Anomalous Hall Effect of Calcium-doped Lanthanum Cobaltite Films

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The Hall resistivity, magnetoresistance, and magnetization of La$_{1-x}$Ca$_x$CoO$_3$ epitaxial films with $0.25 \geq x \geq 0.4$ grown on lanthanum aluminate were measured in fields up to 7 T. The $x=1/3$ film, shows a reentrant metal insulator transition. Below 100 K, the $x=1/3$ and 0.4 films have significant coercivity which increases with decreasing temperature. At low temperature the Hall resistivity remains large and essentially field independent in these films, except for a sign change at the coercive field that is more abrupt than the switching of the magnetization. A unique magnetoresistance behavior accompanies this effect. These results are discussed in terms of a percolation picture and the mixed spin state model for this system. We propose that the low-temperature Hall effect is caused by spin-polarized carriers scattering off of orbital disorder in the spin-ordered clusters.

INTRODUCTION

In doped lanthanum cobaltites, cobalt ions exist in many different charge and spin states. The relative number of ions in each state changes with temperature, giving rise to a complex arrangement of spins and to the unusual magnetic and transport properties of these compounds. Calcium doped lanthanum cobaltite has the largest reported anomalous (proportional to magnetization) Hall effect [1]. As usual, the maximum effect occurs near the ferromagnetic transition temperature, where there is considerable spin disorder. However we report here that the Hall resistivity remains unusually large at low temperatures. We propose that the low-temperature Hall effect is caused by spin-polarized carriers scattering off orbital disorder in the spin-ordered clusters. Further, a unique magnetoresistance behavior accompanies this effect.

Growth, sample quality, etc.

La$_{1-x}$Ca$_x$CoO$_3$ films were grown by laser ablation from targets with $x=0.25$, 0.33, and 0.4. Polycrystalline targets of each composition were prepared by pressing and sintering powders produced by a polymeric steric entrapment method [2]. The films were grown in 150 mTorr of O$_2$ at 1050 K, and then cooled at 5 K/min to room temperature in 1 atm of O$_2$. A section of each film was patterned via photolithography and ion-milled into a five contact Hall pattern. Gold pads were then deposited for electrical contact. Rutherford backscattering (RBS) was used to determine the thickness of each film. The thicknesses were 560 Å, 590 Å, and 400 Å for the films with calcium doping of 0.4, 1/3, and 1/4, respectively. X-ray diffraction indicated epitaxial growth. The growth and patterning conditions were optimized for the 1/3 calcium doped sample, and then repeated for the other samples. As part of the optimization process, the transition temperature was measured by ac magnetic susceptibility, surface roughness was measured by AFM, and composition was measured by x-ray photospectroscopy and energy dispersive x-ray analysis. This information was used along with electrical resistivity and x-ray diffraction data to improve the laser power/fluence, growth temperature, oxygen pressure, and cooling rate. The compositions listed for each film are the nominal doping levels. The RBS data are consistent with these values, but indicate a ten percent cobalt deficiency for the $x=0.4$ sample.

Measurements

Magnetoresistivity and Hall resistivity were measured in out-of-plane fields up to 7 T using a Quantum Design Physical Property Measurement System. Magnetization measurements were made with the field in the same orientation with respect to the sample (i.e., perpendicular to the (001) plane) in a Quantum Design 7 T Magnetic Property Measurement System, so that demagnetization corrections are not needed to calculate the Hall coefficient. A linear temperature independent term is subtracted from the magnetization vs. field data to account for the diamagnetic substrate signal. The Hall resistivity

![FIG. 1: La$_{1-x}$Ca$_x$CoO$_3$ resistivity vs. temperature. The $x=1/4$ resistivity is scaled by a factor of 1000.](image-url)
and magneto resistance were measured every 0.5 T from 7 T to -7 T and back. Hall and magneto resistance measurements are performed by applying a 37 Hz alternating current to the current leads, and recording the voltage between all possible combinations of the three voltage contacts. The weighted sum of these voltages is calculated to yield the resistivity. Subtracting two of these voltages yields the Hall voltage plus a term proportional to the magneto resistance and the imbalance of the contacts. Sweeping the field in both directions allows one to average out this additional term, leaving only the Hall voltage.

RESULTS

The resistivity for each film is shown in Fig. 1. The resistivity of the x=0.4 sample shows only a slight temperature dependence near room temperature. The resistivity drops rapidly below the ferromagnetic transition temperature (near 180 K). The resistivity of the x=1/3 sample rises more rapidly at room temperature, then decreases below the ferromagnetic transition temperature, and increases again below 80 K. The x=1/4 sample has a much higher resistivity, and is semiconducting at all temperatures. The behavior of the higher-doped films conflicts with previously reported data for calcium doped cobaltite films [3], but is similar to that of strontium doped cobaltite (except that the phase boundaries are at slightly higher doping levels) [3].

Below 100 K, the x=1/3 and 0.4 doped films have significant coercivity which increases with decreasing temperature. The resistivity of the x=0.4 film increases linearly as the applied magnetic field decreases in magnitude. When the sign of the applied field is changed, the resistivity continues to increase until switching abruptly at the coercive field. The magneto resistance curves are reversible at fields larger than the coercive field. This magneto resistance is reminiscent of that of magnetic multilayers, except that the shape of the curves is different and cobaltite shows this behavior in much higher fields. Fig. 2 shows a striking example of this behavior. The Hall data shown in Fig. 2 includes both sweep directions with the average value subtracted. Thus removing the imbalance of the contacts, but neglecting a contribution of up to 3% from the magneto resistance. The relative magnitude of the magneto resistance of the 0.4 calcium doped film is temperature independent. The x=1/3 film behaves in a similar manner except that the magnitude of the magneto resistance changes with temperature, and has opposite sign below 60 K. The anomalous Hall resistance of the higher doped samples peaks near the ferromagnetic transition temperature, but still remains quite significant at low temperatures. Although the Hall resis-

FIG. 2: La$_{0.6}$Ca$_{0.4}$CoO$_3$ $\rho_{xx}$ and $\rho_{xy}$ vs. applied field at 10 K. Only a fixed resistance contribution has been subtracted from $\rho_{xy}$: magneto resistance contributes a systematic error of up to 3%.

FIG. 3: La$_{2/3}$Ca$_{1/3}$CoO$_3$ magnetization and Hall resistivity vs. applied field while sweeping from 7 T to -7 T. Both sweep directions are averaged to appropriately remove any magneto resistance contribution and reduce the noise.
tivity switches at the coercive field, the change is much more abrupt than that of the magnetization (Fig. 3). The Hall resistivity is nearly field independent about and below the switching field, depending on the sign of the magnetization, but not its magnitude.

**DISCUSSION**

Calcium doped cobaltite behaves similar to strontium doped cobaltite, except that the phase boundaries are at slightly higher doping levels. In M. A. Señarís-Rodríguez and J. B. Goodenough’s model for strontium doped cobaltite, cobalt atoms exist in two different ionization states, and many different spin states. The intermediate-spin trivalent and low-spin tetravalent cobalt ions have 5 electrons in the $t_{2g}$ levels. Jahn-Tellier distortion splits the $t_{2g}$ levels into doublet and singlet states. The doublet $t_{2g}$ state is degenerate because it contains 3 electrons, and this results in large spin-orbit coupling. At higher calcium doping levels, double-exchange hopping between aligned sites creates a conducting percolation path through an insulating matrix. This path is ferromagnetic with large coercivity below 100 K. The insulating matrix has a magnetization which simply follows the applied magnetic field (i.e., paramagnetic behavior). For the 0.4 calcium doped sample, the effective width of the percolation path is proportional to the degree of alignment of the spin of the matrix with that of the percolation path. When the field is high, the path widens, because the spins tend to line up, and the path is narrowest when the matrix has spins antiparallel to those of the percolation path. The electrons on the percolating cluster are fully polarized, and therefore immune to changes in field (once the percolation cluster itself is saturated). There is spin order on the cluster, but significant orbital disorder. The Hall effect, then, results from spin-orbit scattering of the spin-polarized electrons off the orbital disorder. The sign of the Hall effect depends only on the magnetization direction of the half-metallic percolating pathway. Below 80 K the 1/3 calcium doped sample has ferromagnetic order, but does not percolate electrically. Thermally populated spin states apparently contribute to the percolation path. As the temperature decreases the number of low-spin cobalt states in the insulating matrix increases, suppressing the conductivity at low temperature. It is possible that decreasing the number of thermally populated spin states creates regions where minority spins are scattered more strongly than majority spins and other regions where the opposite is true. These differential spin scattering rates may change as a function of temperature. If this is the case then it is reasonable for the shape of the magnetoresistance curves to remain the same while changing in sign and magnitude. Similar behavior has been observed in multilayer films when the differential spin scattering rate differs in alternating magnetic layers. At higher doping the percolation path remains stable and as a result there is little change in the magnetoresistance ratio.

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