Magnetoresistance in La$_{1-x}$Sr$_x$CoO$_3$ for 0.05 ≤ $x$ ≤ 0.25

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(March 23, 2022)

The dc resistivity, magnetoresistance and magnetic susceptibility of La$_{1-x}$Sr$_x$CoO$_3$ compounds have been investigated in the temperature range of 4K to 300K for magnetic fields up to 7 T. In the doping range studied (0.05 ≤ $x$ ≤ 0.25), the electronic properties of the material exhibit a crossover from semiconducting to metallic behavior. The magnetoresistance is highest in the semiconducting state. A correlation was found between the energy gap determined from the dc conductivity and the energy scale identified from neutron scattering data. The results are interpreted in terms of a double exchange model.

PACS: 72.15.Gd, 72.20.My, 71.45.Gm

The recent discovery of colossal magnetoresistance (MR) in thin films of La- Ca-Mn-O [1] and giant magnetoresistance in a ferromagnetic perovskite of La-Ba-Mn-O [2] generated a renewed interest in this family of compounds. Magnetization and resistivity studies of La$_{1-x}$Sr$_x$MnO$_3$ single crystals [3] revealed several phases with the highest magnetoresistance observed at the paramagnetic insulator to ferromagnetic metal transition. Neutron scattering measurements on La$_{0.7}$Sr$_{0.3}$MnO$_3$ [4] demonstrated that the ferromagnetism in La$_{0.7}$Sr$_{0.3}$MnO$_3$ is itinerant in character.

Although most of the recent attention has been focused on the MnO$_3$ perovskites, similar properties have been observed in materials based on CoO$_3$. The first studies of magnetic and transport properties of La$_{1-x}$Sr$_x$CoO$_3$ by Jonker and van Santen [5] were interpreted by Goodenough [6]. Recently Señarís-Rodríguez and Goodenough performed extensive magnetic and transport studies of pure LaCoO$_3$ [7] and doped La$_{1-x}$Sr$_x$CoO$_3$ [8]. Itoh et al. [9] deduced the magnetic phase diagram of La$_{1-x}$Sr$_x$CoO$_3$ from magnetization measurements. Three phases were identified: at low temperatures spin-glass (for $x < 0.18$) and cluster-glass (for $x > 0.18$) phases and, at high temperatures, a paramagnetic phase. The magnetization dependence of the resistivity of La$_{1-x}$Sr$_x$CoO$_3$ single crystals was investigated for $x > 0.2$ by Yamaguchi et al. [10]. The electronic structure of the material was studied near the semiconductor-metal transition in La$_{1-x}$Sr$_x$CoO$_3$ by using electron-spectroscopy [11].

The negative magnetoresistance in the transition metal perovskites is usually interpreted in terms of the “double exchange” mechanism, suggested by Zener [12], and developed by Anderson [13] and DeGennes [14]. The principal idea is that most of the electrons on the outer shells of the transition metal reside on localized orbits, coupled by Hund’s rule to large magnetic moments, whereas others participate in the conduction via overlapping orbits. Due to the exchange interaction between the two types of electrons, the conduction is conditional on the appropriate orientation of the underlying localized moments. A related approach, suggested for metals by DeGennes and Friedel [15] and adapted to semiconductors by Haas et al. [16] treats the magnetic moments in a mean field approximation. The “perfect” ferromagnetic order leads to a spin splitting of the conduction band, whereas the magnetic disorder is viewed as a source for extra scattering processes.

The magnetoresistance, and the electrical conduction in general, is strongly influenced by the spin state of the Co ions, which was the subject of recent neutron scattering measurements by Asai et al. [17]. Motivated by this study, we investigated the low and high field magnetization, dc electrical resistivity and the magnetoresistance, for magnetic fields up to 7 T, on a set of ceramic samples of composition La$_{1-x}$Sr$_x$CoO$_3$. In contrast to the work by Yamaguchi et al. [10], we concentrated on the low doping range, 0.05 ≤ $x$ ≤ 0.25.

La$_{1-x}$Sr$_x$CoO$_3$ polycrystalline samples were prepared by solid state reaction method similar to that described in [10]. The appropriate mixture of La$_2$O$_3$, SrCO$_3$ and CoO was ground and calcined repeatedly at 950°C for 10 days, fired at 1300°C for about 28 hours and then cooled in air at a rate of approximately 100°C/hour. This cooling rate is considered to be “fast”, as opposed to “slow” cooling rate of 100°C/day used by Itoh et al. [18]. Fast cooling (60°C/hour) has been also used in the recent work of Señarís-Rodríguez and Goodenough [19]. The samples were confirmed to be of a single phase with rhombohedrally distorted perovskite structure by powder X-ray diffraction analysis. The low field magnetic properties of the samples produced here agreed well with the published results [10] and the resistivity curves for $x=0.2$ and 0.25 were similar to those obtained in Ref. [10]. We found, however, that the temperature dependent resistivity of different cuts from the same specimen were different. In order to remedy this shortcoming, we performed an additional heat treatment at 950°C for 5 hours and we cooled the samples slowly, at a rate of 100°C per day as suggested by Itoh et al. [10]. After the heat treat-
ment the low field magnetic properties did not change significantly, but the resistivity did: In contrast to the fast cooled specimens [9] the resistivity curves for $x=0.2$ and 0.25 had positive slope for the whole temperature range measured. The resistivity measurements were very reproducible for all compositions. The data reported here were obtained on the slow cooled material.

Magnetization measurements on our samples (Fig. 1) led to results similar to those observed by Itoh et al. [10]. At the higher $x$ values the samples exhibit ferromagnetism, with a Curie temperature of 220K for $x=0.25$. At low $x$ the magnetic response is much weaker; note the difference in the scale for the upper two curves on Fig. 1. This behavior was interpreted by Itoh et al. [10] as evidence for a spin glass like phase.

The high field magnetizations at 10K are presented in Table 1 along with the average magnetizations per Co and per Sr atoms in units of $\mu_B$. We found about 30% higher magnetization than Sennaris-Rodriguez and Goodenough [9] did for similar compositions. The high field magnetization per Co atom measured by Itoh et al. [10] on the $x=0.5$ sample is also higher than that reported in ref [9]. The difference may be due to the different cooling rates of the samples.

According to the data, the magnetization per Co atom increases approximately linearly with doping concentration. Each Sr atom brings 5-7 spins to the system. The high value of magnetization per Sr site indicates that each dopant atom converts about two Co atoms into high (or intermediate) spin configuration.

In Figure 2 the continuous lines represent the dc resistance of the samples. The room temperature resistivity of $x=0.2$ sample turned out to be higher than that of $x=0.18$ compound. A systematic error, caused by geometrical factors, may be responsible for this [9]. In the Figure the curve corresponding to $x=0.18$ was scaled up and the curve corresponding to $x=0.20$ was scaled down by a factor of 1.4. For low concentrations of Sr the samples are semiconductors. There are two distinct energy gaps in the semiconducting state: at higher temperatures (> 30K) the conductivity is characterized by a larger gap; at low temperatures (< 30K) a lower gap is observed. The cross-over behavior is common for doped semiconductors [20]; we will discuss this matter later. For $x=0.18$ the conductivity shows the signs of a metal-insulator transition. The resistivity of this sample drops dramatically at high temperature and approaches the metallic resistance of the highly doped samples. The

![FIG. 1. Low field magnetization measurements on samples of various Sr content $x$. For each $x$, the lower magnetization was obtained in the zero field cooled measurement, the higher one corresponds to field cooling. The curves are shifted for better view; the high temperature magnetization is close to zero for each samples. The vertical bars indicate the magnetization scale. For $x=0.05$ and $x=0.1$ the scale is expanded by a factor of 50.](image)
the magnitude and temperature dependence of the resistivity of the $x=0.20$ and 0.25 samples is metallic.

In the Mn analogue of the material, the highest magnetoresistance has been observed in the neighborhood of the ferromagnetic transition. Figure 3 illustrates that a similar behavior was found in our metallic samples: there is an MR peak near the Curie temperature of the $x=0.18-0.25$ compounds. However, we found even larger values of MR in the semiconducting phase, and the highest MR was observed in the low temperature spin glass regime. The magnetoresistance exhibits a hysteresis as it follows the internal magnetic fields in the sample, which lags behind the externally applied magnetic field (Fig. 3, inset). The resistivity in 7 T magnetic field, as obtained from field sweeps similar to that shown in the inset of the Fig. 3., is represented in Fig. 2 by empty symbols.

In order to understand the electronic transport in the doped samples, we first consider the pure material, LaCoO$_3$. The ground state electronic configuration of Co atom is $t^3_{2g}e^0_{g}$ with zero spin [8]. The thermal excitation of Co atoms to the high spin $t^4_{2g}e^2_{g}$ (Co$^{3+}$) state is responsible for the anomalous thermal expansion of pure LaCoO$_3$ [18]. The concentration $n$ of excited Co atoms can be estimated as [18]

$$n = \frac{\nu}{\nu + \exp(\Delta/k_B T)}$$  

where $\nu = 15$ is the multiplicity of the high spin state.

FIG. 2. Logarithm of resistivity vs. inverse temperature for a set of samples of various doping level $x$. The solid line is the result of the measurement in zero magnetic field. Note the crossover between two distinct activation energies for low $x$ and the metallic behavior at high $x$. The symbols are resistivities measured in $H=7T$. The inset shows (open symbols) the activation energies evaluated from the slopes of resistivity curves for semiconducting samples. Also shown in the inset (filled square) is the energy gap obtained for the $x=0$ sample from thermal expansion measurements by Asai et al. [18]. The solid line in the inset is guide to the eye.

Remarkably, the Co low spin → high spin transition gap in pure LaCoO$_3$, estimated from thermal expansion [8], coincides very well with the activation energy determined from our low temperature resistivity measurements, if the data are extrapolated to $x = 0$ (Fig. 3 inset). This coincidence suggests that the low temperature conduction is intimately related to the thermal activation of high spin states with a gap modified with doping, presumably due to lattice distortion. At high temperatures another activated process dominates the conduction, characterized by a conductivity of $\sigma_2 \exp(-\Delta_2/k_B T)$. The experimental data for $x = 0.05$, 0.10 and 0.15 on Fig. 2 are reasonably well fitted by the empirical formula

$$\rho^{-1} = \sigma_1 n' + \sigma_2 \exp(-\Delta_2/k_B T)$$  

where $n' = \nu/\nu + \exp(\Delta_1/k_B T)$ is the number of excited Co$^{3+}$ atoms. The parameters $\sigma_1$, $\Delta_1$, $\sigma_2$, $\Delta_2$ are...
The authors wish to thank J.M. Tranquada for initiating this study and for useful discussions, and L. Henderson Lewis for help in sample preparation. Work at SUNY, Stony Brook, is supported by the NSF grant DMR9321575. Work at BNL is supported by the US Department of Energy, Division of Materials Science, under contract DE-AC02-76CH00016.

Table I. Magnetizations of La$_{1-x}$Sr$_x$CoO$_3$ for different $x$ at 5 T and 10K.

| $x$  | 0.05 | 0.10 | 0.15 | 0.18 | 0.20 | 0.25 |
|------|------|------|------|------|------|------|
| $\mu_B$ | 8.24 | 11.62 | 19.14 | 29.05 | 31.88 | 36.31 |
| magnetic moment per Sr atom, $\mu_B$ | 7.2  | 5.0  | 5.4  | 6.8  | 6.7  | 6.1  |

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