Structural studies of a mixed-valence state in the incommensurate composite crystal Sr$_{1.261}$CoO$_3$

Masaaki Isobe$^1$, Hiroyuki Yoshida$^1$, Eiji Takayama Muromachi$^1$ and Kenji Ohoyama$^2$

$^1$ Superconducting Materials Center, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
$^2$ Institute for Materials Research (IMR), Tohokus University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

E-mail: ISOBEMasaaki@nims.go.jp

Received 1 September 2010
Accepted for publication 24 October 2010
Published 6 December 2010
Online at stacks.iop.org/STAM/11/065004

Abstract

The incommensurate modulated crystal structure of the hexagonal cobalt oxide Sr$_{1.261}$CoO$_3$ has been studied using a four-dimensional (4D) superspace profile analysis of neutron powder diffraction data. Sr$_{1.261}$CoO$_3$ is a composite crystal that consists of the [CoO$_3$] and [2Sr] subsystems. The [CoO$_3$] subsystem forms 1D chains that run parallel to the $c$-axis and consist of face-sharing Co$_6$ polyhedra with octahedral ($Oh$) and trigonal prismatic ($TP$) coordinations. The structure analysis reveals that the [CoO$_3$] chains contain 73.9% $Oh$ and 26.1% $TP$ sites, and that the $TP$ sites have longer Co–O bonds than the $Oh$ sites: $d_{av} = 2.039(4)$ Å ($TP$) and 1.895(3) Å ($Oh$). The averaged Co bond valences are Co$^{3.56(3)+}$ in the $Oh$ sites and Co$^{2.45(3)+}$ in the $TP$ sites, suggesting that a considerable amount of Co$^{3+}$ ions are mixed with Co$^{4+}$ ions in the $Oh$ sites and with Co$^{2+}$ ions in the $TP$ sites. The observed magnetic susceptibility can be well explained assuming that the compound has the Co mixed-valence state with the spin configurations of $S=0$ low-spin state for Co$^{3+}$($d^{5}$), $S=1/2$ low-spin state for Co$^{4+}$($d^{5}$) and $S=3/2$ high-spin state for Co$^{5+}$($d^{5}$)($d^{y}$). The Weiss temperature, approximately 0.8 K, implies that Sr$_{1.261}$CoO$_3$ naturally assumes a Curie paramagnetic state, probably owing to the obstruction of the intrachain magnetic interaction by the nonmagnetic Co$^{5+}$ ions. These results suggest that the nonmagnetic Co$^{5+}$ ions play an essential role in the magnetism of Sr$_{2}$CoO$_3$ systems.

Keywords: cobalt oxide, hexagonal perovskite structure, neutron diffraction, modulated structure, Rietveld analysis

1. Introduction

Recently, extensive studies have been carried out on the structural chemistry and magnetism of hexagonal perovskite-related compounds. Several interesting magnetic properties have been reported, such as complex magnetism in Sr$_3$MM$'$O$_6$ (M = Ni, Cu, Zn, M$'$ = Pt, Ir) [1, 2], random spin-chain paramagnetism in Sr$_3$CuPt$_{0.5}$Ir$_{0.5}$O$_6$ [3] and low-dimensional magnetism in Sr$_5$Co$_5$O$_{15}$ [4]. These intriguing magnetic properties seem to be related to the crystal structure through atomic coordination, orbital overlap, ionic valence, crystal field and spin configurations of the magnetic ions. Over the past several years the precise structural determination and relationship between the magnetic properties and structure of the hexagonal perovskites have become significant in the field of solid-state physics and chemistry.

The structure of hexagonal perovskite-related compounds is formulated as $A_{3n+1}A'_nB_{3n+a}O_{9n+a+6}$ ($A$: alkali or alkali-earth, $A'$: alkali-earth, transition-metal, etc,
B: transition-metal elements; \( m, n \): integers, which is derived from the stacking of \( m[A_1O_3] \) layers and \( n[A_2A'_1O_6] \) layers along the hexagonal c-axis, followed by the filling of the interstitial octahedral B sites in the \( a-b \)-plane [5, 6]. The stacking of the layers leads to one-dimensional (1D) chains of face-sharing \([A'O_6]\) trigonal prisms (TPs) and \([BO_6]\) octahedra (Oh) along the c-axis. The polyhedral chains are well separated by the A cation arrays running parallel to the chains. This 3D formalism (\(A_{x+y}B_xA''_yB_{3x+y}O_{6x+y+6}\)) can well describe typical hexagonal compounds such as Sr\(_2\)InO\(_6\) [7] or Ca\(_2\)CoO\(_4\) [8]. However, it is inappropriate to describe all the structures within the hexagonal perovskite system. For instance, Sr\(_{14}\)Co\(_{11}\)O\(_{33}\) [9] would require a fractional number of \( m = 5/3 \) if this formula is applied to the compound. In addition, the 3D formalism is not applicable to incommensurate structure compounds such as Sr\(_{2.872}\)NiO\(_3\) [10], Sr\(_{15}\)(Co,Mn\(_{1-\gamma}\))O\(_3\) [11], [Ba\(_3\)][(Pt,Cu)O\(_2\)] [12], or Sr\(_{1.45}\)Ti\(_2\)O\(_6\) [13].

\( \text{A}_{2y} (\text{A}', \text{B}) \text{O}_3 \) is another description of the hexagonal system. This description is derived from the definition of composite crystals consisting of the \([\text{A}', \text{B}] \text{O}_3\) first subsystem and the \([\text{A}] \) second subsystem [14], where \( y \) is the size of the modulation wave vector (\( q = y\varepsilon \)). In this case, \( y \) corresponds to an incommensurable (irrational) or commensurable (rational) ratio of the c-axis dimensions between the two subsystems (\( y = c_1/c_2 \)). The title compound Sr\(_{1.261}\)CoO\(_3\) is a member of the \( \text{A}_{2y} (\text{A}', \text{B}) \text{O}_3 \) system (\( \text{A} = \text{Sr}, \text{A}' = \text{B} = \text{Co} \)) that includes several compounds such as Sr\(_6\)Co\(_{15}\)O\(_{35}\) (= Sr\(_2\)Co\(_3\)) [4], Sr\(_{14/11}\)Co\(_3\) (= Sr\(_{1.273}\)Co\(_3\)) [9] and Sr\(_{24/19}\)Co\(_3\) (= Sr\(_{1.261}\)Co\(_3\)) [9]. The structure of the Sr\(_{2y}\)Co\(_3\) phases is built up from infinite Co\(_3\) 1D chains and Sr arrays running parallel to the c-axis. The Co\(_3\) chain consists of face-sharing Co\(_6\) polyhedra with octahedral and trigonal prismatic coordinations. The structure of Sr\(_{1.261}\)CoO\(_3\) is similar to that of Sr\(_{14/11}\)Co\(_3\) (= Sr\(_{1.273}\)Co\(_3\)) or Sr\(_{24/19}\)Co\(_3\) (= Sr\(_{1.261}\)Co\(_3\)) [9]. However, Sr\(_{1.261}\)CoO\(_3\) is not the same as Sr\(_{14/11}\)Co\(_3\) because of the different \( y \) values. Another compound, Sr\(_{24/19}\)Co\(_3\), is quite similar to or may possibly be the same as Sr\(_{1.261}\)Co\(_3\), because the \( y \) value of Sr\(_{24/19}\)Co\(_3\) (\( y = 2/19 = 0.6316 \)) is close to the \( y \) value of Sr\(_{1.261}\)Co\(_3\) (\( y = 0.6305 \)). To the best of our knowledge, however, detailed data on the structure of these compounds has not been reported in the literature.

We are interested in the structural chemistry and magnetism of the Sr\(_{1.261}\)CoO\(_3\) phase. Elucidation of the relationship between the crystal structure and magnetic properties is important in understanding the physics and chemistry of Sr\(_{1.261}\)CoO\(_3\) and the Sr\(_{2y}\)CoO\(_3\) series. In particular, the charge balance in the Oh and TP sites should be considered in connection with the magnetic state in Sr\(_{2y}\)CoO\(_3\). Gourdon et al. expected that Sr\(_{14/11}\)Co\(_3\) possesses the oxidation state of the separate Co ions: with the Co\(_{2+}\) in TP sites and Co\(_{4+}\) in Oh sites [9]. This charge balance, i.e. complete separation of Co\(_{2+}\)-Co\(_{4+}\), seems to be a reasonable hypothesis when considering the Co–O bond lengths (2.05 Å (TP) and 1.90 Å (Oh) [9]). This is also the premise for studying the charge balance with respect to the Co–O bond lengths in the Sr\(_{1.261}\)CoO\(_3\) compound. Our idea was that the intermediate oxidation state (Co\(_{5.5+}\)) may be mixed somewhat with the Co\(_{2+}\) and Co\(_{4+}\) states in the Oh and TP sites, because such a mixed valence state has often been observed in many other transition-metal oxides. The Co\(_{5.5+}\) ions should play an essential role in the magnetism of the Sr\(_{2y}\)CoO\(_3\) system. The mixed oxidation states, Co\(_{2+}\), Co\(_{4+}\) and Co\(_{5.5+}\), are also discussed in this article in connection with magnetic susceptibility data. Determination of the ‘real’ charge balance in the Sr\(_{2y}\)CoO\(_3\) system should be reconsidered not only in terms of bond lengths but also physical properties, such as the magnetic properties.

In this paper, we report on the detailed crystal structure and magnetic properties of Sr\(_{1.261}\)CoO\(_3\). Firstly, we refine the structural parameters of the Sr\(_{1.261}\)CoO\(_3\) compound using a four-dimensional (4D) superspace group approach for the incommensurate composite crystal and neutron powder diffraction data. The known advantages of the 4D superspace group approach are: (i) the large unit cell structure in the 3D presentation can be described using two uniform small unit cells and superspace groups for the two subsystems, (ii) the 4D description can reduce the number of adjustable parameters needed to define the structure and (iii) both the commensurate and incommensurate structures can be described using the same model with the only difference in the \( y \) value [14]. We will compare the obtained Co–O bond lengths with those in Sr\(_{14/11}\)CoO\(_3\) [9]. Secondly, we will evaluate the Co ionic valence for each site using the bond-valence sum calculation method [15] with the obtained Co–O bond lengths. The Sr\(_{1.261}\)CoO\(_3\) phase has a higher average valence of Co ions than 3+. However, the charge balance in the Oh and TP sites is still not clear. In particular, the Oh and TP sites should have different bond lengths and coordinations, yielding different valences for the Co ions. The bond-valence sum calculation is a simple and useful method of estimating the charge balance not only for conventional but also incommensurate crystals [16]. Thirdly, we consider spin configurations in the Co ions on the basis of the obtained charge balance. The spin configurations should be consistent with not only the crystal fields in the Oh and TP sites but also the magnetic properties observed in this work. The Co ions are expected to exhibit different crystal fields for the Oh and TP sites, which may affect the spin configuration of the Co ions. Finally, we evaluate essential magnetic correlations in Sr\(_{1.261}\)CoO\(_3\) from the Curie–Weiss analysis of the magnetic susceptibility data. Through these studies, we discuss the magnetic state in Sr\(_{1.261}\)CoO\(_3\) from the viewpoint of the crystal structure.

2. Experimental details

We used polycrystalline samples prepared by the conventional solid-state reaction method from a mixture of SrCO\(_3\) (4N) and CoO\(_3\) (4N). The starting reagents with an atomic ratio of Sr/Co = 1.273 were mixed in an agate mortar. The mixture was prereduced in an alumina crucible at 1173–1253 K in air for over one week with several regrinding steps in between to decompose the carbonate completely. The preheated powder was then reground and fired at 1293 K in air for four days,
followed by quenching to room temperature. Bulk specimens for electrical resistivity measurements were prepared by another sintering process under the same condition of the final firing after pelletization.

A phase purity check of the final products and a preliminary structural study were carried out using conventional powder x-ray diffraction (XRD). The XRD data were collected in the Bragg–Brentano geometry, using a Rigaku diffractometer (RINT2200HF-ULTIMA) equipped with a CuKα radiation source and a conventional slit system. Lattice constants were determined from the least-squares fit using 2θ values of the Bragg reflections. The atomic composition of the samples was measured with an inductively coupled plasma (ICP) atomic emission spectrometer for cations (Sr, Co) and a nondispersive infrared (NDIR) detector for oxygen.

Neutron powder diffraction experiments were carried out using the HERMES diffractometer (Kinnen powder diffractometer for high-efficiency high-resolution measurements, operated by the Institute of Materials Research of Tohoku University) [17], installed at the T1–3 beam line in the guide hall of the JRR-3M reactor of the Japan Atomic Energy Agency (JAEA) Tokai, Japan. Incident thermal neutrons with a wavelength of 1.8265(1) Å were obtained with the 331 reflection of a bent crystalline Ge monochromator and 12°-open-sample-22° collimation. The powder sample (about 5 g) was loaded into a cylindrical vanadium can with a diameter of 10 mm and mounted on a sample stage of a goniometer. Diffraction data were collected at room temperature (295 K) for about 6 h in a 2θ range from 7° to 157.95°, with a step of 0.05°, using 150 °He detectors set at 1.0° intervals.

Magnetic data were collected for the pulverized samples using a SQUID magnetometer (Quantum Design, MPMS-XL). The magnetic moment (M) for susceptibility data was measured in the temperature (T) range of 2–300 K on warming after zero-field cooling (ZFC), and then on field cooling (FC), in a magnetic field (H) of 100 Oe. The electrical resistivity was measured with a commercial setup (Quantum Design, PPMS), in a standard four-probe configuration, applying a DC current of 0.1 μA.

3. Characterization

3.1. Symmetry

Figure 1 shows the XRD pattern of the Sr1.26CoO3 sample. All the Bragg reflections can be systematically indexed using a set of four integers, hklm, with the reciprocal-lattice vector h given by \( h = h a^* + k b^* + l c_1^* + m c_2^* \), where \( a^*, b^*, c_1^* \) and \( c_2^* \) are reciprocal unit vectors of the hexagonal lattice. The lattice parameters are \( a = b = 9.5039(8) \) Å, \( c_1 = 2.5183(5) \) Å, \( c_2 = 3.9928(7) \) Å and \( \gamma = c_1/c_2 = 0.6307(2) \). No extra peaks were observed, suggesting that the sample consists of a single Sr1.26CoO3 phase. The observed sharp Bragg peaks confirm the high crystalline quality of the sample. The γ value of the present compound is close to the rational number 12/19 = 0.6316, but differs from it beyond the experimental errors, meaning that the \( \gamma \) is an irrational number and that the atomic positions in Sr1.26CoO3 are incommensurately modulated owing to the interaction between the two subsystems.

The reflection condition, \( -h + k + l = 3n \) for \( hklm \), was observed in the XRD pattern. Possible space groups of the basic structure for the [CoO3] part (subsystem-1) are \( R\overline{3}m \) and \( R\overline{3}m \). For the main reflections of the [2Sr] part (subsystem-2), the reflection conditions are \( -h + k = 3n \) for \( h\overline{0}lm \) and \( m = 2n \) for \( h\overline{0}lm \) and \( 0\overline{0}lm \) reflections. The reflection condition, \( -h + k + l = 3n \) for \( h\overline{0}lm \), was observed in the XRD pattern. Possible space groups of the basic structure for the [CoO3] part (subsystem-1) are \( R\overline{3}m \) and \( R\overline{3}m \). For the main reflections of the [2Sr] part (subsystem-2), the reflection conditions are \( -h + k = 3n \) for \( h\overline{0}lm \) and \( m = 2n \) for \( 3\overline{j}00m \). These conditions can be simplified into \( m = 2n \) for \( HH\overline{0}lm \) with another set of unit vectors \( A^* (= 2a^* - b^*) \) and \( B^* (= a^* + b^*) \), where the reciprocal-lattice vector \( h \) is given by \( h = H A^* + K B^* + l c_1^* + m c_2^* \). This indicates that \( P3\overline{1}c \) and \( P3\overline{1}c \) are possible space groups of the basic structure for the [2Sr] part. The superspace groups deduced from the systematic reflection conditions \( -h + k + l = 3n \) for \( h\overline{0}lm \) and \( m = 2n \) for \( h\overline{0}lm \), \( 0\overline{0}lm \) and the Laue symmetry (3m) are \( P-R3\overline{3}m/1s \) or \( P-R3\overline{3}m/1s \) for the first subsystem and \( R-P3\overline{1}c/111 \) or \( R-P3\overline{1}c/111 \) for the second subsystem. The possible superspace group of the composite crystal, which can be given by the combination of the superspace groups of the subsystems, is therefore either \( P-R3\overline{3}m/1s:R-P3\overline{1}c/111 \) or \( P-R3\overline{3}m/1s:R-P3\overline{1}c/111 \). In this study, \( P-R3\overline{3}m/1s:R-P3\overline{1}c/111 \) was employed as a superspace group of the composite crystal for determining the crystal structure [12, 13]. The corresponding symmetry operations, i.e., elements of the superspace group, are summarized in table 1.
Table 1. Four-dimensional space group symmetry for Sr$_{26}$CoO$_3$.

| Subsystem | 1: [CoO$_3$] | 2: [Sr] |
|-----------|-------------|--------|
| Modulation vector $q$ | $\gamma e_1^2$ | $\gamma^{-1} e_2^2$ |
| Generators | | |
| Centering translation | $x + 1/3, y + 2/3, z + 2/3, t$ | $x + 1/3, y + 2/3, z, t + 2/3$ |
| $x + 2/3, y + 1/3, z + 1/3, t$ | $x + 2/3, y + 1/3, z, t + 1/3$ |
| Symmetry operators | $-y, -x - y, z, t$ | $-y, -x, z, t$ |
| $-y, -x, z, t + 1/2$ | $-y, -x, z + 1/2, t$ |
| Group symbol | Composite crystal | $P-R 3m / 1s$ |
| Modulated structure | $R 3m(00l) Os(0.160.2)^a$ | $R-P 31c / 111$ |
| Atomic ratio | 1.261$^a$ | 21.3(1)$^b$ |

$^a$ Measured by ICP.
$^b$ Measured by NDIR.
$^c$ Fixed at $2\gamma$ (see text).

3.2. Composition

Table 2 shows the composition of the Sr$_{26}$CoO$_3$ sample. The atomic ratio of Sr/Co is 1.287 (24.5(1)/19.0(1)). This ratio is slightly larger than the composition in the starting mixture (1.273), probably owing to the slight evaporation of Co during the heat treatment. The obtained mole ratio (1.287) is larger than the $2\gamma$ value (1.261; i.e. atomic site ratio of Sr/Co), suggesting the presence of a small amount of defects in the Co site, provided the Sr sites are fully occupied by the Sr ions. The third line of the table indicates the expected atomic ratio assuming full occupation of the Sr site. The finally obtained chemical composition is Sr$_{26}$Co$_{0.98(1)}$O$_{2.91(4)}$, and the averaged Co and Sr valence is +3.36(7). The deviation from stoichiometry indicates the presence of defects in the Co and O sites.

Table 2. Chemical composition of the Sr$_{26}$CoO$_3$ sample.

| Sr | Co | O |
|----|----|---|
| Content (wt%) | 50.5(2)$^a$ | 26.4(2)$^a$ | 21.3(1)$^b$ |
| Content (at.%) | 24.5(1) | 19.0(1) | 56.5(5) |
| Atomic ratio | 1.261$^c$ | 0.981(1) | 2.91(4) |

$^a$ Measured by ICP.
$^b$ Measured by NDIR.
$^c$ Fixed at $2\gamma$ (see text).

4. Structure analysis

The neutron diffraction data were analyzed using the Rietveld refinement software PREMOS91 designed by Yamamoto for modulated structure analysis [18, 19]. Crystal structures were drawn using PRJMS and interatomic distances were calculated with MODPLT. Restrictions of harmonic amplitudes of modulation functions were calculated using SPLITPOS. These computer programs are included in the REMOS95.1 software package [20].

For the refinement, the occupation factor $g$ was fixed at 1.0 for Sr, 0.98 for Co and 0.97 for O so that they correspond to the net composition Sr$_{26}$Co$_{0.98}$O$_{2.91}$ determined by chemical analyses. Isotropic thermal displacement parameters were assigned for all the sites. The preferred orientation due to a needle-like crystal habit was corrected with a preferred-orientation vector of $e^*$. The $2\theta$ range used in the analysis, 10.00$^\circ$ to 157.95$^\circ$, corresponds to the lattice-plane spacing $d$ between 10.478 and 0.930 Å. Bound coherent scattering lengths for Sr, Co and O were taken from [21]. Absorption correction was carried out using absorption coefficients calculated from the chemical composition (Sr$_{26}$Co$_{0.98}$O$_{2.91}$), elemental absorption cross sections [21], and density of the sample powder filled into the vanadium cell (about 1.7 g cm$^{-3}$).

For a modulated structure, the atomic positions can be described using the sum of the fundamental structure and the deviations [22-27]. The coordinates ($x_i$: $x_1 = x$, $x_2 = y$, $x_3 = z$) of atom $j$ can be written as

$$x_i(j) = \tilde{x}_i(j) + u_i(j)(\tilde{\mathbf{x}}_{i\mathbf{d}}), \quad i = 1, 2, 3, \quad j = \text{Co, O, Sr},$$

where $\tilde{x}_i(j)$ represents the coordinates of the fundamental structure ($\tilde{x}_i$: $\tilde{x}_1 = \tilde{x}$, $\tilde{x}_2 = \tilde{y}$, $\tilde{x}_3 = \tilde{z}$) and $u_i(j)$ is the displacement modulation of the atoms. The bar denotes averages over the period of $\mathbf{a}$, which is the fourth dimension of the fractional coordinates of the fundamental structure in superspace. Modulation in the isotropic thermal parameter $B(j)$ and the occupation factor $g(j)$ are also described similarly to equation (1).

In the case of the hexagonal $A_2Y$ ($A’$, $BO_3$) system, a sawtooth function or a crenel function is often used for the modulation function [9-11, 14]. In this study, we employed a Fourier series description to approximate the modulation function [12, 13]:

$$u_i(j)(\tilde{\mathbf{x}_{i\mathbf{d}}}) = A_{i0}^j + \sum_{n=1}^{m} \left[ A_n^j \cos(2\pi n \tilde{x}_n) + B_n^j \sin(2\pi n \tilde{x}_n) \right].$$

In equation (2), the maximum order of harmonics, $m$, was set at 6 in the displacement modulations for all the atoms. For the modulations of the isotropic thermal parameters $B(j)$, the modulation-wave functions of the Fourier series were taken up to the fourth order for Co and O, and up to the third order for Sr. For the occupation factor $g(j)$, all the Fourier amplitudes were zeroed: $A_0 = A_n = B_n = 0$ (n = 1–6) for $g(j)$; i.e. $g(j)$ was fixed at certain initial values (Vide supra.).

For the atoms located in special positions in the superspace group, the modulation–function shapes are...
shows the modulated fractional coordinates.

Table 3. Crystallographic data and structure refinement for Sr₁₋₂ₓCoO₃.

| Parameter                      | Value                   |
|--------------------------------|-------------------------|
| Formula (net)                  | Sr₁₂₆Co₉₆O₃₉₁           |
| (= [2Sr]₆[Co₀₉₆O₂₉₁](γ = 0.6305)) |                         |
| Formula weight                 | 214.8 g mol⁻¹           |
| Color                          | Black powder            |
| Measurement temperature        | 295 K                   |
| Wavelength                     | Neutron, 1.8265 Å       |
| Diffractometer                 | HERMES, T1-3 at JAEA    |
| Crystal system                 | Hexagonal (subsystem-1), hexagonal (subsystem-2) |
| Superspace group               | P-R3m/1r [CoO₃]        |
| Lattice constants              | a = b = 9.5038(2) Å, c₁ = 2.51954(9) Å |
|                                | γ = c₁/c₂ = 0.630525(5), viz., |
|                                | c₂ = 3.9959(5) Å        |
| Cell volume                    | 197.09 Å²               |
| Z                              | 3                       |
| Density (calculated)           | 5.429 g cm⁻³            |
| 2θ scan range used             | 10.00–157.95° (d = 10.478–0.930 Å) |
| Step interval                  | 0.05°                   |
| Maximum intensity              | 26 077 counts           |
| No. of observations used       | 2940                    |
| No. of reflections             | 516                     |
| No. of refined parameters      | Fourier amplitudes (structural parameters): 51 |
| Others: 22 (background: 7, profile: 11, zero-point shift: 1, lattice parameters: 3) |
| R-factor                       | R_wp = 6.23%            |
| Refinement software            | PREMOS91 (with pseudo-Voigt peak shape functions [18]) |

\* R_wp = |\sum w(Io - Ic)²/ \sum wIc²|¹/².

restricted. In this case, some of the Fourier coefficients are zeroed. In addition, some of the other coefficients can be expressed as a linear combination of variable coefficients because of symmetry arguments. These constraints reduce the number of Fourier coefficients to be refined. As a result, the total number of structural parameters (Fourier amplitudes in the modulation functions) refined in the analysis was 51, including 38 parameters for fractional coordinates and 13 parameters for thermal displacement parameters.

Figure 2 shows the neutron powder diffraction pattern of Sr₁₋₂ₓCoO₃ and the best Rietveld analysis profile fit. The Rietveld refinement details and characteristics of the final refinement are summarized in table 3. The reliability factor of the fit, R_wp = 6.23%, is already at the practical minimum limit. Table 4 lists the final coordinates of the fundamental structure and Fourier amplitudes of the modulation functions.

5. Results and discussion

5.1. Structural properties

Figure 3 shows the modulated fractional coordinates x (= x₁) and y (= x₂) of O atoms, plotted as a function of \(\bar{x}_{44}\). The y-curve modulates around the average position \(\bar{y} = 0.076\); its shape resembles a square-wave or a crenel function. The step boundaries that can be defined as intersections between y and \(\bar{y}'\) (solid dots) are \(\bar{x}_{44} = 0.187(= \tau)\) and \(\bar{x}_{44} = 0.687(= \tau + 1/2)\); i.e. \(\bar{y}'(\tau) = y(\tau + 1/2) = \bar{y}'\). The averaged y-value in each step is \(\bar{y}'\). The step boundaries that can be defined as intersections between y and \(\bar{y}'\) (solid dots) are \(\bar{x}_{44} = 0.187(= \tau)\) and \(\bar{x}_{44} = 0.687(= \tau + 1/2)\); i.e. \(\bar{y}'(\tau) = y(\tau + 1/2) = \bar{y}'\). The averaged y-value in each step is \(\bar{y}'\). The step boundaries that can be defined as intersections between y and \(\bar{y}'\) (solid dots) are \(\bar{x}_{44} = 0.187(= \tau)\) and \(\bar{x}_{44} = 0.687(= \tau + 1/2)\); i.e. \(\bar{y}'(\tau) = y(\tau + 1/2) = \bar{y}'\). The averaged y-value in each step is \(\bar{y}'\). The step boundaries that can be defined as intersections between y and \(\bar{y}'\) (solid dots) are \(\bar{x}_{44} = 0.187(= \tau)\) and \(\bar{x}_{44} = 0.687(= \tau + 1/2)\); i.e. \(\bar{y}'(\tau) = y(\tau + 1/2) = \bar{y}'\). The averaged y-value in each step is \(\bar{y}'\).
step B (0 ≤ ∼x_{id} ≤ τ or τ + 1/2 ≤ ∼x_{id} < 1); \bar{y}_{B} equals the average value of x (= \bar{x}'_i = \bar{x}'). The actual coordinates x and y are modulated around these averaged positions, meaning that the O atoms are placed around the averaged position (\bar{x}', \bar{y}') = (0.152, 0) in a half range of ∼x_{id} (τ ≤ ∼x_{id} < τ + 1/2; Case-A), or another position (\bar{x}', \bar{y}') = (0.152, 0.152) in a remaining half range of ∼x_{id} (0 ≤ ∼x_{id} < τ or τ + 1/2 ≤ ∼x_{id} < 1; Case-B). The O positions (case-A and case-B) in the a–b-plane of the hexagonal lattice are illustrated in figure 4(b). The O triangle in the a–b-plane rotates by π/3 radian around the c-axis, from A to B (or from B to A).

Figure 4(a) is a schematic representation of the positions of the Co and O atoms in the 4D real superspace. The horizontal line \textbf{R}_4 represents physical 3D real space, which includes the a-, b- and c-axes. In this illustration, periodicity on the \textbf{R}_4 space is representatively given by \textbf{c}_1. The \textbf{a}_{id} is an additional dimension. \textbf{a}_{id}(i = 1–4) are unit vectors in the 4D superspace. \textbf{c}_1 is a projection of \textbf{a}_{i3} onto \textbf{R}_4. The solid

### Table 4. Refined structural parameters. The fractional coordinates (x, y, z), isotropic thermal parameter B, and occupation factor g are given by the equation: C(\vec{x}_{id}) = C + A_0 + \sum_{m=1}^{6}[A_m \cos(2\pi n \vec{x}_{id}) + B_m \sin(2\pi n \vec{x}_{id})] (m = 6), where C = x, y, z, B, or g, \vec{x}_{id} is the fourth dimension of the fractional coordinates in superspace and the bar denotes quantities belonging to the fundamental structure.

| Atom | x   | y   | z   | B (Å²) | g   |
|------|-----|-----|-----|--------|-----|
| **Subsystem 1: [CoO₃]** |     |     |     |        |     |
| Co   | Fundamental | 0   | 0   | 0     | 0.98 |
|      | A₁   | 0   | 0   | -0.02(3) | 0 (fixed) |
|      | A₂   | 0.023(2) | 0.6(1) | 0 (fixed) |
|      | A₃   | 0.024(2) | 0.7(1) | 0 (fixed) |
|      | A₄   | 0.011(3) | 0.9(1) | 0 (fixed) |
|      | A₅   | -0.055(2) | 0.2(1) | 0 (fixed) |
|      | A₆   | -0.008(4) | 0 (fixed) | 0 (fixed) |
|      | B₁   | 0.015(2) | 0 (fixed) | 0 (fixed) |
|      | B₂   | 0.015(2) | 0 (fixed) | 0 (fixed) |
|      | B₃   | 0.0005(1) | 0 (fixed) | 0 (fixed) |
|      | B₄   | 0.0006(1) | 0 (fixed) | 0 (fixed) |
| **Subsystem 2: [2Sr]** |     |     |     |        |     |
| Sr   | Fundamental | 0.33333 | 0   | 0     | 1.0 |
|      | A₀   | 0.0207(1) | 0.0163[2] | 0.081(2) | -0.22(1) | 0 (fixed) |
|      | A₁   | 0.0069(3) | -0.0144[2] | -0.0071(3) | -0.0123[2] |
|      | A₂   | 0.0101(2) | -0.0011[3] | 0.0117(6) | -0.00057(7) | -0.11(5) | 0 (fixed) |
|      | A₃   | -0.0007(1) | -0.0011[2] | 0.00008(2) | 0.0002[1] |
|      | A₄   | 0.0042(7) | -0.0061[4] | 0.0095(3) | 0.0084[6] |
|      | A₅   | 0.0270(4) | 0 (fixed) | 0 (fixed) | 0 (fixed) |
|      | A₆   | 0 (fixed) | 0 (fixed) | 0 (fixed) | 0 (fixed) |

\(a\) Numbers in parentheses are estimated standard deviations: ( ): independent, [ ]: propagated.

\(b\) Blank columns represent a null coefficient, derived from the constraint on the crystallographically special position of the site.

\(c\) Linear constraints: \(A_j^n = (1/2)A_j^n + (1/2)B_j^n\) for O.

\(d\) Linear constraints: \(A_j^n = (1/2)A_j^n + (3/2)B_j^n\) for Co.
parallelogram indicates a unit cell; $\mathbf{a}_{sd}$ is a complementary element of the coordinates corresponding to the fourth axis $\mathbf{a}_{sd}$; $t(=x_{sd}-y \times z_{sd})$ is an element in another expression of the 4D superspace coordinates $(x, y, z, t)$, and it can be defined as a distance from the 3D real space $\mathbf{R}_3$ along the $\mathbf{a}_{sd}$-axis. Modulated atomic positions in the 4D superspace can be expressed as wavy strings given by equations (1) and (2) with structural parameters in table 4. In figure 4(a), the averaged atomic positions are depicted as a straight line for the Co atoms and step functions for the O atoms. The Co atoms are located at $(x' = 0.152, y' = 0.076)$ and $(x_0 = 0)$ and $y_0 = 0.152$ are the averaged values of $x$ and $y$, and $\bar{y}$ is the averaged value of $y$ for step A and step B, respectively. The intersections between $y$ and $\bar{y}$ give the step boundaries at $x_{sd} = 0.187 (=\tau)$ and $x_{sd} = 0.687 (=\tau+1/2)$.

The vertical line at $z = 0$ represents the Co atoms at $(x', y', z', t) = (0, 0, 0, t)$. The step function at $z = 1/2$ corresponds to the $y$-coordinate of O(+) atoms above the Co atom, whereas another step function at $z = -1/2$ represents the $y$-coordinate of O(−) atoms below the Co atom. The actual $y$-coordinate of O(+) (or O(−), red curves in figure 4) can be obtained by shifting the phase of the $y$-modulation function in figure 3 to $+y \bar{z} = +y/2$ (or $-y \bar{z} = -y/2$). We determined the boundaries between the polyhedral types (TP and Oh) in the range of $t$ using the parameters $\tau$ and $\gamma$ as follows. The $y$-coordinate of O(+), $y(t + \gamma/2)$, crosses the average value $\bar{y} = 0.076$ at $t = \gamma - 2/\pm 2$ and $t = \gamma - 2/1/2 \pm 2n$ (where $n$ is an integer), whereas the $y$-coordinate of O(−), $y(-\gamma/2)$, crosses the average value $\bar{y} = 0.076$ at $t = \gamma + 2/\pm 2n$ and $t = \gamma + 2/1/2 \pm 2n$, because $y(\pm 2n) = y(\pm 1/2 \pm 2n) = y'$. The O(+) atoms take the A-position within $\gamma - 2/\pm 2 \leq t < \gamma - 2/1/2 \pm 2n$ or the B-position within $\gamma - 2/1/2 \pm 2n < t < \gamma - 2/1/2 \pm 2n$, whereas the O(−) atoms take the A-position within $\gamma + 2/\pm 2 \leq t < \gamma + 2/1/2 \pm 2n$ or the B-position within $\gamma + 2/1/2 \pm 2n < t < \gamma + 2/1/2 \pm 2n$. According to the combination of the A- and B-positions for the O(+) and O(−) atoms, $t$ can belong to one of four ranges: e.g. (i) $t + \gamma - 2/1/2 \leq t < \gamma - 2/1/2 \Delta t = 1 - \gamma$ for O(−) = B and O(+) = A, (ii) $\tau - 2/1/2 \leq t < \tau - 2/1/2 \Delta t = 1 - \gamma$ for O(−) = B and O(+) = B, (iii) $\tau - 2/1/2 \leq t < \tau - 2/1/2 \Delta t = 1 - \gamma$ for O(−) = A and O(+) = B, and (iv) $\tau - 2/1/2 \leq t < \tau - 2/1/2 \Delta t = 1 - \gamma$ for O(−) = A and O(+) = B. The O atoms in the $a-b$-plane form O triangles of type A or B, depending on $t$ (figure 4(b)). The O(−) atoms belong to type A for (i) and (ii) and to type B for (i) and (ii), while the O(+) atoms form type-A triangles for (i) and (iv) and type-B triangles for (ii) and (iii). When O(−) and O(+) are of the same O triangle type, the polyhedron is a trigonal prism, and when they are of the dissimilar type, the polyhedron is an octahedron. Therefore, the CoO$_6$ octahedra are formed in the range of (i) and (iii), while the CoO$_6$ trigonal prisms are formed in the range of (ii) and (iv). The contents of each polyhedron type, which can be determined from the width of $\Delta t$ for (i), (ii), (iii) and (iv), are $2(1-\gamma) = 0.739 (=2\Delta t)$ for (i) and (iii) for the octahedra and $2y-1 = 0.261 (=\Delta t)$ for (ii) and (iv) for the trigonal prisms (see figure 4(c)). Thus, the polyhedron type (octahedron or trigonal prism) can be determined as a function of the fourth coordinate $t$ in the 4D superspace.

Because the actual atomic positions are modulated around the average positions as shown in figure 3, the shapes of the polyhedra (octahedron and trigonal prism) are distorted from the ideal shapes ((i)-(iv)) illustrated in figure 4(c). Figures 5(a) and (b) show crystal structures constructed using the refined structure parameters for Sr$_{1,230}$CoO$_3$. Figure 5(a) is a projection viewed along the $[001]$ direction, while figure 5(b) indicates a part of a [CoO$_3$] chain and its neighboring Sr arrays projected along the $[\overline{1}10]$ direction. The lattice parameters are $a = b = 9.5038(2)$ Å, $c_1 = 2.519549(9)$ Å and $c_2 = 3.9959(5)$ Å. Figure 5(b) reveals an arrangement pattern in the sequence of the polyhedra of the prismatic and octahedral coordinations around the Co atoms. The sequence is $\ldots$-TP-Oh-Oh-TP-\ldots$-TP-Oh-Oh-TP-\ldots$; the TP repeatedly appears every four sites in the usual case, but occasionally follows two successive Oh sites, as one looks along the chain. This sequence in the incommensurate Sr$_{1,230}$CoO$_3$ phase is slightly different from the idealized periodic sequence $<$TP-3Oh-TP-3Oh-TP-2Oh-$>$
Figure 4. (a) Description of atomic positions of Co and O atoms in Sr\(_{261}\)CoO\(_3\) in the 4D real superspace. \(a_i\) (\(i = 1 \sim 4\)) are unit vectors in the 4D superspace. The solid parallelogram is a unit cell. The horizontal line \(R_{\parallel}\) represents the physical 3D space, and \(R_{\parallel}(t)\) gives an equivalent description of \(R_{\parallel}\). \(t\) is a complementary element of the superspace coordinates, which represents the position of the unit cell placed somewhere in the crystal. Atomic positions can be expressed as wavy strings, and the average positions are indicated by a straight line for Co and step functions for O. (b) Two cases of the O position (A and B) in the \(a\)-\(b\)-plane in the hexagonal lattice. (c) Four CoO\(_h\) polyhedron types: (i) octahedron: \(\Delta t = \tau + \gamma / 2 \leq t < \tau - \gamma / 2 + 1 / 2 (\Delta t = 1 - \gamma)\), (ii) trigonal prism: \(\Delta t = \gamma / 2 + 1 / 2 \leq t < \tau + \gamma / 2 (\Delta t = \gamma - 1 / 2)\), (iii) octahedron: \(\Delta t = \gamma / 2 \leq t < \tau - \gamma / 2 + 1 (\Delta t = 1 - \gamma)\) and (iv) trigonal prism: \(\tau - \gamma / 2 + 1 \leq t < \tau + \gamma / 2 + 1 / 2 (\Delta t = \gamma - 1 / 2)\).

The commensurate Sr\(_{14/1}\)CoO\(_3\) phase [9]. This is due to a slight difference between the idealized composition 7/11 = 0.6364 and the obtained \(\gamma = 0.6305\). The Co–O bonds in TP sites look longer than the Co–O bonds in Oh sites. The upper (or lower) oxygen ions of the trigonal prism are shifted away from the lower (or upper) oxygen ions. This is probably due to the Coulomb repulsion between the oxygen ions along the \(c\)-axis. The elongation of Co–O bonds may weaken the crystal-field splitting of the 3d-orbit energy band. This situation should stabilize the high-spin state of the Co ion along the \(c\)-axis. The elongation of Co–O bonds may strengthen the crystal-field splitting of the 3d-orbit energy band.

Figure 4(a) indicates that in the TP sites, both the Co–O bonds are lengthened simultaneously. In contrast, in the Oh site, whenever one bond is lengthened, another bond is shortened. The average bond lengths Co–O(av.) clearly indicate that the TP sites tend to have longer Co–O distances than the Oh sites. The average bond lengths for the TP and Oh sites are 2.039(4) Å and 1.895(3) Å, respectively. These values are almost the same as the values for Sr\(_{14/1}\)CoO\(_3\): 2.05 Å (TP) and 1.90 Å (Oh) [9].

For Sr\(_{261}\)CoO\(_3\), the averaged bond length for the Oh site (1.895 Å) is slightly shorter than the typical Co\(^{3+}\)–O length (1.945 Å), which was calculated from Shannon’s ionic radii: 0.545 Å for Co\(^{3+}\) low-spin ion (6-fold coordination) and 1.40 Å for O\(^{2-}\) ion (6-fold coordination) [28]. This suggests that the Oh sites partly include Co\(^{3+}\) small-radius ions. On the other hand, the averaged bond length for the TP site (2.039 Å) is almost intermediate between the typical Co\(^{3+}\)–O length (1.945 Å) and the typical Co\(^{3+}\)–O length (2.145 Å), which was calculated from the ionic radii: 0.745 Å for Co\(^{3+}\) high-spin.
Figure 5. Modulated crystal structure of Sr$_{1.261}$CoO$_3$ viewed along the [00-1] direction (a). Structural arrays of the CoO$_6$ polyhedra and Sr ions viewed along the [-110] direction (b). The solid rhombus and rectangles indicate unit cells of two subsystems. The lattice parameters are $a = b = 9.5038(2)$ Å, $c_1 = 2.51954(9)$ Å and $c_2 = 3.9959(5)$ Å ($\gamma = c_1/c_2 = 0.63052(5)$). The ‘Oh’ (octahedron) and ‘TP’ (trigonal prism) indicate the CoO$_6$ polyhedron types.

ion (6-fold coordination) and 1.40 Å for O$^{2-}$ ion (6-fold coordination) [28]. This suggests that the Co ion in the TP sites takes the mixed valence of Co$^{3+}$ and Co$^{2+}$ ions. Figure 6(b) shows the bond-valence sum at the Co sites, plotted as a function of $t$. These values were calculated from the Co–O bond lengths of figure 6(a). In general, the
bond-valence sum is an empirical measure of the net oxidation state for cations; in the present case, it should correspond to a Co valence for each site [15]. It is noteworthy that the bond-valence sum keeps intermediate values between 3+ and 4+ in the range of 0 ≤ t < 0.37 (or 0.5 ≤ t < 0.87), and subsequently decreases to 2+ in the range of 0.37 ≤ t < 0.5 (or 0.87 ≤ t < 1.0). This suggests that the Oh sites contain Co3+ and Co4+ ions, and the TP sites are composed of Co2+ and Co3+ ions; i.e. the three types of Co valence state ions, Co3+, Co4+, and Co2+, are mixed in a chain. Averaged bond valences are Co0.36(0.37) in the Oh sites and Co0.24(0.35) in the TP sites, indicating that 56% Co4+ ions are mixed in the Co sites in Oh and that 55% Co2+ ions are mixed in the Co sites in TP. The remaining sites are occupied by Co3+ ions. The component ratios of the Co ions in all the Co sites are 42% for Co4+, 44% for Co3+, and 14% for Co2+. The averaged bond valence over all the Co sites is +3.27(6). This value is close to the Co valence (+3.36(7)) determined from the chemical analysis.

It is worth commenting on the validity of the structure analysis results. We employed a Fourier series to approximate the modulation functions for the atomic coordinates. In the present system, the CoO6 polyhedral structure depends mainly on the coordinates of the oxygen site. In particular, the accuracy of γ(O) strongly affects the validity of the structure. In figure 3, the obtained Fourier-series modulation function γ(O) approximates a step-like function. The difference between the Fourier-series function and the crenel function (discontinuous function [9, 10]) is the sharpness of the step boundary at x = τ and τ + 1/2 and the amplitude of the modulation around each step, A or B. The Fourier-series function has a smoothed step (continuous change of y) and a large modulation amplitude around the average y (yA and yB) for each step, as compared with the crenel function. These differences may affect the Co–O distance and the bond valence at local sites. According to the change in the bond-valence curve (figure 6(b)), most parts are consistently in between Co4+ and Co3+ in the Oh region and Co2+ and Co3+ in the TP region. However, in the Oh region around t ∼ 0.35 (or ∼0.85), the bond valence partly exceeds 4+, and in the TP region, it takes the minimum below 2+. This is probably due to excessively amplified y(O)-modulation with artificial humps superimposed on the steps (figure 3). This suggests that for the Sr2/CoO3 system, the local structure obtained from Fourier-series functions may include somewhat excessive modulation.

To cancel out the excessive modulation, an averaged structure was used for further discussion. In figure 3, the averaged γ(O) values are 0 (yB) for step A and 0.152 = yA for step B. The latter is exactly the same as the averaged x (xA). This result is reasonable because x and y are essentially equivalent in trigonal symmetry. The Fourier amplitudes of γ(O) naturally converged without constraints on the structural symmetry to give the suitable average structural parameters on the steps. In figure 6(a), the averaged Co–O bond lengths are 2.04 Å (TP) and 1.90 Å (Oh). These values agree well with the bond lengths in Sr141/CoO3: 2.05 Å (TP) and 1.90 Å (Oh), which were determined using the crenel function [9]. Thus, the obtained average structure is method independent, reliable and useful for further analysis, such as the evaluation of magnetic properties.

5.2. Magnetic properties and electrical resistivity

Figure 7 shows the temperature dependence of the magnetic susceptibility (χ) of Sr1.26CoO3. This behavior is typical
Figure 8. Schematic representation of the $d$-energy levels of Co ions in an octahedral CoO$_6$ cluster and a trigonal prismatic CoO$_6$ cluster. It is assumed that the Co ion is located on the 3-fold rotational axis in the center of the polyhedron. In Sr$_{1.26}$CoO$_3$, the actual CoO$_6$ cluster is distorted by the structural modulation of each site. However, the Co$^{3+}$ $d^6$($S=0$) configuration occurs in the strong and medium crystal field, independent of the trigonal or octahedral distortion in the polyhedra.

The Curie–Weiss paramagnetic state, and neither magnetic transition nor low-dimensional behavior is observed. There is also no difference between the zero-field-cooling (ZFC) and field-cooling (FC) data. The susceptibility values in the temperature range $2 \, \text{K} \leq T \leq 300 \, \text{K}$ were fitted with a Curie–Weiss law: $\chi(T) = \chi_0 + C/(T - \theta)$, where $\chi_0$ is a constant, $C = N p_{\text{eff}}^2 \mu_B^2 / 3 k_B$ is the Curie constant, and $\theta$ is the Weiss temperature. The fitting parameters are $\chi_0 = 0.000 \, 15(36) \, \text{emu} \, [\text{Co}]^{-1}$, $C = 0.434(8) \, \text{emu} \, \text{K} \, [\text{Co}]^{-1}$, and $\theta = 0.76(4) \, \text{K}$, where [Co] is the molar cobalt concentration. The effective number of Bohr magnetons is $p_{\text{eff}} = 1.86(2)$ per Co ion. The resultant Curie–Weiss fit is shown by the broken line in figure 7, and it reproduces well the experimental data (open circles).

The Curie constant $C$ can be calculated theoretically if the spin states of the magnetic ions are known. The spin configuration of the transition-metal elements depends on the ionic valence, atomic coordination and bond lengths. In either case of MO$_6$ ($M$: transition metal)—octahedral or trigonal prism—when the metal atom of the MO$_6$ polyhedron lies on the 3-fold rotational axis, its energy levels are divided into $d_\gamma$($2e$) and $d_\epsilon$($1a, 1e$) levels by the crystal field $\Delta$ [29]. The $2e$ and $1e$ levels are doubly degenerate, while the $1a$ level is nondegenerate. The crystal field strength strongly depends on the M–O bond lengths. Figure 8 shows the expected spin configurations of Co$^{4+}$, Co$^{3+}$ and Co$^{2+}$ ions with 6-fold coordination and 3-fold rotational axis in the ideal CoO$_6$ octahedra and trigonal prisms. The Co$^{4+}$ and Co$^{3+}$ ions have a strong crystal field owing to their short Co–O bonds. The spins simply occupy the $d_\epsilon$ levels, suggesting that Co$^{3+}$($d^5$) takes an $S=1/2$ state and Co$^{4+}$($d^6$) takes an $S=0$ state, regardless of the polyhedron type (Oh or TP). In contrast, the Co$^{2+}$ ion should have a weak crystal field owing to its long Co–O bonds. The spins can occupy not only the $d_\epsilon$ levels but also the $d_\gamma$ levels, by obeying the Hunt rule. As a result, Co$^{2+}$($d^7$) in the trigonal prism should take an $S=3/2$ state.
In the actual crystal structure in Sr$_{1.26}$CoO$_3$, the CoO$_6$ octahedra consist of the Co$^{3+}$ and Co$^{4+}$ ions, while the CoO$_4$ trigonal prisms consist of the Co$^{3+}$ and Co$^{2+}$ ions. This is because the octahedron and trigonal prism sites have mixed-valence states of Co$^{3.5+}_0$ and Co$^{2.5+}_{10}$, respectively. The shape of the actual CoO$_6$ cluster is distorted by the structural modulation of each site. The CoO$_3$ clusters of the Co$^{3+}$ sites and the Co$^{2+}$ sites are comparatively close to the ideal shapes of the octahedron (the left end in figure 8) and the trigonal prism (the right end in figure 8), respectively. However, the CoO$_6$ clusters of the Co$^{3+}$ sites are neither ideal octahedron nor ideal trigonal prism (the middle two clusters in figure 8), but have an intermediate structure; the Co$^{3+}$ octahedra include trigonal distortion, and the Co$^{3+}$ trigonal prisms are distorted octahedrally. Nevertheless, it can be expected that the electronic configurations of two Co$^{3+}$ states with octahedral or trigonal prismatic coordination are essentially the same. The Co$^{3+}$ states with octahedral or trigonal prismatic coordination are 3+

Recently, we have studied the effect of Ni doping on the structure and the magnetic properties of the Sr$_2$(Co, Ni)O$_3$ system [30] and found that the Ni atoms selectively occupy the trigonal prismatic sites, and that the effective magnetic moment is suppressed by the Ni doping. The Ni$^{2+}$($d^8$) ion should take an $S = 1$ high-spin state ($d^5$$e^2$) owing to the doubly degenerate $dy$ (2e) levels. The suppression of the magnetic moment can be understood from the cancellation of the spins at the 1e level. This fact supports the expectation that Co$^{3+}$($d^7$) at the trigonal prismatic site in Sr$_{1.26}$CoO$_3$ assumes an $S = 3/2$ high-spin state.

On the basis of the above expectations of the spin configuration of the Co ions, we calculated the Curie constant (i.e. effective magnetic moment) of Sr$_{1.26}$CoO$_3$. We assumed spin configurations of the Co ions as follows: (i) the Co$^{3+}$ ions have $S = 0$ ($d^6$) for both the Oh and TP sites, (ii) the Co$^{3+}$ ions have $S = 1/2$ ($d^5$) because of the strong crystal field at the Oh sites and (iii) the Co$^{3+}$ ions have $S = 3/2$ ($d^5$$d^2$) because of the weak crystal field and Hund energy gain in the TP sites. These assumptions and the obtained composition of the Co$^{3+}$, Co$^{3+}$ and Co$^{2+}$ ions at all the Co sites (i.e. 0.42 $\times$ Co$^{3+}$, 0.44 $\times$ Co$^{3+}$, 0.14 $\times$ Co$^{2+}$; vide supra) result in the Curie constant of 0.425 emu K[Co]$^{-1}$; i.e. the effective magnetic moment is 1.84$\mu_B$. This calculated Curie constant agrees well with the measured value of 0.434 emu K[Co]$^{-1}$, suggesting that the above assumptions (1)–(3) on the mixed valence states of the Co ions and their spin configurations are consistent with the experiment.

The obtained value of $\chi_0 \sim 1.5 \times 10^{-4}$ emu K[Co]$^{-1}$ is almost the same as those in other cobalt oxides, such as (CaOH)$_{1.14}$CoO$_2$ [31]. There could be several contributions to $\chi_0$, such as the van Vleck paramagnetic term, spin–orbit interaction [32], electron correlation, closed-shell diamagnetic term, and so on. The low Weiss temperature ($\theta \sim 0.8$ K) is an indication of the negligible interspin correlation in Sr$_{1.26}$CoO$_3$, which may be attributed to the obstruction of the long-range magnetic interaction by nonmagnetic ions (Co$^{3+}$) intervening between the magnetic ions (Co$^{3+}$, Co$^{2+}$).

The magnitude of the Curie constant and negligibly small Weiss temperature suggest that a considerable amount of nonmagnetic Co$^{3+}$ ions are present in the material. The analysis of the magnetic data reveals that Sr$_{1.26}$CoO$_3$ is essentially in a Curie (not Curie–Weiss) paramagnetic state. Note that the observed magnetic data can be well understood by assuming that nonmagnetic Co$^{3+}$ ions are mixed with the Co$^{3+}$-based octahedron sites and the Co$^{2+}$-based trigonal prism sites in Sr$_{1.26}$CoO$_3$.

The charge balance of the Co ions in the Sr$_{2}$CoO$_3$ system was discussed in terms of the structure and magnetic properties. Gourdon et al. expected that Sr$_{14/11}$CoO$_3$ possesses the oxidation state of the separate Co ions, with the Co$^{3+}$ in TP sites and Co$^{4+}$ in Oh sites [9]. However, if the complete Co$^{3+-}$Co$^{4+}$ separation is realized also in Sr$_{1.26}$CoO$_3$, then the Curie constant should become 0.767 emu K[Co]$^{-1}$ ($\mu_B = 2.48\mu_B$), which is much larger than the observed Curie constant of 0.434 emu K[Co]$^{-1}$. The complete Co$^{3+-}$Co$^{4+}$ separation seems excessive and unrealistic for Sr$_{1.26}$CoO$_3$. Nonmagnetic ions are necessary for explaining the size of the magnetic moment observed in Sr$_{1.26}$CoO$_3$. Whanbgo et al. theoretically expected that in Sr$_{14/11}$CoO$_3$, the double CoO$_6$ octahedra (adjacent to Co$^{3+}$($d^5$) in the chain) form a nonmagnetic Co$_2$O$_6$ dimer, and that adjacent triple CoO$_6$ octahedra form a magnetic Co$_3$O$_{12}$ trimer with an $S = 1/2$ moment [29]. It is desirable to test their theoretical predictions experimentally. However, even if the nonmagnetic dimers and an $S = 1/2$ moment per trimer are taken into account for Sr$_{1.26}$CoO$_3$, the estimated Curie constant ($C = 0.580$ emu K[Co]$^{-1}$, $\mu_B = 2.15\mu_B$) is still larger than the observed value. The magnetic susceptibility data suggest that a larger number of nonmagnetic sites should exist in the chain, in agreement with our structure analysis.
Figure 9 shows the temperature dependence of the electrical resistivity (ρ) of Sr$_{1.26}$CoO$_3$. The semiconductor-like behavior is observed with the resistivity following the Arrhenius law (see inset). The deduced activation energy of $\Delta E \sim 0.15$ eV may correspond to the electron hopping along the polyhedral chains. The conduction properties can be attributed to the indirect overlap of the Co d orbitals, which may be affected by the mixing of the different energy levels (d$_x$ and d$_y$) in a chain (see figure 8). The resistivity value is rather high at low temperatures. These data suggest that the localized spin model with the Curie–Weiss behavior is applicable to the analysis of the magnetic data in Sr$_{1.26}$CoO$_3$.

6. Conclusions

We have characterized the crystal structure and magnetic properties of the hexagonal 1D cobalt oxide Sr$_{1.26}$CoO$_3$ using a modulated-structure analysis technique combined with neutron powder diffraction and magnetic susceptibility data. Sr$_{1.26}$CoO$_3$ is a composite crystal that consists of [CoO$_{2.5}$] and [2Sr] subsystems. The [CoO$_3$] sublattice forms 1D chains along the c-axis composed of two types of face-sharing CoO$_6$ polyhedra: octahedra (Oh) and trigonal prisms (TPs). The structure analysis revealed that the [CoO$_3$] chain contains 73.9% Oh and 26.1% TP sites and that the TP sites have longer Co–O bonds and consequently lower bond valence than the Oh sites: $d_{\text{av}} = 2.039(4)$ Å (TP) and 1.895(3) Å (Oh). The bond length may affect the strength of the crystal field at the Co sites. The Co bond valence takes intermediate values of Co$^{3+}$ in the Oh sites and Co$^{4+}$ in the TP sites, suggesting that Co$^{3+}$ ions are mixed with Co$^{4+}$ ions in the Oh sites and Co$^{2+}$ ions in the TP sites. The Co sites contain about 42% Co$^{4+}$, 44% Co$^{3+}$ and 14% Co$^{2+}$ ions. The measured magnetic susceptibility can be well explained assuming that the compound has Co mixed-valence states with the spin configurations of the d$_x^0S = 0$ low-spin state for Co$^{3+}$, d$_{5/2}S = 1/2$ low-spin state for Co$^{4+}$ and d$_{3/2}S = 3/2$ high-spin state for Co$^{5+}$. The deduced Weiss temperature value of approximately 0.8 K implies that the Sr$_{1.26}$CoO$_3$ usual state is a Curie paramagnetic state. The paramagnetic state is attributed to the obstruction of the intrachain magnetic interaction by the nonmagnetic Co$^{3+}$ ions. These results suggest that the nonmagnetic Co$^{3+}$ ions play an essential role in the magnetism of the Sr$_{2y}$CoO$_3$ systems.

Acknowledgment

We thank Dr Onoda (NIMS) for helpful advice on the crystal structure analysis and Mr Takenouchi (NIMS) for technical assistance with the ICP analysis. This research was supported by the Superconducting Materials Research Project and Thermoelectric Materials Research Project of NIMS administered by the Ministry of Education, Culture, Sports, Science and Technology of Japan, and by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Grant Nos. 22246083 and 22560676).

References

[1] Nguyen T N, Giaquinta D M and zur Loye H-C 1994 Chem. Mater. 6 1642
[2] Nguyen T N and zur Loye H-C 1995 J. Solid State Chem. 117 300
[3] Nguyen T N, Lee P A and zur Loye H-C 1996 Science 271 489
[4] Sun J, Li G, Li Z, You L and Lin J 2006 Inorg. Chem. 45 8394
[5] Darriet J and Subramanian M A 1995 J. Mater. Chem. 5 543
[6] Dussarrat C, Grasset F and Darriet J 1995 Eur. J. Solid State Inorg. Chem. 32 557
[7] Powell A V, Battle P D and Gore J G 1993 Acta Crystallogr. C 49 852
[8] Fjellvåg H, Gulbrandsen E, Aasland S, Olsen A and Hauback B C 1996 J. Solid State Chem. 124 190
[9] Gourdon O, Petricek V, Dusek M, Bezdicka P, Durovic S, Gyepesova D and Evain M 1999 Acta Crystallogr. B 55 841
[10] Evain M, Boucher F, Gourdon O, Petricek V, Dusek M and Bezdicka P 1998 Chem. Mater. 10 3068
[11] Jordan N A, Battle P D, van Smaalen S and Wunschel M 2003 Chem. Mater. 15 4262
[12] Ueki K, Yamamoto A, Watanabe Y, Shishido T and Fukuda T 1993 Acta Crystallogr. B 49 67
[13] Onoda M, Saeki M, Yamamoto A and Kato K 1993 Acta Crystallogr. B 49 929
[14] Perez-Mato J M, Zakhour-Nakkhi M, Weill F and Darriet J 1999 J. Mater. Chem. 9 2795
[15] Brown I D and Altermatt D 1985 Acta Crystallogr. B 41 244
[16] van Smaalen S 1992 Acta Crystallogr. A 48 408
[17] Ohoyama K, Kanouchi T, Nemoto K, Ohashi M, Kajitani T and Yamaguchi Y 1998 Japan. J. Appl. Phys. 37 3319
[18] Yamamoto A 1993 Acta Crystallogr. A 49 831
[19] Yamamoto A 1996 Acta Crystallogr. A 52 509
[20] Yamamoto A http://www.nims.go.jp/apperiodic/yamamoto/index.html
[21] Prince E (ed) 2004 International Tables for Crystallography vol C 3rd edn (Dordrecht: Kluwer) p 445
[22] van Smaalen S, Meetsma A, Wiegers G A and de Boer J L 1991 Acta Crystallogr. B 47 314
[23] van Smaalen S and de Boer J L 1992 Phys. Rev. B 46 2750
[24] de Wolff 1974 Acta Crystallogr. A 30 777
[25] Onoda M 1998 J. Crystallogr. Soc. Japan 40 161
[26] Onoda M 1998 J. Crystallogr. Soc. Japan 40 202 [in Japanese]
[27] van Smaalen S 2007 Incommensurate Crystallography (Oxford: Oxford University Press)
[28] Shannon R D 1976 Acta Crystallogr. A 32 751
[29] Whangbo M-H, Koo H-J, Lee K-S, Gourdon O, Evain M, Jobic S and Brec R 2001 J. Solid State Chem. 160 239
[30] Isobe M et al in preparation
[31] Shizuya M, Isobe M, Baba Y, Nagai T, Osada M, Kosuda K, Takenouchi S, Matsui Y and Takayama-Muromachi E 2007 J. Solid State Chem. 180 249
[32] Kotani M 1949 J. Phys. Soc. Japan 4 293