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Journal of Solid State Chemistry 178 (2005) 3431–3436

JOURNAL OF SOLID STATE CHEMISTRY

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Magnetic and transport properties of high-pressure synthesized perovskite cobalt oxide $(Sr_{1-x}Ca_x)CoO_3$ $(0\leqslant x\leqslant 0.8)$

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Received 29 March 2005; received in revised form 1 August 2005; accepted 29 August 2005

Abstract

Polycrystalline perovskite cobalt oxides $(Sr_{1-x}Ca_x)CoO_3$ $(0\leqslant x\leqslant 0.8)$ were synthesized under high pressure (6 GPa) and high temperature (1200–1300 °C) conditions. Powder X-ray diffraction data confirmed that they have cubic perovskite structures. The end member of the solid solution, $SrCoO_3$, exhibited a ferromagnetic transition with Curie temperature of $T_c{\sim}266$ K and metallic electric conductivity. With increasing the Ca content x, T_c increased slightly to 286 K at $x = 0.2$ then decreased rapidly to 148 K for $x = 0.8$. The origin of the ferromagnetism is discussed in relation to the spin state of the Co^{4+} ions. The present system showed a relatively large (~5.5%) negative magnetoresistance for $x = 0$ or 0.2 in the vicinity of T_c.

Keywords: Perovskite; $(Sr,Ca)CoO_3$; HP–HT synthesis; Ferromagnetism

1. Introduction

The perovskite cobalt oxide $LaCoO_3$ and its hole-doped divalent substitution have been intrigued by many researchers because of their complex electronic and magnetic properties [1–3]. Their rich physical properties are associated to the proximity of the crystal field splitting and the exchange energy of Co^{3+} in the octahedral coordination, with a small energy difference between low-spin (LS) state (t_{2g}^6, $S = 0$) and high-spin (HS) state ($t_{2g}^4e_g^2$, $S = 2$) or intermediate-spin (IS) state ($t_{2g}^5e_g^1$, $S = 1$). At low temperatures, $LaCoO_3$ is a diamagnetic insulator with the LS state of Co^{3+}. Upon increasing the temperature, its magnetization increases and has a broad maximum around 100 K [4,5]. Above 100 K, it undergoes a spin transformation from the LS state (diamagnetic insulator) to a IS state (paramagnetic insulator) [4,5]. The paramagnetic behavior above 100 K is attributed to the thermal population of the excited IS state [6–11]. But the appearance of the IS state is still controversial and remains to be solved. The spin state and electron configuration of $LaCoO_3$ and its related systems have been subject of various investigations and debates over the past few decades. Our focus here is confined to the synthesis and study of the cubic perovskite cobalt oxide $SrCoO_3$.

$SrCoO_{3-\delta}$ prepared under high oxygen pressure has a perovskite structure [12,13]. A large number of papers have been published for this system [12–20]. Watanabe [12] and Watanabe and Takeda [13] synthesized this compound for the first time under oxygen pressure (up to 20 MPa) and they found that this perovskite exhibited ferromagnetism with Curie temperature (T_c) of ~200 K and metallic resistivity. The oxygen deficient $SrCoO_{3-\delta}$ contains both Co^{4+} and Co^{3+} ions and magnetic measurements suggested that both Co^{4+} and Co^{3+} ions were in the LS states [12,13]. With increasing oxygen deficiency δ, it is expected that the Curie temperature will have a value lower than that of stoichiometric $SrCoO_3$ if we assume the nonmagnetic LS state for Co^{3+}. Indeed, Taguchi et al. [14] synthesized the cubic perovskite $SrCoO_{3-\delta}$ $(0.05\leqslant\delta\leqslant 0.26)$ under high oxygen pressures of 5–260 MPa, and examined its crystallographic and magnetic properties to find systematic decrease of T_c with increasing δ. They suggested that the Co^{4+} ion was essentially in the LS state but some

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0022-4596/$ - see front matter
doi:10.1016/j.jssc.2005.08.019

of the t_{2g} electrons were transferred into the e_g band. Since then, various results have been reported and most of them have supported that the Co^{4+} ion is in the LS state [14–18]. Recently, however, the possibility of the IS state (t_{2g}^4, e_g^1) has been proposed [19,20]. According to Potze et al. [19], the comparison between the experimental Co 2p X-ray absorption spectra and the atomic multiplet theoretical calculations indicated that the ground state of $SrCoO_3$ is the IS state. Zhuang et al. [20] have also theoretically suggested that the ground state of $SrCoO_3$ is the IS state, in agreement with the Co 2p X-ray absorption spectrum.

To the best of our knowledge, there is no report in literature on the substitution of Ca for Sr in the perovskite cobalt oxide $SrCoO_3$. A couple of reports exist on the synthesis of nonstoichiometric compound $CaCoO_{3-\delta}$ ($\delta = 0.48$) [21,22]. However, $CaCoO_{2.52}$ prepared by a drip pyrolysis method at ~1000 °C under ambient pressure was identified as an orthorhombic system with a brown millerite structure [22] rather than perovskite. The substitution of Ca for Sr in the perovskite will work to shrink the Co–O bond length due to its smaller ionic radius and we expect as a result larger crystal field splitting and significant changes in physical properties.

In the present investigation, we have synthesized the perovskite cobalt oxide $(Sr_{1-x}Ca_x)CoO_3$ ($0 \leqslant x \leqslant 0.8$) samples under high pressure (6 GPa) and high temperature (1200–1300 °C) conditions, and studied the substitution effects on the structural, magnetic and transport properties, and the spin states of the Co^{4+} ions. The end member of $SrCoO_3$ undergoes ferromagnetic transition with $T_c \sim 266$ K. The observed Curie temperature (T_c) is much higher than that reported for the nonstoichiometric $SrCoO_{3-\delta}$ compound. A fairly large negative magnetoresistivity was observed for this system.

2. Experimental

The polycrystalline samples of $(Sr_{1-x}Ca_x)CoO_3$ ($0 \leqslant x \leqslant 0.8$) were synthesized by high pressure and high temperature (HP–HT) technique. The required amounts of high purity (>99.9%) fine powders of SrO_2, Co, Co_3O_4, CaO and $KClO_4$ (oxidizing agent) were thoroughly mixed and ground in an agate mortar with pestle in a glove box. $KClO_4$ was needed to adjust the oxygen content to 3 when a sample with $x > 0.33$ was prepared because we used CaO instead of CaO_2 which could not be obtained in pure form. Approximately 0.2–0.3 g of each mixture was sealed in a gold capsule and allowed to react in a flat belt type high pressure apparatus at 6 GPa and heated to 1200–1300 °C for 1–3 h then quenched to room temperature followed by releasing of pressure. For some selected compositions, two different samples were prepared in the same experimental conditions and their properties were compared, to see that the results were essentially reproducible.

The structure and phase purity of the HP–HT synthesized $(Sr_{1-x}Ca_x)CoO_3$ ($0 \leqslant x \leqslant 0.8$) samples were checked by powder X-ray diffraction (XRD) performed on a *Rigaku–Ultima* diffractometer using the Ni-filtered Cu $K\alpha$ radiation at 40 kV and 40 mA. The diffraction patterns were collected at room temperature over the angular range $5^\circ \leqslant 2\theta \leqslant 80^\circ$ with a step size 0.02°. The magnetic properties of the samples were measured using a commercial magnetometer with the superconducting quantum interference device (MPMS-XL, Quantum Design) between 2 and 400 K in magnetic fields up to 70 kOe. The magnetotransport measurements were carried out in a commercial apparatus (PPMS-6600, Quantum Design) between 5 and 320 K in magnetic fields up to 70 kOe.

3. Results and discussions

The XRD patterns of the $(Sr_{1-x}Ca_x)CoO_3$ samples are shown in Fig. 1. The samples with $x \leqslant 0.3$ were found to be single phase and all the reflections were indexed on the basis of cubic perovskite structure. For $0.8 \geqslant x \geqslant 0.4$, main phase was also cubic perovskite and only an impurity was KCl which was formed from $KClO_4$ used as the oxidizer. We tried to synthesize $CaCoO_3$ but the high-pressure product of the mixture with $x = 1.0$ did not contain any perovskite phase. The lattice parameters of the perovskite given in Table 1 show a slight decrease in the values with a progressive increase in x from 0 to 0.8. This is viewed as due to partial substitution of Ca for Sr, since the ionic radius of Ca^{2+} ($r^{XII}_{Ca^{2+}} = 1.34$ Å) is smaller than that of Sr^{2+} ($r^{XII}_{Sr^{2+}} = 1.44$ Å).

Fig. 2 shows the temperature dependence of electrical resistivity, ρ for the $(Sr_{1-x}Ca_x)CoO_3$ system. The pristine compound $SrCoO_3$ and the compound with $x = 0.1$ showed metallic resistivity with a positive temperature dependency. For $0.2 \leqslant x \leqslant 0.4$, semiconducting behavior was seen in the low temperature region while for $x = 0.6$, almost metallic behavior was seen again even under low temperature region. Finally for $x = 0.8$, slight increase of resistivity was observed compared with $x = 0.6$. At present, we do not know what caused these complicated features, but at least three factors seem to be considered: (i) effect of

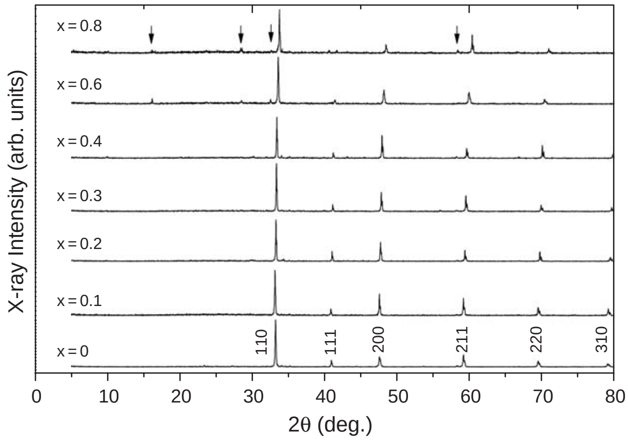

Fig. 1. XRD patterns of the $(Sr_{1-x}Ca_x)CoO_3$ system. The arrow marks indicate peaks due to the impurity KCl.

Table 1
Summary of $(Sr_{1-x}Ca_x)CoO_3$ system: composition (x), lattice parameter (a), Curie temperature (T_c), Curie–Weiss temperature (Θ), effective number of Bohr magnetons (P_{eff}), saturation magnetization (M_s), coercive field (H_c) at 1.8 K, spin (S) and $2S/M_s$ value

x	a (Å)	T_c (±2 K)	Θ (K)	P_{eff} (μ_B/Co)	M_s (μ_B/Co)	H_c (Oe)	S	$2S/M_s$
0	3.8246(7)	266	263.6	3.17	1.78	70	1.16	1.31
0.1	3.8165(4)	283	277.5	3.18	1.97	75	1.17	1.19
0.2	3.8132(5)	286	276.5	3.09	1.84	100	1.12	1.22
0.3	3.8074(2)	270	269.9	3.00	1.54	100	1.08	1.40
0.4	3.8021(6)	247	264.3	2.92	1.48	180	1.04	1.41
0.6	3.7848(3)	218	239.3	2.74	1.23	880	0.96	1.56
0.8	3.7569(8)	148	196.7	2.86	1.08	4800	1.02	1.88

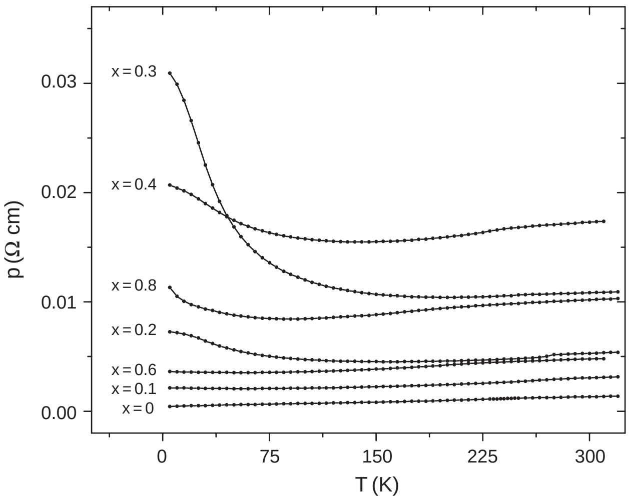

Fig. 2. Temperature dependence of electrical resistivity ρ of the $(Sr_{1-x}Ca_x)CoO_3$ system.

random potential due to the substitution of Ca for Sr which is expected to be the most pronounced at $x\sim0.5$; (ii) changes in the electronic structure and in the Co spin state with replacing Ca for Sr; and (iii) extrinsic effects such as the contamination of KCl which was the most serious for $x = 0.8$. As a whole, the phases were fairly conductive with positive temperature dependencies of resistivity in higher temperature range.

The electric resistivity under magnetic field was measured for $(Sr_{1-x}Ca_x)CoO_3$ with $x = 0.2$ applying the magnetic field of 70 kOe. As shown in Fig. 3(a), there is a kink near ~280 K in the zero magnetic field $\rho-T$ curve. This kink corresponds to the ferromagnetic transition at T_c of 286 K (see below). By applying the magnetic field of 70 kOe, the resistivity decreased and the kink seen at ~280 K disappeared completely. The magnetoresistance was defined as $MR = (\rho_H - \rho_0)/\rho_0$, where ρ_0 and ρ_H stand for the electrical resistivities under zero magnetic field and magnetic field, respectively. MR was negative (negative magnetoresistance) for the entire range of temperature and it had two peaks near T_c and at a low temperature of ~20 K. In particular, the absolute MR around T_c was fairly large with a maximum value of 5.5%. The peak near T_c is explained by the intrinsic mechanism of magnetoresistance [23]; the ferromagnetic order is enhanced by the external magnetic field causing a decrease in the electric resistivity. On the other hand, enhancement of the absolute MR under the low temperature region seems to be explained in terms of tunneling magnetoresistance at grain and/or magnetic domain boundaries where the hopping of spin-polarized electrons is affected by the relative angle between the magnetic moments of the grains (domains) and is controlled by the external field [23]. However, the reason for the downturn of absolute MR below ~20 K has not been clarified yet. Essentially the same behavior was observed for the $x = 0$ sample. Similar magnetoresistance phenomenon has been reported in other Co perovskite $La_{0.5}Ba_{0.5}CoO_3$ [3].

The dc-magnetization (M) measurements were carried out for the $(Sr_{1-x}Ca_x)CoO_3$ samples in the field cooling condition at several applied magnetic fields. As examples,

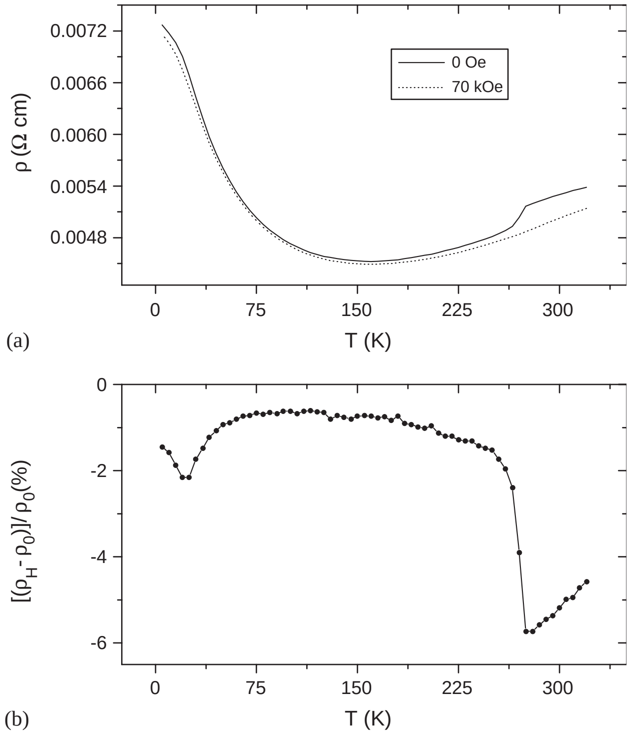

Fig. 3. Temperature dependence of electrical resistivity under and 0 and 70 kOe (a) and magnetoresistance defined as $MR = (\rho_H - \rho_0)/\rho_0$ (b) obtained for $Sr_{0.8}Ca_{0.2}CoO_3$.

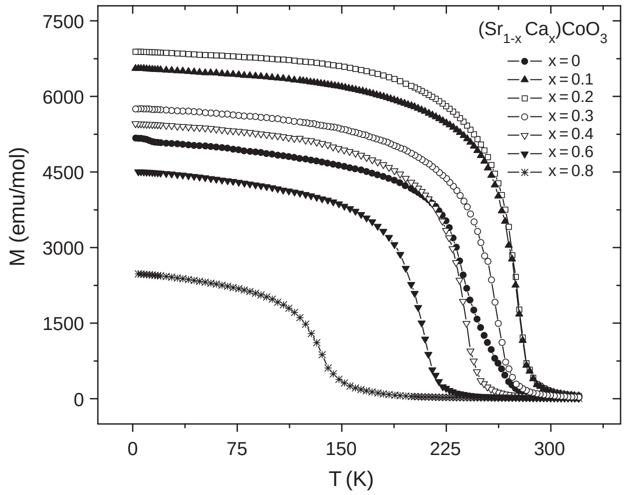

Fig. 4. Temperature dependence of the dc-magnetization M of the $(Sr_{1-x}Ca_x)CoO_3$ system measured at an applied field of 1 kOe by the field cooling mode.

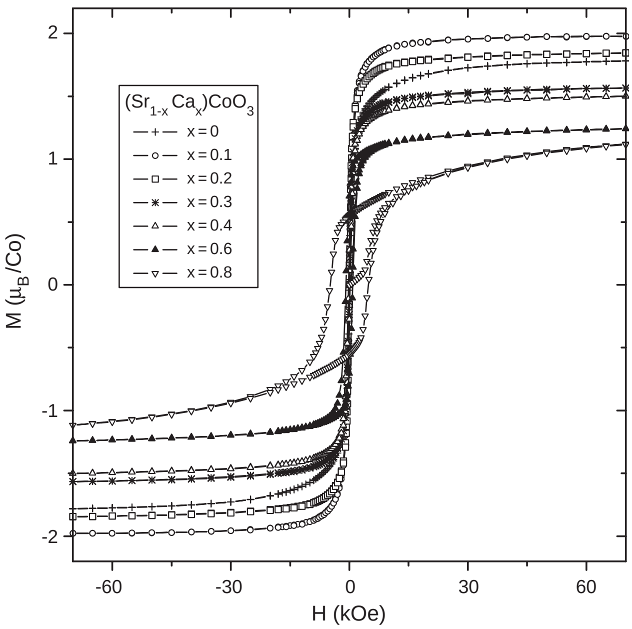

Fig. 5. Magnetic hysteresis loops for the $(Sr_{1-x}Ca_x)CoO_3$ system generated at 1.8 K.

M–T curves measured in the magnetic field of 1 kOe are shown in Fig. 4. The ferromagnetic transition occurred in the temperature range of 286–148 K depending on the Ca content x of the sample (see Table 1). The observed Curie temperature for $SrCoO_3$ is much higher than that reported for the non-stoichiometric $SrCoO_{3-\delta}$ compound (<220 K). On the other hand, the $SrCoO_3$ perovskite prepared by electrochemical oxidization of $Sr_2Co_2O_5$ brownmilleite showed higher T_c (~280 K) [24] than our HP–HT synthesis technique. Taguchi et al. found that the lattice parameter of $SrCoO_{3-\delta}$ increased with δ and they estimated a value for $\delta = 0$ to be 3.836 Å by extrapolation [25]. As shown in Table 1, the lattice parameter of our $SrCoO_3$ (3.824 Å) was even smaller than the value estimated by them implying that δ was minimal. The increase of the Curie temperature was probably caused by the diminishment of the oxygen deficiency.

The isothermal magnetization versus magnetic field (M–H) hysteresis loops were generated at 1.8 K and are given in Fig. 5. The $SrCoO_3$ perovskite showed a very narrow hysteresis loop at 1.8 K with a small coercive field of 70 Oe. The small coercive field of $SrCoO_3$ suggests a small anisotropy energy of magnetization and seems to correspond to its isotropic cubic structure. As shown in Table 1, the coercive field increased with increasing x and the maximum coercive field of ~4.8 kOe was observed for the $x = 0.8$ sample suggesting that it is magnetically more anisotropic than $SrCoO_3$, though it also belongs to the cubic system. Saturation magnetization M_s of the system was obtained from extrapolation of high magnetic field ($H > 4.5$ T) magnetization data to zero field. M_s was 1.78 μ_B/Co atom for $x = 0$ and changed with increasing x synchronizing with T_c, i.e., it first increased slightly for $x = 0.1$ and 0.2 then decreased to 1.08 μ_B/Co atom for $x = 0.8$ (Table 1).

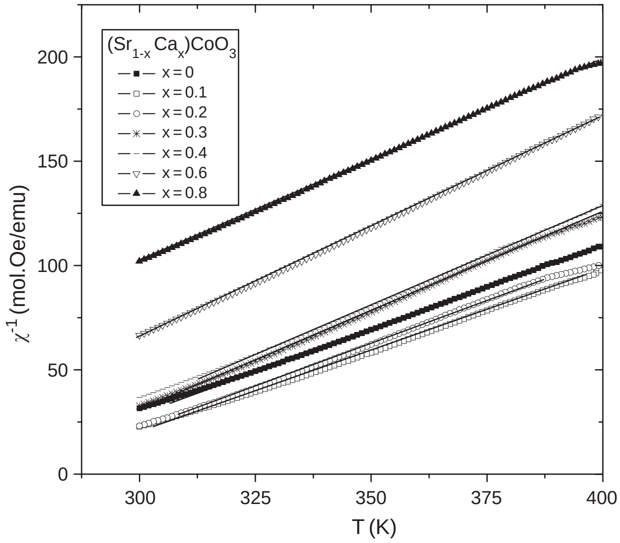

Fig. 6. Temperature dependence of inverse molar magnetic susceptibility for the $(Sr_{1-x}Ca_x)CoO_3$ system. Susceptibilities were measured under an applied magnetic field of 2 kOe in the field-cooling mode. The solid line represents the Curie–Weiss fit.

Magnetic susceptibility χ of the $(Sr_{1-x}Ca_x)CoO_3$ system was measured under a magnetic field of 2 kOe in field-cooled mode for temperature above T_c. The temperature dependence of the inverse magnetic susceptibility is shown in Fig. 6. It is seen that the inverse susceptibility obeys Curie–Weiss law, $\chi^{-1} = C/(T-\Theta)$, where C is Curie constant and Θ is Curie–Weiss temperature. From the Curie constant, effective number of Bohr magnetons P_{eff} was calculated, and then, spin S was estimated according to $P_{\text{eff}} = g\sqrt{S(S+1)}$ assuming that the g-factor was equal to 2 (spin only moment). The Θ, P_{eff}, S thus obtained are listed in Table 1. Based on an ionic model, $S = 1/2, 3/2$

and 5/2 are expected for the LS (t_{2g}^5), IS ($t_{2g}^4e_g^1$) and HS ($t_{2g}^3e_g^2$) state of Co^{4+}. The experimental value is close to $S = 1$ for the entire range of x as shown in Table 1. From this result, we can conclude that electrons are introduced into the e_g orbitals (e_g band) because t_{2g}^5 state (LS state) will give $S = 1/2$ at most even when fully polarized.

The magnetic properties of perovskite cobalt oxide $SrCoO_3$ is under dispute owing to its miscellaneous magnetic properties. Potze et al. took notice of strong hybridization between Co e_g and O 2p states, and showed using atomic multiplet calculations that the IS state can become the ground state due to the relative stability of the ligand hole state of e_g symmetry that it hybridizes with [19]. They excluded the LS state from the comparison of observed and calculated Co 2p X-ray absorption spectra and explained the ferromagnetism of the system by a mechanism that the mobile oxygen holes couple the Co moments ferromagnetically when their spins are conserved during transport. This mechanism is very close to the Zener double exchange model [26] and consistent with a half-metallic electronic structure. Zhuang et al. carried out calculations based on the unrestricted Hartree–Fock approximation of the multiband d–p model Hamiltonian and the real-space recursion method [20]. They concluded that the IS state is the most suitable candidate for the ground state of $SrCoO_3$. Furthermore, they found from features of majority- and minority-spin densities of states that Co t_{2g} electrons tend to be highly localized while the e_g electrons to be quite itinerant with the half-metallic nature. Thus, two independent theoretical studies gave essentially the same picture on the electronic structure of the system.

If we assume the localized t_{2g} electrons and the itinerant e_g electrons with the $t_{2g}^4e_g^1$ configuration and spin depolarization for the itinerant electrons, $S = 1$ is expected. Indeed, S is close to unity when $T > T_c$ for the entire range of x in $(Sr_{1-x}Ca_x)CoO_3$ as shown in Table 1. For the ferromagnetic state of $T < T_c$, on the other hand, if we assume the half-metallic electronic structure based on the IS configuration with the fully polarized e_g electrons, $S = 3/2$, i.e., $M_s = 3\,\mu_B$/Co, is expected. Actually, experimental results indicate that M_s is close to $2\,\mu_B$/Co when x is small decreasing to $\sim 1\,\mu_B$/Co for $x = 0.8$. Thus, the simple half-metallic picture based on the IS configuration does not account well for the ferromagnetism of the present system. In the ferromagnetic region, the e_g electrons may not be fully polarized and/or the LS-like configuration may be mixed with transferring electrons from e_g to t_{2g}. It is notable that M_s decreased to $\sim 1\,\mu_B$/Co for $x = 0.8$ where the lattice constant shrank to 3.76 Å from 3.82 Å in $x = 0$. Such shrinkage of the lattice would increase the crystal field splitting making the t_{2g} state relatively stable. Thus, it seems reasonable to assume that the mixing of the LS-like configuration is more pronounced with increasing the Ca content resulting in the smaller M_s values. X-ray absorption studies are desirable for the Ca-rich phases to see the contribution of the LS configuration.

Other possibility for the ferromagnetism is an itinerant electron ferromagnetism picture. For a simple ionic model, we expect $gS = 2S = M_s$ in Table 1, but this relation is not valid but $2S/M_s$ has a value of 1.2–1.9. An itinerant electron ferromagnet sometimes obeys Curie–Weiss law above T_c and Rhodes–Wohlfarth relationship [27] is often applicable for such a system. According to Rhodes and Wohlfarth [27], the ferromagnets with the Curie–Weiss behavior can be classified into two groups and first group of compounds show $2S/M_s{\sim}1$. In the second group, $2S/M_s$ varies as a universal function of T_c increasing from 1 to ∞ with decreasing T_c. As seen in Table 1, $2S/M_s$ increased with decreasing T_c having the maximum value of $\sim$1.9 at $x = 0.8$. Thus, it may be qualitatively considered that the present system belongs the second group obeying the Rhodes–Wohlfarth relationship. We need further studies, in particular studies using microscopic tools, for the definite conclusion of the origin of the ferromagnetism and the spin state of the present system.

4. Conclusions

The perovskite $(Sr_{1-x}Ca_x)CoO_3$ ($0 \leqslant x \leqslant 0.8$) samples were synthesized by high pressure and high temperature (HP–HT) method. All the samples were characterized by powder X-ray diffraction, and their magnetic and transport properties were measured. The pristine perovskite $SrCoO_3$ exhibited ferromagnetic transition at $T_c{\sim}266$ K and metallic resistivity with a positive temperature dependency. The $(Sr_{1-x}Ca_x)CoO_3$ system showed a relatively large ($\sim$5.5%) negative magnetoresistance for $x = 0$ or 0.2 in the vicinity of T_c. With increasing the Ca content x, T_c increased slightly to 286 K at $x = 0.2$ then decreased rapidly to 148 K for $x = 0.8$. Magnetic susceptibilities above the Curie temperature can be fitted by Curie–Weiss law and effective numbers of Bohr magneton determined from the Curie–Weiss constants indicated that electrons are introduced into the e_g orbitals (e_g band) of the Co^{4+} ions. A half-metallic picture and an itinerant electron picture are discussed regarding origin of the ferromagnetism.

Acknowledgments

One of the authors (SB) is thankful to NIMS for awarding the NIMS-Post doctoral fellowship. We also thank Dr. K. Yamaura and Dr. H. Sakurai for their helpful suggestions. This study was supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (16076209, 16340111).

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