Transition metal oxide compounds have been a fertile field for the discovery of new materials with unusual physical properties. Among these, high-T_c superconductivity has been one of the major fields of activity of solid state chemistry and physics during the past 14 years. Although the main focus of the activity has been concentrated in the study of cuprates, we believe it to be scientifically challenging and rewarding to search for superconductivity in new systems. Of the 3d transition metal elements, the oxidation state of cobalt exists within the same valence ranges as that of copper. Cobalt also adopts fairly similar coordination and forms layered compounds where electronically active sites are found, and thus they appeared worthy of detailed study.

In our search for possible new copper-free superconducting materials, we have synthesized three cobalt oxychlorides of compositions Sr_2CoO_3Cl, $Sr_3Co_2O_5Cl_2$, and $Sr_4Co_3O_{7.5}Cl_2$ and here report their structural characterization by neutron powder diffraction data. The $Sr_3Co_2O_5Cl_2$ compound has been previously identified in the literature as an impurity in samples of the $Sr_4Co_3O_{7.5}Cl_2$ compound.[1] Both its structure and that of Sr_2CoO_3Cl have recently been determined from single-crystal X-ray diffraction data.[2] These materials have perovskite-related structures and are analogous to alkali-earth-based Fe oxychlorides of formulas Ca_2FeO_3Cl and $Sr_3Fe_2O_5Cl_2$.[3] Examples of cuprates found with a similar structure are $Ca_3Cu_2O_4Cl_2$[4] and $SrLnCuO_3Cl$.[5] Some alkali-earth Cu-based oxychlorides become superconducting when doped with sodium.[6] Superconductivity has not yet been observed in cobalt-based oxides. The current study was undertaken to define more precisely the crystal structure as a basis for further analysis of the physical properties.

Experimental Section

Synthesis and Neutron Powder Diffraction. Powder samples of nominal composition Sr_2CoO_3Cl, $Sr_3Co_2O_5Cl_2$, and $Sr_4Co_3O_8Cl_2$ were prepared by mixing stoichiometric amounts of SrO_2, Co_3O_4, and $SrCl_2$ and heating at 830 °C in air (Co-1L and Co-2L) or 960 °C in nitrogen (Co-3L) for 24 h. The synthesis of any of these compounds without the coexistence of other members of the series seems to be extremely sensitive to small variations of temperature, annealing time, and atmosphere. X-ray powder diffraction showed that, with the exception of small amounts of identified impurities ($Sr_6Co_5O_{15}$ + $Sr_6Co_5O_{15}Cl_4$ for the Co-1L sample and $Sr_6Co_5O_{15}$ for the Co-2L sample), the compounds were nearly single phase.

The neutron powder diffraction intensity data were collected using the BT-1 high-resolution powder diffractometer located at the reactor of the NIST Center for Neutron Research, employing a Cu (311) monochromator to produce a monochromatic neutron beam of wavelength 1.5401 Å. Collimators with horizontal divergences of 15-, 20-, and 7-min. arc were used before and after the monochromator and after the sample, respectively. The intensities were measured in steps of 0.05° in the 2θ range 3°−168°. Data were collected at room temper-

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* To whom correspondence should be addressed.
† Princeton University.
‡ Johannes Guttenberg-Universität.
§ National Institute and Standards and Technology.
|| University of Maryland.

(1) Müller-Buschbaum, H.; Boje, J. *Z. Anorg. Allg. Chem*. **1991**, *73*, 592.
(2) McGlothlin, N.; Khalifah, P.; Ho, D.; Cava, R. J. To be published in *Mater. Res. Bull.* **2000**.
(3) Ackerman, J. *J. Solid State Chem*. **1991**, *92*, 496.
(4) Lee, J.-G.; Ramanujachary, K. V.; Greenblatt, M. *Mater. Res. Bull.* **1991**, *26*, 1207.
(5) Fuller, R. L.; Greenblatt, M. *J. Solid State Chem*. **1991**, *92*, 386.
(6) Hiroi, Z.; Kobayashi, N.; Takano, M. *Nature* **1994**, *371*, 139.

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Table 1. Structural Parameters of Sr_2CoO_3Cl (1L) at Room Temperature (Sr_2CoO_3Cl (86.9 wt %), space group *P*4/*nmm* (#129), $a = 3.90262(7)$ Å, $c = 14.3089(3)$ Å, $V = 217.92(1)$; $R_p = 0.0302$, $R_{wp} = 0.0360$, $\chi^2 = 1.649$)[a,b]

atom	Wyckoff	*x*	*y*	*z*	U_{iso} (Å^2)	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	*n*
Co	2*c*	$^1/_4$	$^1/_4$	0.2069(3)	0.0072(9)				1.0
Sr_O	2*c*	$^3/_4$	$^3/_4$	0.0981(1)	0.0099(4)				1.0
Sr_{Cl}	2*c*	$^3/_4$	$^3/_4$	0.3442(1)	0.0090(4)				1.0
Cl	2*c*	$^1/_4$	$^1/_4$	0.42470(8)		0.0117(3)	0.0117(3)	0.013(1)	1.0
O_{ip}	4*f*	$^1/_4$	$^3/_4$	0.22960(8)		0.0122(6)	0.0103(5)	0.0103(8)	1.0
O_{ap}	2*c*	$^1/_4$	$^1/_4$	0.0745(1)		0.0173(5)	0.0173(5)	0.008(1)	1.0

[a] Note: $U_{12} = U_{13} = U_{23} = 0$. [b] Additional phases: $Sr_6Co_5O_{15}$, (7.5 wt %), space group *R*32, $a = 9.4450(8)$ Å, $c = 12.487(2)$ Å, and $V = 964.7(2)$ Å^3; $Sr_6Co_5O_{15}Cl_4$, (5.6 wt %), space group *I*4/*mmm*, $a = 3.9167(3)$ Å, $c = 31.637(5)$ Å, and $V = 485.3(1)$ Å^3.

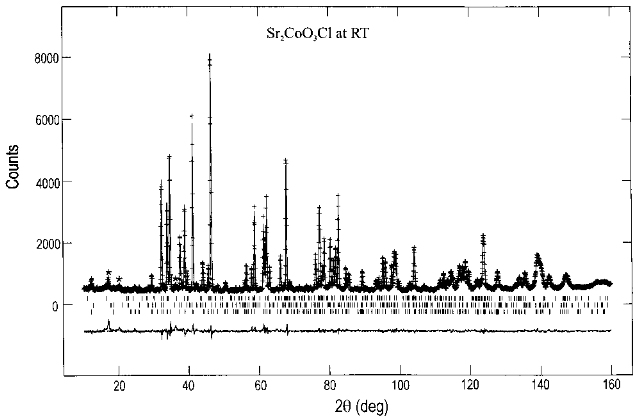

Figure 1. Observed (+) and calculated (continuous line) intensities from the Sr_2CoO_3Cl refined sample. The difference curve between (observed−calculated) intensities is shown in the bottom of the figure. The excluded regions are affected by a minimal amount of an unknown impurity. The refinement included three phases, Sr_2CoO_3Cl, $Sr_6Co_5O_{15}$, and $Sr_6Co_5O_{15}Cl_4$ (top to bottom).

ature and the structural parameters were refined using the program GSAS.[7] The neutron scattering amplitudes used in the refinements were 0.702, 0.253, 0.581, and 0.958 ($\times 10^{-12}$ cm) for Sr, Co, O, and Cl, respectively.

The initial refinement procedure for the Co-1L and −2L was carried out using the structural parameters previously reported for single-crystal X-ray diffraction data on identical phases. For the Sr_2CoO_3Cl, the initial refinement was in space group *P*4/*nmm* (#129) (origin 2) with both Sr_O and Sr_{Cl} atoms (defined as Sr in the SrO layer and Sr in the SrCl layer, respectively) and Co in position 2*c*, the in-plane (O_{ip}) oxygen in 4*f*, the apical (O_{ap}) oxygen in 2*c*, and chlorine (Cl_{ap}) in position 2*c*. The *z*-coordinates were simultaneously refined while keeping the thermal parameters isotropic and at a reasonable and constant value of 1 Å^2. Subsequent refinement of the oxygen and chlorine atoms with anisotropic thermal parameters yielded better agreement between the calculated and observed intensities. The full profile refinement for this sample included hexagonal $Sr_6Co_5O_{15}$[8] (space group *R*32) and $Sr_3Co_2O_{7.5}Cl_4$ (space group *I*4/*mmm*) as additional phases, with 7.5 and 5.6 wt % phase proportion, respectively. The final structural parameters for Sr_2CoO_3Cl are displayed in Table 1 and the Rietveld plot showing the difference between observed and calculated intensities is shown in Figure 1.

The initial refinement parameters for $Sr_3Co_2O_5Cl_2$ placed Sr_O and Sr_{Cl} in positions 2*a* and 4*e*, respectively, Co in 4*e*, O_{ip} and O_{ap} in 8*g* and 2*b*, respectively, and Cl in position 4*e* in space group *I*4/*mmm*. The refinement procedure was similar to the one described for the previous phase, with the exception that isotropic thermal parameters resulted in good agreement between calculated and observed intensities. An additional phase, $Sr_6Co_5O_{15}$ (space group *R*32), with 16 wt % phase proportion was included in the refinement. The final structural parameters for $Sr_3Co_2O_5Cl_2$ are displayed in Table 2. The Rietveld plot for the refined sample showing the difference between observed and calculated intensities is shown in Figure 2.

Table 2. Structural Parameters for $Sr_3Co_2O_5Cl_2$ (2L) at Room Temperature ($Sr_3Co_2O_5Cl_2$, (84 wt %), Space Group *I*4/*mmm* (#139), $a = 3.9142(1)$ Å, $c = 24.0098(7)$ Å, $V = 367.85(2)$; $R_p = 0.0373$, $R_{wp} = 0.0453$, $\chi^2 = 1.162$)[a]

atom	Wyckoff	*x*	*y*	*z*	U_{iso} (Å^2)	*n*
Co	4*e*	0	0	0.4219(2)	0.0068(9)	1.0
Sr_O	2*a*	0	0	0	0.012(1)	1.0
Sr_{Cl}	4*e*	0	0	0.15723(8)	0.0082(4)	1.0
Cl	4*e*	0	0	0.29469(6)	0.0102(3)	1.0
Oi_p	8*g*	$^1/_2$	0	0.0899(6)	0.0146(3)	1.0
O_{ap}	2*b*	0	0	$^1/_2$	0.012(1)	1.0

[a] Additional phases: $Sr_6Co_5O_{15}$, (16 wt %), space group *R*32, $a = 9.4572(5)$ Å, $c = 12.460(1)$ Å, and $V = 965.1(1)$ Å^3.

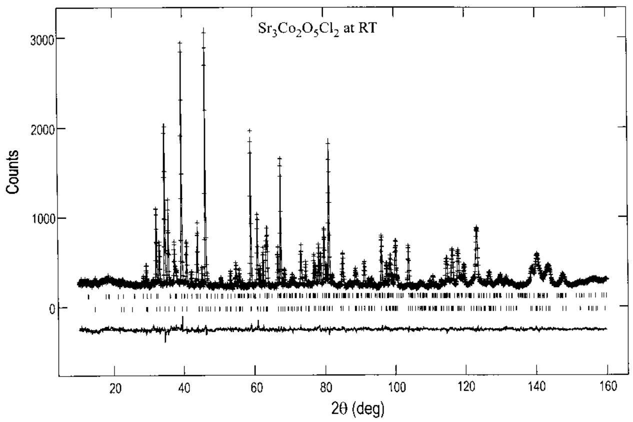

Figure 2. Observed (+) and calculated (continuous line) intensities from the $Sr_3Co_2O_5Cl_2$ refined sample. The difference curve between (observed−calculated) intensities is shown in the bottom of the figure. The refinement included $Sr_6Co_5O_{15}$ as additional impurity.

The initial refinement for $Sr_4Co_3O_{7.5}Cl_2$ (Co-3L) was carried out using the parameters given by Müller-Buschbaum and Boje.[1] In this model the occupation and thermal parameters of the $O_{ip(CoO)}$ located at the 4*c* site (0, 1/2, 0) were refined and found to be correlated. The occupancy of the site was subsequently fixed at 0.75. The refinement of the temperature factor showed that this atom had an unusually large isotropic temperature factor (≈4.3 Å^2). An anisotropic refinement yielded temperature factors $U_{11} = 0.140$ Å^2, $U_{22} = 0.017$ Å^2, and $U_{33} = 0.007$ Å^2, indicating that the oxygen was shifted from the ideal position to (*x*, $^1/_2$, 0). The final refinement with $O_{ip(CoO)}$ in position (*x*, $^1/_2$, 0) gave $\chi^2 = 1.355$ with a reasonable value for the temperature factor (≈1.5 Å^2). All the final structural parameters for $Sr_4Co_3O_{7.5}Cl_2$ are displayed in Table 3. The Rietveld plot for the refined sample showing the difference between observed and calculated intensities is shown in Figure 3.

Physical Properties. The magnetic measurements were carried out using a SQUID magnetometer operating at 1 T.

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(7) Larson, A. C.; von Dreele, R. B. *General Structure System Analysis*; Report No. LAUR086-748; Los Alamos National Laboratory, Los Alamos, NM, 1990.

(8) Harrison, W. T. A.; Hedgwood, S. L.; Jacobson, A. J. *J. Chem. Soc., Chem Commun.* **1995**, *19*, 1953.

Table 3. Structural Parameters for $Sr_4Co_3O_{7.5}Cl_2$ (Co-3L) at Room Temperature ($Sr_4Co_3O_{7.5}Cl_2$, (100 wt %), Space Group *I*4/*mmm* (#139), $a = 3.9012(2)$ Å, $c = 31.688(2)$ Å, $V = 482.27(5)$ Å^3; $R_p = 0.0277$, $R_{wp} = 0.0344$, $\chi^2 = 1.355$)[a]

atom	Wyckoff	*x*	*y*	*z*	U_{iso} (Å^2)	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	*n*
Co_O	2*a*	0	0	0	0.012(2)				1.0
Co_{Cl}	4*e*	0	0	0.1195(4)	0.012(2)				1.0
Sr_{Cl}	4*e*	0	0	0.4364(2)	0.012(1)				1.0
Sr_O	4*e*	0	0	0.3206(2)	0.012(1)				1.0
Cl	4*e*	0	0	0.2160(1)	0.0147(9)				1.0
$O_{(ipCoCl)}$	8*g*	0	$^1/_2$	0.1279(1)		0.017(3)	0.013(2)	0.020(2)	1.0
O_{ap}	4*e*	0	0	0.0602(3)		0.026(3)	0.026(3)	0.021(4)	1.0
$O_{ip(CoO)}$	8*j*	0.0742(34)	$^1/_2$	0	0.019(3)				0.375

[a] Note: $U_{12} = U_{13} = U_{23} = 0$.

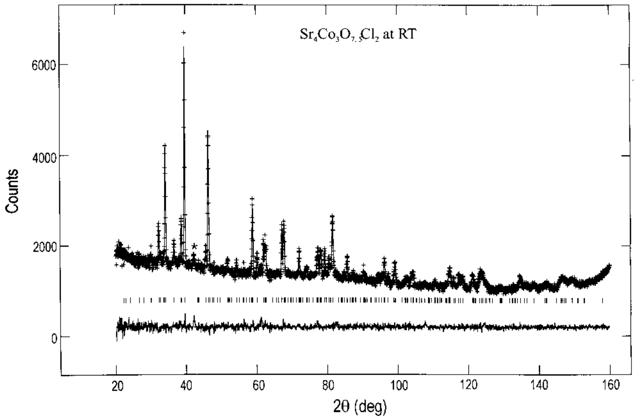


Figure 3. Observed (+) and calculated (continuous line) intensities from the $Sr_4Co_3O_{7.5}Cl_2$ refined sample. The difference curve between (observed−calculated) intensities is shown in the bottom of the figure.

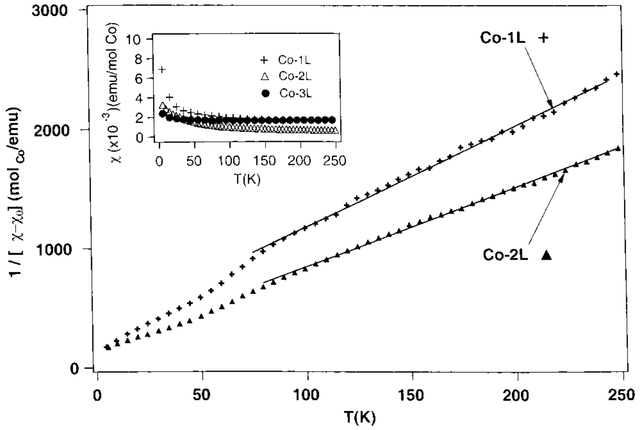
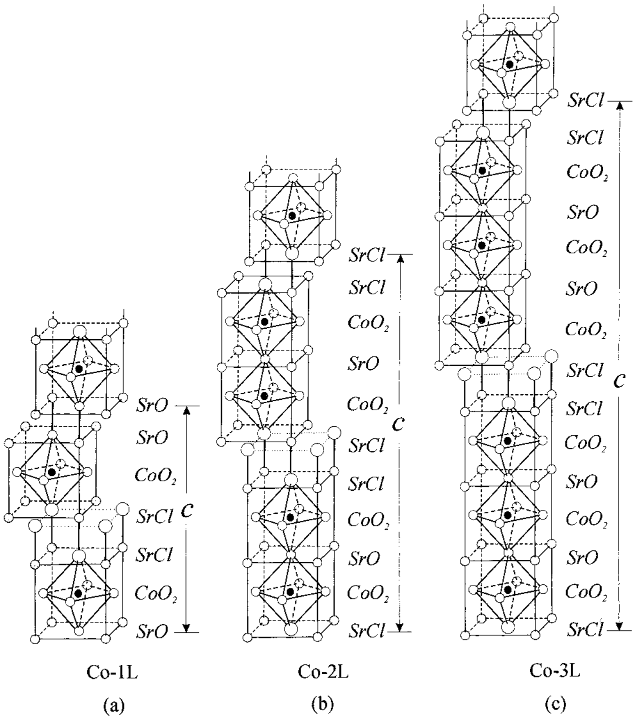


Figure 4. Inverse magnetic susceptibility data vs temperature for samples Sr_2CoO_3Cl (Co-1L) and $Sr_3Co_2O_5Cl_2$ (Co-2L). Data collected at 1 T. The inset shows magnetic susceptibility data vs temperature for samples Sr_2CoO_3Cl (Co-1L), $Sr_3Co_2O_5Cl_2$ (Co-2L), and $Sr_4Co_3O_{7.5}Cl_2$ (Co-3L).



Co-1L (a) Co-2L (b) Co-3L (c)

Figure 5. Crystal structures of the first three members of the Ruddlesden−Popper series of compounds of general formula $Sr_{n+1}Co_n(O,Cl)_{2n+1}$.

Figure 4 displays the inverse molar magnetic susceptibility vs temperature data for samples Sr_2CoO_3Cl and $Sr_3Co_2O_5Cl_2$. The inset shows the molar magnetic susceptibility data vs temperature for the three samples. The behavior was typically Curie−Weiss for Co-1L and Co-2L and no magnetic ordering was detected for any of the samples. The susceptibility is basically temperature independent for Co-3L. The magnetic moment was found to decrease consistently with the increase of the number of Co layers, being 0.80 μ_B/Co for Sr_2CoO_3Cl and 0.56 μ_B/Co for $Sr_3Co_2O_5Cl_2$. The antiferromagnetic interaction temperature was in the range 5−20 K. The transition found with $T_c \approx 75$ K, visible for both Co-1L and Co-2L, is likely due to the hexagonal $Sr_6Co_5O_{15}$ phase, an impurity common in both samples (this phase has previously been identified as the low-temperature form of $SrCoO_{3-x}$, which is known to be ferromagnetic with T_c changing with the amount of Co^{4+}).[9] The temperature-independent Pauli paramagnetism of $Sr_4Co_3O_{7.5}Cl_2$ is on the order of 10^{-3} emu/mol of Co. Preliminary transport property measurements on these materials have shown that they are insulating, although the resistance decreases several orders of magnitude with the increase of the number of Co layers.

Results and Discussion

As shown in Figure 5, the crystal structures, which are analogous to the Ruddlesden−Popper phases of general formula $Sr_{n+1}Co_n(O,Cl)_{2n+1}$, can be considered as formed by blocks of the $CrCo(O,Cl)_3$ perovskite units. Each unit cell contains two blocks stacked along the *c*-axis with an origin shift ($^1/_2$ *a* × $^1/_2$ *b*) from one to another and interleaved with the adjacent layers of SrO and SrCl (for Cl-1L) and SrCl (for Co-2L and Co-3L) and connected by Sr−O or/and Sr−Cl bondings (see Table 4). All the chlorine atoms are ordered and located in the adjacent layers. The structure of Sr_2CoO_3Cl can be seen in Figure 6. It is primitive tetragonal with space group *P*4/*nmm* symmetry and lattice parameters $a = 3.9026(1)$ Å and $c = 14.3089(3)$ Å. This compound

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(9) Taguchi, H.; Shimada, M.; Koizumi, M. *J. Solid State Chem.* **1979**, *29*, 221.

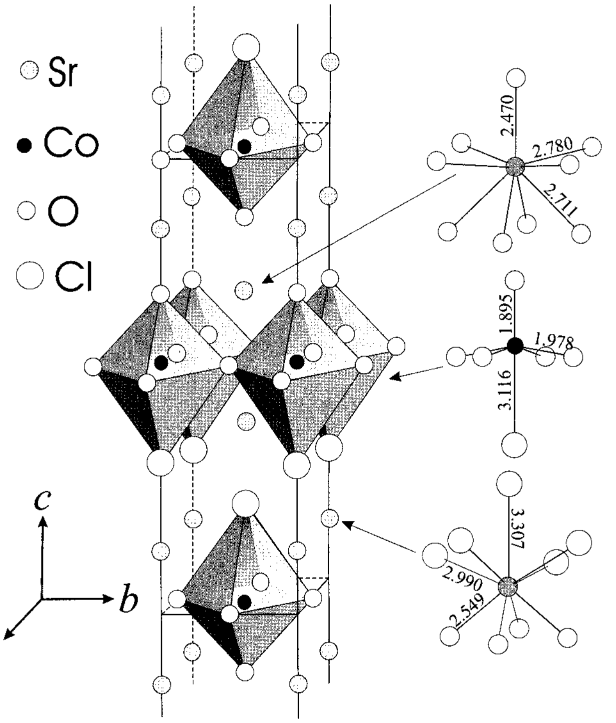

Figure 6. Crystal structure model of the Sr_2CoO_3Cl (Co-1L) phase, showing the coordination polyhedra of the Sr and Co atoms.

Table 4. Selected Bond Distances and Angles for Co-1L, Co-2L, and Co-3L Phases

bonds (Å) and angles (deg)	Co-1L	Co-2L	Co-3L
$Co_{Cl}-O_{ip}$	1.9781(6)	1.9774(7)	1.969(2)
$Co_{Cl}-O_{ap}$	1.895(4)	1.876(5)	1.88(2)
$Co_{Cl}-Cl$	3.116(4)	3.053(5)	3.06(1)
$O_{ip}-Co_{O}-O_{ip}$	161.1(2)	163.6(3)	164.4(7)
$Sr_{O}-O_{ip(CoO)}$	2.711(1) × 4	2.914(1) × 8	2.612(9)–3.014(11) × 3
$Sr_{O}-O_{ap}$	2.7801(3) × 4	2.76779(9) × 4	2.7607(4) × 4
Sr(1)–O(2)	2.470(2)		2.820(5) × 4
$Sr_{Cl}-O_{ip}$ × 4	2.549(1)	2.538(1)	2.544(4)
$Sr_{Cl}-Cl$ × 4	2.990(1)	2.9990(9)	2.992(2)
$Sr_{Cl}-Cl$ × 1	3.307(2)	3.300(3)	3.314(7)
$Co_{O}-O_{ip}$			1.972(3) × 3
$Co_{O}-O_{ap}$			1.907(8)
$O_{ip}-Co_{Cl}-O_{ip}$			180

consists of infinite planes of highly distorted corner-shared CoO_5Cl octahedra sandwiched between alternate double layers of $(SrCl)_2$ and $(SrO)_2$ with the following stacking of planes $(CoO_2)(SrCl)_2(CoO_2)(SrO)_2$(...). Because of the large value of the Co–Cl bond length (≈3.10 Å), it is questionable whether the Co atom is indeed bonded to chlorine. The compound can also be seen, then, as consisting of infinite layers of CoO_5 pyramids with cobalt shifted from the 4-oxygen basal plane along the *z*-direction. The $(SrCl)_2$ double layers are ≈3.3 Å apart and thus very weakly connected through van der Waals forces. Because of the large deviation of the $O_{ip}-Co-O_{ip}$ bond angle [161.1(2)°] from the ideal value of 180°, the corner-shared CoO_4 plane is not regular as found in many cuprates. Because the degree of overlap between the M 3*d* and O 2*p* orbitals changes as a function of the $O_{ip}-Co-O_{ip}$ bond angle, and because these are the electronically active sites of the structure where conduction occurs, the transport and magnetic properties are expected to be severely affected by this deviation.

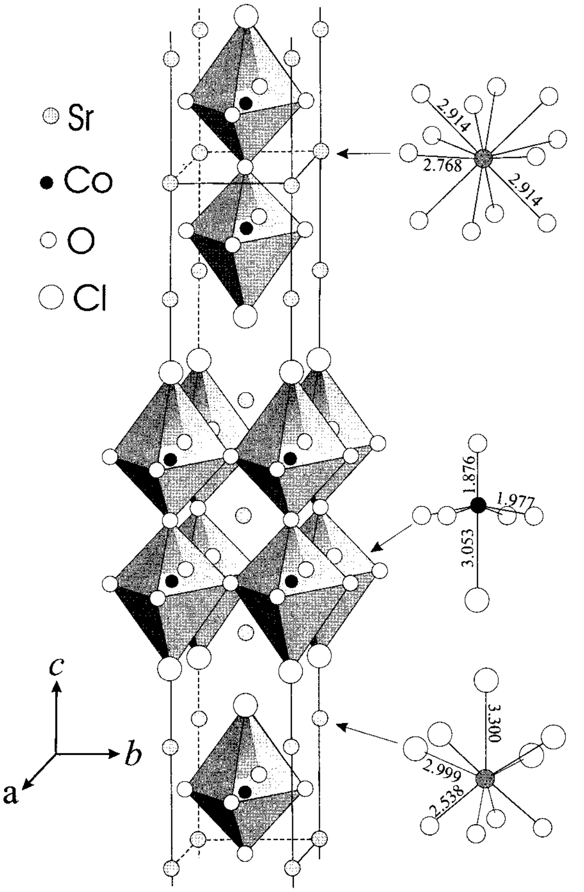

Figure 7. Crystal structure model of the $Sr_3Co_2O_5Cl_2$ (Co-2L) phase, showing the coordination polyhedra of the Sr and Co atoms.

$Sr_3Co_2O_5Cl_2$ has also tetragonal symmetry with a = 3.9142(1) Å and c = 24.010(1) Å (see Figure 7). The ≈7-Å increase in the *c*-parameter is due to the inclusion of the SrCoOCl block. This compound also has double layers of distorted CoO_5Cl octahedra, but they are connected by the apical oxygen position in the vertexes of each octahedron. These layers are sandwiched between double layers of $(SrCl)_2$ with the following stacking sequence $(CoO_2)(SrO)(CoO_2)(SrCl)_2$(...). The $O_{ip}-Co-O_{ip}$ bond angle [163.6(3)°] in the (*a*,*b*) plane is also much smaller than the ideal 180°; however, in this structure, unlike Sr_2CoO_3Cl, there is one set of 180° bond angles, between the $O_{ap}-Co-O_{ap}$ atoms, due to the common apical oxygen position.

$Sr_4Co_3O_{7.5}Cl_2$ is once again tetragonal with space group *I*4/*mmm* and lattice parameters a = 3.9012(2) Å and c = 31.688(2) Å. This compound had two different Co sites, a CoO_6 octahedron and the CoO_5Cl distorted octahedra already described for the Co-1L and Co-2L compounds. The stacking sequence $(CoO_2)(SrO)(CoO_2)(SrCl)_2$(...) shows that the layers of corner-shared CoO_6 octahedra are sandwiched between two layers of corner-shared distorted CoO_5Cl octahedra (see Figure 8). In the distorted CoO_5Cl octahedra, the four in-plane bond lengths are ≈0.1 Å larger than the apical one, and the Co atom is shifted from the basal plane along the *z*-direction. This is valid for both Co-1L and -2L

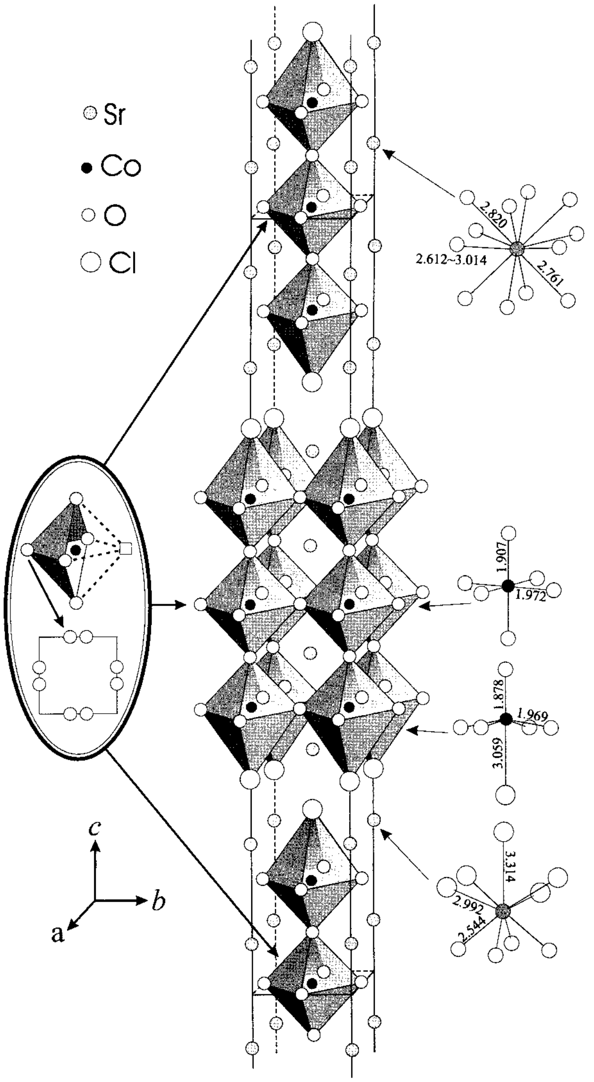

Figure 8. Crystal structure model of the $Sr_4Co_3O_{7.5}Cl_2$ (Co-3L) phase, showing the coordination polyhedra of the Sr and Co atoms. The partial occupation of the oxygen in the CoO_6 octahedra and its subsequent change of coordination to a pyramid can also be viewed.

compounds. In $Sr_4Co_3O_{7.5}Cl_2$, the Co atom is coplanar with the four oxygen atoms, but the in-plane oxygen position is both shifted along *a* and partially occupied. This partial occupation changes the coordination around some of the cobalt atoms, and instead of octahedra, there are pyramids with basal planes parallel to the *z*-direction. These pyramids may have their vertexes randomly oriented (in−out) and may form clusters from which superstructures may arise. Transmission electron microscopy studies are underway to confirm this hypothesis.

There are two types of Sr atoms. In the Sr_O position, strontium is coordinated to 12 oxygen atoms, $4O_{ip} + 4O_{ap} + 4O_{ip}$, while in the Sr_{Cl} position, strontium is coordinated to 9 atoms ($4O_{ip}$ + 4Cl + 1Cl). The Sr_O-O_{ap} bond length remains fairly constant throughout the series, but the Sr_O-O_{ip} bond length changes from Co-1L [2.711(1) Å] to Co-2L [2.914(1)] to Co-3L [3.01(1)−2.61(1) Å]. This indicates that the coupling between adjacent layers of (CoO_2) planes changes throughout the series, probably being stronger for Co-3L, favoring delocalization. This may explain our preliminary resistance measurements that showed a decrease in resistance with an increase of the number of Co layers in the series.

The main difference between the three compounds seems to be the existence of two types of Co-coordination octahedra for the three-layered member of the series. Each compound has distorted CoO_5Cl octahedra, but in $Sr_4Co_3O_{7.5}Cl_2$, in addition to this, there are also CoO_6 octahedra or CoO_5 pyramids. Within the Co-3L compound, the Co_O-O_{ip} bond length is slightly larger than that in the CoO_5Cl octahedra. The $Co_{Cl}-O_{ap}$ remains almost the same as well. The value of the $O_{ip}-Co-O_{ip}$ bond angle [164.4(7)°], even though larger, remains also fairly constant when compared to the Co-2L [163.6(3)°] and Co-1L [161.1(2)°] compounds.

Conclusions

The crystal structure of three cobalt oxychlorides has been refined by neutron powder data. These compounds are tetragonal and have (CoO_2) electronically active layers that are distorted due to a $\approx$20° deviation of the $O_{ip}-Co-O_{ip}$ bond angle from the ideal value of 180°. This deviation changes the overlap between the M−O orbitals relevant to the electronic properties of the compounds. The compounds are insulating, although the resistance decreases with increasing *n* in the series probably due to an increase between the coupling of the (CoO_2) planes and delocalization phenomena. The magnetic moment per Co_{atom} also decreases with the increase of the number of Co layers in this series. Even though all three members are nominally Co^{3+} in a low spin state, we cannot exclude valence fluctuations that may decrease the charge and reduce the moment when increasing the number of Co layers. More detailed studies on the physical properties of these compounds are currently underway.

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