

Magnetic Interactions in Ternary Cobalt Oxides with Cubic Perovskite Structure

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Magnetic properties were measured on the cubic perovskite systems $\text{SrCoO}_{3-\delta}$, $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0.5 \leq x \leq 1.0$), and $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$). It is found that Sr^{2+} and La^{3+} ions strongly affect the spin state of the Co^{3+} ion and that the Mn^{4+} ion located at the octahedral site affects the spin state of Co^{4+} ion. The magnetic properties (T_c , T_θ , and σ) are explained by the magnetic interaction $\text{Co}^{3+}-\text{O}-\text{Co}^{3+}$, $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Co}^{4+}$, $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$, and $\text{Mn}^{4+}-\text{O}-\text{Co}^{4+}$ in these systems.

Introduction

In the oxides containing the tetravalent state of the first-row transition metal ions, Me^{4+}O_2 (Me : Ti, V, Cr, and Mn), oxides with rutile structure are well known and their physical properties are also systematically examined in detail. In the oxides containing Fe, Co, and Ni ions, however, these ions are normally in the di- or trivalent state. But a tetravalent state of Fe, Co, and Ni ions exists only in the oxides with perovskite structure in CaFeO_3 (1), SrFeO_3 (2), BaCoO_3 (3), SrCoO_3 (4), and BaNiO_3 (5), whose chemical formulas are generally presented as $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ (A : alkaline earth metal, B : transition metal). In the cubic perovskite-type oxides, the B^{4+} ion is at the octahedral site, each octahedron shares corners, and the angle $\text{B}-\text{O}-\text{B}$ is 180° .

SrCoO_3 has the cubic perovskite struc-

ture and exhibits ferromagnetism below 200K, the electron configuration of Co^{4+} ion is the low-spin state with $(d\epsilon)^5(d\gamma)^0$ (4). We have synthesized nonstoichiometric cubic perovskite $\text{SrCoO}_{3-\delta}$ under high oxygen pressures of 5-260 MPa, and its crystallographic and magnetic properties have been examined (6). These results indicate that the oxygen deficiency in $\text{SrCoO}_{3-\delta}$ strongly influences the cell constant and the magnetic properties.

In the system $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$, Co^{4+} and Co^{3+} ions coexist at the octahedral sites in the cubic perovskite structure (7). The Co^{4+} ion content increases with increasing Sr^{2+} ion content. Raccach and Goodenough have reported that the magnetic properties of $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0 \leq x \leq 0.5$) change from antiferromagnetic to ferromagnetic with increasing Sr^{2+} ion content (8). We have synthesized the cubic $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ without oxygen deficiency in the range of $0.5 \leq x \leq 1.0$ under high oxygen pressures (9). From the magnetic measurement, it was found that all samples showed ferro-

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magnetism, the Co^{4+} ion was in the low-spin state with $(d\epsilon)^5(d\gamma)^0$, and the Co^{3+} ion was in the high-spin state with $(d\epsilon)^4(d\gamma)^2$.

SrMnO_3 has a cubic perovskite structure with $a = 0.3808$ nm (10) and is an antiferromagnet with Néel temperature at 260K (11). From a neutron diffraction study, SrMnO_3 was determined to show a G-type antiferromagnetic ordering. The magnetic moment of Mn^{4+} ion is $2.6 \pm 0.2 \mu_B$ at 77K. A solid solution of $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ was prepared under high oxygen pressures to study the effect of the replacement of the Mn^{4+} ion with Co^{4+} ion on the magnetic properties (12).

In the present study, an attempt is made to provide some information on the magnetic interaction of $\text{Co}^{3+}-\text{O}-\text{Co}^{3+}$, $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Mn}^{4+}$, and $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ in the systems $\text{SrCoO}_{3-\delta}$, $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$, and $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$.

Experimental

A. Preparation

$\text{SrCoO}_{3-\delta}$. The starting materials were prepared by mixing reagent-grade powders of SrCoO_3 and CoCO_3 . The mixture was calcined in air at 800°C , then ground and fired at 1000°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 5–260 MPa at 250– 400°C for 24–72 hr.

$(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0.5 \leq x \leq 1.0$). The starting materials were prepared by mixing reagent-grade powders of La_2O_3 , SrCoO_3 , and CoCO_3 . The mixture was calcined in air at 800°C , then ground and fired at 1000– 1300°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 140 MPa at 300°C for 72 hr.

$\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$). The starting materials were prepared by mixing reagent-grade powders of SrCO_3 , CoCO_3 ,

and MnCO_3 . The mixture was calcined in air at 800°C , then ground and fired at 1000– 1350°C in a pure oxygen stream for 24 hr. The oxygen-deficient materials obtained in this way were annealed under high oxygen pressures of 140 MPa at 300°C for 72 hr.

B. Chemical Analysis

The oxygen content in $\text{SrCoO}_{3-\delta}$ and the Co^{4+} ion content in $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ were determined by chemical analysis (3). The total amount of cobalt (Co^{3+} and Co^{4+} ions) was determined as follows: A sample was dissolved in hydrochloric acid and α -nitroso- β -naphthol was added to this solution. The precipitate was filtered off and burnt in a crucible at 650 – 750°C . The cobalt content was weighed as Co_3O_4 . The ratio $\text{Co}^{3+}/\text{Co}^{4+}$ was determined by a 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 thiosulfate solution.

C. X-Ray Diffraction

The samples were identified by X-ray powder diffraction with filtered $\text{CuK}\alpha$ and $\text{CoK}\alpha$ radiations. The cell constants of the samples were calculated from high-angle reflections using Si as a standard material.

D. Magnetic Properties

Magnetic properties were measured using an automatic recording balance in the temperature range from 77 to 350K in a field of 8 kOe. The temperature was measured with an AuCo–Cu thermocouple.

According to a Jonker's report (13), the signs and magnitudes of the exchange interactions of $\text{Co}^{3+}-\text{O}-\text{Co}^{3+}$, $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Mn}^{4+}$, and $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ in the systems $\text{SrCoO}_{3-\delta}$, $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0.5 \leq x \leq 1.0$) and $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$) were determined. In the system $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$, for example, the interaction energies in term of T_θ were expressed as follows: θ_a for $\text{Co}^{3+}-$

O–Co³⁺, θ_b for Co³⁺–O–Co⁴⁺ and θ_c for Co⁴⁺–O–Co⁴⁺. The fraction of the Co³⁺ and Co⁴⁺ ions were $1 - x$ and x , respectively. The fractions of neighboring pairs were then $(1 - x)^2$ for Co³⁺–O–Co³⁺, $2x(1 - x)$ for Co³⁺–O–Co⁴⁺ and x^2 for Co⁴⁺–O–Co⁴⁺. If θ_a , θ_b , and θ_c were considered as constants in the system, the compositional dependence of T_θ were calculated using the following equation:

$$T_\theta = (1 - x)^2\theta_a + 2x(1 - x)\theta_b + x^2\theta_c$$

By putting the value of T_θ into each x , the signs and magnitudes of the exchange interactions of Co³⁺–O–Co³⁺, Co⁴⁺–O–Co³⁺ and Co⁴⁺–O–Co⁴⁺ were calculated.

Results and Discussion

In the system SrCoO_{3- δ} , the Co⁴⁺ and Co³⁺ ions are in the low-spin state with $(d\epsilon)^5(dy)^0$ and $(d\epsilon)^6(dy)^0$, respectively, and the Co³⁺ ion has no magnetic moment (6). The magnetic interactions of Co³⁺–O–Co³⁺ and Co³⁺–O–Co⁴⁺ are absent, and that of Co⁴⁺–O–Co⁴⁺ is ferromagnetic. With increasing oxygen deficiency, the Co⁴⁺ ion content decreases and the magnetic interac-

tion of Co⁴⁺–O–Co⁴⁺ is weak. The signs of the magnetic interactions of Co³⁺–O–Co³⁺, Co³⁺–O–Co⁴⁺, and Co⁴⁺–O–Co⁴⁺ in SrCoO_{3- δ} are listed in Table I.

In the system (La_{1- x} Sr _{x})CoO₃, the Co⁴⁺ ion is in the low-spin state with $(d\epsilon)^5(dy)^0$ and the Co³⁺ ion is in the high-spin state with $(d\epsilon)^4(dy)^2$ (9). Since the Co³⁺ ion has a magnetic moment, the magnetic interactions of Co³⁺–O–Co³⁺, Co³⁺–O–Co⁴⁺, and Co⁴⁺–O–Co⁴⁺ occurs in this system. T_θ of (La_{1- x} Sr _{x})CoO₃ with cubic structure forms a parabolic curve for $0.5 \leq x \leq 1.0$. By putting the value of T_θ into each x into an equation, the best-fitting results are calculated as listed in Table I. Since the magnetic interaction of Co³⁺–O–Co⁴⁺ is the strongest, T_θ and T_c increase with decreasing x from 1.0 to 0.7, and has maximum values ($T_\theta = 310\text{K}$ and $T_c = 280\text{K}$) at around $x = 0.7$. However, as the content of the La³⁺ ion increases, the magnetic interaction of Co³⁺–O–Co³⁺ begins to play an important role in the total magnetic interaction, and T_θ and T_c decrease monotonically.

In the system Sr(Co_{1- x} Mn _{x})O₃, it is considered that the spin state of the Co⁴⁺ ion changes from low to high at around $x = 0.3$

TABLE I
MAGNETIC INTERACTION OF Co³⁺, Co⁴⁺, AND Mn⁴⁺ IONS

	Magnetic interaction		Spin state of Co ³⁺	Spin state of Co ⁴⁺	Magnetic properties
SrCoO _{3-δ}	Co ³⁺ –O–Co ³⁺	none	low	low	ferro
	Co ³⁺ –O–Co ⁴⁺	none	$(d\epsilon)^6(dy)^0$	$(d\epsilon)^5(dy)^0$	
	Co ⁴⁺ –O–Co ⁴⁺	ferro			
(La _{1-x} Sr _{x})CoO ₃	Co ³⁺ –O–Co ³⁺	~–200K	high	low	ferro
	Co ³⁺ –O–Co ⁴⁺	~440K	$(d\epsilon)^4(dy)^2$	$(d\epsilon)^5(dy)^0$	
	Co ⁴⁺ –O–Co ⁴⁺	~280K			
Sr(Co _{1-x} Mn _{x})O ₃ (0 $\leq x \leq$ 0.3)	Co ⁴⁺ –O–Co ⁴⁺	~280K		low	ferro
	Co ⁴⁺ –O–Mn ⁴⁺	~–146K		$(d\epsilon)^5(dy)^0$	
	Mn ⁴⁺ –O–Mn ⁴⁺	~–750K			
0.3 < $x \leq$ 1.0	Co ⁴⁺ –O–Co ⁴⁺	~–1080K		high	antiferro
	Co ⁴⁺ –O–Mn ⁴⁺	~420K		$(d\epsilon)^5(dy)^2$	
	Mn ⁴⁺ –O–Mn ⁴⁺	~–750K			

(12). Since the change of the spin state in the Co^{4+} ion strongly influences the cell constant and the magnetic properties, $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ changes from ferromagnet to antiferromagnet at around $x = 0.3$. The magnetic interactions of $\text{Co}^{4+}\text{-O-Co}^{4+}$, $\text{Co}^{4+}\text{-O-Mn}^{4+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ are calculated by the same method as made in the system $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$. The variation of T_θ is shown in Fig. 1. In the range $0 \leq x \leq 0.3$, T_θ decreases parabolically with increasing x . The magnetic interactions are calculated from the observed T_θ , and are listed in Table I. The magnetic interaction of $\text{Co}^{4+}\text{-O-Co}^{4+}$ is ferromagnetic and the others are antiferromagnetic. The decrease in σ_0 also suggests that the magnetic moment of the Mn^{4+} ion aligns in the direction antiparallel to that of the Co^{4+} ion. In the case where x is larger, the magnetic interactions of $\text{Co}^{4+}\text{-O-Mn}^{4+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ play an important role in the total magnetic interaction, T_θ , T_c , and σ_0 decrease with increasing x .

In the range 0.3–1.0, T_θ is negative and parabolic. The magnetic interactions of $\text{Co}^{4+}\text{-O-Co}^{4+}$, $\text{Co}^{4+}\text{-O-Mn}^{4+}$, and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ are also listed in Table I. The magnetic interaction of $\text{Co}^{4+}\text{-O-Co}^{4+}$ changes from ferromagnetic (280K) to strongly antiferromagnetic (–1080K), according to the change of the spin state of Co^{4+} ion, and that of $\text{Co}^{4+}\text{-O-Mn}^{4+}$ changes from antiferromagnetic (146K) to

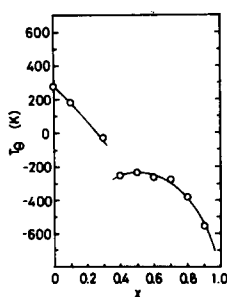


FIG. 1. Paramagnetic Curie temperature vs x in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$.

ferromagnetic (420K). Since the magnetic interactions of $\text{Co}^{4+}\text{-O-Co}^{4+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ are larger than that of $\text{Co}^{4+}\text{-O-Mn}^{4+}$, $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ is antiferromagnetic in the range of $0.3 \leq x \leq 1.0$.

Goodenough reported the 180K supermagnetic interaction of Me-O-Me (Me : the transition metal) in various oxides (14). The magnetic interaction of $3d^5\text{-O-}3d^5$, for example, $\text{Fe}^{3+}(\text{high})\text{-O-Fe}^{3+}(\text{high})$, is strongly antiferromagnetic. This is in agreement with the results of $\text{Co}^{4+}(\text{high})\text{-O-Co}^{4+}(\text{high})$ in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$. In the oxides containing Fe^{3+} ions, since the spin state of Fe^{3+} ions at the octahedral site is usually high, we did not examine the magnetic interaction between low-spin state $\text{Fe}^{3+}(3d^5)$ in perovskite and spinel oxides (14). From the results of $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$, it is assumed that the magnetic interaction of $\text{Fe}^{3+}(\text{low})\text{-O-Fe}^{3+}(\text{low})$ would be ferromagnetic.

In the system $\text{SrCoO}_{3-\delta}$, both Co^{4+} and Co^{3+} ions are in the low-spin state. In the system $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$, the Co^{4+} ion is the low-spin state and the Co^{3+} ion is the high-spin state. And, in the system $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$, the spin state of the Co^{4+} ion changes from low to high at around $x = 0.3$. The difference of the spin states of the Co^{3+} ion in the systems $\text{SrCoO}_{3-\delta}$ and $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ suggests that the A cations (Sr^{2+} and La^{3+}) play a significant role in determining the electron configuration of the other cations located at the octahedral sites. Considering the ionic radii of La^{3+} of 0.132 nm and that of Sr^{2+} ion of 0.144 nm (15), it is expected that the bonding between $\text{La}^{3+}\text{-O}^{2-}$ is stronger than that between $\text{Sr}^{2+}\text{-O}^{2-}$. An increasing La^{3+} ion content in $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$, causes the electron cloud of $2P\pi$ in oxygen to be attracted to the La^{3+} ion, and therefore the Co^{3+} ion with the high-spin state would be stabilized in the octahedral site.

It is considered that the change of the spin state of the Co^{4+} ion in the system

$\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ is caused by the replacement of Mn^{4+} ions, whose polarization power is larger than that of the Co^{4+} ion (16). In the range of $0.3 \leq x \leq 1.0$, the oxygen located at the chain of $\text{Co}^{4+}-\text{O}-\text{Mn}^{4+}$ deviates from the center, i.e., larger CoO_6 octahedra and small MnO_6 octahedra, which are connected to each other via the oxygens of the apex of the octahedra, are distributed statistically (17).

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