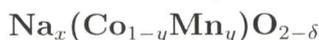


Neutron Diffraction Study of Layered Oxides



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Structure parameters of layered oxides $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$ ($y=0.0, 0.1, 0.3, 0.5$ and 0.7) were refined by means of powder neutron diffraction. Disordered sodium ions are unequally distributed at two non-equivalent sites. Cobalt and manganese ions are situated at a rhombohedrally distorted octahedral site. Average formal valence for these ions was evaluated from charge neutrality condition in the chemical formula. The effective magnetic moments μ_{eff} were calculated assuming the presence of magnetic ions, $\text{Co}^{4+}(S=1/2)$ and $\text{Mn}^{3+}(S=2)$, based on the average formal valence. There is a good agreement between μ_{eff} and the experimentally determined ones at $y=0.0, 0.1$ and 0.3 .

KEYWORDS: thermoelectric material, Na_xCoO_2 , neutron diffraction, strong electron-electron correlation

§1. Introduction

Layered cobalt oxide Na_xCoO_2 ($x \approx 0.5$) is a potential thermoelectric material with unusually large thermopower ($\alpha=100 \mu\text{V}/\text{K}$) and low electric resistivity ($\rho=200 \mu\Omega\text{cm}$) at 300 K .¹ A good thermoelectric material having low thermal conductivity κ is needed to attain higher figure of merit $Z=\alpha^2/\rho\kappa$. Takahata *et al.*² observed poor thermal conduction ($\kappa=20 \text{ mW}/\text{cmK}$ at 280 K) in polycrystalline Na_xCoO_2 , which possibly originates from the point-defect phonon scattering in highly vacant sodium layers.²

It has been pointed out that strong electron-electron correlation plays an important role in enhancement of the thermopower of Na_xCoO_2 .^{1,3,4} However, the mechanism of this enhancement is not fully understood yet. In this compound, the highly vacant Na layer and CoO_2 conducting layer are alternately stacked parallel to the c -axis.⁵⁻⁷ Cobalt ions are situated at the centers of CoO_6 octahedra and form two-dimensional triangular sublattice. The electron-electron correlation is possibly related to the frustration of antiferromagnetically interacting spins at cobalt ion sites.¹ Recently, Ray *et al.*⁸ reported that two kinds of cobalt ions in the low spin state, $\text{Co}^{3+}(S=0)$ and $\text{Co}^{4+}(S=1/2)$, coexist with a population ratio 2:1 in polycrystalline Na_xCoO_2 . But, in earlier structure determinations, all the cobalt ions were located at the equivalent sites.⁵⁻⁷

In order to get more insight into the origin of the large α and the low κ , we have studied the effects of Mn-substitution on crystal structure, magnetism and electric transport of Na_xCoO_2 . In this paper, we report structural changes and magnetic behavior in $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$ system.

§2. Experimental

Polycrystalline samples, $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$ with $y=0.0, 0.1, 0.3, 0.5$ and 0.7 , were prepared by a conventional solid state reaction. Starting powders of Na_2CO_3 ,

Co_3O_4 and Mn_3O_4 were mixed with an appropriate molar ratio and calcined at 1123 K for 12 hours in air. Nominal sodium content in each sample was fixed to 0.70 . The products were thoroughly reground, pressed into pellets and sintered at 1173 K for 12 hours in air. Neutron diffraction intensities were measured at room temperature using double-axis diffractometer HERMES ($\lambda=1.8196 \text{ \AA}$) implemented with multi-counter detection system at JAERI. The $\text{P6}_3/\text{mmc}$ type space symmetry (No.194) was assigned to all the samples based on their observed systematic absence.⁷ The structure parameters were refined using a Rietveld analysis program, RIETAN.⁹ The magnetic measurements were carried out in the range from 300 K down to 4.2 K by a SQUID magnetometer.

§3. Results

No impurity peak was detected in the present powder diffraction measurements. As an example, Fig.1 shows observed, calculated and difference intensities in powder neutron diffraction of $\text{Na}_{0.70}\text{CoO}_2$ ($y=0.0$). Sodium ions at $2b(0\ 0\ 1/4)$ and $2d(2/3\ 1/3\ 1/4)$ sites have an anomalously large thermal parameter B ($\approx 3 \text{ \AA}^2$), implying disorder of sodium ions around these sites. In the present

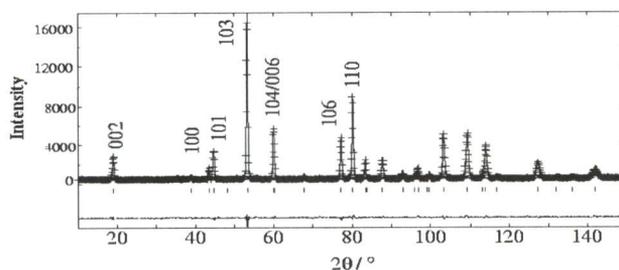


Fig.1. Observed (+) and calculated (solid line) intensities in powder neutron diffraction of $\text{Na}_{0.70}\text{CoO}_2$. Tick marks represent the positions of possible Bragg reflections. A solid line at the bottom is the difference between observed and calculated intensities.

Table I. Structure parameters, R -factors and Goodness of fits of $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$.

| Atom | Site | | $y=0.0$ | 0.1 | 0.3 | 0.5 | 0.7 |
|--------------------|-------------------|------------------|------------|------------|------------|-----------|-----------|
| Na1 | $6h(x\ 2x\ 1/4)$ | <i>occ.</i> | 0.071(2) | 0.076(2) | 0.074(3) | 0.067(3) | 0.063(4) |
| | | x | 0.057* | 0.053* | 0.042* | 0.045* | 0.052* |
| | | $B (\text{Å}^2)$ | 0.5** | 1.0** | 1.2** | 0.4** | 0.3** |
| Na2 | $6h(x\ 2x\ 1/4)$ | <i>occ.</i> | 0.162(2) | 0.152(3) | 0.123(3) | 0.094(4) | 0.097(5) |
| | | x | 0.724(2) | 0.719(2) | 0.709(5) | 0.712(7) | 0.719(5) |
| | | $B (\text{Å}^2)$ | 0.5(2) | 1.0(3) | 1.2(4) | 0.4(6) | 0.3(6) |
| Co/Mn | $2a(0\ 0\ 0)$ | <i>occ.</i> | 1.0/0.0 | 0.9/0.1 | 0.7/0.3 | 0.5/0.5 | 0.3/0.7 |
| | | $B (\text{Å}^2)$ | 0.45(6) | 0.40(8) | 1.7(7) | 0.5(6) | 1.5(3) |
| O | $4f(1/3\ 2/3\ z)$ | <i>occ.</i> | 1.0 | 1.0 | 1.0 | 1.0 | 0.94(3) |
| | | z | 0.09041(9) | 0.0906(1) | 0.0904(1) | 0.0896(2) | 0.0899(2) |
| | | $B (\text{Å}^2)$ | 0.46(3) | 0.36(3) | 0.50(4) | 0.41(6) | 0.82(7) |
| Lattice parameters | $a (\text{Å})$ | | 2.8288(1) | 2.8273(1) | 2.8257(2) | 2.8276(4) | 2.8510(6) |
| | $c (\text{Å})$ | | 10.8922(3) | 10.9421(3) | 11.0220(6) | 11.181(1) | 11.183(2) |
| Na content | x | | 0.70(1) | 0.68(2) | 0.59(2) | 0.48(2) | 0.48(3) |
| R -factors | R_{wp} (%) | | 5.07 | 5.43 | 6.44 | 4.00 | 3.34 |
| | R_I (%) | | 1.58 | 1.93 | 2.77 | 3.73 | 4.56 |
| Goodness of fit | S | | 1.40 | 1.34 | 1.68 | 1.53 | 1.36 |

*) x parameters for Na1 and Na2 were constrained through a relation of $x(\text{Na1})=x(\text{Na2}) - 2/3$.

**) B factors for Na1 and Na2 were constrained to be equal.

analysis, we assumed that Na1 and Na2 ions occupy $6h$ ($x\ 2x\ 1/4$) sites with $x \approx 0.05$ and $x \approx 0.72$, respectively. Refined structure parameters, final R -factors and Goodness of fits are given in Table I. The sodium content of $\text{Na}_{0.70}\text{CoO}_2$ is in good agreement with the nominal one. In $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$, however, the sodium content continuously changes from 0.70 at $y=0$ to 0.48 at $y=0.5$. Oxygen deficiency was noticed for only the sample with $y=0.7$.

Figure 2 shows crystal structure of $\text{Na}_{0.70}\text{CoO}_2$ and the schematic representation of possible sites in the Na layers at $z=1/4$ and $3/4$. Calculated M–O distances and M–O–M angles are plotted in Fig.3, where M represents Co or Mn at $2a(0\ 0\ 0)$ site. The M–O distance gradually increases with increasing y ($0 \leq y \leq 0.5$) and then jumps from 1.915(1) Å at $y=0.5$ to 1.928(1) Å at $y=0.7$. The M–O–M angles are significantly larger than 90° in the whole range of y , corresponding to a rhombohedral distortion

of the MO_6 octahedra. The minimum M–O–M angle, $95.15(6)^\circ$, was found at $y=0.5$.

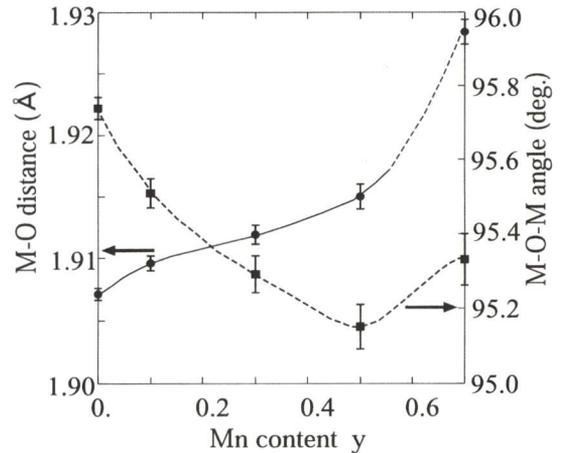


Fig.3. M–O distance and M–O–M angle vs. Mn content y . M represents Co or Mn at $2a(0\ 0\ 0)$ site.

The magnetic susceptibilities observed above 50 K were fitted to Curie-Weiss law by the least-squares calculation. Adjusted parameters, Curie constant C , Weiss temperature Θ and χ_0 , are summarized in Table II. Figure 4 shows the observed χ - T curve and the best fit (solid line) of $\text{Na}_{0.70}\text{CoO}_2$. Figure 5 shows the magnetization

Table II. Adjusted parameters to Curie-Weiss law.

| parameter | $y=0.0$ | 0.1 | 0.3 | 0.5 | 0.7 |
|--------------------------------------|-----------|----------|---------|----------|----------|
| $\chi_0 (10^{-3} \text{emu/moleOe})$ | 0.454(3) | 1.03(7) | 0.52(8) | 0.450(9) | 3.66(6) |
| $C (\text{emuK/moleOe})$ | 0.0590(8) | 0.304(6) | 0.84(3) | 0.791(3) | 0.325(9) |
| $\Theta (\text{K})$ | -40.7(9) | -4.1(2) | -4(2) | -46.2(3) | -19.4(7) |

(M) as a function of magnetic field (H) at 4.2 K. Only the sample with $y=0.3$ exhibits non-linear field dependence and small hysteresis in the M - H curve.

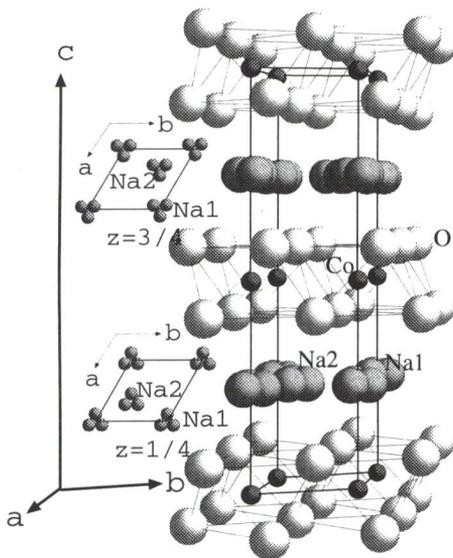


Fig.2. Crystal structure of $\text{Na}_{0.70}\text{CoO}_2$.

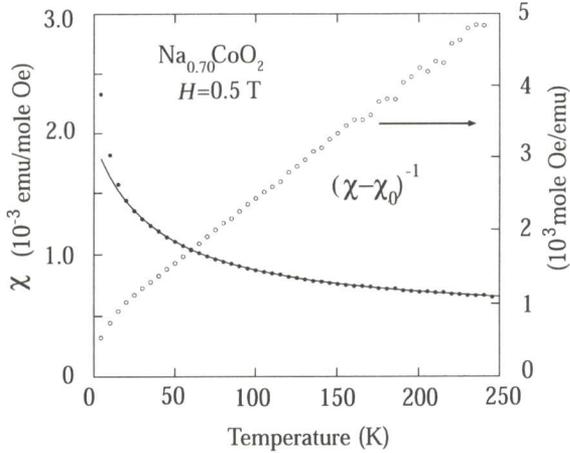


Fig. 4. Temperature variation of magnetic susceptibility (filled circles) for $\text{Na}_{0.70}\text{CoO}_2$. A solid line is the best fit to the Curie - Weiss law. Open circles represent the inverse plot of $\chi - \chi_0$, where χ_0 is temperature-independent term in Curie -Weiss law.

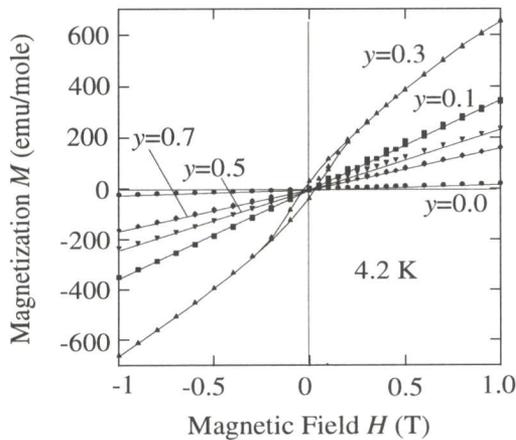


Fig. 5. M - H curves at 4.2 K.

§4. Discussion

Disordered Na1 and Na2 ions are coordinated by six oxygen atoms forming a trigonal prism.^{5,6)} In spite of large ionic radius of Na^+ (1.02 Å) for six-coordination,¹⁰⁾ the Na1 site is only 1.24–1.97 Å distant from the Na2 site in $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$. The sodium ions are too large to occupy the adjacent Na1 and Na2 sites simultaneously. Hence, the sodium vacancies, *i.e.*, the point-defects, are generated to stabilize the two-dimensional layered structure. The amount of the point-defects at the Na1 site is larger than that at the Na2 site. Low thermal conductivity observed in $\text{Na}_{0.5}\text{CoO}_2$ ²⁾ possibly originates from not only the sodium disorder but also the point-defects.

The formal valence v at the $2a$ site was evaluated from the charge neutrality condition in the chemical formula $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$, where the valences of the sodium and the oxygen atoms were assumed to be +1 and -2, respectively (Table III). In $\text{Na}_{0.70}\text{CoO}_2$, the magnitude of v can be interpreted in terms of the coexistence of Co^{3+} and Co^{4+} ,⁸⁾ *i.e.*, $\text{Na}_{0.70}[\text{Co}^{3+}]_{0.70}[\text{Co}^{4+}]_{0.30}\text{O}_2$. If both cobalt ions are in the low spin state, only the Co^{4+}

spin ($S=1/2$) is responsible to the magnetic susceptibility. From the Curie constant (Table II), the effective magnetic moment of the Co^{4+} becomes $\mu_{exp} = 1.25 \mu_B$, which is smaller than $\mu_{eff} = 1.73 \mu_B$ expected from localized $S=1/2$ spin ($\mu_{eff} = 2\sqrt{S(S+1)}\mu_B$). Probably,

Table III. Average formal valence v at $2a$ site and effective magnetic moments.

| | $y=0.0$ | 0.1 | 0.3 | 0.5 | 0.7 |
|--------------------|---------|------|------|------|------|
| v | 3.30 | 3.32 | 3.39 | 3.50 | 3.51 |
| $\mu_{exp}(\mu_B)$ | 1.25 | 2.41 | 3.11 | 2.52 | 1.61 |
| $\mu_{eff}(\mu_B)$ | 1.73 | 2.49 | 3.10 | 3.32 | 3.95 |

this discrepancy is ascribed to partially delocalized d electrons showing the metallic conduction.¹⁾ For the Mn-substituted samples, it was assumed that $\text{Mn}^{3+}(S=2)$ ions preferentially substitute for the non-magnetic Co^{3+} ions. In this case, the population ratio at the $2a$ site is given by $\text{Co}^{3+}:\text{Mn}^{3+}:\text{Co}^{4+} = 4-v-y : y : v-3$, but $\text{Mn}^{3+}:\text{Co}^{4+} = 0.7:0.3$ for the sample with $y=0.7$. We calculated μ_{exp} and μ_{eff} as the average value per one magnetic ion based on this population ratio (Table III). There is a good agreement between μ_{exp} and μ_{eff} at $y=0.1$ and 0.3, but large discrepancy was found at $y=0.5$ and 0.7.

The sample with $y=0.3$ is in the weak ferromagnetic ordered state at 4.2 K. Spontaneous magnetization was determined to be about 126 emu/mole by linearly extrapolating $M(H)$ into $H=0$. This value is considerably small relative to that estimated from the localized spins in this sample.

Further study by means of neutron scattering is underway for full understandings of the magnetic properties in $\text{Na}_x(\text{Co}_{1-y}\text{Mn}_y)\text{O}_{2-\delta}$.

Acknowledgements

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