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Magnetic Properties in the System $(La_{1-x}Ca_x)CoO_3$ $(0 \leqq x \leqq 0.6)$

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The perovskite $(La_{1-x}Ca_x)CoO_3$ $(0 \leqq x \leqq 0.6)$ was prepared under high oxygen pressures. The rhombohedral distortion decreases with increasing x and the phase becomes cubic at $x = 0.5$. From the results of magnetic measurement, it was found that the cobaltite with $x \geqq 0.05$ is ferromagnetic. This result is explained by the itinerant-electron model.

Introduction

In recent years many investigations have been reported on the substitution of La^{3+} ion by Sr^{2+} or Ba^{2+} ions in $LaCoO_3$. Jonker and Van Santen (*1*) first showed that $(La_{1-x}Sr_x)CoO_3$ had ferromagnetic and metallic behavior. Raccah and Goodenough (*2*) also investigated the magnetic and electrical properties of $(La_{1-x}Sr_x)CoO_3$ $(0 \leqq x \leqq 0.5)$ and obtained the following results. All cobaltites are indexed as a rhombohedral perovskite structure with the most probable space group $R3C$ at room temperature. The hexagonal c_H and rhombohedral α_R have a definite discontinuity in the range $0.1 \leqq x \leqq 0.15$. However, the unit cell volume increases with a positive slope, and has no resolvable discontinuity. The paramagnetic Curie temperature (T_θ) appears to have a discontinuity within $0.1 \leqq x \leqq 0.15$, as found for the cell constants. The saturation magnetization (σ) and T_θ do not agree with the theoretical values. In order to account for those results, Raccah and Goodenough postulated an overlapping band between σ spin (up) and π spin (down).

Patil *et al.* (*3*) synthesized the $(La_{1-x}Ba_x)CoO_3$ system in the range $0 \leqq x \leqq 0.5$. The rhombohedral distortion decreases with increasing x, and at $x = 0.4$ the phase becomes cubic. No discontinuity has been observed in c_H and α_R. The cobaltites are ferromagnetic in the range $0.2 \leqq x \leqq 0.5$, and metallic at $x = 0.5$. They explained these magnetic and electrical properties using Zener's double-exchange model (*4*) and Goodenough's itinerant-electron ferromagnetism (*2*).

In the present study, an attempt was made to synthesize the compound $(La_{1-x}Ca_x)CoO_3$, where the ionic radius of Ca^{2+} ion is nearly equal to that of La^{3+} ion (*5*), in order to study its magnetic properties. These results will provide some information for discussing the behavior of $3d$

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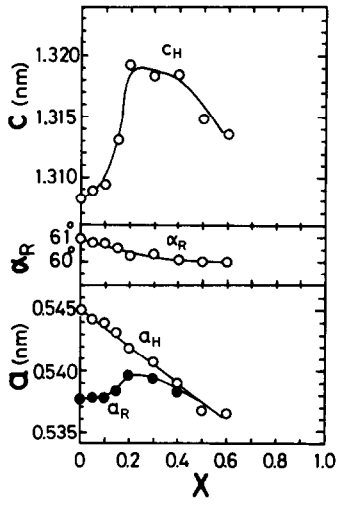

FIG. 1. Cell constants vs composition in the system $(La_{1-x}Ca_x)CoO_3$.

electrons of Co ions in this system in comparison with $(La_{1-x}Sr_x)CoO_3$ (*1*, *6*, *7*).

Experimental

All $(La_{1-x}Ca_x)CoO_3$ ($0 \leqq x \leqq 0.6$) samples were prepared using a standard ceramic technique. 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 the mixed powders were dried at 100°C, they were calcined in air at 800°C, then fired at 1200°C for 24 hr in a flow of pure oxygen gas. The oxygen-deficient materials obtained in this way

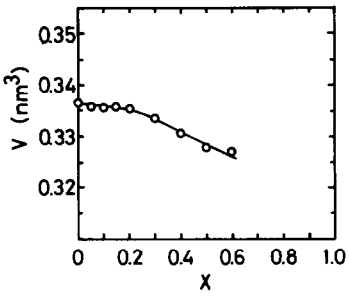

FIG. 2. Unit cell volume vs composition in the system $(La_{1-x}Ca_x)CoO_3$.

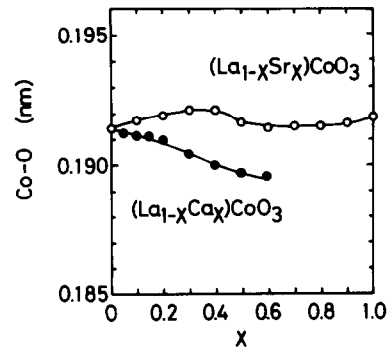

FIG. 3. Co–O distance vs composition in the systems $(La_{1-x}Sr_x)CoO_3$ and $(La_{1-x}Ca_x)CoO_3$.

were annealed under high oxygen pressures of 140 MPa at 300°C for 72 hr.

Phases of the powdered samples were identified by X-ray powder diffraction. Cell constants of the samples were determined using Si as a standard material.

Magnetic properties were measured by a magnetic torsion balance in the temperature range from 77 to 300 K.

Results and Discussion

X-Ray powder diffraction patterns of all samples of $(La_{1-x}Ca_x)CoO_3$ ($0 \leqq x \leqq 0.6$)

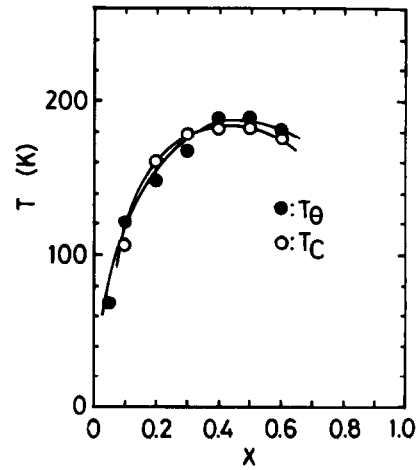

FIG. 4. Paramagnetic Curie temperature and Curie temperature vs composition in the system $(La_{1-x}Ca_x)CoO_3$.

were completely indexed as hexagonal and rhombohedral structures. The relation between the composition and the cell constants is shown in Fig. 1. Rhombohedral distortion decreases with increasing x and the phase becomes cubic at $x = 0.5$. The hexagonal c_H and the rhombohedral a_R increase with increasing x from 0 to 0.2 and have maximum values at $x = 0.2$, then monotonically decrease with increasing x. The hexagonal a_H linearly decreases with increasing x. Unit cell volume (V) decreases monotonically with increasing x, as shown in Fig. 2.

Although the discontinuous change of hexagonal c_H and the rhombohedral angle a_R in the system $(La_{1-x}Sr_x)CoO_3$ ($0 \leqq x \leqq 0.5$) was observed at $x = 0.125$ (*2*), the hexagonal a_H and rhombohedral a_R of the present system do not show any discontinuity. The distance Co–O calculated from the cell constants in both systems of $(La_{1-x}Sr_x)CoO_3$ and $(La_{1-x}Ca_x)CoO_3$ is shown in Fig. 3. In the system $(La_{1-x}Sr_x)CoO_3$, the distance Co–O increases with increasing x. On the other hand, the distance Co–O monotonically decreases with increasing x in the system $(La_{1-x}Ca_x)CoO_3$. Although the ionic radius of Ca^{2+} ion is nearly equal to that of La^{3+} ion (*5*), the unit cell volume and the distance Co–O decrease with increasing Ca^{2+} ion contents in the system $(La_{1-x}Ca_x)CoO_3$. This is due to the fact that the ionic radius of tetravalent cobalt is smaller than that of trivalent cobalt.

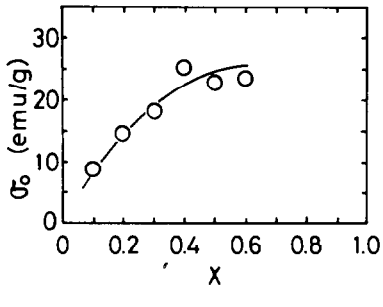

FIG. 5. Saturation magnetization at 0 K vs composition in the system $(La_{1-x}Ca_x)CoO_3$.

The paramagnetic Curie temperature (T_θ) and the Curie temperature (T_C) are shown in Fig. 4 as a function of x. In the range $0.05 \leqq x \leqq 0.6$, T_θ is positive and has a maximum value of 190 K at $x = 0.4$. T_C also has a maximum value of 185 K at $x = 0.4$. The values of saturation magnetization at 0 K (σ_0) were extrapolated from the σ–T curve, and the compositional dependence of the saturation magnetization (σ_0) is shown in Fig. 5. As seen in this figure, σ_0 increases monotonically with increasing x. From the results of the electrical resistivity measurements, $(La_{1-x}Ca_x)CoO_3$ was metallic in the range $0.2 \leqq x \leqq 0.5$.

Raccah and Goodenough proposed the itinerant-electron model to explain the magnetic and electrical properties in the system $(La_{1-x}Sr_x)CoO_3$ (*2*). According to this model, Co^{IV} ions ($3d$ hole) introduced by a small quantity of Sr^{2+} ions remain tightly bound to all the nearest-neighbor cobalt ions and act as a deep acceptor level. $3d$ 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 interaction is introduced. It is necessary to postulate the overlapping band of the $\alpha^*(\uparrow)$ and $\pi^*(\downarrow)$ bands. $(La_{1-x}Ca_x)CoO_3$ exhibits metallic and ferromagnetism in the range $0.2 \leqq x \leqq 0.6$, and the saturation magnetization (σ_0) increases with increasing x. These properties are well explained by the itinerant-electron model. The Fermi energy (E_F) moves into the σ^* orbital at $x = 0.2$, and deeper into the σ^* orbital with increasing x in the range $0.2 \leqq x \leqq 0.6$. The number of electrons in the $\sigma^*(\downarrow)$ bands decrease and σ_0 increases with increasing x, as shown in Fig. 5. Such an itinerant-electron model is also consistent with the crystallographic data, which shows a distinct change at $x = 0.2$, as shown in Fig. 1.

It is concluded that single-phase perovskite can be synthesized in the system $(La_{1-x}Ca_x)CoO_3$ up to $x = 0.6$. $(La_{1-x}Ca_x)CoO_3$ is ferromagnetic in the range $0.05 \leqq x \leqq 0.6$ and metallic in the range $0.2 \leqq x \leqq 0.5$. These properties are explained by the itinerant-electron model proposed by Raccah and Goodenough (*2*).

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