JOURNAL OF SOLID STATE CHEMISTRY 105, 550–560 (1993)

Studies of Nonstoichiometry and Magnetic Properties of the Perovskite $Gd_{1-x}Sr_xCoO_{3-y}$ System

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Received June 22, 1992; in revised form January 12, 1993; accepted January 14, 1993

A series of samples in the $Gd_{1-x}Sr_xCoO_{3-y}$ ($x = 0.00, 0.25, 0.50, 0.75$, and 1.00) system with perovskite-type oxide have been prepared at 1200°C under an atmosphere with and without oxygen gas flow. X-ray diffraction analysis of the solid solution assigns the structure of the compositions of $x = 0.00$, 0.25, and 1.00 to the orthorhombic system, $x = 0.50$ to the cubic system, and $x = 0.75$ to the tetragonal system. The reduced lattice volume of the system is increased as the x value gets higher. The amount of Co^{4+} ion or the mixed valence state between Co^{3+} and Co^{4+} ions is quantitatively analyzed by the iodometric titration method. The mole ratio of the Co^{4+} ion, the τ value, is maximized at the composition of $x = 0.50$ and the y value, the oxygen deficiency, increases as the x value increases. Nonstoichiometric chemical formulas are obtained with the x, τ, and y values. The electrical conductivity of the $GdCoO_{3.00}$ sharply increases within the experimental temperature range; therefore, the activation energy of this compound is higher than those of the other compositions. The electrical conductivity measurement of the composition ($x = 0.50$) indicates a metallic property. The compounds of the compositions ($x = 0.00 \sim 0.75$) show a paramagnetic property. The magnetic measurement shows that the paramagnetic Curie temperature (θ_p) is a positive value in the case of $x = 0.50$ with the maximum amount of the Co^{4+} ion. The μ_{eff-Co} is decreased as the τ value gets higher. The $SrCoO_{2.52}$ has the Néel temperature of 550 K.

Introduction

In perovskite-type ABO_3 compounds, the higher valence state of the transition metal is generally stabilized with larger A-site ion (*1–6*). Therefore, the perovskite-type compounds have extensively been studied because of their unique and interesting properties.

Raccah and Goodenough (*7*) and Bhide *et al.*(*8*) have investigated a $LaCoO_3$ system in which cobalt ions predominently exist in the low spin state Co^{3+} ($t_{2g}^6e_g^0$) at low temperature. According to these studies, the equilibrium between the low and high spin states can be changed with temperature because of the small energy difference between the states ($\simeq$0.08 eV). They have also suggested that the $LaCoO_3$ undergoes a first-order transition at 1210 K and then becomes metallic. Their interpretation of the transition mechanism involves the σ^* band broadening which makes the t_{2g} level lie within the σ^* band in the metallic phase.

Thornton *et al.* (*9*), however, have suggested that the $LnCoO_3$ (Ln: La, Nd, Gd, Ho, and Y) system should show broad and high-order semiconductor-to-metal transitions over the temperature ranges of La: 385–570 K and Gd: 490–770 K. These transitions involve $t_{2g}^6e_g^0 \rightarrow t_{2g}^4e_g^2$ excitation and delocalization of e_g orbitals to form a collective σ^* band.

The $SrCoO_{2.5}$ has brownmillerite or hexagonally deficient perovskite structure depending on annealing temperature and oxygen pressure during the sample preparation (*10–12*). The high temperature phase of

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$SrCoO_{2.5}$ is a brown millerite-type, orthorhombic structure, and has the Néel temperature of 550 K (*10*).

The magnetic properties of the cobaltite with perovskite structure are dependent upon the spin states of Co^{3+} and Co^{4+} whether they are the low spin state or the high spin state. They also depend on the indirect exchange interaction between cobalt ions through an intermediate oxygen ion (*13*, *14*). Due to this interaction, the Co^{3+}–O^{2-}–Co^{4+} and the Co^{3+}–O^{2-}–Co^{3+} systems show a ferromagnetic and antiferromagnetic property, respectively (*5*, *15*, *16*).

The Co^{4+} ion is formed in $La_{1-x}Sr_xCoO_3$ in accordance with the x value ($0.00 \leq x \leq 0.60$) and induces ferromagnetic interaction with the Co^{3+} ion (*6*). The Co^{4+} ion is delocalized over all the cobalt ions. The $La_{1-x}Sr_xCoO_3$ system becomes ferromagnetic when $x > 0.15$ due to an increased amount of the itinerant Co^{4+} ions. The itinerent electron has a ferromagnetic property. The compounds of compositions ($x > 0.15$) become metallic and their paramagnetic Curie temperatures are positive.

The transition metals with mixed valence states, which are produced due to the divalent cation substituted for the trivalent cation on the *A*-site of the perovskite, have been investigated by us and several other research groups previously (*1–6*). In the transition metal oxides, it is possible to study their properties in terms of the mixed valence states. In this present study, the $Gd_{1-x}Sr_xCoO_{3-y}$ ($0.00 \leq x \leq 1.00$) system has been prepared and their structures are analyzed by X-ray diffraction and a thermal analysis method. The amount of Co^{4+} ions to the total cobalt ions is determined by an iodometric titration. The nonstoichiometric chemical formula of the $Gd_{1-x}Sr_xCo^{3+}_{1-\tau}Co^{4+}_{\tau}O_{3-y}$ ($y = (x - \tau)/2$) system is determined. The magnetic and other physical properties of this system with the nonstoichiometry are discussed.

Experimental

The solid solutions of the $Gd_{1-x}Sr_xCoO_{3-y}$ system were prepared with the compositions of x = 0.00, 0.25, 0.50, 0.75, and 1.00, and the starting materials for these compositions were Gd_2O_3, $SrCO_3$, and $Co(NO_3)_3 \cdot 6H_2O$. Appropriate amounts of the mixtures were dissolved in dilute nitric acid. The solution was evaporated over a burner flame and then fired at 800°C for 4 hr. After being ground, the samples were heated at 1200°C under an atmosphere for 24 hr. The weighing, grinding, and heating processes were repeated in order to produce a homogeneous solid solution. In order to compare the physical properties of the composition which has the mixed valence state and oxygen vacancy, the composition of $x = 1.00$ was prepared in an atmosphere with and without oxygen. Each powdered sample was shaped into a pellet, then sintered under the same conditions.

The mole ratio of the element of the starting materials was confirmed by energy dispersion X-ray spectroscopy (EDX). By the X-ray diffraction analysis with monochromatized $CuK\alpha$ ($\lambda = 1.5418$ Å) radiation, the lattice parameter, the reduced lattice volume of the unit cell, and the crystal structure of the prepared samples were determined. DTA and TGA were carried out in the range 300 ~ 1000 K. The oxidation states of the cobalt ion were specified by the chemical analysis in which the samples were dissolved in an acidified KI solution and followed by redox titration. The amount of Co^{4+}, the oxygen vacancy, and the nonstoichiometric chemical formulas for the system were also determined.

The electrical conductivity measurements of the samples, using a polycrystalline disk form, have been carried out by the four probe dc technique in the temperature range 78 ~ 1000 K. The electrical conductivities were calculated using Laplume's equation. The magnetic susceptibilities were measured using a Faraday balance from room temperature to 800 K.

Results and Discussion

The mole ratio of each material in the samples was quantitatively confirmed by EDX analysis.

TABLE I

LATTICE PARAMETERS, REDUCED LATTICE VOLUME, AND CRYSTAL SYSTEM FOR THE $Gd_{1-x}Sr_xCoO_{3-y}$ SYSTEM

x	Lattice parameter (Å) (±0.001 Å) a	b	c	Reduced lattice volume (Å^3)	Crystal system
0.00	5.228	5.387	7.463	52.55	Orthorhombic
0.25	5.256	5.413	7.461	53.06	Orthorhombic
0.50	3.805	—	—	55.08	Cubic
0.75	3.849	—	3.846	56.98	Tetragonal
1.00 (Air)	5.463	15.735	5.565	59.80	Orthorhombic
1.00 (O_2)	5.456	15.738	5.568	59.77	Orthorhombic

The X-ray diffraction patterns of the compositions of $x = 0.00$ and 0.25 are indexed on the basis of a distorted perovskite-type structure with orthorhombic symmetry like $GdFeO_3$ (*17*). According to the spectra of the compositions of $x = 0.50$ and 0.75, the symmetries of these compositions are cubic and tetragonal, respectively. In the tetragonal system ($x = 0.75$), the lattice parameter a is slightly larger than c. The composition of $x = 1.00$, $SrCoO_{2.52}$ and $SrCoO_{2.60}$, shows the brownmillerite-type structure which is similar to the $SrCoO_{2.50}$ suggested by Grenier *et al.* (*10, 11, 18*). They suggested that $SrCoO_{2.50}$, the brownmillerite-type structure, contains oxygen vacancies which are ordered along the [101] rows (*18*). The lattice parameters of the crystal system of $SrCoO_{2.52}$ and $SrCoO_{2.60}$ are similar to those of $SrCoO_{2.50}$. We guess that their residue oxygens are randomly distributed.

The lattice parameters, the reduced lattice volume of the unit cell, and the crystal system of the compositions are listed in Table I. According to the previous studies (*1, 2*), the unit cell volume of the ABO_3 system is affected by the factors such as ionic radius of the substituted ion in A-site, the oxygen vacancy, and the mixed valence state of B-site ions. The reduced lattice volume increases with the substitution of Sr^{2+} for Gd^{3+} as shown in Fig. 1. The ionic radius effect of the substituted ions in the system is predominent because the ionic radius of the Sr^{2+} ion (1.58 Å) is larger than that of the Gd^{3+} ion (1.25 Å).

The τ value, y value, and nonstoichiometric chemical formula corresponding to each composition are listed in Table II. The composition of $x = 0.00$, $GdCoO_{3.00}$, is a stoichiometric compound and the others are nonstoichiometric ones. As shown in Fig. 2, the mole ratio of the Co^{4+} ion to total cobalt ions, the τ value, increases as the x value increases within the range of $0.00 \leq x \leq 0.50$ and the τ value is maximized at the composition of $x = 0.50$. However, the τ value decreases as the x value increases for the composition of $x > 0.50$, in which the formation of the oxygen vacancies might be easier than the formation of the Co^{4+} ion. In the case of $x = 1.00$, the compound prepared under an oxygen atmosphere contains larger amounts of the Co^{4+} ion than that prepared under an air atmosphere.

The experimental data of DTA and TGA for the compositions of $x = 0.00 \sim 0.75$ show that there is neither weight loss nor phase transition in the temperature range of $300 \sim 1000$ K. These compositions, therefore, are thermally stable in this temperature range. Since there is no oxygen decomposition, it is considered that the amounts of the oxygen vacancy and the Co^{4+} ion are stationary to 1000 K.

The electrical conductivity measure-

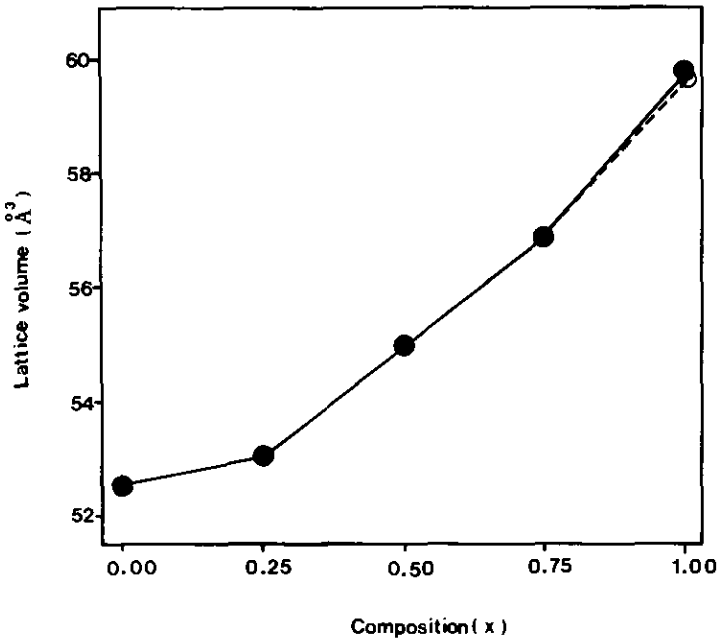

FIG. 1. Plot of reduced lattice volume vs composition (x) for the $Gd_{1-x}Sr_xCoO_{3-y}$ system. (○, the composition of x = 1.00 prepared under the oxygen atmosphere.)

ments have been carried out in the temperature range 78 ~ 1000 K under an atmospheric condition. These conductivity data are shown in Fig. 3. The activation energies of electrical conduction are listed in Table III for all the compositions in the given temperature ranges.

In $GdCoO_{3.00}$, the activation energy for $T < 350$ K corresponds to the excitation from a t_{2g} band to a conduction σ^* band in the trivalent cobalt ion. The short range ordering is established between low and high spins of the trivalent cobalt ions in the temperature range of 360 to 540 K. $GdCoO_{3.00}$ shows high conductivity as well as metallic behavior above 800 K because of overlapping of π^* and σ^* band.

In the $Gd_{1-x}Sr_xCoO_{3-y}$ (x = 0.25, 0.50, 0.75, and 1.00) system, there exists the low spin state of the Co^{4+} ion ($t_{2g}^5 e_g^0$) by replacing the Gd^{3+} ion with the Sr^{2+} ion. The activation energy decreases with the x value in

TABLE II

x, τ, y VALUES, AND NONSTOICHIOMETRIC CHEMICAL FORMULA FOR THE $Gd_{1-x}Sr_xCo^{3+}_{1-\tau}Co^{4+}_{\tau}O_{3-y}$ ($y = (x - \tau)/2$) SYSTEM

x	τ (±0.005)	y	Chemical formula
0.00	0.00	0.00	$Gd_{1.00}Co^{3+}_{1.00}O_{3.00}$
0.25	0.19	0.03	$Gd_{0.75}Sr_{0.25}Co^{3+}_{0.81}Co^{4+}_{0.19}O_{2.97}$
0.50	0.31	0.09	$Gd_{0.50}Sr_{0.50}Co^{3+}_{0.69}Co^{4+}_{0.31}O_{2.91}$
0.75	0.17	0.29	$Gd_{0.25}Sr_{0.75}Co^{3+}_{0.83}Co^{4+}_{0.17}O_{2.71}$
1.00 (in Air)	0.04	0.48	$Sr_{1.00}Co^{3+}_{0.96}Co^{4+}_{0.04}O_{2.52}$
1.00 (in O_2)	0.20	0.40	$Sr_{1.00}Co^{3+}_{0.80}Co^{4+}_{0.20}O_{2.60}$

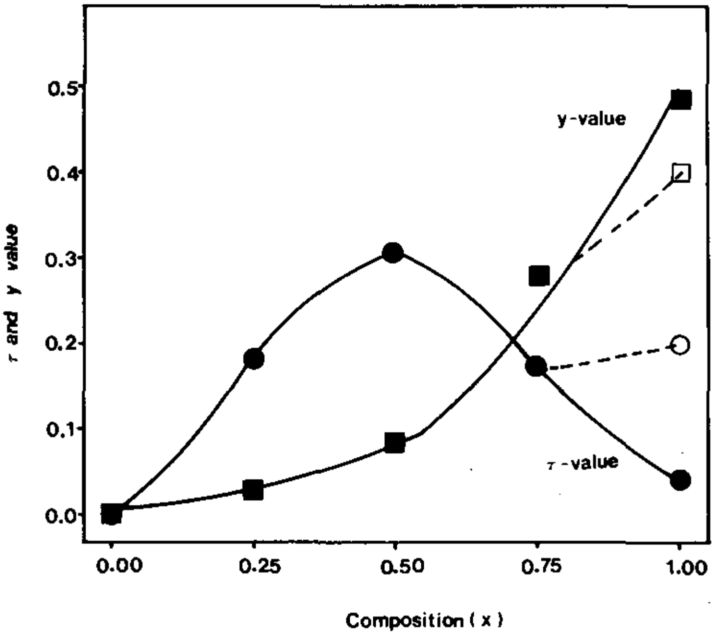

FIG. 2. Plot of the τ and y values vs composition (x) for the $Gd_{1-x}Sr_xCoO_{3-y}$ system. (○ and □, *the composition of* $x = 1.00$ *prepared under the oxygen atmosphere.*)

$x \leq 0.50$ but shows an irregular pattern in $x > 0.50$. The conductivity for the composition of $x = 0.50$ is independent of temperature in the temperature $T < 450$ K, and then decreases as the temperature increases for $T > 450$ K as a metallic behavior. The activation energy depends on the concentration of the Co^{4+} ion which has the $3d$ electron hole in the t_{2g} level. The $3d$ holes are delocalized over all the cobalt ions which is made possible by indirect interaction between the cobalt ions through the intermediate oxygen ions. The delocalization of the $3d$ electron hole induces ferromagnetic interaction to $x = 0.50$ which contains the large amount of the Co^{4+} ion ($\tau = 0.31$).

The activation energy of the $x = 0.75$ composition is considerably larger than that of $x = 0.25$ even though they have similar τ values. The activation energies of the compositions of $x = 0.25$ and $x = 0.75$ are 0.03 and 0.16 eV, respectively. The oxygen vacancies formed by the replacement of the Gd^{3+} ion with the Sr^{2+} ion interrupt the delocalization of the $3d$ holes over all the cobalt ions in the composition $x > 0.50$. The $SrCoO_{2.60}$ sample contains a larger amount of the Co^{4+} ion; however, it has a higher activation energy than that of the $x = 0.25$. Since there are many oxygen vacancies in $SrCoO_{2.60}$, the delocalization of the Co^{4+} ion is interrupted in the same way as the case of $x = 0.75$. Both the activation energy and the resistivity are decreased in proportion to the amount of collective Co^{4+} ions and increased in proportion to the oxygen vacancies.

The reciprocal magnetic susceptibilities as a function of temperature are shown in Figs. 4–6 within the temperature range of 300 ~ 800 K. The compositions of $x = 0.00 \sim 0.75$ show paramagnetism within the temperature range of the magnetic measurement. In contrast with the $LaCoO_3$ (*8*) compound, a plot of $1/\chi_M$ vs T of $GdCoO_{3.00}$ does not indicate any plateau region, but it shows the change of the slope of the susceptibility curve at about 500 K. Also, the compositions of $x = 0.25$ and 0.50 show the change of slope at about the same temperature as

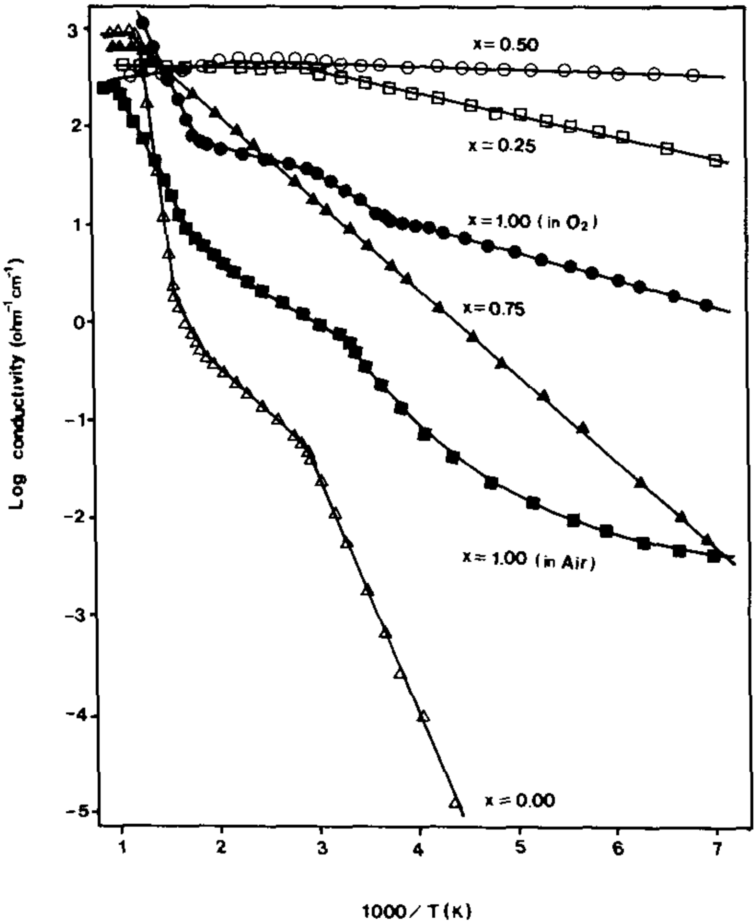

FIG. 3. Plot of log conductivity vs 100/T for the $Gd_{1-x}Sr_xCoO_{3-y}$ system.

the above. However, the composition of $x = 0.75$ does not show any slope change in the plot. The antiferromagnetic behavior of the $SrCoO_{2.52}$ below the Néel temperature of 550 K can be described by the superexchange model (5) in which the antiferromagnetic Co^{3+}–O^{2-}–Co^{3+} interaction is predominent. The $SrCoO_{2.60}$ prepared under an oxygen atmosphere shows an anomaly in $1/\chi_M$ vs T curve below 360 K. This anomaly results from a weak ferromagnetic behavior caused by the canting of the spin. Since $SrCoO_{2.60}$ with a brownmillerite structure contains residue oxygens, excess oxygens distribute randomly in the tetrahedral layer. Such a distribution causes the spin canting of the cobalt-sublattice, which produces a

TABLE III

ACTIVATION ENERGIES OF THE ELECTRICAL CONDUCTIVITY FOR THE $Gd_{1-x}Sr_xCoO_{3-y}$ SYSTEM

x	Temperature range (K)	Activation energy (eV)
0.00	$78 \leq T \leq 360$	0.46 ± 0.01
	$360 \leq T \leq 540$	0.18 ± 0.01
	$540 \leq T \leq 800$	0.76 ± 0.03
0.25	$78 \leq T \leq 350$	0.03 ± 0.002
0.50	$78 \leq T \leq 450$	0.01 ± 0.001
0.75	$78 \leq T \leq 700$	0.16 ± 0.005
1.00 (in O_2)	$78 \leq T \leq 500$	0.05 ± 0.002

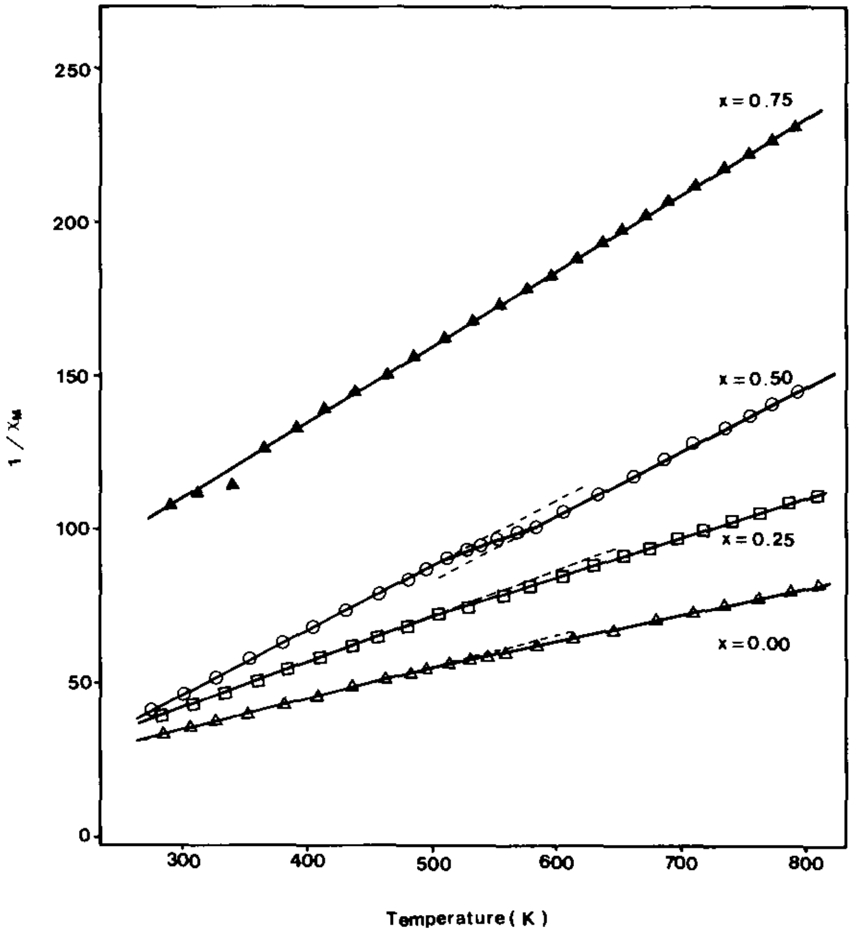

FIG. 4. Plot of $1/\chi_M$ vs temperature for the $Gd_{1-x}Sr_xCoO_{3-y}$ $(0.00 \leq x \leq 0.75)$ system.

weak ferromagnetism in $SrCoO_{2.60}$ and gives rise to small residual magnetization. The perovskite $GdCoO_{3.00}$ contains only the Co^{3+} ion and it has a slightly distorted perovskite-type structure like an orthoferrite. Since the sublattice spin of $GdCoO_{3.00}$ is canted with the hidden one, it does not produce any residual magnetization similar to that of $GdFeO_3$ (*19*) but has only antiferromagnetic interaction.

The Curie constant (C), the paramagnetic Curie temperature (θ_p), and the effective magnetic moment (μ_{eff}) obtained from the $1/\chi_M$ vs T plot for each composition in the temperature ranges are listed in Table IV. The paramagnetic Curie temperature (θ_p) is increased as the τ value increases and is positive only for the composition of x = 0.50 having the maximum τ value. A large amount of the collective Co^{4+} ion causes the ferromagnetic interaction due to delocalization of the 3d hole over all the cobalt ions. The θ_p decreases sharply as the x value increases in $x > 0.50$ due to the interruption of the delocalization of the collective 3d holes. This interruption is caused by the formation of the oxygen vacancies. The Curie constant and the μ_{eff} are decreased as the x value increases.

It can be assumed that for the $Gd_{1-x}Sr_x CoO_{3-y}$ system the exchange interactions between the Gd^{3+} ions ($\mu_{eff} = 7.94\ \mu_B$) and

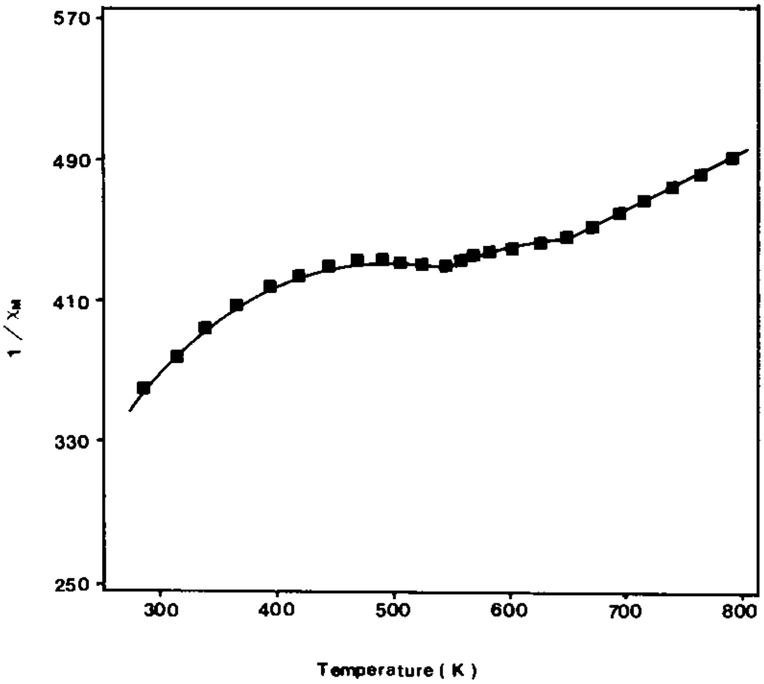

FIG. 5. Plot of $1/\chi_M$ vs temperature for the $SrCoO_{2.52}$.

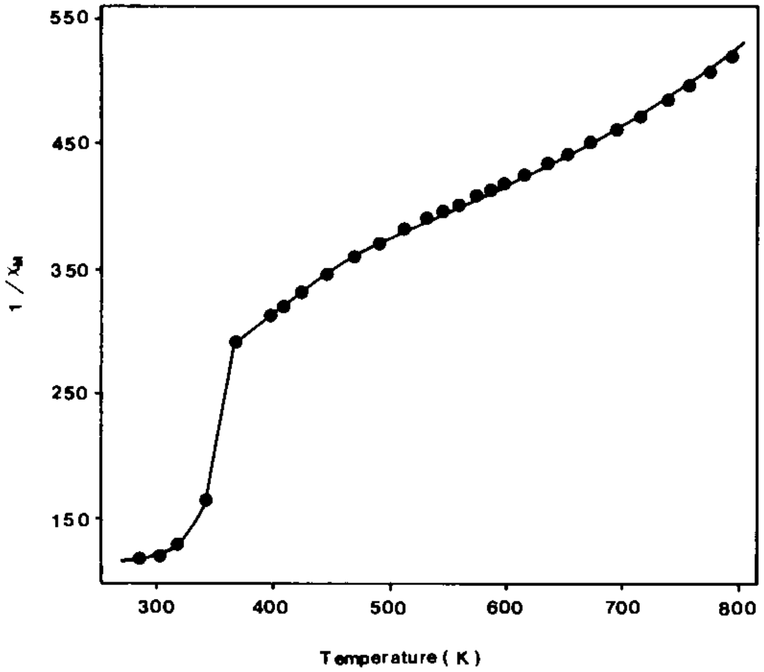

FIG. 6. Plot of $1/\chi_M$ vs temperature for the $SrCoO_{2.60}$.

TABLE IV

MAGNETIC SUSCEPTIBILITY PARAMETERS OF THE $Gd_{1-x}Sr_xCoO_{3-y}$ SYSTEM AS A FUNCTION OF THE x VALUES

x	Temperature range (K)	C ($\pm$0.01)	θ_p	μ_{eff}	μ_{eff} of the Co-ion only; μ_{eff-Co}
0.00	$500 \leq T \leq 800$	10.78	−80	9.29	4.89
	$280 \leq T \leq 500$	9.96	−40	8.92	4.16
0.25	$400 \leq T \leq 800$	7.83	−60	7.91	3.98
	$280 \leq T \leq 400$	6.73	−20	7.34	2.65
0.50	$580 \leq T \leq 800$	4.88	70	6.25	2.81
	$280 \leq T \leq 520$	4.70	110	6.13	2.53
0.75	$280 \leq T \leq 800$	3.95	−120	5.62	4.15
1.00 (in Air)	$680 \leq T \leq 800$	3.16	−759	5.03	5.03
1.00 (in O_2)	$370 \leq T \leq 800$	2.06	−254	3.85	3.85

the cobalt ions do not exist in paramagnetic ranges. From the assumption, we can denote

$$\chi_{TOT} = \chi_{Co} + \chi_{Gd},$$

where χ_{TOT} is total magnetic susceptibility and χ_{Co} and χ_{Gd} are magnetic susceptibilities of the cobalt and the gadolinium ions, respectively. Consequently, the effective magnetic moment of the cobalt ion-only, μ_{eff-Co}, can be calculated as a function of composition. The calculated values are shown in Table IV and Fig. 7.

The μ_{eff-Co} vs composition curve in Fig. 7 shows the opposite trend to the τ value in Fig. 2. The spin angular momentum of the cobalt ion calculated from the μ_{eff-Co} value that the trivalent cobalt ions exist as a mixed state of low and high spins below the transition temperature and mainly as a high spin state above the transition temperature. In the perovskite structure, the Co^{4+} ion within the octahedral site is stable with a low spin state ($t_{2g}^5e_g^0$).

In the case of $GdCoO_{3.00}$, the effective magnetic moment and the spin angular momentum of the cobalt ion are 4.89 μ_B and 2 above 500 K, respectively. From the above result, we believe that the trivalent cobalt ion in $GdCoO_{3.00}$ exists only as a high spin state ($t_{2g}^4e_g^2$) above 500 K.

The electrical properties of $GdCoO_{3.00}$ can be explained with one of the following mechanisms. According to the first model proposed by Raccah and Goodenough (*7*) and Bhide *et al.* (*8, 16, 21*), it is possible that the trivalent cobalt ion undergoes the transition from a low spin state to a high spin state with the increasing temperature. The $LnCoO_3$ (Ln: rare earth metal) systems have low activation energy such as 0.1 eV for the $LaCoO_3$ and 0.2 ~ 0.3 eV for the $GdCoO_3$ in the temperature range of 78 to 200 K due to the low energy gap between the high spin state and low spin state of the Co^{3+} ions at low temperature. Above 200 K, the Co^{4+} and Co^{2+} ions can be produced by electron transfer from the low spin state to the high spin state of the Co^{3+} ion through the intermediate oxygen. The metallic transition is a first order transition in which the localized t_{2g} levels locate within the collective σ^* band at about 1200 K.

The second model proposed by Thornton *et al.* (*9*) is that the semiconducting phase consists of localized $\sigma^*(e_g)$ and $\pi^*(t_{2g})$ orbitals and, in order to get the metallic transition from the semiconducting phase, the $t_{2g}^6e_g^0 \rightarrow t_{2g}^4e_g^2$ excitation should occur, resulting in the change in the spin transition from low spin state and high spin state of the Co^{3+} ions and the delocalization of the e_g orbital to form a collection σ^* band. The gradual increase in the population of the delocalized

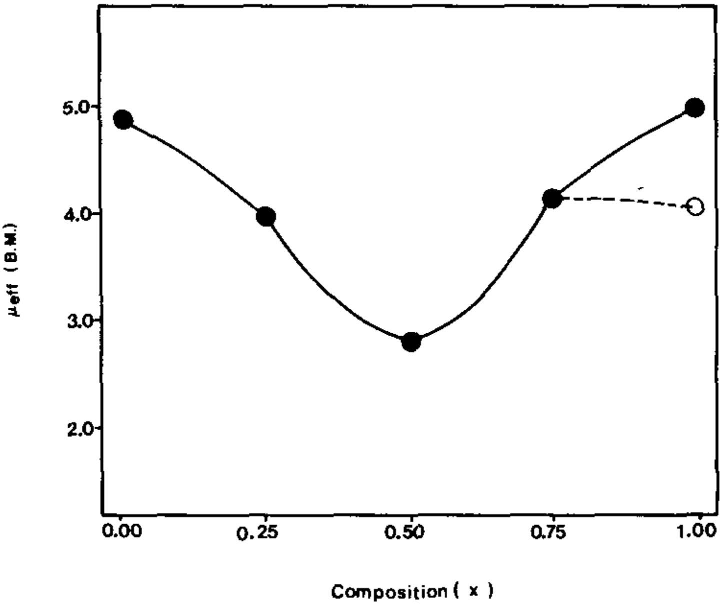

FIG. 7. Plot of the effective magnetic moment (Co-ion only) vs composition (x) for the $Gd_{1-x}Sr_xCoO_{3-y}$ system. (○, the composition of x = 1.00 prepared under the oxygen atmosphere.)

σ^* $3d$ band causes the metallic transition of the $LnCoO_3$ to be a higher order transition at the temperature region of 520 ~ 750 K.

In the present study, it is found that the $GdCoO_{3.00}$ has no Co^{4+} ions. The magnetic measurement shows that the $GdCoO_{3.00}$ predominently involves the high spin state of Co^{3+} ions above 500 K, and the low spin state Co^{3+} ions in this system exist in the low temperature. The transition of the trivalent cobalt ion from the low spin ($t_{2g}^6e_g^0$) to the high spin ($t_{2g}^4e_g^2$) with an increase of the temperature leads to an increase in the population of the e_g electrons and the formation of the σ^* band. The population of the σ^* band causes the σ^* band broadening as well as the band gap narrowing. The metallic transition occurs by overlapping of the π^* and σ^* bands above the short range ordering temperature. The σ^* band is not localized at a particular cobalt ion but delocalized over all the cobalt ions through the intermediated oxygen ions, which results the long range ordering.

Acknowledgments

This work was supported by Grant 89-0306-08 from the Korea Science and Engineering Foundation in 1990 and therefore we express our appreciation to the authorities concerned.

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