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Electric Properties of Ferromagnetic $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 0.9$)

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The electrical resistivity of ferromagnetic $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 0.9$) was measured in the temperature range from 77 to 300 K. All cobaltites are good conductors and have a metallic coefficient. The magnetic transitions are independent of the electrical conductivity in this system. The logarithm of the specific electrical resistivities ($\log \rho$) at 80 and 290 K monotonically increase with mole fraction of X, and these increases are explained by the itinerant-electron model.

Introduction

The perovskite-type system $La_{1-X}Sr_X CoO_3$ was prepared in the range $0 \leqq X \leqq 0.5$, and magnetic and electrical properties were first studied by Jonker and Van Santen (*1*). $LaCoO_3$ ($X = 0$) was a semiconductor (*2*) with conductivity given as $\sigma = \sigma_0 \exp(-\Delta E/kT)$ below 398 K. With increasing X in the range $0 \leqq X \leqq 0.2$, ΔE in the low-temperature region decreased and became zero at $X = 0.2$ (*3*). In the range $0.3 \leqq X \leqq 0.5$, the cobaltites were good conductors and had a metallic temperature coefficient. In the range $0 \leqq X \leqq 0.2$, Rao *et al.* proposed a hopping conduction model from the experimental results of electrical conductivity and Mössbauer measurement (*3, 4*), and in the range $0.3 \leqq X \leqq 0.5$, Raccah and Goodenough reported that the $3d$ electrons of Co ions were collective and gave ferromagnetism at low temperature and metallic conductivities (*5*).

Since the cobaltites, $La_{1-X}Sr_XCoO_{3-\delta}$, tend to have oxygen deficiency in the range $0.5 \leqq X \leqq 1.0$, we prepared powdered samples of $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 1.0$) under high oxygen pressures and measured their magnetic properties (*6*). All cobaltites exhibited ferromagnetism, and the Curie temperature (T_c), the paramagnetic Curie temperature (T_θ), and the saturation magnetization (σ) had maximum values at $X = 0.6 \sim 0.7$.

In the present study, we discuss the behavior of $3d$ electrons of Co ions of $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 1.0$) from the results of magnetic and electrical measurements in comparison with the model proposed by Raccah and Goodenough (*5*).

Experimental

All the $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 0.9$) samples were prepared using the standard ceramic technique. The powders of $SrCO_3$, $CoCO_3$, and La_2O_3 were weighed in the desired proportions and milled for

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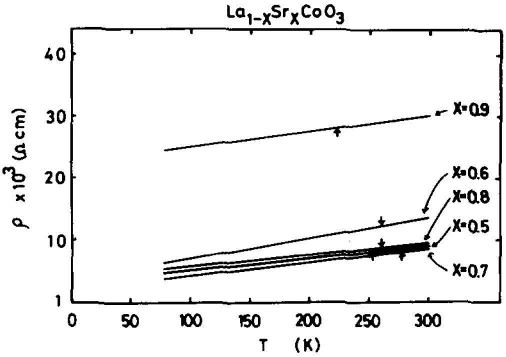

FIG. 1. Specific electrical resistivity vs absolute temperature for the system $La_{1-X}Sr_XCoO_3$.

24 hr with acetone. After drying the mixed products at 100°C, they were prefired in air at 800°C for 24 hr. The products obtained were reground and milled, and then fired again for 24 hr at 1100–1300°C in a flow of pure oxygen gas. For measuring the electrical conductivity, the powder of each compound was compressed into pellet form under a pressure of about 1000 kg/cm², and then the pellets of pressed samples were sintered at 1100°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 1400 bars at 300°C for 1 week.

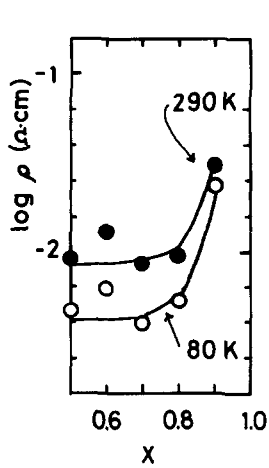

FIG. 2. Specific electrical resistivities at 80 and 290 K for the system $La_{1-X}Sr_XCoO_3$.

The phase of the pellets was identified by X-ray powder diffraction with filtered Co$K\alpha$ radiation. The electrical resistivity was measured by a standard four-electrode technique in the temperature range from 77 to 300 K.

Results and Discussion

X-Ray powder diffraction patterns of all pellet samples were completely indexed as the cubic perovskite structure, and their lattice parameters agreed with those of powdered samples of $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 1.0$) (*6*). The Curie temperature (T_c) of these pellet samples also agreed with the previous data. These facts suggest that all samples have no oxygen deficiency in the range $0.5 \leqq X \leqq 0.8$.

The electrical resistivity data in the temperature range from 77 to 300 K are shown in Fig. 1. All samples are good conductors and have a metallic temperature coefficient, and also the specific electrical resistivity (ρ) increases linearly with increasing temperature (T). In Fig. 1, the arrows indicate the Curie temperature (T_c) of each sample. It is found that the magnetic transitions are independent of the electrical conductivities in the $La_{1-X}Sr_XCoO_3$ ($0.5 \leqq X \leqq 0.9$) system. In Fig. 2, the values of log ρ at 80 and 290 K are plotted against X. As seen in this figure, log ρ monotonically increases with increasing X. Since the samples annealed under high oxygen pressures have little porosity, the measured values of electrical resistivity of the samples are still higher. Raccah and Goodenough proposed an itinerant-electron model to account for the ferromagnetic moment ($\bar{n}$) of $La_{1-X}Sr_XCoO_3$ (*5*) and the model is shown schematically in Fig. 3. The average magnetic moments of Co ion are given as

$$\bar{n} = (X + 2n)\mu_B, \quad (1)$$

where n is the number of up-spin, σ^* orbital electrons per molecule. For $\bar{n}$ = 1.5 in

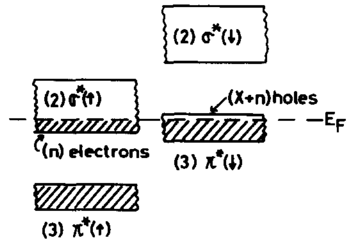

FIG. 3. Schematic 3*d* band for ferromagnetic region (after Raccah and Goodenough, Ref. (*5*).

$La_{0.5}Sr_{0.5}CoO_3$, the intermediate-spin configuration would be $\pi^{*5.0}\sigma^{*0.5}$. In the range $0.5 \leqq X \leqq 1.0$, the values of magnetic moments ($\bar{n}$) at 0 K, calculated from the value of the saturation magnetization (σ), are shown in Table I. The number of electrons in the σ^* orbitals and the π^* orbitals calculated from Eq. (1) are also shown in Table I. Figure 4 shows the relation between X and the number of electrons in the σ^* orbitals and π^* orbitals. In the range $0.5 \leqq X \leqq 0.8$, the number of electrons in the π^* orbitals decreases with increasing X, but that in the σ^* orbitals increases with increasing X. This fact suggests that an increase of X would add electrons to the broad σ^* orbitals more rapidly than to the π^* orbitals and the π^* orbitals shift upward relative to the σ^* orbitals with increasing X. In the range $0.8 \leqq X \leqq 1.0$, the number of electrons in the π^* orbitals increases and that in the σ^* orbitals decreases with increasing X. However, the number of electrons in the $\sigma^*(\uparrow)$ orbitals and the $\pi^*(\downarrow)$ orbitals below E_F (Fermi energy) decreases according to the function $(3 - X)$ calculated from $3 + n - (X + n)$ (Fig. 3) in the range $0.5 \leqq X \leqq 0.9$. This idea is confirmed by the results of the increase of log ρ at 80 and at 290 K.

TABLE I

THE VALUES OF MAGNETIC MOMENTS ($\bar{n}$) AND THE NUMBER OF ELECTRONS IN THE π^* ORBITALS AND σ^* ORBITALS

X	$\bar{n}$	σ^*	π^*
0.5	1.57	0.54	4.97
0.6	1.46	0.43	4.97
0.7	1.73	0.52	4.79
0.8	2.02	0.61	4.59
0.9	1.43	0.27	4.84
1.0	1.39	0.20	4.81

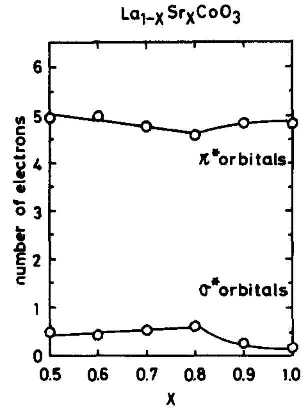

FIG. 4. The number of electrons in the π^* orbitals and σ^* orbitals as a function of X in the system $La_{1-X}Sr_XCoO_3$.

It is concluded that $La_{1-X}Sr_XCoO_3$ has a metallic temperature coefficient in the range $0.5 \leqq X \leqq 0.9$, though all cobaltites exhibit ferromagnetism and the electrical resistivity has no relation to the magnetic transitions. The increase of log ρ at 80 and 290 K is explained by the itinerant-electron model proposed by Raccah and Goodenough (*5*); in the range $0.5 \leqq X \leqq 0.8$, the electrons are added to the broad σ^* orbitals more rapidly than to the π^* orbitals, and the π^* orbitals shifts upward relative to the σ^* orbitals with increasing X, but in the range $0.8 \leqq X \leqq 0.9$, the π^* orbitals shift downward relative to the σ^* orbitals with increasing X.

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