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Magnetotransport Properties of Cobalt Doped Manganites $(Nd_{0.5}Sr_{0.5})_{0.93}(Mn_{1-x}Co_x)O_3$

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The change in electric, magnetic and magnetoresistive properties with the substitution of Mn by Co were investigated on *A*-site ion defected manganite. The manganites except manganite with x=0.0 show spin glass-type magnetism. The x=0.0 manganite shows semiconductor to metal transition at 172 K when reducing temperature. The manganites with x=0.1~0.8 show semiconductive behaviors and those with x=0.9 and 1.0 show metallic behaviors below room temperature. The x=0.0 manganite shows larger negative magnetoresistance at 168 K, which is close to its semiconductor-metal transition temperature. The negative magnetoresistance of the manganite with x=0.1 increases to –79 % at 25 K with reducing temperature. Further Co doping suppresses occurrence of magnetoresistance. The manganite with x=0.8 shows magnetoresistance again and shows an inflection point at 100 K in the magnetoresistance-temperature curve. Hysteresis loops were observed in the magnetic field dependence of magnetoresistance at lower temperature for the manganites containing Co.
Key words: Magnetoresistance, Magnetic impurity, Spin glass, Manganite, Perovskite-type structure

1. INTRODUCTION

Manganites with perovskite-type structure have been studied extensively, because they have larger magnetoresistance and are expected to be applied to novel magnetic devices, such as magnetoresistance head (MR head) and magnetoresistive random access memory (MRAM). The compounds have been studied mainly by control carrier concentration and mobility due to substitution of *A*-site ions in the perovskite structure.

For example, $Nd_{0.5}Sr_{0.5}MnO_3$, of which Nd-sites are substituted by Sr ions, shows magnetic field induced insulator – metal transition and colossal magnetoresistance [1]. Further substitution by Sr ion, $Nd_{0.45}Sr_{0.55}MnO_3$, of which manganese ions have the average valence of 3.55, shows antiferromagnetism with Néel temperature of 225 K [2]. We had been preparing *A*-site deficient perovskite-type manganite $(Nd_{0.5}Sr_{0.5})_{1-z}MnO_3$, and we found that $(Nd_{0.5}Sr_{0.5})_{0.93}MnO_3$, of which manganese ions have the average valence of 3.68, shows ferromagnetism with Curie temperature of 226 K. We are interested in the difference between change in magnetic properties due to ionic substitution and one due to ionic deficiency.

Magnetoresistance was reported for alloy, which is made by dispersing particles of ferromagnetic metal (Co) in non-magnetic metal (Cu) [3,4]. Itinerant electrons are scattered because of correlation between spins of the electrons and magnetic moments of the ferromagnetic metals so that the alloy has high resistivity when magnetic field is not applied. Under external magnetic field, the magnetic moments align one direction and the electrons are not hard to be scattered, subsequently, the electric resistivity decreases and the magnetoresistance occurs. Therefore, we are interested in the effect of doping magnetic impurity as "magnetic seed" to manganese oxide compounds.

We select cobalt ion as a magnetic impurity. In the present study, the manganites with chemical composition of $(Nd_{0.5}Sr_{0.5})_{0.93}(Mn_{1-x}Co_x)O_3$ were prepared and their electric, magnetic, and magnetoresistive properties were investigated.

2. EXPERIMENTALS

The samples were prepared by a conventional ceramic process. Mixtures of Nd_2O_3 (99.9%), $SrCO_3$ (99.9%), Mn_3O_4 (99.9%) and CoO (99.9%) were calcined at 1200 °C in air for 12 h. The calcined powders were ground using a planetary mill (Pulverrisette 5, Fritsch) and ethanol. After drying, the ground powders were pressed into pellets by cold isostatic pressing. The pellets were sintered at 1300 °C - 1500 °C in O_2 for 12 h. The sintering temperature was lowered with increasing nominal Co content.

Chemical compositions of the samples were determined by ICP method. Crystalline phases were identified by means of X-ray diffractometer (RINT2500VHF, Rigaku) equipped with graphite monochrometer. The lattice constants were calculated by a least square method from diffraction angles which were corrected by the angles of Si as an internal standard.

The temperature dependence of magnetization was measured with a vibrating sample magnetometer (BHV-55LHCS, Riken Denshi) below room temperature under magnetic field of 2.5 kOe. The temperature dependence of electric resistivity was measure by dc four-probe method below room temperature under magnetic field of 0 or 15 kOe.

Magnetoresistance is defined as reduction rate of the electric resistivity when magnetic field is applied in this study.

3. RESULTS AND DISCUSSIONS

Chemical compositions determined by ICP method were listed in Table 1. The compositions agree well with the nominal compositions. All samples have no impurity

Table 1 Chemical composition determined by ICP and lattice constants of $(Nd_{0.5}Sr_{0.5})_{0.93}(Mn_{1-x}Co_x)O_3$

x	Chemical composition				Lattice constants		
	Nd	Sr	Mn	Co	a / nm	b / nm	c / nm
0	0.48	0.47	1.00	0.00	0.54307(4)	0.54754(3)	0.76440(5)
0.1	0.46	0.46	0.90	0.10	0.54214(5)	0.54660(4)	0.76300(6)
0.2	0.47	0.47	0.80	0.20	0.54110(3)	0.54561(3)	0.76317(3)
0.3	0.45	0.44	0.70	0.30	0.54041(4)	0.54496(3)	0.76321(5)
0.4	0.49	0.49	0.61	0.39	0.54060(7)	0.54389(5)	0.76325(8)
0.5	0.46	0.45	0.51	0.49	0.53936(6)	0.54366(6)	0.76254(13)
0.6	0.46	0.46	0.41	0.59	0.53884(6)	0.54327(7)	0.76096(11)
0.7	0.47	0.46	0.32	0.68	0.53843(5)	0.54300(3)	0.76105(7)
0.8	0.46	0.45	0.22	0.78	0.53845(5)	0.54254(3)	0.76134(9)
0.9	0.46	0.45	0.10	0.90	0.53773(7)	0.54224(4)	0.76024(10)
1.0	0.47	0.45	0.00	1.00	0.53793(7)	0.54186(6)	0.75996(12)

phases and have orthorhombically distorted perovskite cells from XRD study. No evidence of ordering Mn ions and Co ions was detected so that Co ions substituted randomly Mn ion sites. Lattice constants of the samples are also listed in Table 1. They decrease with increasing x, because radius of Co ion is smaller than one of Mn ion.

The sample with x=0.0 shows semiconductive behavior below room temperature to 172 K and shows metallic one below the temperature. Manganite of $Nd_{0.45}Sr_{0.55}MnO_3$ shows semiconductive behavior below room temperature to 225 K, metallic one below 225 K to 80 K, and semiconductive one below 80 K [5]. The sample with $0.1 \leq x \leq 0.8$ shows semiconductive behavior and the sample with x = 0.9 and 1.0 shows metallic behavior below room temperature. Figure 1 shows logarithmic electric resistivity as function of $T^{-1/4}$. Good linear relations are seen for the sample with $0.1 \leq x \leq 0.7$. The electric resistivity at a fixed temperature increases with increase in x to 0.5 and decreases with increase in x from 0.5. The linear relations indicate variable range hopping conduction in the samples. The variable range hopping is due to random potential, which originates from Co ions located randomly on Mn sites in the present samples. The relation between ln ρ and $T^{-1/4}$ is not linear for the sample with x = 0.8, because Mn ions doped as magnetic impurities in $(Nd_{0.5}Sr_{0.5})_{0.93}CoO_3$ may not make strong random potential.

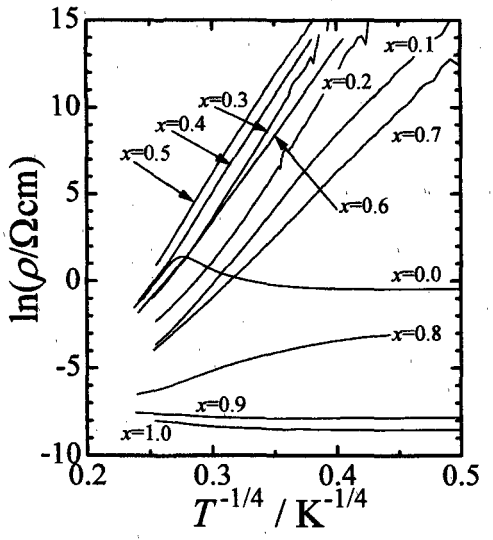

Figure1 Logarithmic electric resistivity as functions of $T^{-1/4}$.

Temperature dependence of magnetic susceptibility (χ) was measured in the temperature range between 300 K and 500 K (not shown here). All samples show no magnetic transition in the range and their temperature dependences are well fitted by Curie-Weiss law, $\chi = C/(T - \theta) + \chi_0$, where C is Curie constant, θ is Curie temperature, and χ_0 is the temperature independent term. These magnetic parameters are summarized in Table 2. The Curie temperature is positive for all samples so that ferromagnetic correlations between magnetic moments exist in the samples. Curie temperature decreases monotonously with increase in x to 0.5 and increases monotonously with further increase in x. Effective Bohr magnetons (p_{cal}) for the samples are estimated from the fraction and the magnetons of magnetic ions (Nd, Mn, and Co ions) and listed with the magnetons (p_{exp}) derived from Curie constants in Table 2. Our best agreement between the experimental values and the calculated ones is obtained with x larger than 0.5 when Co^{3+} ions are assumed to be under the intermediate spin state ($t_{2g}^5 e_g^1$). The discrepancy between the experimental values and the calculated ones with $0 < x < 0.3$ are considered to be due to local clustering of moments of the Mn ions, as found in $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ system [6].

The upper panels of Figure 3 indicate the temperature dependence of magnetization for the samples, which were cooled under magnetic field of 15 kOe (Field Cooling mode) or under no magnetic field (Zero Field Cooling mode) previously. The sample with x=0.0 shows no difference between the magnetizations measured on FC mode and that on ZFC mode. The samples with $0.1 < x < 1.0$ show abrupt increases in magnetization at low temperatures. They seem to be ferromagnets but they show obvious differences between both the magnetizations. The difference in magnetizations is often found in samples under spin glass state. Short-range ferromagnetic correlation between magnetic moments exists and consequently ferromagnetic clusters are formed in the sample under the state. Sample under spin glass state due to zero field cooling is hard to be magnetized and the volume fraction of the magnetic cluster is small when applied external

Table 2 Magnetic parameters of $(Nd_{0.5}Sr_{0.5})_{0.93}(Mn_{1-x}Co_x)O_3$

x	C / emu mol^{-1}K	θ / K	χ_0 / emu mol^{-1}	p_{exp}	p_{cal}*
0	4.48	226	-2.47×10^{-3}	5.99	4.98
0.1	4.69	172	-2.51×10^{-3}	6.12	4.75
0.2	3.90	137	-1.32×10^{-3}	5.59	4.67
0.3	3.51	100	-5.44×10^{-4}	5.30	4.37
0.4	2.63	89.0	7.10×10^{-4}	4.59	4.50
0.5	2.22	65.8	1.14×10^{-3}	4.21	4.14
0.6	1.87	68.4	1.35×10^{-3}	3.87	4.00
0.7	2.06	98.1	8.66×10^{-4}	4.06	3.87
0.8	1.80	149	7.56×10^{-4}	3.79	3.63
0.9	1.45	187	1.30×10^{-3}	3.40	3.45
1.0	1.36	202	7.94×10^{-4}	3.30	3.26

*Calculated on the assumption of cobalt ions under intermediate spin state (see text)

magnetic field. Then, its magnetization is smaller than that of the field cooled sample.

The lower panels of Figure 3 indicate temperature dependence of magnetoresistance. The samples were also cooled on FC (closed circles) or ZFC (open circles). We suggested in the introductory section that ferromagnets dispersed in electric conductive matrix scatter conducting electrons and magnetoresistance occurs. The difference in the volume fraction of ferromagnetic clusters between FC mode and ZFC mode has been referred just above. Therefore, we expected the difference in magnetoresistance between FC mode and ZFC mode. On the contrary of our expectation, no differences in the magnetoresistances are found within experimental error. Conducting electrons during the measurement may promote magnetization and grow size of the ferromagnetic cluster due to the double exchange interaction [7].

The sample with x=0.0 shows maximum negative magnetoresistance of –37% at 168 K, which is very close to the semiconductor – metal transition temperature shown in Figure 1. It is often found in Perovskite-type manganese oxide compounds that he temperature at which the maximum magnetoresistance occurs agrees well with electric or magnetic transition temperature. The magnetoresistance decreases monotonously with reducing temperature for the samples with $0.1 \leq x \leq 0.3$. It is noteworthy that the sample with x=0.3 shows giant magnetoresistance (–79%), which is larger than magnetoresistance of –26% for x=0.0 sample at low temperature of 25 K. However, occurrence of magnetoresistance is tend to be suppressed with increasing x. The samples with $0.4 \leq x \leq 1.0$ except x=0.8 sample show no magnetoresistance within experimental error. The sample with x=0.8 having magnetic transition temperature of 149 K shows negative magnetoresistance of several percent below the temperature.

Figure 4 indicates magnetic field dependences of magnetization and magnetoresistance for selected samples. These properties were measured at 50 K for the samples cooled previously under magnetic field of 15 kOe. The sample with x=0.0 is a soft ferromagnet, because its magnetization is saturated under magnetic field of 15 kOe and its coercive force is very small. The sample with x=0.1 has faintly hysteresis loop, but its magnetization is small and is not saturated. Further increasing x, the magnetization becomes to decrease and

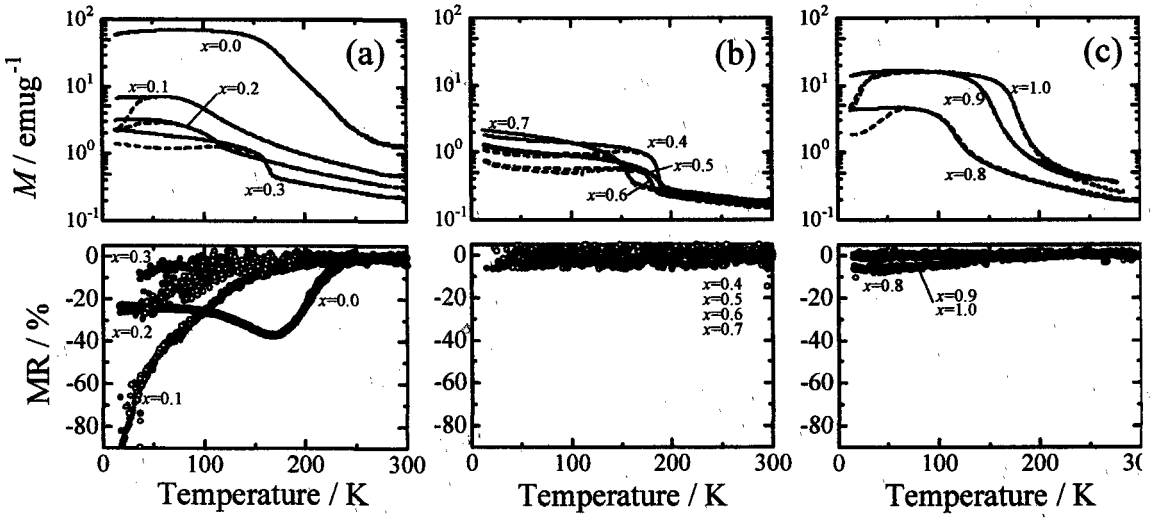

Figure2 Temperature dependence of magnetization (upper panels) and magnetoresistance (lower panels) measured under magnetic field of 15 kOe for the samples with (a) $0.0 \leq x \leq 0.3$, (b) $0.4 \leq x \leq 0.7$, and (c) $0.8 \leq x \leq 1.0$. Solid lines and broken ones in the upper panels, and closed circles and open ones in the lower panels indicate the measurements on field cooling mode and zero field cooling mode.

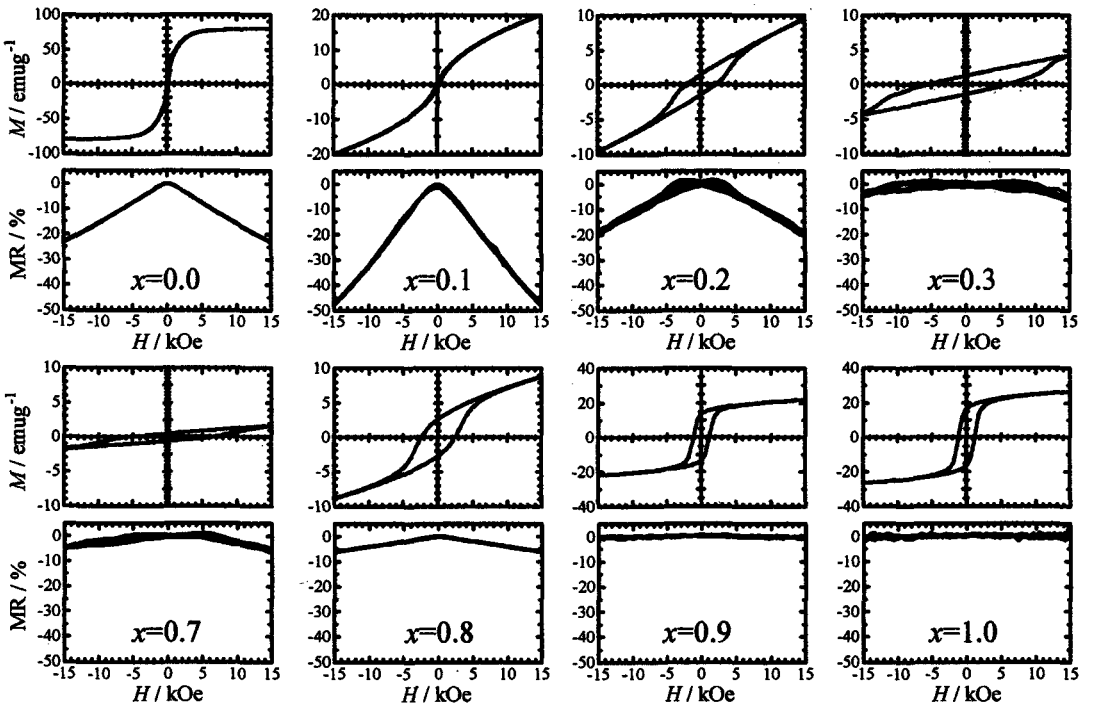

Figure 3 Magnetic field dependences of magnetization (upper panels of each figure) and magnetoresistance (lower panels of each figure) measured at 50 K. The samples were cooled under magnetic field of 15 kOe before the measurements.

the coercive force becomes to increase abruptly. The coercive forces are large and the magnetizations are no saturated for the samples with x=0.9 and 1.0, although the samples are metallic. They are under spin glass state so that their magnetizations are hard to turn around.

The negative magnetoresistance increases monotonously with increasing magnetic field for the samples with x=0.0 and 0.1. The samples with x=0.2, 0.3 and 0.7 show hysteresis loops in the magnetic field dependences of magnetoresistance. The magnetic field under which the magnetoresistance is positive maximum is close to the coercive force. On the other hand, the negative magnetoresistance increases monotonously with increasing magnetic field for the sample with x=0.8, although the sample has hysteresis loop in the magnetization curve.

4. SUMMARY

The manganites with the chemical composition of (Nd0.5Sr0.5)0.93(Mn1-xCox)O3 were prepared and the effects of substitution by Co ions on physical properties were investigated. The substitution tends to suppress magnetoresistance, however, the substitution by 10% of Co ions increases remarkably magnetoresistance at low temperature. Spin glass states occur in the samples containing Co ions, and the evidences of ferromagnetic clusters are found in magnetic properties. Hysteresis loops are found in the magnetic field dependences of magnetoresistance, which reflect unique magnetization of the samples including the clusters. Size or volume fraction of the clusters in the FC samples differ from ones in the ZFC samples, however they do not affect the temperature dependence of magnetoresistance.

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