Role of the rare-earth on the electrical and magnetic properties of cobalt perovskites

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The magnetic and electrical properties of $R_{1-x}Sr_xCoO_3$ materials (R=La, Pr, Nd, Gd) ($0 \le x \le 0.50$) are studied. Rare-earths with angular momentum $L \ne 0$ enhance coercive field values. They are maximum for R=Nd (the highest *L*) and much smaller for Gd and La (*L*=0). The result is interpreted as the contribution of the L–S coupling in the rare-earth to the magnetic anisotropy of the system. Electrical conductivity is improved with Sr doping, but increases of rare-earth atomic number lead to decreases of conductivity. This is attributed to the increase of lattice distortions, due to the smaller R³⁺ ionic size, and to the effect of the rare-earth on the spin state of cobalt ions. © 2000 American Institute of Physics. [S0021-8979(00)92608-2]

I. INTRODUCTION

The complexity of the magnetic and electrical properties of hole-doped lanthanum cobaltites $La_{1-x}Sr_xCoO_3$ has been known since long ago.^{1–3} However, the interest on these materials has increased recently due to the finding of colossal magnetoresistive effects in parent hole-doped manganesebased perovskites.^{4,5} Sr doping favors the onset of ferromagnetic interactions but, in contrast with the manganites, the Co^{3+} spin state changes with temperature, adding a new aspect to the physics of the system. The complete phase diagram has already been described by Señarís–Rodríguez and Goodenough.⁸

Although LaCoO₃ and La_{1-x}Sr_xCoO₃ have been extensively studied,^{6,7} the behavior of other members of the series $R_{1-x}Sr_xCoO_3$, with R=rare-earth, has not. The purpose of this work is to deepen into the effects that variations in the rare-earth induce in the magnetic and electrical properties of the resulting perovskite. For this, $R_{1-x}Sr_xCoO_3$ samples, with R=La, Pr, Nd and Gd and $0 \le x \le 0.50$ have been synthesized and their dc magnetization and resistivity analyzed.

II. EXPERIMENTAL DETAILS

Single phase polycrystalline $R_{1-x}Sr_xCoO_3$ series (R=La, Pr, Nd, Gd) ($0 \le x \le 0.50$) were prepared by the nitrate decomposition method in the case of R=La and Nd, and the so-called ''liquid-mix'' method in the case of R=Pr and Gd.⁸ The so-obtained materials were characterized by means of x-ray powder diffraction. In this context, while the La compounds are rhombohedrally distorted perovskites, the x-ray diffraction (XRD) patterns of the R=Nd and Gd series were indexed in the orthorhombic perovskite GdFeO₃ structure ($\sim \sqrt{2}a_c \times \sim \sqrt{2}a_c \times \sim \sqrt{2}a_c$), and those of R=Pr were indexed on the basis of orthorhombic structures with ($\sim 2a_c \times \sim 2a_c \times \sim 2a_c$).

To compare the lattice parameters of the different series pseudocubic lattice constants (a') were calculated. a' repre-

sents the lattice parameter of a cubic unit cell containing one ABO₃ unit, and can be defined as $a' = (V/Z)^{1/3}$, where V is the volume of the unit cell and Z is the number of ABO₃ units in one unit cell of the crystal.

III. RESULTS

The general trend of the variation of the pseudocubic lattice constant, a', as a function of both x and R, is that in each of the series the cell expands upon Sr doping and that a'-Pr_{1-x}Sr_xCoO₃ series >a'-Nd_{1-x}Sr_xCoO₃ series >a'-Gd_{1-x}Sr_xCoO₃ series.

In Fig. 1(a) field cooled dc magnetic susceptibility versus temperature of $Nd_{1-x}Sr_xCoO_3$ is shown. As for R=La, the material exhibits an ordered magnetic phase below a critical temperature T_C , which increases with the doping ratio, x. For $La_{1-x}Sr_xCoO_3$ the ordered magnetic phase sets in at x=0.20 and further increase in the Sr content hardly alters T_C . But this does not seem to be the case here, where dependence of T_C with x is observed in the whole doping range. Magnetization versus magnetic field curves taken at 77 K [Fig. 1(b)] indicate that the magnetic state is, for low doping rates, paramagnetic, and for $x \ge 0.20$, ferromagnetic, as expected. The magnetization grows with x, but does not saturate within the available field range. It is worth mentioning the high coercive fields, which reach a maximum of about 4000 Oe for x=0.30, decrease thereafter.

For R=Pr the behavior is similar. The ferromagnetic phase sets in at x = 0.20, but T_C 's are higher and their dependence on x is more important. Hysteresis loops show also evidence of ferromagnetic phase, with coercive fields near R=Nd (measured after maximum applied fields of 13 000 Oe) for x = 0.30. This concentration of divalent ions at the rare-earth site is close to x = 1/3, which in manganites yields a ratio 2:1 Mn³⁺/Mn⁴⁺, found to be optimal for the development of the ferromagnetic state via double exchange mechanism.⁹ In cobaltites, coercive fields decrease after x = 1/3, but their T_C 's keep on growing, in some contrast to what happens in manganites.

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50 100

1000

100

10

0.01

1E-3

x=0.3

=0 4

x = 0.5

ρ**(Ω.cm)**

FIG. 3. Resistivity vs temperature of the $Pr_{1-x}Sr_xCoO_3$ series.

T (K)

150

200

250

300

field, and much lower values of coercive fields (maximum of 1380 Oe for the x=0.30 samples). The form of the hyteresis loops was found to be dependent on the thermomagnetic history of the samples, which does not happen for other *R*'s.

As for their electrical behavior, hole doping increases electrical conductivity (Fig. 3). $La_{0.80}Sr_{0.20}CoO_3$ is already metallic, but as the atomic number of the lanthanide increases (i.e., as its ionic radius decreases) the onset of metallic state occurs at higher *x*. Doping values of x=0.35 and 0.40 are required for R=Pr and Nd, respectively. No metallic state is observed in any of the $Gd_{1-x}Sr_xCoO_3$ samples, although the conductivity is notably improved upon Sr doping by 6 orders of magnitude from x=0 to 0.50.

IV. DISCUSSION

Two main parameters are altered upon substitutions at the rare-earth site: (a) the ionic radius, and (b) the magnetic state of the R^{3+} ion.

Reducing ionic radii means increasing the distortion of the perovskite. In particular, the Co-O-Co bond angle is reduced, with the subsequent diminution of the electronic transfer integral between Co sites, that controls the electronic (hole) conduction.¹⁰ It would also make more difficult the stabilization of ferromagnetic interactions via double exchange, which would explain the low T_C 's of $Gd_{1-x}Sr_xCoO_3$. In addition, the spin state of the Co ions is likely to be altered. In fact, it is well accepted that Co^{3+} undergo a thermal activated spin-state transition in LaCoO₃, form low S = 0 to intermediate S = 1 or high S = 2 spin states already at moderate temperatures.⁷ It determines not only the magnetic but also the electrical properties of the material. Sr doping introduces holes in the system, expands the cell and favors higher spin states, but the physics of $La_{1-x}Sr_xCoO_3$ are still strongly influenced by the changing state of Co^{3+}/Co^{4+} ions.⁶ On the other hand, as the rare earth becomes smaller and more acidic (higher q/r ratio), it competes more strongly with the cobalt for bonding to the oxygen atoms, which results in a progressive stabilization of the $\pi^*(\text{Co-O})$ levels and a large splitting between t_{2g} and e_g ones, and therefore in lower spin states for the cobalt.⁶ In

FIG. 1. (a) Field-cooled dc-magnetic susceptibility of several $Nd_{1-x}Sr_xCoO_3$ samples, measured under a magnetic field of H=1000 Oe. (b) Hysteresis loops of some of the above samples.

When R=Gd important differences appear with respect to the two precedent cases. Samples are ferromagnetic for $x \ge 0.20$, but their T_C 's are lower (~160 K) and do not show appreciable dependences on x. Also, magnetization versus field curves (Fig. 2) indicate a less developed ferromagnetic state, that does not saturate under the maximum available



FIG. 2. Hysteresis loops of some $Gd_{1-x}Sr_xCoO_3$ samples at T = 77 K.

Pr_{1-x}Sr_xCoO₃

these cases, transitions to higher spin configurations take place at higher temperatures. For example, spin–state transitions in RCoO₃ systems with low-radius ions like Lu³⁺ and Ho³⁺ have been reported to occur at temperatures above 500 and 800 K, respectively.¹¹ This is in agreement with our results, which show that on passing from Pr³⁺ to Gd³⁺ the effective magnetic moments for the cobalt ions get smaller. For x=0.30 the values of μ_{eff} (Co) at room temperature are 3.0, 1.7, and ≈ 0 for R=Pr³⁺, Nd³⁺, and Gd³⁺, respectively. Also, the maximum values of magnetization of R_{1-x}Sr_xCoO₃ decrease when increasing the atomic number of R. Also, the conductivity of the undoped RCoO₃ is improved with lighter rare-earths, due to the high portion of Co³⁺ in excited states that facilitate electronic conduction.

Concerning (b), the rare-earths involved in this work were chosen in order to have different values of spin and angular moment, S and L:La³⁺, can be considered as a "neutral" case (L=S=0), and consequently La_{1-x}Sr_xCoO₃ is regarded as reference. Nd³⁺ posess the highest value of L among the lanthanides and Gd³⁺ the maximum value of *S*, but with L=0. Pr³⁺ is taken as an intermediate situation, more similar to Nd. First, it is observed that the presence of R³⁺ ions with L≠0 induces a notable increase in coercive field values. They are maximum for the maximum value of L, corresponding to Nd³⁺. On the other hand, in Gd_{1-x}Sr_xCoO₃ samples, coercive fields are at minimum values, in the order of those of La_{1-x}Sr_xCoO₃. Here Gd³⁺ is an L=0 ion, i.e., the opposite case to Nd³⁺. We interpret this as evidence of the contribution of the L–S coupling in the rareearth to the magnetic anisotropy of the system. The mechanism would then be not active in L=0 ions like La³⁺, and Gd³⁺. Gd³⁺ has also high values of spin angular momentum. The high magnetic moment created by this rare earth, with no L–S anisotropy, can be easily oriented with a small magnetic field. This might be the origin of the thermomagnetic dependence of hysteresis loops in Gd_{1-x}Sr_xCoO₃ samples.

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