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Electrical Properties in the System $(La_{1-x}Ca_x)CoO_3$ $(0.1 \leqq x \leqq 0.5)$

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The electrical resistivity of $(La_{1-x}Ca_x)CoO_3$ $(0.1 \leqq x \leqq 0.5)$ was measured in the temperature range from 80 to 300K. Cobaltite with $x \leqq 0.15$ is a semiconductor, but the specimen with chemical composition $0.2 \leqq x \leqq 0.5$ is metallic. The change of temperature dependence of electrical resistivity has a break point around T_c. The value of the logarithm of the specific electrical resistivity ($\log \rho$) at 300K has a minimum at $x = 0.4$, and this result is explained by the Zener double-exchange mechanism.

Introduction

The perovskite-type system $(La_{1-x}Ca_x)CoO_3$ was prepared in the range $0 \leqq x \leqq 0.6$ under high oxygen pressures (*1*). All cobaltites were indexed as having a rhombohedral structure. A rhombohedral distortion decreased with increasing x, and above $x = 0.5$ the samples were indexed as having a cubic perovskite structure. From the results of magnetic measurements, it was found that the cobaltite with $x \geqq 0.05$ was ferromagnetic.

$(La_{1-x}Sr_x)CoO_3$ also was a perovskite-type structure and both Co^{3+} and Co^{4+} ions were located at the octahedral site (*2, 3*). Jonker and Van Santen first showed that $(La_{1-x}Sr_x)CoO_3$ was ferromagnetic in the range $0.15 \leqq x \leqq 0.5$. Although $LaCoO_3$ was a semiconductor, $(La_{1-x}Sr_x)CoO_3$ was metallic in the range $0.3 \leqq x \leqq 0.5$ (*4*). The saturation magnetization (σ) and the paramagnetic Curie temperature (T_θ) were larger than the theoretical values. To account for these results, Raccah and Goodenough proposed the itinerant-electron model (*5*).

In the present study, we measured the electrical resistivity of $(La_{1-x}Ca_x)CoO_3$ $(0.1 \leqq x \leqq 0.5)$ to examine the behavior of $3d$ electrons of Co ions, introducing the itinerant-electron model proposed by Raccah and Goodenough (*5*) and the Zener double-exchange mechanism (*6*).

Experimental

All $(La_{1-x}Ca_x)CoO_3$ $(0.1 \leqq x \leqq 0.5)$ samples were prepared using standard ceramic techniques. The powders of La_2O_3, $CaCO_3$, and $CoCO_3$ were weighed in the desired proportions and milled for a few hours with acetone. After drying the mixed products at 100°C, they were calcined in air at 800°C,

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then fired at 1200°C for 24 hr in a flow of pure oxygen gas. For measuring the electrical resistivity, the powders of each compound were compressed into a pellet form under a pressure of about 100 MPa, and then the pellet was sintered at 1200°C for 24 hr in a flow of pure oxygen gas. The oxygen-deficient samples obtained in this way were annealed under oxygen pressures of 140 MPa at 300°C for 1 week.

The phase of the pellets was identified by X-ray powder diffraction with filtered Cu$K\alpha$ radiation. The electrical resistivity was measured by a standard four-electrode technique in the temperature range from 80 to 300K.

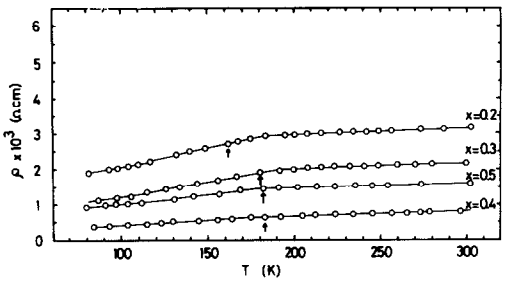

FIG. 1. Specific electrical resisitivity vs temperature for the system $(La_{1-x}Ca_x)CoO_3$.

Results and Discussion

X-Ray diffraction patterns of all the pellet samples were completely indexed as the perovskite-type structure and their lattice parameters were in good agreement with those of the powder samples of $(La_{1-x}Ca_x)CoO_3$ (*1*).

In the range $0 \leqq x \leqq 0.15$, cobaltite was a semiconductor with conductivity given as $\sigma = \sigma_0 \exp(-\Delta E/kT)$. For $0.2 \leqq x \leqq 0.5$, cobaltite was a good conductor and had a metallic temperature coefficient. The electrical resistivity data in the temperature range from 80 to 300K are shown in Fig. 1. In Fig. 1, the arrows indicate the Curie temperature (T_c) of each sample. The electrical resistivity of cobaltites for $0.2 \leqq x \leqq 0.5$ had a break point around T_c. In Fig. 2, the values of log ρ at 300K are plotted against x. Log ρ had a minimum value at $x = 0.4$.

Zener proposed the double-exchange mechanism to explain the magnetic and electrical properties of the ferromagnetic $(La_{1-x}Sr_x)MnO_3$ (*6*). These manganites change from metallic to semiconductive at T_c (*7*). Bhide *et al.* studied the Mössbauer measurement of $(La_{1-x}Sr_x)CoO_3$ at various temperature (*2*). A single six-line pattern was observed at 78K and a single-line pattern was observed above T_c. Although these results of Mössbauer measurements support the double-exchange mechanism, no marked change in conductivity was found at T_c. From these results, the magnetic and electrical properties of $(La_{1-x}Sr_x)CoO_3$ were explained by an itinerant-electron model proposed by Raccah and Goodenough (*5*). According to this model, Co^{IV} ions (3*d* hole) induced by a small quantity of Sr^{2+} ions remain tightly bound to all nearest-neighbor cobalt ions and act as a deep acceptor level. 3*d* holes are not localized at particular cobalt ions but belong to all cobalt atoms. At higher Sr^{2+} ion contents, the acceptor complex interacts to form an impurity band and ferromagnetic

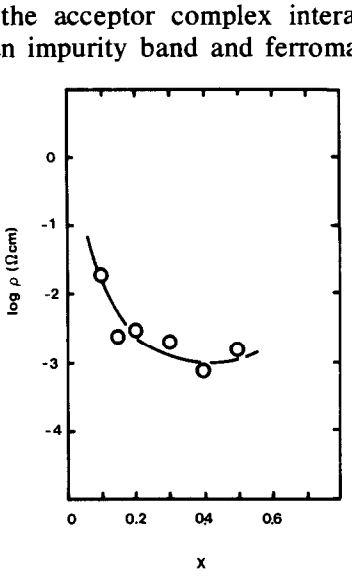

FIG. 2. Specific electrical resistivity at 300K for the system $(La_{1-x}Ca_x)CoO_3$.

interaction is introduced. It is necessary to postulate an overlapping band of the $\sigma^*(\uparrow)$ and $\pi^*(\downarrow)$ bands. Patil *et al.* synthesized the perovskite-type system $(La_{1-x}Ba_x)CoO_3$ in the range $0 \leqq x \leqq 0.5$ (*8*). $(La_{1-x}Ba_x)CoO_3$ was ferromagnetic in the range $0.2 \leqq x \leqq 0.5$. The electrical resistivity of cobaltites decreased with increasing x and had a minimum value at $x = 0.3$, and $(La_{0.5}Ba_{0.5})CoO_3$ was metallic. These magnetic and electrical properties were explained by an itinerant-electron model (*5*).

$(La_{1-x}Ca_x)CoO_3$ exhibited ferromagnetism in the range $0.05 \leqq x \leqq 0.6$, and T_c had maximum value 185K at $x = 0.4$ (*1*). The saturation magnetization (σ_0) increased monotonically with increasing x and was not larger than the theoretical value. $(La_{1-x}Ca_x)CoO_3$ ($0.2 \leqq x \leqq 0.5$) were metallic in the temperature range from 80 to 300K and $d\rho/dT$ changed at T_c. From these results, it is considered that the magnetic and electrical properties of $(La_{1-x}Ca_x)CoO_3$ are explained by using the Zener double-exchange mechanism (*6*).

It is concluded that $(La_{1-x}Ca_x)CoO_3$ is a semiconductor in the range $0 \leqq x \leqq 0.15$ and metallic in the range $0.2 \leqq x \leqq 0.5$. The change of temperature dependence of electrical resistivity has a break point around T_c. Log ρ at room temperature has a minimum value at $x = 0.4$. These properties are explained by the Zener double-exchange mechanism (*6*).

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