

Crystal Structure, Electric and Magnetic Properties of Layered Cobaltite β -Na_xCoO₂

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The layered oxide thermoelectric material β -Na_{0.67}CoO₂ has been studied by powder neutron diffraction, electric and magnetic measurements. This compound includes an edge-sharing CoO₆ slab and a highly vacant Na⁺ sheet in a unit cell (space group symmetry $C2/m$, $a = 4.9023(4)$ Å, $b = 2.8280(2)$ Å, $c = 5.7198(6)$ Å and $\beta = 105.964(6)^\circ$ at 300 K). The evaluated formal valence of cobalt ion, +3.33(1), is ascribed to the coexistence of Co³⁺ and Co⁴⁺ in the ratio 2:1. Polycrystalline β -Na_{0.67}CoO₂, a p -type thermoelectric material, exhibits metallic behavior of the electric resistivity below 300 K. The Curie–Weiss-type magnetic susceptibility indicates antiferromagnetic interactions between magnetic cobalt ions in the edge-sharing CoO₆ slab. © 2002 Elsevier

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INTRODUCTION

Recent discovery of excellent thermoelectric properties in NaCo₂O₄ single crystal has stimulated broad interest in layered oxide thermoelectric materials (1). In the NaCo₂O₄, a highly vacant Na⁺ sheet and a CdI₂-type CoO₂ conducting layer are alternately stacked parallel to the c -axis. Recently, several research groups observed large Seebeck coefficient in the misfit-layered cobaltites, [Ca₂CoO_{3.34}]_{0.614}[CoO₂] and Bi₂Sr₃Co₂O₉ (2–4). These compounds also have the CdI₂-type CoO₂ layers interleaved by a modulated cation-oxygen layer. It has been pointed out that the strongly correlated electrons in such a CoO₂ layer play an important role in the enhancement of the Seebeck coefficient (5). The magnetic susceptibility of polycrystalline sample of NaCo₂O₄ was successfully explained by the coexistence of Co³⁺ and Co⁴⁺, both of which are in the low-spin state (6). Koshibae *et al.* (7) established

a theory generalizing Heikes' formula and suggested that the low-spin state is a key factor for the large Seebeck coefficient.

The thermoelectric material, γ -Na_xCoO₂ (NaCo₂O₄) (1, 8), is a member of Na_xCoO₂ type layered oxides (9). There are other three members with different sodium contents, namely, α ($0.90 \leq x \leq 1.0$), α' ($x = 0.75$), β ($0.55 \leq x \leq 0.60$) phases, respectively. They are also potential candidates for the thermoelectric material because of their layered structures similar to γ -Na_xCoO₂. Unfortunately, there is no report on their thermoelectric properties, i.e., Seebeck coefficient, electric resistivity and thermal conductivity. The crystal structures of α and α' -phases are believed to be isomorphous to the well-known α -NaFeO₂ and α' -NaMnO₂ (10, 11), respectively, while that of the β -phase has not been definitely determined yet. In this report, the crystal structure of β -Na_xCoO₂ is determined by means of powder neutron diffraction measurement. The electric resistivity and Seebeck coefficient are measured and compared with those of γ -Na_xCoO₂. The spin state of cobalt ion in β -Na_xCoO₂ is discussed based on observed and calculated effective magnetic moments.

EXPERIMENTAL

Polycrystalline samples of β -Na_xCoO₂ were prepared by a conventional solid-state reaction. Starting materials, Na₂O₂ (98%, Wako Pure Chemical Industries, Ltd.) and Co₃O₄ (99.9%, High purity Chemicals Lab.), were mixed in a molar ratio of Na:Co = 0.70:1.0, pressed into pellets and calcined at 530°C for 12 h in flowing oxygen gas. After intermediate grindings and pelletizing, the product was sintered at 530°C for 24 h in flowing oxygen gas. In this study, single-phase β -Na_xCoO₂ was not obtained in the range $0.55 \leq x \leq 0.65$.

The molar ratio of metal ions in the samples was chemically analyzed by inductively coupled plasma atomic-emission spectrometry (ICP-AES) and determined to be

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Na:Co = 0.674:1.0, indicating that about 4% sodium ions are missing from the initial composition. This discrepancy is likely related to the sodium evaporation occurring above 500°C as observed in the phase-formation process of γ -Na_{0.55}CoO₂ (12).

Powder neutron diffraction measurement of β -Na_xCoO₂ were carried out at 10 and 300 K using high-resolution powder diffractometer (HRPD, $\lambda = 1.8251$ Å) implemented with multi-counter detection system at Japan Atomic Energy Research Institute. The diffraction intensities were measured in the 2θ -range from 5° to 160° with a 0.05° step width. The electric resistivity, ρ , was measured by a standard four-probe method below 300 K. The Seebeck coefficient was measured by a conventional DC method with a temperature gradient of about 0.5 K and the contribution of copper lead wires was carefully subtracted. Magnetization, M , was measured under a magnetic field of $H = 0.5$ T by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5) in the range from 4.2 to 300 K.

STRUCTURE DETERMINATION

The structure determination of β -Na_xCoO₂ was performed using a Rietveld analysis program RIETAN (13). Fouassier *et al.* (9) reported an approximated structure model of β -Na_{0.60}CoO₂ with space symmetry $R3m$ (No. 160). Unfortunately, their model did not fit for the present neutron diffraction intensities. Recently, Cushing and Wiley (14) adopted a monoclinic unit cell in this compound, but did not give structural data. In the present study, a monoclinic unit cell with $\mathbf{a}_m = \mathbf{a}_h - \mathbf{b}_h$, $\mathbf{b}_m = \mathbf{a}_h + \mathbf{b}_h$ and $\mathbf{c}_m = (\mathbf{c}_h - \mathbf{a}_h + \mathbf{b}_h)/3$ was assumed, where subscripts m and h denote the monoclinic and a hexagonal $R3m$ cell, respectively. This relation is schematically illustrated in Fig. 1. Space group, $C2/m$ (No. 12), was assigned to the monoclinic unit cell based on the systematic absence of Bragg reflections

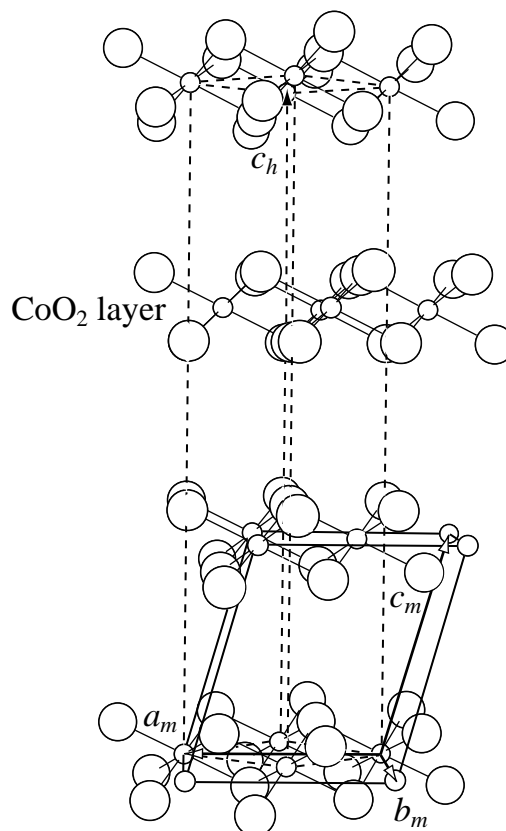


FIG. 1. Relation of a monoclinic $C2/m$ cell (solid lines) to a hexagonal $R3m$ cell (broken lines). Na⁺ sites are not shown.

(hkl reflections with $h + k = \text{odd}$ number are absent) in the present intensity data. At the initial stage of the analysis, sodium ion at $4i(x, 0, z)$ site with $x \sim 0.83$ and $z \sim 0.50$ showed an anomalously large thermal parameter, B , implying disorder of the sodium ions as in γ -Na_{0.70}CoO₂ (8). For this reason, the sodium ion was assumed to statistically occupy $8j(x, y, z)$ site with $x \sim 0.81$, $y \sim 0.10$ and

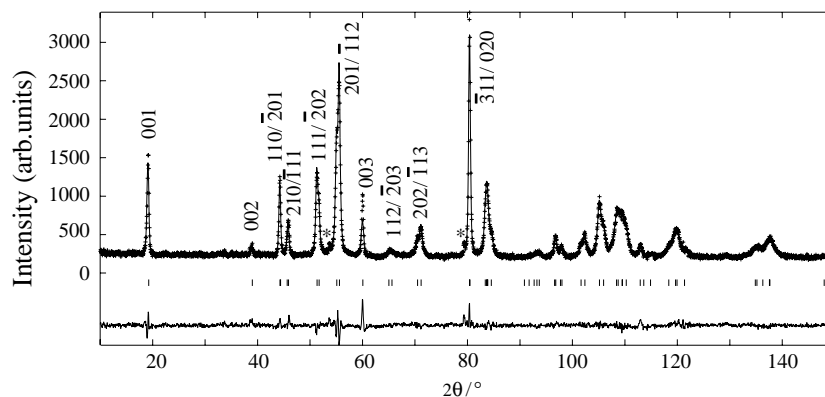


FIG. 2. Observed (+) and calculated (solid line) intensities of powder neutron diffraction pattern of β -Na_{0.67}CoO₂ at 10 K. Tick marks represent the positions of possible Bragg reflections. A solid line at the bottom is the difference between the observed and calculated intensities. Tracer peaks marked by * ($2\theta \sim 54^\circ$ and 79°) correspond to γ -phase impurity.

TABLE 1
Structure Parameters, *R*-Factors and Goodness-of-Fits of β -Na_{0.67}CoO₂ at 10 K and 300 K (Space Group *C2/m*, *Z* = 2)

Atom	site		10 K	300 K
Na	8 <i>j</i> (<i>x,y,z</i>)	occ.	0.168(3)	0.168
		<i>x</i>	0.811(2)	0.810(2)
		<i>y</i>	0.084(5)	0.097(4)
		<i>z</i>	0.495(3)	0.495(1)
Co	2 <i>a</i> (000)	<i>B</i> (Å)	0.5(3)	0.7(3)
		occ.	1.0	1.0
		<i>B</i> (Å)	0.3(1)	0.44(9)
O	4 <i>i</i> (<i>x,0,z</i>)	occ.	1.00(1)	1.0
		<i>x</i>	0.3891(5)	0.3898(6)
		<i>z</i>	0.1793(3)	0.1790(3)
		<i>B</i> (Å)	0.08(4)	0.36(5)
Lattice parameters	<i>a</i> (Å)		4.9003(4)	4.9023(4)
		<i>b</i> (Å)	2.8274(2)	2.8280(2)
		<i>c</i> (Å)	5.6968(5)	5.7198(6)
		β (°)	106.014(5)	105.964(6)
		<i>R</i> -factors	<i>R</i> _{wp} (%)	7.33
	<i>R</i> _f (%)	2.54	2.99	
Goodness of fit	<i>S</i>	1.32	1.29	

$z \sim 0.50$. The possibility of substitution for cobalt ion by sodium ion is negligible due to a large difference in ionic radius (15). Oxygen occupancy was also refined, but noticeable oxygen deficiency was not detected. As shown in Fig. 2, the powder neutron diffraction pattern at 10 K, there is satisfactory agreement between the observed and calculated intensities, except for four peaks, 001, $\bar{1}12$, 003 and $\bar{3}11$. Tracer peaks marked by * ($2\theta \sim 54^\circ$ and 79°) are originated from the γ -phase impurity. The amount of this impurity phase is negligibly small relative to that of β -Na_xCoO₂. Sodium content x was determined to be 0.67(1) at 10 K, which is in good agreement with that obtained by the ICP chemical analysis. In the refinement for the 300 K data, the sodium and oxygen occupancies were assumed to be identical with those at 10 K. The refined structure parameters, final *R*-factors and goodness of fits are given in Table 1. A close similarity of the structure parameters at 10 and 300 K is noticed.

MAGNETIC AND ELECTRIC MEASUREMENTS

Magnetic susceptibility and inverse susceptibility, $\chi(T) = M/H$ and $\chi^{-1}(T)$, are given in Fig. 3. $\chi(T)^{-1}$ linearly increases with increasing temperature above 30 K, but the deviation from the Curie-Weiss law is noticed below 30 K. The *M*-*H* curve of β -Na_{0.67}CoO₂ shows no evidence of long-range magnetic ordering at 4.2 K. Figure 4 shows the ρ -*T* curve of the polycrystalline β -Na_{0.67}CoO₂. The $\rho(T)$ monotonically decreases with decreasing temperature from 12 mΩ cm at 280 K to 3 mΩ cm at 4.2 K, i.e., metallic

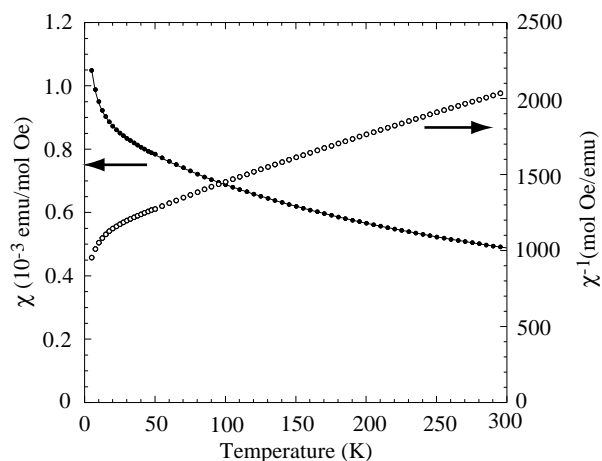


FIG. 3. χ -*T* (filled circles) and χ^{-1} -*T* (open circles) curves of β -Na_{0.67}CoO₂. A solid line is the best-fit to $\chi(T) = \chi_0 + C_1/(T-\theta) + C_2/T$.

behavior. But, the magnitude of $\rho(T)$ is considerably larger than that of γ -Na_xCoO₂ over the whole temperature range (5). This difference is presumably ascribed to low density of the sample and small grain size insufficiently grown at low sintering temperature. Figure 5 shows the temperature variation of the Seebeck coefficient. The positive Seebeck coefficient reaches about 70 μ V/K at 290 K, which is comparable with that of γ -Na_xCoO₂ (5).

DISCUSSION

Figure 6 represents the determined crystal structure of β -Na_{0.67}CoO₂. Six oxygen atoms forming a prism coordinate to the sodium ion. The sodium ions are randomly distributed at the 8*j* sites in a plane at $z \sim 0.5$. Na-Na site distances are in the range from 1.06(2) to 1.93(2) Å at 300 K. Judging from the ionic radius of Na⁺ for six coordinations

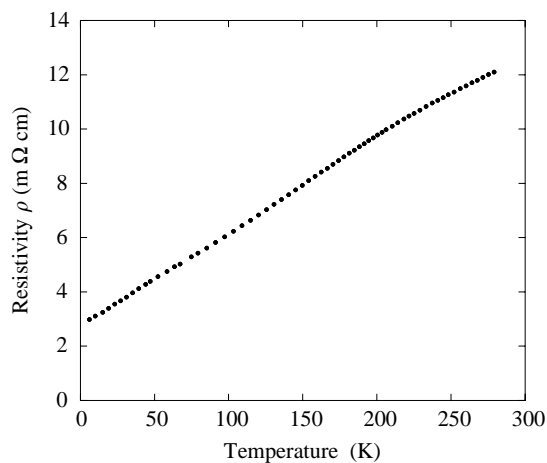


FIG. 4. ρ -*T* curve of β -Na_{0.67}CoO₂.

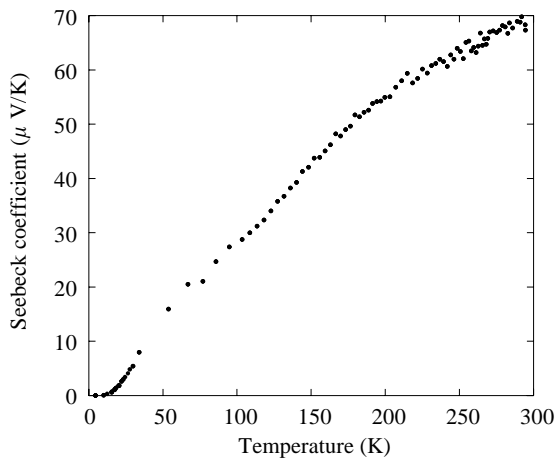


FIG. 5. Seebeck coefficient vs T of β - $\text{Na}_{0.67}\text{CoO}_2$.

(1.02 Å, (15)), the sodium ions cannot fully occupy the adjacent $8j$ sites. Selected Co–O distances and O–Co–O angles are listed in Table 2. Six Co–O distances in the CoO_6 octahedron at 300 K, 1.903(3) Å \times 2 and 1.909(1) Å \times 4, are nearly equal and practically remain unchanged at 10 K. But, the CoO_6 is slightly distorted from a regular octahedron due to the O–Co–O angles larger than 90°, e.g., O–Co–O⁽ⁱ⁾ = 95.84(8)° at 300 K. The observed Co–O distances and O–Co–O angles are comparable with those reported in γ - $\text{Na}_{0.70}\text{CoO}_2$ (8) and the misfit-layered cobaltite $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$ (16).

Figure 7 shows the stacking of NaO_6 prisms and CoO_6 octahedra in β - $\text{Na}_{0.67}\text{CoO}_2$ and γ - $\text{Na}_{0.70}\text{CoO}_2$. In β - $\text{Na}_{0.67}\text{CoO}_2$, upper oxygen atoms of the prism are shared with a CoO_6 octahedron, but lower oxygen atoms are shared with three CoO_6 octahedra. In γ - $\text{Na}_{0.70}\text{CoO}_2$, there are two kinds of prisms, namely, $\text{Na}(1)\text{O}_6$ and $\text{Na}(2)\text{O}_6$ (8). The $\text{Na}(1)\text{O}_6$ prism shares two sets of three oxygen atoms with one upper and one lower CoO_6 octahedra, respective-

TABLE 2
Selected Co–O Distances (Å) and O–Co–O Angles (°)
of β - $\text{Na}_{0.67}\text{CoO}_2$

	10 K	300 K
Co–O	1.899(2)	1.903(3)
Co–O ⁽ⁱ⁾	1.909(1)	1.909(1)
O–Co–O ⁽ⁱ⁾	95.97(7)	95.84(8)
O–Co–O ⁽ⁱⁱ⁾	95.97(7)	95.84(8)
O ⁽ⁱ⁾ –Co–O ⁽ⁱⁱ⁾	95.56(8)	95.58(9)

Note. Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$.

ly. On the other hand, the $\text{Na}(2)\text{O}_6$ prism shares two sets of three oxygen atoms with upper and lower three CoO_6 octahedra, respectively.

The formal valence of cobalt ion evaluated from the formula, $\text{Na}_{0.67}\text{CoO}_2$, is +3.33(1), where the valences of the sodium and the oxygen ions were assumed to be +1 and –2, respectively. This fractional cobalt valence is due to the coexistence of Co^{3+} and Co^{4+} (6, 8), leading to the mixed-valence cobaltite, $\text{Na}_{0.67}[\text{Co}^{3+}]_{0.67}[\text{Co}^{4+}]_{0.33}\text{O}_2$. The bond-valence sum, $v_i = \sum \exp[(R_i - r_{ij})/0.37]$, also indicates the similar cobalt valence, +3.429(7), where $R_i = 1.70$ is an empirically determined parameter for cobalt–oxygen bond and r_{ij} is a distance between cobalt ion and the j th coordinating oxygen atom (17).

Magnetic susceptibility, χ , was fitted to the formula, $\chi(T) = \chi_0 + C_1/(T-\theta) + C_2/T$, by the least-squares calculation, where χ_0 , C_i ($i = 1$ and 2) and θ are the temperature-independent susceptibility, Curie constants and the asymptotic Curie temperature, respectively. The best-fit curve (solid line) in Fig. 3 was obtained with $\chi_0 = 1.11 \times 10^{-4}$ (emu/mol Oe), $C_1 = 0.219(4)$ (emu K/mol Oe), $\theta = -285(4)$ K and $C_2 = 9.41(9) \times 10^{-4}$ (emu K/mol Oe). The Curie constant, C_2 , is so small that the Curie term, C_2/T , was tentatively attributed to unknown paramagnetic impurity. Thus,

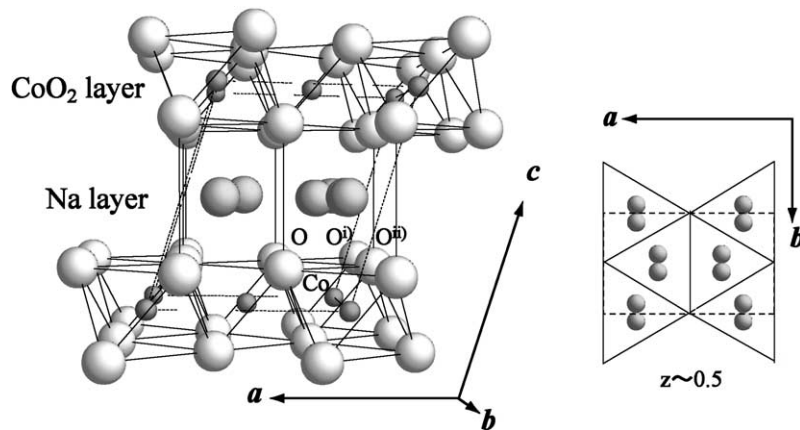


FIG. 6. Crystal structure of β - $\text{Na}_{0.67}\text{CoO}_2$. Broken lines indicate the unit cell edges.

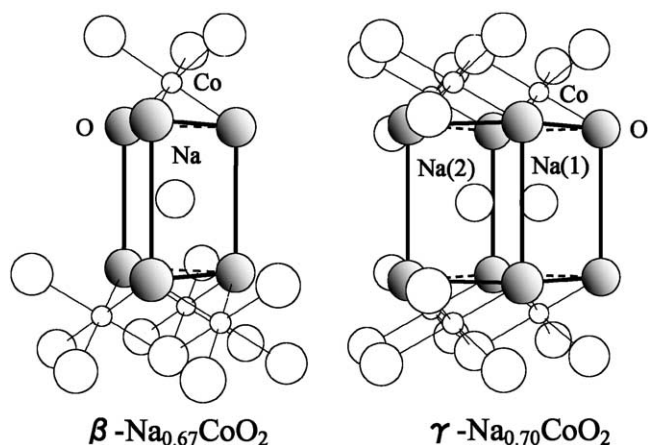


FIG. 7. Stacking of NaO_6 prisms and CoO_6 octahedra in β - $\text{Na}_{0.67}\text{CoO}_2$ and γ - $\text{Na}_{0.70}\text{CoO}_2$. Shaded circles represent the oxygen atoms forming NaO_6 prisms with Na^+ sites at their centers.

the Curie-Weiss term, $C_1/(T - \theta)$, corresponds to the intrinsic magnetic response from β - $\text{Na}_{0.67}\text{CoO}_2$. The negative θ suggests the antiferromagnetically interacting spins. The adjusted Curie constant gives the effective magnetic moment, $\mu_{\text{exp}} = 1.32(6) \mu_B$, per chemical formula, where μ_B is the Bohr magneton.

Since Na^+ is non-magnetic, the Curie-Weiss behavior of $\chi(T)$ is attributed to the distinct Co^{3+} and Co^{4+} randomly arranged at the cobalt ion sites. In the localized-spin approximation, there are three kinds of possible spin states for each cobalt ion, i.e., $\text{Co}^{3+}(3d^6)$: $S = 0(t_{2g}^6 e_g^0)$, $S = 1(t_{2g}^5 e_g^1)$, $S = 2(t_{2g}^4 e_g^2)$, and $\text{Co}^{4+}(3d^5)$: $S = \frac{1}{2}(t_{2g}^5 e_g^0)$, $S = \frac{3}{2}(t_{2g}^4 e_g^1)$, $S = \frac{5}{2}(t_{2g}^3 e_g^2)$, respectively. In this study, the effective magnetic moment was calculated using the formula, $\mu_{\text{calc}} = [0.67 \times 4S(\text{Co}^{3+})(S(\text{Co}^{3+}) + 1) + 0.33 \times 4S(\text{Co}^{4+})(S(\text{Co}^{4+}) + 1)]^{1/2}$, where the ratio, $[\text{Co}^{3+}]:[\text{Co}^{4+}] = 0.67:0.33$, was assumed. The closest value obtained from the above formula, $\mu_{\text{calc}} = 0.99 \mu_B$, where $S(\text{Co}^{3+}) = 0$ and $S(\text{Co}^{4+}) = \frac{1}{2}$, is unreasonably small relative to the experimental value. In the similarly synthesized γ - $\text{Na}_{0.70}\text{CoO}_2$, both cobalt ions take the low-spin states, $S(\text{Co}^{3+}) = 0$ and $S(\text{Co}^{4+}) = \frac{1}{2}$ (8). Recently, Masset *et al.* (3) found the spin state transition at 420 K in the misfit-layered cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$ with Co^{3+} and Co^{4+} . This transition is accompanied by clear anomalies of $\chi(T)^{-1}$ and $\rho(T)$ at this temperature. However, such anomalies were not observed in the present study as shown in Figs. 3 and 4. Further study on magnetic properties would be needed to understand the spin state of the mixed-valent cobalt ion in the present compound.

SUMMARY

The crystal structure of layered oxide β - $\text{Na}_{0.67}\text{CoO}_2$ has been determined from the powder neutron diffraction data. The sodium ions are statistically distributed at prism sites coordinated by six oxygen atoms. The conducting layer consisting of edge-sharing CoO_6 octahedra, i.e., the CdI_2 -type CoO_2 slab, is alternately stacked with the highly vacant Na^+ sheet. The estimated cobalt valence, $+3.33(1)$, is fairly close to the value, $+3.429(7)$, determined by the bond-valence sum calculation. These features are closely related to the crystal structure of a good thermoelectric material, γ - Na_xCoO_2 . The Seebeck coefficient of the present material, $+70 \mu\text{V/K}$ at 290 K, is comparable to that of γ - Na_xCoO_2 .

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