

## The Effect of Oxygen Vacancy on the Magnetic Properties in the System $\text{SrCoO}_{3-\delta}$ ( $0 < \delta < 0.5$ )

H. TAGUCHI,\* M. SHIMADA, AND M. KOIZUMI

*The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan*

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The cubic perovskite  $\text{SrCoO}_{3-\delta}$  ( $0.05 \leq \delta \leq 0.26$ ) was prepared under high oxygen pressures of 50–2600 bars, and its crystallographic and magnetic properties were examined. From the results, it was found that oxygen deficiency strongly influences the unit-cell parameters and the Curie temperatures. The unit-cell parameter  $a_0 = 3.836 \text{ \AA}$  and the Curie temperature  $222^\circ\text{K}$  for  $\text{SrCoO}_3$  were determined.

### Introduction

Cobalt ion is normally in a divalent or trivalent state for oxides such as  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ . A higher valence state of cobalt ion, however, exists in oxides with perovskite-type structure such as  $2\text{H-BaCoO}_3$  (1) with hexagonal symmetry and cubic  $\text{SrCoO}_3$  (2). In the cubic perovskite-type oxide  $A^{2+}B^{4+}\text{O}_3$  ( $A =$  alkaline earth metal,  $B =$  transition metal), the  $B^{4+}$  ion is at the octahedral site and each octahedron shares corners.

Much interest has been paid to the nonstoichiometric perovskite oxide ( $\text{ABO}_{3-\delta}$ ), because both  $B^{4+}$  and  $B^{3+}$  ions coexist at the octahedral site of the oxide. Anion-deficient nonstoichiometry has often been reported on  $\text{SrFeO}_{3-\delta}$  (3),  $\text{SrMnO}_{3-\delta}$  (4), and  $\text{SrCoO}_{3-\delta}$  (5).  $\text{SrFeO}_3$  is metallic and antiferromagnetic below  $130^\circ\text{K}$ , but its cell constant and electrical resistivity increase and the Néel temperature falls with decreasing oxygen deficiency. Mössbauer spectra of  $\text{SrFeO}_{3-\delta}$  were measured by

Gallagher *et al.* (6) in various temperature regions. The isomer shift indicates an electron charge density at the nucleus much smaller than that predicted by theoretical calculation assuming a purely ionic model. Watanabe *et al.* synthesized  $\text{SrCoO}_{3-\delta}$  having various crystal structure types such as brownmillerite, orthoferrite, tetragonal, and perovskite under oxygen pressures up to 200 bars. According to their report,  $\text{SrCoO}_3$  exhibits ferromagnetism below  $200^\circ\text{K}$  and metallic conductivity in the temperature range 77 to  $250^\circ\text{K}$ . The results of magnetic measurement indicated that the electron configuration of  $\text{Co}^{4+}$  ions of  $\text{SrCoO}_3$  was a low-spin state  $(d\epsilon)^5(d\gamma)^0$ , and  $\text{Co}^{3+}$  ions were assumed to be a low-spin state  $(d\epsilon)^6(d\gamma)^0$  (7). With increasing oxygen deficiency, it is expected that the Curie temperature will have a value lower than that of  $\text{SrCoO}_3$  due to the increase in the number of  $\text{Co}^{4+}\text{-O-Co}^{3+}$  interactions due to the increase of  $\text{Co}^{3+}$  ions in cubic  $\text{SrCoO}_{3-\delta}$ .

In the  $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$  system, both  $\text{Co}^{4+}$  and  $\text{Co}^{3+}$  coexist at the octahedral site in cubic perovskite structure (8). With increasing  $\text{Sr}^{2+}$  ion content,  $\text{Co}^{4+}$  ion content and

\* Present address: Osaka Prefectural Industrial Research Institute, Osaka 550, Japan.

the number of  $\text{Co}^{4+}\text{-O-Co}^{3+}$  interactions increase. Raccach and Goodenough (9) reported that magnetic properties change from antiferromagnetism to ferromagnetism and also that electric properties change from semiconductivity to metallic conductivity with increasing  $\text{Sr}^{2+}$  ion content.

In the present study, cubic  $\text{SrCoO}_{3-\delta}$  was synthesized under high oxygen pressures and temperatures so that the effect of the oxygen deficiency on the lattice constant and magnetic properties could be examined. These results will provide some information on the electron configurations of  $\text{Co}^{4+}$  and  $\text{Co}^{3+}$  located at the octahedral site and on the magnetic interactions of  $\text{Co}^{4+}\text{-O-Co}^{4+}$ ,  $\text{Co}^{4+}\text{-O-Co}^{3+}$ , and  $\text{Co}^{3+}\text{-O-Co}^{3+}$ .

### Experimental

The starting materials were prepared by mixing reagent-grade powders of  $\text{SrCO}_3$  and  $\text{CoCO}_3$ . The mixture was calcined in air at  $800^\circ\text{C}$ , then ground and fired at  $1000^\circ\text{C}$  in a pure oxygen gas stream for 24 hr. The oxygen-deficient materials obtained in this way were annealed under high oxygen pressures of 50–2600 bars at  $250\text{--}400^\circ\text{C}$  for 24–72 hr (10).

The products were identified by X-ray diffraction with filtered  $\text{CoK}\alpha$  radiation. Cell

constants were calculated from high-angle reflections using Si as a standard material.

The oxygen content in each sample of  $\text{SrCoO}_{3-\delta}$  was determined by chemical analysis. The total amount of cobalt ( $\text{Co}^{4+}$  and  $\text{Co}^{3+}$ ) was determined as follows: The sample was dissolved in hydrochloric acid and  $\alpha$ -nitroso- $\beta$ -naphthol was added to this solution. The precipitate was filtered off and burnt in a crucible at  $650\text{--}750^\circ\text{C}$ . The cobalt content was weighed as  $\text{Co}_3\text{O}_4$ . The ratio  $\text{Co}^{3+}/\text{Co}^{4+}$  was determined by the oxidation-reduction (redox) method. After KI solution and hydrochloric acid were added to dissolve the sample in a flask, the solution was titrated with a standard sodium thio-sulfate solution (1).

Magnetic properties were measured using an automatic recording magnetic balance in the temperature range 77 to  $350^\circ\text{K}$ .

### Results and Discussion

X-Ray powder diffraction patterns of all samples annealed under high oxygen pressures were completely indexed as cubic perovskite structures. Table I shows the values of  $\delta$  in  $\text{SrCoO}_{3-\delta}$  prepared under different annealing conditions. The relation between lattice constants and  $\text{Co}^{4+}$  concentration is shown in Fig. 1. As seen in Fig. 1, the lattice constants decrease linearly with

TABLE I  
THE VALUE OF  $\delta$  IN  $\text{SrCoO}_{3-\delta}$

Specimen number	Annealing Conditions					$\delta$
	Temp. ( $^\circ\text{C}$ )	Oxygen pressure (bar)	Time (hr)	$\text{Co}^{4+}/\text{Co}$ (%)		
1	350	50	24	49	0.26	
2	250	80	72	53	0.24	
3	350	200	72	61	0.20	
4	350	500	72	62	0.19	
5	300	500	72	70	0.15	
6	400	2600	72	80	0.10	
7	300	1000	72	84	0.08	
8	300	2000	72	90	0.05	

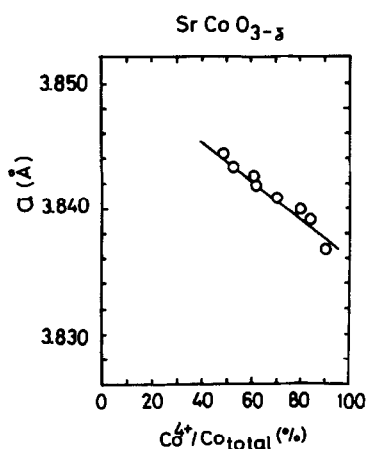


FIG. 1. Cell parameter vs Co<sup>4+</sup> concentration in the system SrCoO<sub>3-δ</sub>.

increasing Co<sup>4+</sup> concentration. It is expected that the decrease of the *a*-axis is caused by the difference in ionic radius between Co<sup>3+</sup> and Co<sup>4+</sup> ions at the octahedral site. From the extrapolation of the present results, it was determined that the lattice constant of SrCoO<sub>3</sub> without oxygen deficiency was  $a = 3.836 \text{ \AA}$ , as shown in Fig. 1. In the cubic perovskite SrCoO<sub>3</sub>, the ionic radius of the Co<sup>4+</sup> ion was calculated using the simple equation  $r_{\text{Co}^{4+}} = \frac{1}{2}(a_0 - 2r_{\text{O}^{2-}})$ , where  $r_{\text{O}^{2-}} = 1.40 \text{ \AA}$ . By putting the values of  $a_0 = 3.836 \text{ \AA}$  and  $r_{\text{O}^{2-}} = 1.40 \text{ \AA}$  into the above equation,  $r_{\text{Co}^{4+}}$  at the octahedral site was determined to be  $0.518 \text{ \AA}$ . Assigning the average ionic radius of the trivalent cobalt ion at the octahedral site to be  $0.61 \text{ \AA}$  for the high-spin state and  $0.525 \text{ \AA}$  for the low-spin state as reported by Shannon and Prewitt (11), the tendency of the lattice constant to decrease for SrCoO<sub>3-δ</sub> was well understood to be due to decreasing oxygen deficiency. For the ionic radius of the tetravalent cobalt ion, the present authors determined  $0.476 \text{ \AA}$  from the results of single-crystal X-ray analysis for 2H-BaCoO<sub>3</sub> with hexagonal symmetry (12). The crystal structure of BaCoO<sub>3</sub> was described in terms of the hexagonal close-packed BaO<sub>3</sub> layer and Co ions located in the oxygen octahedra. Within

the BaO<sub>3</sub> layer, the O-O distance between the layers is  $2.783 \text{ \AA}$ , the O-O distance within the layer is much shorter, and these three oxygens forming a short O-O distance make a triangular plane sharing the face of the CoO<sub>6</sub> octahedra columns. The Co<sup>4+</sup> ions in the columns face each other at a very short distance of  $2.38 \text{ \AA}$ . This will produce a large electrostatic repulsion between the metal ions. As the oxygen atoms of face-sharing triangles mutually approach, the O ions are caused to screen the coulomb interaction between Co<sup>4+</sup> ions and weaken the repulsion.

The Goldschmidt tolerance factor (*t*) is  $t = 1.046$  in SrCoO<sub>3</sub> and  $t = 1.13$  in BaCoO<sub>3</sub>. For all the compounds with the ideal cubic perovskite-type structure, the value of *t* lies between approximately 0.9 and 1.0, but for higher or lower values of *t* the hexagonal perovskite-type structure is found. This fact suggests that the cubic phase, rather than the hexagonal phase, is stable for SrCoO<sub>3</sub>.

In the system SrCoO<sub>3-δ</sub>, it is known that SrCoO<sub>3</sub> is a ferromagnet with a Curie temperature of  $200^\circ\text{K}$ , and SrCoO<sub>2.5</sub> whose structure is brownmillerite is an antiferromagnet with a Néel temperature of  $570^\circ\text{K}$ . All specimens of SrCoO<sub>3-δ</sub> under the present investigation exhibited ferromagnetism below  $215^\circ\text{K}$ , and their Curie temperatures ( $T_c$ ) are shown as a function of Co<sup>4+</sup> concentration in Fig. 2.  $T_c$  increases linearly with increasing Co<sup>4+</sup> content. By extrapolation from the present results,  $T_c$  of SrCoO<sub>3</sub> was estimated to be about  $222^\circ\text{K}$ .

From the values of saturation magnetization, the magnetic moment  $\bar{n}$  at  $0^\circ\text{K}$  was calculated. The results are shown as a function of the Co<sup>4+</sup> concentration in Fig. 3. As shown in this figure, the cobalt ion is in a low-spin state with  $(d\varepsilon)^5(d\gamma)^0$ .  $\bar{n}$  increases with increasing Co<sup>4+</sup> content and the value of  $\bar{n}$  for SrCoO<sub>3</sub> is estimated by extrapolation to be 1.60, which is relatively larger than expected.

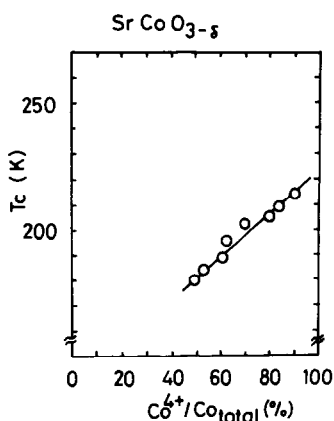


FIG. 2. Curie temperature as a function of  $Co^{4+}$  concentration in the system  $SrCoO_{3-\delta}$ .

The temperature dependence of the paramagnetic susceptibility of samples under investigation was examined in the paramagnetic temperature range, and the relation of  $1/\chi$  vs temperature was linear. The effective magnetic moment was calculated from the linear portion of this curve according to the usual relation  $\mu_{eff} = 2.82[\chi_m \cdot (T - \theta)]^{1/2}$ , where  $\mu_{eff}$  is the moment per molecule in Bohr magnetons,  $\chi_m$  is the molar susceptibility,  $T$  is the temperature in degrees Kelvin and  $\theta$  is the paramagnetic Curie temperature. The variations of  $\theta$  and  $\mu_{eff}$  are shown in Figs. 4 and 5 as a function of the  $Co^{4+}$  concentration. In Fig. 5, open circles indicate the observed values and a broken

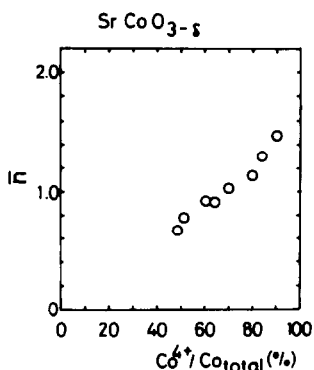


FIG. 3. Magnetic momenta as a function of  $Co^{4+}$  concentration in the system  $SrCoO_{3-\delta}$ .

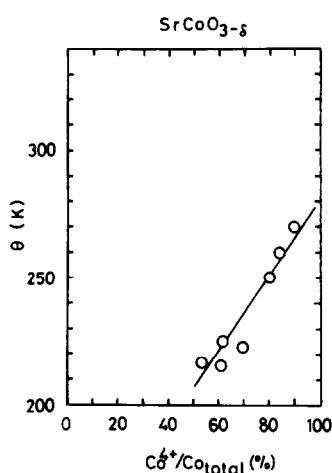


FIG. 4. Paramagnetic Curie temperature as a function of  $Co^{4+}$  concentration in the system  $SrCoO_{3-\delta}$ .

line is drawn for the theoretical values calculated under the following assumptions of the spin state of  $Co^{4+}$  and  $Co^{3+}$  ions: one is the high-spin state of  $Co^{3+}$  with  $(d\epsilon)^4(d\gamma)^2$  and the low-spin state of  $Co^{4+}$  with  $(d\epsilon)^5(d\gamma)^0$ , and the other is the low-spin state of  $Co^{3+}$  with  $(d\epsilon)^6(d\gamma)^0$  and the low-spin state of  $Co^{4+}$  with  $(d\epsilon)^5(d\gamma)^0$ . As seen in Fig. 5,  $\mu_{eff}$  for  $SrCoO_3$  at  $Co^{4+}/Co_{(total)} = 100\%$  is extrapolated to be approximately  $\mu_{eff} = 3$ .

Goodenough (13) has pointed out that the  $\bar{n} = 1.5$  in metallic  $Sr_{0.5}La_{0.5}CoO_3$  can be rationalized with an intermediate-spin model having localized  $t_2^5$  configurations on each cobalt and an itinerant  $\sigma^*$  band containing 0.5 electron per Co ion

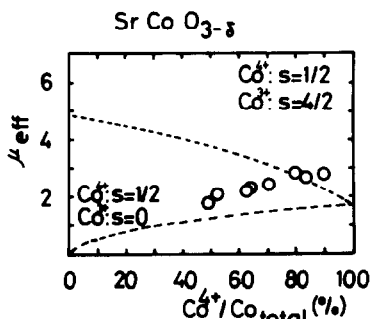


FIG. 5. Effective magnetic Bohr magneton as a function of  $Co^{4+}$  concentration in the system  $SrCoO_{3-\delta}$ .

magnetized ferromagnetically. The model could account for the observed  $\bar{n}$  in metallic SrCoO<sub>3</sub> if the itinerant  $\sigma^*$  band overlaps the localized  $t_2^5$  level (or strongly correlated  $\pi^{*5}$  band). For  $g=2.0$  and  $\bar{n}=1.6$ , the intermediate-spin configuration would be  $\pi^{*4.7}\sigma^{*0.3}$ . Moreover, increasing  $\delta$  would add electrons to the  $\pi^*$  band more rapidly than to the broader  $\sigma^*$  band, so  $\bar{n}$  should decrease with increasing  $\delta$ , as shown in Fig. 3. It should reach a minimum value of about 1.3 if the overlapping bands retain their relative positions. If the  $\sigma^*$  band shifts upward relative to the  $\pi^*$  band with increasing  $\delta$ , the minimum  $\bar{n}$  would correspond to the low-spin value  $\bar{n}_{\min} = (1 - 2\delta)$ . At  $\text{Co}^{4+}/\text{Co}_{\text{total}} = 0.5$ , the minimum would be  $\bar{n}_{\min} = 0.5$ , just a little smaller than observed. The paramagnetic data can also be accounted for with the model.

The itinerant-electron model given above would also account for the change in  $T_c$  and  $\theta$  with  $\delta$ . For ferromagnetic materials, Curie temperature,  $T_c$ , and paramagnetic Curie temperature,  $\theta$ , are expressed as  $T_c \approx \theta = 2zJs(s+1)/3k$ . With increasing  $\delta$  in SrCoO<sub>3-δ</sub>, the values of effective magnetic spins ( $S$ ) of cobalt ions decrease, and  $T_c$  and  $\theta$  decrease with increasing  $\delta$  as shown in Figs. 2 and 4.

Finally, the oxygen deficiency plays an important role in controlling the properties of SrCoO<sub>3</sub>; the decrease of lattice parameter

and the increase of  $T_c$ ,  $\theta$ ,  $\sigma$ , and  $\mu_{\text{eff}}$  with increasing  $\text{Co}^{4+}$  concentration support the idea that  $\text{Co}^{4+}$  ions are in a low-spin state.

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