PhD Thesis

The study of the giant magnetoresistance effect in the LaNi_{1-x}Co_xO₃ solid solution

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I really think that this is the easiest page to write in a thesis. After so many hours of hard work, so many sleepless nights and endless disappointments you are finally there. Actually, you feel so generous and happy that you practically want to thank everybody! Well, here is my collection...

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Preface

The present work was written in partial fulfillment of the requirements for a Ph.D. degree from the department of *Chemistry* of the *University of Crete*, Greece. The work described here was carried out in the *Superconducting and Magnetic Materials Laboratory* located on the grounds of the *Institute of Electronic Structure and Lasers* (IESL) at the *Foundation for Research and Technology-Hellas* (FORTH), under the supervision of Prof. J. Giapintzakis.

The thesis is divided in three major parts, namely A, B and C. Part A, consists of three chapters which aim to introduce the reader to the field of magnetoresistance and provide useful information regarding the system in consideration. The third chapter of part A explains in full details the synthesis and characterization of the compounds under investigation. Part B, describes the main experimental findings and provides a consistent picture not only for the magnetoresistance effect but also for a number of physical properties of the solid solution. Finally, part C is a collection of appendices that contain description of experimental techniques used and a report on the growth of LaNi_{1-x}Co_xO₃ thin films on Si(100) substrates, which have been used for Hall effect studies (chapter 6), using pulsed laser deposition.

Every time I try to read a thesis or a book, I usually get lost in the hundreds of references piled up in the last few pages. Thus, I have tried to make every chapter of the present thesis quite self-sufficient from this point of view, in the sense that it contains its own references and it can be read independently. Furthermore, since magnetic units can usually prove to be a real headache for non-expert readers, I have included a table in the very last page, which contains the basic measuring units in the SI and cgs systems of units as well as conversion factors from one to the other.

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PART A

INTRODUCTION

Chapter 1

Introduction to the GMR effect

Conventional electronics function successfully on the basis of the electronic charge, neglecting the electronic spin. In recent decades, technology has experienced a breakthrough through the integration of optics with electronics in optoelectronic devices like photodetectors, semiconductor diode lasers etc. To date there has been no comparable integration of electronics with magnetics at a chip level. The first steps toward the creation of a new technological field, which will combine electronics and magnetics for the creation of devices with new and/or enhanced functionality, are just being taken. This new field, soon to emerge, is called spin electronics, spintronics or magnetoelectronics.

A subclass of this new exciting field, which has drawn much attention during the last decade and actually gave the impetus for the development of magnetoelectronics, pertains to the exploitation of the giant or colossal negative magnetoresistance effects, coined as GMR and CMR, respectively. The term magnetoresistance refers to the change in the measured resistance of a material when it is subjected in a magnetic field. Although the study of magnetoresistance in ferromagnets started as early as 1857 with the measurements of anisotropic magnetoresistance (AMR) in nickel and iron by William Thomson (Lord Kelvin), recent years have witnessed a tremendous interest in magnetotransport phenomena merely due to applications in magnetic read-write heads and storing devices (e.g. computer hard disks).

1.1 What (and Where) is Giant Magnetoresistance?

Giant magnetoresistance may be most easily understood through a simple optical analogy. If a beam of unpolarized light is directed through a pair of polarizers, the total transmitted intensity can be modulated by rotating the polarizers with respect to each other. The first polarizer scatters all but one polarization of light, and the second polarizer either transmits that same polarization (0°) or blocks it (90°). For commercially available GMR devices, electrons take the place of photons, thin ferromagnetic materials act as electronic polarizers, and the polarization is in terms of

spin rather than electric field. The magnitude of the effect is measured on a quantitative basis through the relations:

$$MR(\%) = 100 \times \frac{\rho(H) - \rho(0)}{\rho(0)}$$
 or $MR(\%) = 100 \times \frac{\rho(H) - \rho(0)}{\rho(H)}$

where $\rho(H)$ is the resistance in a magnetic field and $\rho(0)$ is the resistance without a magnetic field.



Fig. 1.1.1: Explanation of GMR by optical analogy.

Giant magnetoresistance takes place in a thin-film superlattice stack of at least three films: two ferromagnetic layers, most typically NiFe or Co, separated by a noble metal spacer layer, usually Cu. These films are ultra-thin, of the order of ten atomic layers each. The polarization axis is provided by the magnetization of the ferromagnet through *spin-dependent scattering*. Conduction electrons with spin parallel to the layer magnetization are scattered weakly close to the layer, carrying current more effectively and leading to low resistance, and those with spin antiparallel to the magnetization are scattered strongly, leading to high resistance. Spin-dependent scattering of this sort has been postulated to be a dominant resistance mechanism in bulk ferromagnets since the work of Mott [1]. GMR has been interpreted in terms of spin-dependent scattering from its very first experimental observation in 1988 [2]. For parallel alignment of the two layer magnetizations, the electrons transmitted strongly through one ferromagnetic layer are transmitted strongly through the other, leading to a lowered overall resistance. For antiparallel magnetization, strong scattering will take place in either one of the layers for both spins. By changing the relative magnetization of alternate layers from parallel to antiparallel, a very large room-temperature change in the resistance may be produced. Room-temperature resistance changes (known as the "GMR ratio") as high as 110% percent for [Co90Fe10(20)/Cu(10Å)]x10 multilayers [3] have been produced.

Another class of systems exhibiting the aforementioned effect are transition metal oxides with the perovskite structure [4]. A typical case are the so called perovskite manganites with the chemical formula (RE)_{1-x}A_xMnO₃ (RE= rare earth, A=alkaline earth). Although many of the physical properties of the above have already been studied and a large magnetoresistance effect had been reported, experimental work on manganites has been greatly accelerated during the 1990's. The reason is two fold; (i) the magnitude of the effect was not fully appreciated in previous studies (ii) the underlying mechanisms which control magnetoresistance in the manganites seem to still puzzle physicists, chemists and material scientists all over the world. Indeed, neutron diffraction studies revealed that there is a peculiar competition and coexistence of a long ranged ordered antiferromagnetic phase with a long range ferromagnetic one which drive these oxides to a metallic state below a certain temperature and have been considered widely responsible for typical MR ratios of the order of 10^3 - 10^5 % [4]! Consequently, the above materials have been dubbed CMR materials, which stands for Colossal Magneto-Resistance.

Although the perovskite manganites were the turning point in the 90's for an emerging field, i.e. magnetoresistive perovskite oxides, they are not the only system under consideration. Intense experimental research has pointed out several other compounds like perovskite cobaltites [5], pyrochlore-structured oxides [6], double perovskites [7] and perovskite related ($AA'_{3}B_{4}O_{12}$) oxides [8] to name but a few. One of the above includes the solid solution $LaNi_{1-x}Co_{x}O_{3}$ [9], which was the main focal point of the present thesis.

In summary, giant magnetoresistance is a great example of basic science applied to devices of much relevance to technological applications. The key concept is that electrons can propagate in ferromagnetic regions with the same orientation as the spins, but they cannot propagate when the moment is in the opposite direction. A very similar phenomenon is believed to occur in perovskite manganites at a microscopic level, with phase coexistence leading to ferromagnetic clusters with random orientation of their moments. The latter greatly enhances magnetoresistance values (see Table 1), which increase by several orders of magnitude. Such observations, and detailed experimental work may provide future guidance to design useful devices with new and/or enhanced functionality involving transition metal oxides.

Type of MR	Material	% Change in Resistance*		
MR	Normal metals	~(-1)%		
AMR	Usual ferromagnets (Ni, etc)	~20%		
GMR	Thin film multilayers	~50-200%		
CMR	Perovskite oxides	$\sim 10^3 - 10^5 \%$		

Table 1.1: Types of magnetoresistance and where they can be found.

*The in the resistance is usually negative, thus the minus sign in the first line is to denote that metals exhibit positive MR due to cyclotron resonance.

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Chapter 2 Introduction to the LaNi_{1-x}Co_xO₃ solid solution

2.1 Perovskites

Perovskites are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite. The parent material, perovskite, was first described in the 1830's by the geologist Gustav Rose, who named it after the famous Russian mineralogist Count Lev Aleksevich von Perovski. Perovskites are the most abundant minerals on earth and have been of continuing interest to geologists, chemists, physicists and material scientists due to their exceptional physical properties, which include, ferromagnetism, antiferromagnetism, colossal magnetoresistance, metallicity, superconductivity and ferroelectricity to name but a few.



Fig. 2.1.1: (a) The ideal perovskite $CaTiO_3$ structure. The red sphere in the center of the formed cube (blue lines) is the alkaline earth atom. The gray spheres at the corners of the cube represent Ti cations and the green spheres lying between two Ti atoms are oxygen anions. (b) Schematic of the corner shared octahedra at the cube corners.

Stoichiometric, ideally structured perovskite oxides have the general chemical formula ABO₃ and are of cubic structure. A typical example is that of CaTiO₃ (see

Fig. 2.1.1) in which Ca^{2+} and O^{2-} combine to form a close packed cubic structure with Ti⁴⁺ cations. Notice that Ti cations experience an octahedral environment formed by oxygen anions while Ca lies in the centre of the formed cube. Depending on the oxidation state of A and B cations, the ABO₃ perovskites can be classified in three main categories: (a) $A^{I}B^{V}O_{3}$ (A=Na, Ag, K and rarely Rb, Tl, Cs while B=Nb, Ta, I) (b) $A^{II}B^{IV}O_{3}$ (A=Ba, Sr, Ca, Pb and B=Ti, Sn, Zr, Hf, Mn, Mo, Th, Fe, Ce, Pr, U) and (c) $A^{III}B^{III}O_{3}$ (A=Rare earths, Bi, Y while B=Fe, Cr, Co, Mn, Ni, Ti, V, Al, Sc, Ga, In, Rh).

The stability of the perovskite structure stems from the minimization of the electrostatic (Madelung) energy, which is achieved by the formation of B site corner shared octehedra with oxygen atoms. The corner-shared octahedra form the main building blocks of the perovskite crystal structure and actually this is one out of three prerequisites for the existence of such a stable structure. Another prerequisite is the proper size of the A cation that occupies the space between four corner-shared octahedra and finally the A-O and B-O bond lengths that eventually determine if the formation of the octahedra is possible. Goldschmidt first used a phenomenological coefficient t, called the structure factor, in an attempt to predict the formation of the A, B and O ions (R_A , R_B and R_O respectively) according to the formula:

$$R_A + R_O = t\sqrt{2}(R_B + R_O)$$

In the above relation the ideal cubic perovskite structure is realized for t=1, while deviations from this value normally results in various types of distorted structures i.e. tetragonal, orthorhombic, rhombohedral etc. The perovskite structure has been realized for $0.8 \le t \le 1$.

2.2 The LaNi_{1-x}Co_xO₃ system

2.2.1 Symmetry and Structure

The crystal structure of LaNiO₃ is shown in Fig 2.2.1. The structure is very nearly cubic with a slight rhombohedral (trigonal) distortion, exhibiting a pseudocubic angle of 90.7°. The compound is indexed in the $R\overline{3}c$ space group [1]. It is worth pointing out that substitution of Ni cations by Co ones results in slightly different lattice parameters although the symmetry of the structure is not affected. Thus, the

compounds LaCoO₃ and LaNiO₃ are completely miscible and the series LaNi_{1-x}Co_xO₃ is considered to be a solid solution according to Vegard's law [2]. Therefore, we expect a number of physical properties of the series to vary linearly as a function of composition x.



Fig. 2.2.1: The crystal structure of LaNiO₃. The unit cell has eight formula units. The thick lines indicate the primitive cell, which contains two formula units. Notice the octahedron formed by oxygen anions surrounding a Ni cation. The bigger white spheres represent La atoms.

2.2.2 Electronic structure

At the present time there exists no unified theory for interpreting the electronic properties of transition metal oxides with the perovskite structure. In fact, the very great diversity of their properties makes it very unlikely that it could ever be developed. The simplest way of classifying theories of the electronic structure is to distinguish between those that take a *local* view and those that describe *extended* (*delocalized*) states. An extreme version of the first kind is the **ionic model**, which concentrates on the properties of individual ions, presumed to have integral charges given by the oxidation states of the different elements present. The contrasting picture is that provided by **band theory**, which calculates the wavefunctions of the electrons in a periodic lattice and is obviously applied in metallic solids.

An essential tool for the description of the localized ionic states is the crystal field (CF) theory. The basic idea of the crystal field theory is that all anions around a

metallic cation behave as a group of negative point charges that repel the electrons of the central cation. As a result, the degeneracy of the orbitals of the central cation (2L+1) is lifted. This is called a Stark or CF splitting of the originally degenerate L level. When the CF splitting is large compared to k_BT and the magnetic energies, then the occupation of the various sublevels cannot be altered by temperature or an applied magnetic field. Application of the CF theory for a 3d transition metal in an octahedral environment results in 2 subgroups of degenerate orbitals. The first is a triply degenerate group called t_{2g} and includes d_{xy} , d_{yz} , d_{xz} orbitals while the second is a doubly degenerate group called eg that includes d_{z^2} , $d_{x^2-y^2}$ orbitals. The eg group lies above the t_{2g}.



Fig. 2.2.2: A schematic of the energy diagram of a Stark splitting for a 3d metal cation in an octahedral environment. The splitting Δ_0 is often symbolized as 10Dq.

The chemistry of the perovskite structure LaMO₃ (M=transition metal) requires both Co and Ni to be treated as trivalent cations. Ni³⁺ (d⁷) in this oxide is in a low spin state, i.e. $t_{2g}{}^{6}e_{g}{}^{1}$. However, Co³⁺ is known to assume more than one spin states. The CF splitting, Δ_0 or Δ_{cf} or 10Dq, of Co³⁺ cation is almost identical to the intra-atomic exchange interaction, Δ_{ex} , and thus occupation of the t_{2g} and e_{g} sublevels is expected to be strongly affected by external factors such as temperature. Indeed, the magnetic properties of LaCoO₃ are treated within a thermally activated spin state transition from a low ($t_{2g}{}^{6}e_{g}{}^{0}$) to intermediate ($t_{2g}{}^{5}e_{g}{}^{1}$) to high spin ($t_{2g}{}^{4}e_{g}{}^{2}$) state of Co [3]. Some of the obvious deficiencies in the ionic picture are remedied by the use of **cluster models** where the electronic interactions within a small group of atoms are treated more explicitly.

On the other hand, the traditional approach to band theory starts with a basis of free-electron states, and looks how these are perturbed by the periodic potential of a crystal lattice. However, such a method is not applicable to transition metals or their compounds due to the non-satisfactory representation of d-states by free-electron ones. Thus, the simplest approach to the problem is based on the linear combination of atomic orbitals (LCAO) idea that is used for molecular orbital (MO) theory. In the context of band calculations, this is known as the **tight binding** method.

To illustrate the application of the method to band theory it is simplest to imagine a one-dimensional model, which might represent part of the structure of a perovskite oxide. As in the MO theory, we form orbitals for the electrons in the chain by making linear combinations of the AO basis functions. The symmetry constraints of the problem requires that the crystal orbitals take the form

$$\Psi_K = \sum_n e^{(ikna)} \phi_n$$

In this expression, ϕ_n is an atomic orbital located in unit cell *n* of the lattice, α is the spacing between the unit cells and *k* is the wavevector (the quantum number of crystal orbitals). The form given for Ψ_K would be appropriate for just one basis AO per unit cell. The most important basis functions for transition metal oxides are the metal *d* and the oxygen 2p orbitals. When the overlap between orbitals is included, these may mix together to form bonding and antibonding combinations (bands) just like in MO theory. Depending on the symmetry constraints and the assumptions made for the Hamiltonian of the specific crystal, one may derive different ground states described in band theory as metallic (no gap in the density of electronic states), semiconducting (small band gap ~1.5 eV) or insulating (band gap >5 eV).

Finally, we should mention Goodenough's approach [1] to the description of the physical properties of perovskites, which has proved to be particularly successful although it is based on several phenomelogical assumptions in an attempt to combine the MO theory from a chemists point of view and the tight binding approximation.

2.2.3 Transport Properties

 $LaNiO_3$ is a metallic oxide. The conduction band is formed by the hybridization of low-spin nickel e_g and oxygen p orbitals which form the delocalized

 σ^* band. While LaNiO₃ is metallic, LaCoO₃ is an insulator. The conduction band for LaCoO₃ is almost empty at low temperatures, where Co is predominantly in a low-spin state. However, successive thermal occupation of the σ^* band in LaCoO₃ results in an insulator-to-metal transition with increasing temperature at ~600 K [3].

Replacing Ni for Co cations the resistivity of the solid solution decreases at room temperature. The investigated solid solution retains metallicity throughout the whole temperature range of interest to this study ($5 \le T \le 300$ K) but not for all x. High Co concentration results in a chemically induced metal to insulator transition. Rajeev et al. have studied the very low temperature (T ≤ 2 K) conductivity for $0 \leq x \leq 0.75$ [4]. The aforementioned study defined the chemically induced metal to insulator transition to occur at x=0.65. Hereafter, this value will be called x_c . Below x_c the conductivity σ follows a power law $\sigma(T) = \sigma_0 + \alpha T^m$ with m~0.3-0.4. This result was explained as arising predominantly from electron-electron interactions in terms of present theories on quantum corrections to the conductivity. It is interesting to point out that for $x \rightarrow 0$ the above corrections are quite small but leaving the regime of small corrections and approaching x_c the correction term, $\delta\sigma(T)$, diverges. The authors concluded that actually there is no theory that can explain the data in this regime. Thus, their study was not conclusive on how the metal to insulator transition can be truly explained. This fact is particularly interesting since this is actually the regime where the GMR effect occurs and grows with increasing x.

The electrical transport properties above x_c show a clear exponential temperature dependence which is a fingerprint for semiconducting behavior. Ganguly et al. [5] have tried to explain their results based on Mott's ideas for a minimum metallic conductivity in oxides. The conductivity at x_c is taken as the value of the minimum metallic conductivity, σ_{min} , separating localized and "itinerant" d-electrons in the system. The value of σ_{min} is independent of the transition metal present in the structure and displays a value of $\sim 2 \cdot 10^2 \Omega^{-1} \text{cm}^{-1}$. They concluded that Mott's variable range hopping transport mechanism is valid for $x=x_c$ only for a limited range of low temperature values and that the resistivity of the aforementioned compound is fitted to an empirical equation $\rho=\rho_0 \exp\{E_a/(k_BT+\theta)\}$, where E_a is an activation energy value and θ is a derived characteristic temperature. Nevertheless, the above equation still remains physically unjustifiable and the authors of this work have not extended their measurements for concentrations deep in the insulating range of compositions.

Furthermore, their suggested metal to insulator transition picture does not provide any physical description, which may help reveal the origin of the GMR effect close to and above x_c . Lately, Kobayashi et al. [6] suggested that the transport properties of semiconducting compositions would be better explained with hopping of small polarons. However, their results were based on comparison with a similar oxide system (La_{1-x}Sr_xCoO₃) and not on actual physical arguments like fitting their data to the small polaron hopping transport formula $\rho=\rho_0\text{Texp}(\text{E}_p/\text{k}_B\text{T})$, with E_p being the characteristic energy for hopping of a small polaron. Finally, Pérez et al. has studied the MR of RENi_{0.3}Co_{0.7}O₃ (with RE=La, Nd, Sm) and concluded that GMR can be explained in terms of a double exchange mechanism, which is similar to the manganites [7], an effect for which there is no good evidence that occurs in perovskite cobaltites [8].

Thermal transport properties of the solid solution have revealed that close to x=0.5 the conductivity mechanism changes from n to p type [9]. Interestingly, a nearly linear temperature independent negative thermopower, S for x=0, adopts a hump close to 80 K with increasing Co doping which results in giant thermopower values for x>0.65. The aforementioned effect has not been yet correlated with the observed GMR.

It is clear that up to now there is no consistent explanation regarding the origin of magnetoresistance in conjunction with existing thermal and electrical transport properties (see Fig. 2.2.3). Furthermore, the magnetic behavior of the solid solution, intimately related with magnetoresistance, is still tentative.



Fig. 2.2.3: Magnetoresistance of the solid solution as a function of composition at T=5 K and H=6 T. Data are taken from Ref. 10.

2.2.4 Magnetic Properties

The interesting magnetic properties of the solid solution LaNi_{1-x}Co_xO₃ have been the subject of just a few studies [5, 10]. The magnetic properties of the series have been discussed in terms of ferromagnetism with spin-glass-like character at low temperatures (for $0 \le x \le 0.5$) [11] as well as ferrimagnetism (for $0.1 \le x \le 0.95$) [12]. Of particular interest is the semiconducting regime where the magnetic behavior is surprisingly complex and has been recently discussed for x=0.7 in terms of a spin-glass (SG) state; it has been proposed that the SG state is coupled to the negative GMR exhibited by the system [7, 13]. The claim for the existence of a SG phase at low temperatures was based on the observation of thermomagnetic irreversibility effects in dc magnetization data and the frequency dependence of the real part of the linear ac susceptibility near the freezing temperature (T_{f} ~50K). The conclusion that a SG state exists led the authors to suggest that both ferromagnetic and antiferromagnetic interactions should occur in the system. They have assigned the antiferromagnetic interactions to Ni³⁺-O-Ni³⁺ and Co³⁺-O-Co³⁺ superexchange interactions according to the Goodenough-Kanamori rules, and the ferromagnetic interactions to the simultaneous presence of Ni and Co ions. In particular, they have suggested that either trivalent Co is forced to the intermediate or high spin-state due to the presence of Ni and ferromagnetic interaction is established between these two ions, or that electronic transfer occurs between Ni³⁺ and Co³⁺ leading to the formation of Co⁴⁺ and Ni²⁺. In the latter case, ferromagnetism would occur from the Co³⁺-Co⁴⁺ double exchange interactions as in Sr-doped cobaltates. However, on one hand the evidence on which the authors of Refs. 7 and 13 based their conclusion that a SG phase occurs, characterizes also inhomogeneous clustered systems [14, 15] and on the other hand, they have not provided any direct evidence either for the ferromagnetic or for the antiferromagnetic interactions claimed to occur in the system.

Recent neutron scattering experiments performed on single crystals of $LaNi_{0.1}Co_{0.9}O_3$ have revealed that the Q-dependence of the magnetic scattering at

8.9K exhibits a broad peak around (1,0,0) indicating the existence of strong ferromagnetic correlations in this oxide [6]. However, it has been argued that this ferromagnetic spin fluctuation is suppressed to a finite extent, most likely, due to some antiferromagnetic interactions and thus spin-glass freezing occurs instead of long-range magnetic order. It has also been suggested that the magnetism in LaCo_{1-x}Ni_xO₃ (x=0.05, 0.1) is probably more cluster-glass-like than that of La_{1-x}Sr_xCoO₃ (x=0.05, 0.1). However, there has been no further discussion in that report on whether a spin-glass or a cluster-glass phase occurs at low temperatures.

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Chapter 3

Synthesis and Materials Characterization

3.1 The Pechini (citrate gel method)

Worldwide studies on ceramics, polymers and metals during the past century have resulted in the establishment of materials science as a scientific discipline. A feature of these studies, particularly for ceramics, is their interdisciplinary nature and at the present time chemistry is making an increasingly important contribution to the research, development and manufacture of ceramic materials [1].

The conventional synthesis for multicomponent ceramic powders involves a solid-state reaction between oxide and/or carbonate precursors. Thus, for barium titanate, BaCO₃ and TiO₂ powders are mixed, milled and calcined. Repeated cycles of milling and calcination are carried out to achieve the solid-state reaction. Relatively high temperatures are required for solid-state reactions, typically around 1200°C because of limited diffusion during calcinations, and this can result in decomposition of the ceramic product. Other disadvantages of the method are the formation of undesirable phases such as BaTi₂O₅ during the preparation of BaTiO₃, large grain sizes (detrimental for high-strength ceramic components) due to firing at high temperature and poor chemical homogeneity particularly when dopant oxides are introduced in small amounts as for example during the synthesis of electro-ceramics. In addition, particle size reduction by milling can introduce chemical impurities into the ceramic product.

Therefore, in order to overcome many of the above drawbacks, new synthetic approaches have been exploited and have now become a standard in materials production. One of the above is the Pechini (citrate gel) method [2]. In the Pechini method, polybasic chelates are formed between α hydroxycarboxylic acids containing at least one hydroxy group, for example citric acid, HOC(CH₂CO₂H)₂·CO₂H with metallic ions. The chelate undergoes polyesterification on heating with a multifunctional alcohol, for example ethylene glycol, HOCH₂CH₂OH. Further heating produces a viscous resin, then a rigid, glassy gel and finally a fine oxide powder [3]. Advantages of the Pechini method are the ability to prepare complex compositions, good homogeneity through mixing at the molecular level in solution and control of the stoichiometry. Low firing temperatures are required for decomposition of the resin to the oxide, thus 650°C for BaTiO₃ compared to 1000°C for the conventional solid-state reaction.



Fig. 3.1.1: (a) The structure of the molecule of citric acid. Gray spheres are carbon atoms, red spheres represent oxygen atoms and white spheres hydrogen atoms. Notice that citric acid hosts four carboxyl groups. (b) The structure of the molecule of ethylene glycol. Dark blue spheres represent carbon atoms. When heated in the presence of HNO₃ citric acid and ethylene glycol undergo polyesterification [-COOH+C-OH \rightarrow -CO-O-C- + H₂O]. The existence of the four carboxyl groups is essential for a random substitution to take place and therefore a random three-dimensional network is formed which chelates metal cations.

In the case of $LaNi_{1-x}Co_xO_3$ the citrate-gel (Pechini) method has proved of invaluable help since formation of components with high Ni concentration face an inherent problem: the oxidation state of Ni. In general Ni-oxide perovskites are hard to obtain with Ni in a d⁷ configuration (Ni³⁺). Thus, a conventional solid-state route is preferred followed by high temperature calcinations in a high pressure of oxygen (~100-200 bar). However, the citrate gel method offers a quick reliable and safe way to produce high oxidation state Ni oxides at relatively low temperatures [4].

Ceramic powder samples of LaNi_{1-x}Co_xO₃ ($0.3 \le x \le 1$) were prepared using very high purity (99.999 %) metal nitrates [(La(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O] as starting materials. The nitrates were first dissolved in nano-pure water and then an appropriate mixture of citric acid and ethylene glycol was added to the solution. The preferred ratio is 10gr of citric acid for every 4 ml of ethylene glycol and 4 gr of metal nitrates. The gel formation was catalyzed by the addition of HNO₃. The resulted gel was decomposed at 400 °C and the acquired precursor powders were calcined at 650 °C in an atmosphere of flowing oxygen for a few days, followed by annealing at 1000 °C for 48 hours to improve the crystallinity of the grains (see Fig. 3.1.2). A final heat treatment at 460 °C in an atmosphere of flowing oxygen ensured that the samples were optimally oxygenated.



Fig. 3.1.2: The heat treatment of the produced gel. The produced powder was reground between the step intervals.

3.2 Characterization of produced powders

Figures 3.2.1 to 3.2.7 shows the X-ray diffraction patterns obtained for LaNi_{1-x}Co_xO₃ (0.3 < x < 0.9) at room temperature. The circles represent the measured diffraction pattern, while the red solid line is the calculated one. The difference between the observed and the calculated patterns is plotted at the bottom (blue line). The set of vertical bar marks just below the diffraction spectrum indicate the position of the expected Bragg reflections for the particular space group used in the refinement process. The fit to the obtained pattern as well as the difference between the observed and the calculated using Le-Bail analysis. The refinements were performed with the help of the FullProf program [5].

As evident, the citrate gel method can produce single phase, high purity LaNi₁. $_xCo_xO_3$ members even at 1 atm O₂ pressure. A summary of the results of the powder X-ray diffraction studies can be found in Table 3.2.1. The obtained lattice parameters are in excellent agreement with previously published work [6].



Fig. 3.2.1: Powder X-ray diffraction pattern for LaNi_{0.7}Co_{0.3}O₃.



Fig. 3.2.2: Powder X-ray diffraction pattern for LaNi_{0.6}Co_{0.4}O₃.



Fig. 3.2.3: Powder X-ray diffraction pattern for $LaNi_{0.5}Co_{0.5}O_3$. The second set of vertical bar marks represent expected reflections from the aluminum sample holder.



Fig. 3.2.4: Powder X-ray diffraction pattern for LaNi_{0.4}Co_{0.6}O₃.



Fig. 3.2.5: Powder X-ray diffraction pattern for LaNi_{0.3}Co_{0.7}O₃.



Fig. 3.2.6: Powder X-ray diffraction pattern for LaNi_{0.2}Co_{0.8}O₃.



Fig. 3.2.7: Powder X-ray diffraction pattern for LaNi_{0.1}Co_{0.9}O₃.



Fig. 3.2.8: Evolution of the lattice parameters of the $LaNi_{1-x}Co_xO_3$ solid solution as a function of the Co concentration.

Table 3.2.1. Lattice parameters and statistics of the fit for the produced powder samples as extracted from Le-Bail analysis of the observed diffractionspectra. All spectra were recorded in a Rigaku D-Max 2000 rotating anode (12kW) diffractometer using a Bragg-Brentano configuration with monochromated $Cu-Ka_1$ radiation. All profiles were analyzed in the $R\overline{3}c$ space group.

x(Co)	a, b (Å)	c(Å)	R _B	R _F	Counting time	χ^2	Profile Function	# Refined
								Parameters
0.9	5.45996(2)	13.12069(30)	4.78	3.70	4secs/0.02degs	1.89	TCH* pseudo-Voight	6
0.8	5.45988(1)	13.11921(18)	3.08	2.67	4secs/0.02degs	0.95	TCH pseudo-Voight	6
0.7	5.45987(1)	13.11907(21)	1.35	1.25	4secs/0.02degs	0.95	TCH pseudo-Voight	6
0.6	5.46008(1)	13.12295(19)	2.10	2.15	4secs/0.02degs	0.92	TCH pseudo-Voight	6
0.5	5.46000(1)	13.12149(20)	1.79	2.00	4secs/0.02degs	0.95	TCH pseudo-Voight	$10^{\#}$
0.4	5.46053(3)	13.13131(47)	4.22	2.80	3secs/0.02degs	0.81	TCH pseudo-Voight	6
0.3	5.46090(2)	13.13818(44)	4.49	3.27	3secs/0.02degs	0.89	TCH pseudo-Voight	6

*TCH stands for Thompson-Cox-Hastings.

[#]The fitting included parameters for the Al sample holder contribution in the spectrum.

The oxygen content of each member of the solid solution, after the final stage of the heat treatment illustrated in Fig 3.1.2, was determined through iodometric titrations. 100 mgr of powder samples were placed in a three-neck flask, while concentrated HCl solution was slowly transferred in the flask (see fig 3.2.9). A magnetic stirrer was used to continuously stir the solution. Trivalent Ni/Co cations react with chlorine anions to produce chlorine gas, which was transferred via a stream of pure N₂ gas into an acidified KI solution (5 gr of KI in 200ml of dilute sodium thiosulfate solution); the I₂ generated was then titrated against a standard 0.100N solution of sodium thiosulfate (Na₂S₂O₃). The following chemical reactions take place during the aforementioned experimental procedure:

$$2M^{3+} + 2C\Gamma \leftrightarrow 2M^{2+} + Cl_2$$
$$Cl_2 + 3\Gamma \leftrightarrow 2C\Gamma + I_3^{-1}$$

Note that the addition of starch as an indicator is capable of detecting iodine concentrations as low as 10^{-7} N. Nevertheless, the method is based on optical

$$I_3^- + 2S_2O_3^{2-} \leftrightarrow 3I_3^- + S_4O_6^{2-}$$

observations and thus the results are extracted statistically, i.e. several titrations are
performed and the mean value is used. The results of the titrations indicated that the
samples used in this thesis were optimally oxygenated.



Fig. 3.2.9: Schematic of the experimental set up used to perform iodometric titrations on $LaNi_{1-x}Co_xO_3$ powder samples.

3.3 Microstructure of the produced powders.



Fig. 3.3.1

Figure 3.3.1 shows the microstructure of the produced powders, examined with scanning electron microscopy (SEM), after the final heat treatment. The photograph was taken for LaNi_{0.6}Co_{0.4}O₃ powder sample. The red line inside the blue circle represents a unit length of 1 μ m. Comparing with the grains as observed we conclude that the mean grain size of the produced powders is of the order of ~1 μ m.

Given the fact that we allowed 48 hours of high temperature treatment (1000 °C) in order to

improve the crystallinity of the grains we conclude that the citrate gel method can also be used to produce sub-micron grain size oxide powders and possibly nano-size oxide crystallites. However, such a study goes beyond the scope of this thesis.

For completeness we mention that the cation stoichiometry of certain members of the investigated solid solution has been examined directly through the use of energy dispersive x-ray analysis (EDX). The results indicate that the nominal concentration of cations is in total agreement with the experimentally determined one within the resolution of the instrument used ($\pm 2\%$).

3.4 Conclusions

The samples of this study have been produced through the Pechini (citrate gel) method. The technique has been shown to produce single phase, high quality polycrystalline $LaNi_{1-x}Co_xO_3$ powders.

Powder X-ray diffraction analysis yielded the correct space group and lattice parameters that are in agreement with previously published work. The microstructure of the produced powders revealed a homogeneous assembly of crystallites of the order of 1 µm in size.

The oxygen content of the samples has been systematically examined through iodometric titrations; all samples were found to be optimally oxygenated. This fact is an indirect observation for the correct cation stoichiometry of the samples and has been independently confirmed for certain members of the solution with the use of EDX spectroscopy.

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PART B

RESULTS, DISCUSSION & CONCLUSIONS

Chapter 4

The magnetism of $x > x_c$ as probed by detailed dc and ac magnetic susceptibility studies: Coexistence of ferromagnetic and glassy behavior in semiconducting LaNi_{0.2}Co_{0.8}O₃

In depth analysis of the magnetoresistance effect in any system requires a profound knowledge of the magnetic interactions present. Therefore, we start by presenting a detailed study on the magnetic properties of the GMR x=0.8 compound. The study is based on complementary measurements of the static magnetization (normalized to account for the applied field and sample mass which we shall call dc susceptibility) as well as the ac response of the compound with respect to various frequencies of the ac driving field.

4.1 DC Susceptibility

The temperature dependence of the dc susceptibility, χ , of LaNi_{0.2}Co_{0.8}O₃ measured both under field-cooled (FC) and zero-field-cooled (ZFC) conditions at several magnetic fields, ranging from 0.01 to 6.5T, is depicted in Fig. 4.1.1. It is observed that $\chi(T)$ shows a strong field dependence for T< 60K. For H=0.01T, χ increases rapidly at ~55K indicating the onset of ferromagnetic interactions and exhibits a broad peak at T_p~30K. This peak broadens and shifts to lower temperatures with increasing magnetic field, reaching ~15K for H=1T (not shown here).

A bifurcation in the ZFC and FC susceptibility curves is observed below a certain characteristic temperature T_{irr} , which decreases with increasing applied field. The thermomagnetic irreversibility (TMI) observed in LaNi_{0.2}Co_{0.8}O₃ could be interpreted as a sign for the emergence of a spin-glass state at low temperatures. However, it should be mentioned that TMI is characteristic of both spin-glasses and inhomogeneous clustered systems [1, 2]. It is interesting to note that for low dc fields, e.g., H=0.01T, the ZFC susceptibility exhibits a broad peak rather than a cusp, the FC susceptibility does not level off at low temperatures, and $T_{irr}>T_p$. The aforementioned features are not expected for a canonical spin-glass system and are worth looking into.

The ZFC and FC susceptibility curves taken at high magnetic field (H=6.5T) are presented in Fig. 4.1.2. They show a slight TMI at low temperatures and strongly resemble in shape the characteristic behavior of a ferromagnet; note that the ZFC susceptibility does not show a decrease at low temperatures.



Fig. 4.1.1: Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) dc molar susceptibilities of $LaNi_{0.2}Co_{0.8}O_3$ for various applied magnetic fields. Colors in figure are as following:

 ZFC 0.01 T
 FC 0.01 T
 ZFC 0.1 T
FC 0.1T



Fig. 4.1.2: ZFC (blue line) and FC (red line) curves taken at 6.5 T for $LaNi_{0.2}Co_{0.8}O_3$. The arrow indicate a very weak TMI observed only at low temperature.

The divergence of the magnetic susceptibility at T_c can be studied using the Kouvel-Fischer (KF) scaling analysis [3], which makes use of the scaling law

$$\chi \propto (\mathrm{T} - \mathrm{T}_{\mathrm{c}})^{\gamma}, \tag{1}$$

and defines a new function

$$X_{\rm KF} = \frac{1}{\chi \left(d\chi^{-1} / dT \right)} = \frac{T - T_c}{\gamma}, \qquad (2)$$

in order to determine the Curie temperature, T_c , and the critical exponent, γ .

The KF analysis for our LaNi_{0.2}Co_{0.8}O₃ powder samples yielded $T_c \sim 55.31\pm 5.64$ K and $\gamma \sim 0.5\pm 0.03$. The value obtained for the critical exponent γ is much smaller than the one expected for a 3D-Ising ($\gamma \sim 1.24$) or a 3-D Heisenberg ($\gamma \sim 1.34$) system. More information on the occurrence of ferromagnetic interactions in LaNi_{0.2}Co_{0.8}O₃ and on their nature can be deduced by M (H) studies.

Figure 4.1.3 shows the magnetization versus dc magnetic field curve M (H) taken at 1.8K. The hysteretic behavior observed clearly demonstrates the existence of ferromagnetic interactions in LaNi_{0.2}Co_{0.8}O₃. Several distinct features characterize the hysteresis loop. Namely, even under the highest applied magnetic field (H=5T) the magnetization remains unsaturated pointing out that no true long-range ferromagnetic order exists and / or that high magnetocrystalline anisotropy occurs. It is worth mentioning, that the neutron scattering experiments on single crystals of x=0.9 have also revealed that no long-range FM order exists [4]. Another characteristic feature of the hysteresis loop is that the M (H) curve is narrower around zero-field than at higher fields where hysteresis is more pronounced. Of particular interest is also the behavior of the virgin magnetization branch $M_{\nu}(H)$ that lies outside the loop. The slope of $M_{p}(H)$ remains almost constant until ~0.8T and then rapidly increases, exhibiting a maximum at 1.2T (see bottom right inset of Fig. 4.1.3). Finally, hysteresis loops measured under ZFC and FC conditions show no differences, i.e., they are symmetric about the origin. It is noted that canonical spin glasses exhibit FC hysteresis loops, which are rather asymmetric about the origin due to the polarization of a large number of spins by the magnetic field.



Fig. 4.1.3: Hysteresis loop of LaNi_{0.2}Co_{0.8}O₃ measured at T=1.8K. Bottom right inset represents the derivative of the virgin magnetization curve when increasing the field after zero-field cooling of the sample.

4.2 AC susceptibility

The temperature dependence of the real part of the ac susceptibility, χ' , at 1 kHz is depicted in Fig. 4.2.1 for several dc magnetic fields up to 5T. For H=0T, $\chi'(T)$ displays a single broad peak around 38K, while upon increasing the magnetic field this single peak evolves into two separate peaks. The high-temperature peak broadens and shifts towards higher temperatures, while the low-temperature peak shifts towards lower temperatures with increasing dc magnetic field. The imaginary part of the ac susceptibility, χ'' , is presented as a function of temperature and dc magnetic field in Fig. 4.2.2. For H=0T, $\chi''(T)$ exhibits a broad peak at ~29K. Upon increasing the dc magnetic field, the zero-field broad peak breaks up into two separate peaks whose amplitudes decrease gradually. The position of the high-temperature $\chi''(T)$ peak does not change with increasing field up to 5T (~29K), while the low-temperature $\chi''(T)$ peak shifts to lower temperatures up to 0.5T but then remains constant at ~7K up to 5T (see bottom right inset of Fig. 4.2.2).

Fig. 4.2.3 shows the temperature dependence of χ' at different frequencies of the driving ac field (1 Oe) ranging from 333 Hz to 5 kHz for H_{dc}=0T. There is no frequency dependence at temperatures above 45K. The peak observed at ~38K shifts to higher temperatures with increasing frequency. Note that the frequency dependence becomes smaller with decreasing temperature and vanishes below ~7K. The frequency dependence of the peak in $\chi'(T)$ is qualitatively consistent with either a spin-glass or a cluster-glass phase. In order to gain more information on which phase occurs in LaNi_{0.2}Co_{0.8}O₃ at low temperatures, we performed measurements of the non-linear components χ_2 and χ_3 of the ac susceptibility, which are shown in Fig. 4.2.4 for H_{dc}=0.



Fig 4.2.1: Temperature dependence of the real part of the ac susceptibility, χ' , for various applied dc magnetic fields. Data were taken with a driving ac field of 1 Oe oscillating at 1 kHz. The upper-right inset depicts the low dc biasing field regime, while the bottom-right inset shows the high dc biasing field regime.



Fig 4.2.2: Temperature dependence of the imaginary part of the ac susceptibility, χ'' , for various applied dc magnetic fields. Data were taken with a driving ac field of 1 Oe oscillating at 1 kHz. The upper-right inset depicts the low dc biasing field regime, while the bottom-right inset shows the high dc biasing field regime.



Fig. 4.2.3: Temperature dependence of the real part of the ac susceptibility, χ' , for various frequencies of the ac driving field (H_{ac}=1 Oe) in H_{dc}=0.

In general, the magnetization of a system in the presence of a magnetic field is expressed as

$$m = m_0 + \chi_1 h + \chi_2 h^2 + \chi_3 h^3 + \dots , \qquad (3)$$

where h is the applied field, m_0 is the spontaneous magnetization, χ_1 is the linear susceptibility, and χ_2 , χ_3 are the non-linear susceptibility terms observed as higher harmonic components of frequencies 2ω and 3ω . When the magnetization has inversion symmetry with respect to the applied magnetic field, as in the case of a spin-glass phase, it is expressed as the odd power series of h ($\chi_2 = \chi_4 = ... = 0$). It is important to note that χ_2 is observed only if there is spontaneous magnetization. It has been shown that for a spin-glass χ_3 diverges at T_f, the temperature at which the moments "freeze", and is negative as $h\rightarrow 0$, regardless of the theoretical description of the freezing, i.e., a phase transition in the Anderson-Edwards model or a progressive freezing of the moments of super-paramagnetic clusters [5, 6, 7]. As it can be observed in Fig. 4.2.4, χ_3 exhibits a negative, but non-divergent broad peak at ~38K, while χ_2 shows also a broad peak at around the same temperature. Our data appear to exclude the existence of a canonical spin-glass phase and instead indicate that a cluster-glass phase occurs in LaNi_{0.2}Co_{0.8}O₃. This cluster-glass phase is consistent with the TMI observed in the low-field dc magnetization data, the frequency dependence of the zero-field $\chi'(T)$, and finally the peaks in χ_2 and χ_3 . The clusters formed are randomly distributed in the paramagnetic matrix of LaNi_{0.2}Co_{0.8}O₃, leading to disorder evidenced by the non-saturation of the M (H) curves. The broad peak in $\chi'(T)$ at T \approx 38K accompanied by the peak in $\chi''(T)$ at T \approx 29K can be attributed to intracluster ferromagnetic correlations, which are suppressed with increasing dc field as demonstrated by the abrupt decrease in the amplitude of the zero-field $\chi'(T)$ and $\chi''(T)$ peaks. It is additionally suggested that intercluster FM interactions might be responsible for the increase of the low-field dc magnetization at T≤10K and the low-temperature peak in χ'' (T~7K).



Fig. 4.2.4: The non-linear components of the ac susceptibility, χ_2 and χ_3 , as a function of temperature for H_{dc}=0. The frequency of the ac driving field is 1000 Hz.

4.3 Discussion

In this section several plausible explanations regarding the origin and the nature of the magnetic clusters formed in LaNi_{0.2}Co_{0.8}O₃ are discussed. Pérez *et al.* [8] and Escote *et al* [9] have suggested that electronic transfer might occur between Ni³⁺ and Co³⁺ leading to the formation of Co⁴⁺ and Ni²⁺, and thus Co³⁺-Co⁴⁺ FM interactions could be established. Based on this suggestion, we propose that Co⁴⁺ and Ni²⁺-based clusters could be formed, and intracluster FM correlations occur due to either double exchange interactions of the type Co³⁺-Co⁴⁺ as in Sr-doped cobaltates, or superexchange interactions between Co^s-O-Co^{IV} (s = *iii* which stands for low spin or 3+ which stands for high spin) according to the Goodenough-Kanamori rules.

Another possible explanation for the intracluster FM correlations in LaNi_{0.2}Co_{0.8}O₃ could be related to the disorder introduced by the Ni³⁺ ions placed in the LaCoO₃ matrix since they contribute one extra e_g electron and $E^{3d}(\text{Co})-E^{3d}(\text{Ni}) \approx 1 \text{ eV}$ [10]. The presence of magnetic ions (low-spin Ni^{III}: t_{2g}⁶e_g¹ randomly distributed in LaNi_{1-x}Co_xO₃) could stabilize the nearest-neighboring trivalent Co ions in higher-spin state configurations (either intermediate or high-spin) as it has been suggested for Mn³⁺ and Cr³⁺-doped LaCoO₃ [11]. Based on this suggestion, we propose that Ni^{III}-clusters could be formed, in which the e_g-electron on the Ni^{III} site interacts positively with its nearest-neighboring spins on the Co^s-sites, thus leading to the FM correlation observed in LaNi_{0.2}Co_{0.8}O₃.

The novelty of the experimental results presented in sections 4.1 and 4.2 lies in the definite identification of Ni-Co clusters, which sustain strong ferromagnetic interactions. However, up to now we have not identified any striking features in the magnetic properties of the semiconducting (magnetoresistive) compositions that could serve as the path to reveal the origin of GMR. This is because Vasanthacharya et al have demonstrated that several magnetic properties (that include the critical Curie temperature T_C and the spin only p_{eff} value) of the solution remain almost x independent in the range $0.15 \le x \le 0.85$ [12] as opposed to compounds $LaNi_{1-x}Fe_xO_3$ and $LaNi_{1-x}Cr_xO_3$, which are of similar structure and composition to the investigated system.

Therefore, a systematic comparison of the magnetic and electrical transport properties of members of the solution with x lying above and below x_c is needed in order to

come up with a consistent picture for the evolution the GMR effect. This is the subject of the next chapter.

4.4 Conclusions

We have presented a detailed study of the low-temperature (T<100K) magnetic properties of LaNi_{0.2}Co_{0.8}O₃ powders. Our dc and ac susceptibility measurements are not consistent with the presence of a spin-glass phase at low temperatures and rather point to the occurrence of a cluster-glass phase. The clusters formed are randomly distributed in the paramagnetic matrix of LaNi_{0.2}Co_{0.8}O₃ leading to disorder evidenced by the non-saturation of the M (H) curves. The broad peak in $\chi'(T)$ at T≈38K accompanied by the peak in $\chi''(T)$ at T≈29K can be attributed to intracluster ferromagnetic correlations, which are suppressed with increasing dc field. It is additionally suggested that intercluster FM interactions might be responsible for the increase of the low-field dc magnetization at T≤10K and the peak of χ'' at ~7K.

The apparent similarity of the magnetic properties of the solution with respect to x as suggested by Vasanthacharya et al led us to conclude that a detailed comparison of both the magnetic and the magnetotransport properties between the metallic and the semiconducting compositions would be helpful.

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Chapter 5 A comparative study of the magnetic and magnetotransport properties between metallic and semiconducting compositions of the solid solution $LaNi_{1-x}Co_xO_3$

In this chapter we present a comparative study of both the magnetic and magnetotransport properties for selected members of the perovskite solid solution LaNi_{1-x}Co_xO₃ located on opposite sides of the chemically induced metal-to-insulator (MIT) transition that occurs at x_c [1-4]. Furthermore, we present medium resolution powder neutron diffraction data, which exclude the presence of any type of long range magnetic ordering. In view of the results presented in this chapter as well as the existing bibliography on the magnetic and transport properties on members of the solid solution [5-12] we begin to formulate a plausible picture regarding the origin of the MR in LaNi_{1-x}Co_xO₃ as a function of x.

5.1 DC susceptibility

Fig. 5.1.1 shows the low-field static susceptibility, χ_{dc} (=M_{dc}/H), for both compounds. The magnetic moment was measured under zero field cooled (ZFC) and field cooled (FC) conditions, upon warming the samples in both cases at a constant rate of 0.3 K/min. Both compounds exhibit thermomagnetic irreversibility with qualitatively similar behavior. Specifically, there is a sudden increase in χ_{dc} below 60 K for both compounds, followed by a peak at T_p~32 K for x=0.8 and at T_p~28 K for x=0.4, a minimum at lower temperatures and a subsequent increase below 10 K for all curves. In addition, the irreversibility temperature, T_{irr}, is greater than T_p for both compounds (T_{irr}~38 K for x=0.8; T_{irr}~50.5 K for x=0.4).

The shoulder designated by the arrow around 55 K in the susceptibility curve of x=0.4 is believed to be an effect of the Ni sublattice. According to Vegard's law for solid solutions, it is reasonable to expect the Ni sublattice to have an increasing impact on the magnetic properties with increasing Ni concentration. Moreover, the susceptibility data in the temperature range 30-55 K are fitted relatively well by the expression, $\chi(T)=\chi(0)-\alpha T^2+C/T$, which has been previously used to fit susceptibility data for LaNiO₃ [7]. Finally, it is worth mentioning that in Figs. 4 and 5 of Ref. 7 it is clearly shown that the susceptibility of LaNiO₃ exhibits an enhancement around 50 K and another anomaly at 12 K.



Fig. 5.1.1: Temperature dependence of the molar dc susceptibility for x=0.4 and 0.8 compounds in low field, $H_{dc}=100$ G. (—). The shoulder indicated by the arrow is most likely an effect of the Ni sublattice.

The effect of increasing magnetic field on the static susceptibility of the x=0.4 metallic compound is shown in Fig. 5.1.2. The thermomagnetic irreversibility as well as the upturn at low temperatures are steadily suppressed with increasing magnetic field. Similar effects are also observed for the x=0.8 semiconducting compound [6]. Notice that the peak at 55 K, which was observed on the low-field static susceptibility curves of x=0.4, does not appear at higher fields.

The large increase of χ_{dc} around 60 K for both compounds is an indication for the existence of FM correlations, which were certified by the measurement of hysteresis loops (vide infra). Fits to the Curie-Weiss law, $\chi_{dc}^{-1}=(T-\Theta_C)/C$, for $80 \le T \le 280$ K gave positive mean field temperature values of $\Theta_C=55.6 \pm 1.5$ K for x=0.8 and 51.1 ± 1.3 K for x=0.4. The positive Θ_C values are consistent with the existence of FM interactions. The spin-only value of the effective magnetic moment obtained from the above fit is $\mu_{eff}=2.39 \pm 0.06 \ \mu_B$ for x=0.8 and $\mu_{eff}=2.20 \pm 0.06 \ \mu_B$ for x=0.4.

The divergence of the magnetic susceptibility at the Curie temperature, T_C, has been studied using the Kouvel-Fisher (KF) scaling analysis [13], the KF scaling analysis for x=0.4 is presented in Fig. 5.1.3. The parameters obtained are T_C=55.7±5.68 K and γ =1.05±0.06. The same analysis for x=0.8 yielded T_C=55.31±5.64 K and γ =0.54±0.06. The T_C values obtained from the above analyses are in agreement with the calculated mean field $\Theta_{\rm C}$ values. For completeness, we mention that the value of the critical exponent γ , which describes the divergence of the susceptibility just above T_C, for the mean field approach to the Landau theory is γ =1, for the 3D Ising model is γ =1.25 and for the spin-1/2 Heisenberg model is γ =1.43 [14].

Fig. 5.1.4 presents M(H) curves for both compounds measured at T=2 K. The observation of hysteretic behavior establishes the existence of FM interactions. The magnetization does not reach saturation up to the maximum applied field of H=30 kOe, which indicates that the FM interactions are short range due to the spin-disorder present in the measured compounds. The calculated magnetization at H=30 kOe and T=2 K is 0.44 μ_B /f.u. for x=0.8 and 0.26 μ_B /f.u. for x=0.4. A distinctive difference between the M(H) curves is the relatively large coercive field of the semiconducting compound in comparison to that of the metallic one. The coercive field for x=0.4 reaches H_c~200 Oe, while for x=0.8, H_c~1.6 kOe.



Fig. 5.1.2: Temperature dependence of the molar dc susceptibility for $LaNi_{0.6}Co_{0.4}O_3$ measured under both ZFC and FC conditions in several magnetic fields ($0.8 \le H \le 10 \text{ kOe}$). Notice that the thermomagnetic irreversibility is gradually vanishing with increasing field.



Fig. 5.1.3: KF function (in arbitrary units) versus temperature for the metallic sample (x=0.4). The high-temperature fit (red solid line) defines both T_C and the critical exponent, γ .



Fig. 5.1.4: Magnetic field dependence of the magnetization for (a) x=0.8 and (b) x=0.4 at 2 K. Note the enhanced value of the coercive field for x=0.8.

5.2 AC susceptibility

Fig. 5.2.1 shows the temperature dependence of the ac susceptibility, $\chi_{ac}(T)$, for different values of the applied dc magnetic field. Measurements were made upon warming the ZFC samples at a constant rate of 0.3 K/min and using an ac driving field of 1 Oe oscillating at 1 kHz. In zero dc field both compounds exhibit a broad featureless peak with a maximum in the range 35-40 K (Fig. 5.2.1a). In the presence of a dc field the single peak evolves into two separate peaks. The magnitude of the two new peaks is reduced drastically with increasing dc field intensity (see Figs. 5.2.1b and 5.2.1c). Note also, that the zero-field peak at 55 K, for x=0.4, disappears in moderate dc fields consistent with the dc data.

Fig. 5.2.2 exhibits the frequency dependence of $\chi_{ac}(T)$ for the x=0.4 compound in zero dc field. The overall behavior of $\chi_{ac}(T)$ with respect to frequency around 35 K is consistent with that of glassy systems and similar to the one that has been reported for x=0.8 and 0.7 [5, 6, 11]. Nevertheless, the observation of thermomagnetic irreversibility in χ_{dc} and frequency dependence in $\chi_{ac}(T)$ are not sufficient evidence to safely conclude on the origin of glassy dynamics, since similar effects have been observed even in systems which exhibit long range magnetic ordering [15].

Both the second, χ_2 , and the third, χ_3 , harmonic components of $\chi_{ac}(T)$ for x=0.8 and 0.6 compounds have been measured. Fig. 5.2.3 (a) and (b) depicts the temperature dependence of $|\chi_2 h_0|$ and $|(3/4)\chi_3 h_0^2|$ for x=0.8 and x=0.4 respectively. Both compounds exhibit a strong signal of χ_2 , which pertains to the presence of a spontaneous moment [6, 16]. In addition, χ_3 for both compounds does not exhibit any divergence and thus cannot be attributed to a random freezing of atomic local moments, i.e., a canonical spin glass state. We should point out that similar nondiverging behavior of χ_3 has also been observed in superparamagnetic (SP) systems [17]. To check for the presence of SP in x=0.8, we have measured M(H) curves in the range $30 \le T \le 50$ K (not shown here) where SP behavior is expected to appear. Experimental M(H) isotherms do not scale with H/T, thus excluding the presence of SP and pointing rather to the existence of strong FM correlations. In addition, we have observed neither a T⁻³ dependence of χ_3 above T_f (defined as the peak in the zero-field ac susceptibility) nor a temperature independence of both χ_1 and χ_3 below T_f, which are expected by Wohlfarth's model for SP [17]. A similar analysis for the x=0.4 compound has led to the same conclusion, i.e. it is not a SP system but rather a disordered spontaneously magnetized one.



Fig. 5.2.1: Field dependence of the real part of the linear ac magnetic susceptibility, χ_{ac} ', as a function of temperature for x=0.8 (black lines) and x=0.4 (red lines). Data were taken with a driving ac field of amplitude h₀=1 Oe oscillating at a frequency of 1 kHz [(a) H_{dc}=0 kOe, (b) H_{dc}=1 kOe, (c) H_{dc}=5 kOe].



Fig. 5.2.2: Temperature dependence of the real part of the linear ac magnetic susceptibility, χ_{ac} , for x=0.4 at several frequencies. Data were taken in zero dc magnetic field with an ac field of 1 Oe oscillating at 1 kHz.



Fig. 5.2.3: Temperature dependence of the absolute value of the second, $|\chi_2h_0|$, and the third, ${}^{3}_{4}|\chi_3h_0{}^2|$, harmonic components for x=0.8 (a) and x=0.4 (b) compounds extracted from the signal obtained at frequency 2 ω and 3 ω , respectively (ω =2 π f, f=1 kHz).

5.3 Powder Neutron Diffraction

As it was explained in chapters 2 and 4, Kobayashi et al have performed polarized neutron diffraction experiments which have shown the existence of strong but short-range ferromagnetic interactions for $x > x_c$. On the basis of the above, the purpose of this experiment was to collect neutron diffraction patterns for x = 0.5, i.e. above the critical concentration x_c, at low and high temperatures both in zero and in a non-zero magnetic field in order to determine the magnetic structure of the metallic compositions of the solution. The application of high magnetic fields is necessary to examine the extent to which magnetic interactions are related to the observed magnetoresistance effect (e.g. magnetic cluster growth) as well as to the metal-toinsulator transition. Phase purity of x=0.5 powder samples was checked by X-ray powder diffraction. All the neutron diffraction experiments were performed in the E2 flat-cone diffractometer of the reactor BER II in Berlin. A neutron wavelength of λ = 1.21 Å was chosen by a Ge crystal monochromator with a collimation of 30'. 5 gr of powdered sample were placed in a vanadium can of 5mm diameter in He atmosphere and immersed in a cryostat. The magnetic field was applied, always normal to the scattering vector and only during the heating procedure.

Measurements were performed at 2 K, 120 K and 300 K in zero magnetic field and at 300 K and 2 K in a magnetic field of 6.5 T. The difference diffractograms in temperature and in field didn't show any residual intensity despite the long counting time. We conclude that either the ordered magnetic moment is very weak, at the border sensitivity of the diffractometer (~ 0.3 μ_B), or that the compound does not exhibit a true magnetically long ranged order. All spectra were analysed with the *Rietveld* method in the $R\overline{3}c$ space group. Fig. 5.3.2 presents the results of such an analysis for H=0T and T=300K. For completeness we have collected several useful crystallographic and other information regarding the results of the Rietveld refinement in Tables 5.3.1, 5.3.2, 5.3.3 for future reference.



Fig. 5.3.1: Powder neutron diffraction spectra for $LaNi_{0.5}Co_{0.5}O_3$ collected at various magnetic fields and temperatures. The difference plots of the spectra do not provide any clear evidence for the evolution of long-range ferromagnetic interactions.



Fig. 5.3.2: Refinement of the neutron diffraction pattern at 300 K under H=0 T with the Rietveld method for the $LaNi_{0.5}Co_{0.5}O_3$.

Space Group	$R\overline{3}c$				
Refined lattice constants, a=b	5.420(0) Å				
c	13.026(0) Å				
Diffractometer	E2 flat-cone, (BER II reactor)				
Wavelength	1.21 Å				
Geometry	Bragg-Brentano				
Counting Time	28 sec/step				
20 range	3-80 deg				
20 step	0.1 deg				
Profile Function	Pseudo-Voight				
$R_{wp} = \left\{ \frac{\sum w_i (y_i(obs) - y_i(calc))^2}{\sum w_i (y_i(obs))^2} \right\}^{1/2}$	7.72%				
$R_{p} = \frac{\sum y_{i}(obs) - y_{i}(calc) }{\sum y_{i}(obs)}$	5.16%				
$R_{F} = \frac{\sum (I_{K} (obs)^{1/2} - I_{K} (calc)^{1/2}) }{\sum (I_{K} (obs))^{1/2}}$	2.53%				
$R_{Bragg} = \frac{\sum I_{K} (obs) - I_{K} (calc) }{\sum I_{K} (obs)}$	3.29%				
χ ²	6.71%				

Table 5.2.1: Neutron Diffraction data collection conditions and refinement details for $LaNi_{0.5}Co_{0.5}$ at 300K and in zero magnetic field.

*Note that I_K is the intensity assigned to the Kth Bragg reflection at the end of the refinement cycles

 $\begin{array}{c} \textbf{Table 5.2.2:} \ \mbox{Atomic parameters, isotropic temperature factors and occupancies of} \\ LaNi_{0.5}Co_{0.5}O_3 \ \mbox{at 300K.} \ \mbox{According to the calculated occupancies the chemical formula is:} \\ La_{0.948}Co_{0.585}Ni_{0.426}O_{2.925} \end{array}$

ATOM	Х	Y	Ζ	B _{ISO}	OCCUPANCY
La	0	0	1/4	0.36	0.316
Co	0	0	0	0.21	0.195
Ni	0	0	0	0.21	0.142
0	0.45018(36)	0	3/4	0.55	0.975

A comparative study....

Chapter 5

Table 5.3.3: Miller indices (HKL), multiplicities (Mult.), positions (2θ), calculated (I_{calc}) and observed (I_{obs}) intensities, structure factors ($|F|^2$) and d-spacings (d-hkl) of the observed reflections for LaNi_{0.5}Co_{0.5}O₃ at 300K and zero magnetic field. The first column counts the observed reflections.

No.	Н	K	L	Mult.	20	I _{calc}	I _{obs}	F ²	d-hkl
1	0	1	2	6	18.282	150.6	175.0	0.3889	3.808279
2	1	1	0	6	25.797	494.3	520.1	2.4812	2.710313
3	1	0	4	6	26.136	618.0	618.4	3.1803	2.675740
4	1	1	3	12	30.513	499.0	521.6	1.7189	2.299164
5	2	0	2	6	31.803	1393.2	1410.3	10.3656	2.208180
6	0	0	6	2	32.362	571.2	603.0	13.1675	2.171018
7	0	2	4	6	37.051	3156.8	3225.1	31.0498	1.904140
8	2	1	1	12	40.257	236.8	247.6	1.3502	1.758082
9	1	2	2	12	41.391	30.2	34.0	0.1807	1.711928
10	1	1	6	12	41.838	107.6	113.2	0.6562	1.694436
11	3	0	0	6	45.490	453.9	465.0	6.3952	1.564800
12	2	1	4	12	45.698	533.3	559.4	3.7861	1.558061
13	0	1	8	6	46.317	214.2	256.4	3.1114	1.538354
14	1	2	5	12	48.730	164.3	164.8	1.2987	1.466505
15	2	2	0	6	53.031	1220.1	1233.5	22.1138	1.355156
16	2	0	8	6	53.771	1578.6	1621.2	29.2443	1.337870
17	1	3	1	12	55.678	463.9	446.0	4.5359	1.295537
18	2	2	3	12	55.768	5.4	5.2	0.0525	1.293616
19	2	1	7	12	56.216	125.9	128.6	1.2491	1.284141
20	3	1	2	12	56.571	86.0	91.1	0.8620	1.276732
21	1	1	9	12	56.572	152.7	161.6	1.5296	1.276708
22	0	3	6	6	56.926	1.1	1.2	0.0223	1.269426
23	3	0	6	6	56.926	1.1	1.2	0.0223	1.269426
24	1	0	10	6	57.632	17.0	27.6	0.3505	1.255185
25	1	3	4	12	60.058	182.4	170.8	1.9987	1.208948
26	1	2	8	12	60.570	332.1	323.1	3.6836	1.199672
27	3	1	5	12	62.593	375.3	370.8	4.3629	1.164648
28	0	4	2	6	63.176	164.6	162.3	3.8759	1.154999

29	2	2	6	12	63.509	436.9	431.8	5.1836	1.149582
30	0	2	10	6	64.170	364.8	371.5	8.7820	1.138973
31	4	0	4	6	66.455	721.1	710.9	18.2007	1.104090
32	0	0	12	2	67.744	407.1	412.0	31.6150	1.085509
33	3	2	1	12	68.621	45.5	45.2	0.5990	1.073307
34	1	3	7	12	69.099	316.1	302.3	4.1965	1.066800
35	2	3	2	12	69.415	20.9	19.3	0.2791	1.062541
36	2	1	10	12	70.364	12.3	10.7	0.1669	1.050024
37	4	1	0	12	72.398	279.1	272.7	3.9260	1.024402
38	3	2	4	12	72.553	565.2	560.6	7.9706	1.022504
39	3	1	8	12	73.020	139.3	144.1	1.9786	1.016873
40	1	1	12	12	73.794	164.7	171.5	2.3694	1.007692
41	1	4	3	12	74.717	175.6	175.8	2.5621	0.997030
42	4	1	3	12	74.717	175.6	175.8	2.5621	0.997030
43	2	3	5	12	74.871	39.4	38.9	0.5762	0.995280
44	2	2	9	12	75.409	3.2	2.8	0.0468	0.989227
45	1	2	11	12	75.792	75.0	64.4	1.1115	0.984970
46	0	4	8	6	78.908	556.1	519.5	17.2214	0.952070
47	3	2	7	12	80.941	34.9	22.6	0.5542	0.932119
48	5	0	2	6	81.241	48.2	35.3	1.5397	0.929274
49	1	4	6	12	81.541	6.3	5.4	0.1010	0.926446
50	4	1	6	12	81.541	6.3	5.4	0.1010	0.926446
51	1	3	10	12	82.141	43.6	82.1	0.7645	0.920866

Evidently, the overall magnetic behavior is strikingly similar for both compounds, which suggests that the magnetic interactions involved on both sides of the chemically induced metal-to-insulator transition are most likely of the same origin. Our data seem to exclude the presence of both a conventional spin glass phase as well as the formation of SP clusters in the vicinity of 55 K and instead, point to the formation of magnetic clusters with enhanced FM intra-cluster correlations. Furthermore, it is remarkable that the substitution of an extra 40% of Co by Ni modifies only slightly most of the magnetic quantities examined so far, i.e., the T_C value (obtained by KF analysis), the mean field Θ_C value, the spin-only μ_{eff} value as well as the low-temperature magnetization [M(30 kOe) at 2 K]. An exception is the magnitude of the coercive field, which drops an order of magnitude from x=0.8 to x=0.4. However, when we take into consideration the available transport data for both compounds, this H_c effect has a natural explanation, which will be discussed in section 5.5.

5.4 Magneto-resistivity

Fig. 5.4.1 shows the temperature dependence of the zero-field resistivity for the x=0.8 compound, which exhibits semiconducting behavior. In general, semiconducting transport data can be analyzed using one of the following three theoretical models: (a) The Arrhenius law, $\rho = \rho_0 \exp\{E_g/k_BT\}$, which describes thermally activated behavior due to the presence of a band gap, E_g ; (b) The nearest neighbor hopping of small polarons, which is described by the expression $\rho = \rho_0 \operatorname{Texp}\{E_p/k_BT\}$, where E_p is the characteristic energy for polaron hopping and (c) Mott's variable range hopping (VRH) model described by the expression $\rho = \rho_0 \exp\{T_0/T\}^{1/4}$. T₀ is related to the characteristic fall-off rate, α , of the radial part of the electronic wavefunction around an impurity ion through the relation: $k_B T_0 = 1.5/\alpha^3 N(E_F)$, where $N(E_F)$ is the density of states at the Fermi level [18]. The VRH model originates from the effect of high concentrations of doping that strongly disorders a semiconducting crystal giving rise to the Anderson localization phenomenon [19].



Fig. 5.4.1: Resistivity data for the x=0.8 compound in the temperature range $5 \le T \le 70$ K in zero applied field. Inset: the solid line is the fit to the resistivity data based on Mott's VRH model.

The inset of Fig. 5.4.1 shows a lnp-vs- $T^{-1/4}$ plot of the data. Note that the curve is linear for a wide temperature range $5 \le T \le 70$ K. It is interesting to mention that ln(ρ/T)-vs-(1/T) and a lnp-vs-(1/T) plots exhibit no linearity throughout the whole temperature interval of the measurements (not shown here). Therefore, we can safely conclude that the transport properties of the semiconducting compound, at least down to 5 K, are strongly dominated by the effect of Anderson localization, which introduces a mobility edge above E_F that stabilizes the semiconducting phase. An earlier study of the x=x_c member of the LaNi_xCo_{1-x}O₃ solid solution reported the existence of a limited temperature range for which the VRH model is valid, however, the authors did not extend their analysis to x<x_c [20]. It should be mentioned that transport studies performed on x=0.05 and x=0.1 single crystals suggested that the data are typical of small polaron hopping [21]. However, that suggestion seems to come from a qualitative comparison of the data with those reported for the La₁. _xSr_xCoO₃ system and not from a quantitative fitting of the actual transport data to the small polaron hopping model.

The temperature dependence of the resistivity of the metallic sample (x=0.4) is depicted in Fig. 5.4.2. At high temperatures we observe a linear increase of $\rho(T)$ which is consistent with the metallic nature of x=0.4. On the other hand, the lowtemperature behavior is characterized by an upturn, which has been interpreted as the effect of strong electron-electron correlations in the oxide [9]. Apparently, to date no expression has been proposed that fits the $\rho(T)$ curve over a wide temperature range. In the past, the very low temperature resistivity of the members of the solid solution with x>0.4 was fitted relatively well by a $\sim T^{1/2}$ term, which quantifies electronelectron correlations, plus a power law $\sim T^p$ term to account for inelastic contributions at higher temperatures [22]. The solid line of Fig. 5.4.2 is the result of a fit to the resistivity data using the following expression:

$$\rho(T) = \rho_0 + \alpha_1 T + \alpha_2 T^{1/2} - \alpha_3 \ln T.$$
 (1)

The expression contains three terms besides the residual resistivity term, ρ_0 (where $\rho_0=\rho(T=0)$): (i) a linear term effective at high temperatures to account for phonon scattering, (ii) a T^{1/2}-term that quantifies strong electron-electron interactions at low temperatures and (iii) a lnT-term which normally arises in systems dominated by spin fluctuations [23].



Fig. 5.4.2: Resistivity data for the x=0.4 compound (open circles) in the temperature range $5 \le T \le 300$ K in zero applied field. The solid line is the fit to the data using equation (1). The maximum calculated fitting error using the relation $100 \times [(\rho_{obs}-\rho_{fit})/\rho_{obs}]$ (ρ_{obs} =observed resistivity, ρ_{fit} =calculated resistivity using equation (4)) is 0.6%. Inset: ρ vs. lnT plots and linear fittings for H_{dc}=0 and 20 kOe. Notice the suppression of the lnT term (decreasing slope of the linear part illustrated with the blue straight line) with increasing magnetic field.


Fig. 5.4.3: (a) The magnetic field dependence of magnetoresistance, defined as $100 \times [(\rho(H) - \rho(0))/\rho(0)]$, for x=0.4 (red line) and x=0.8 (black line) compounds at 5 K. All data were collected with the applied field perpendicular to the current direction. (b) The temperature dependence of MR= $100 \times [(\rho(65 \text{ kOe}) - \rho(0))/\rho(0)]$ for the x=0.8 compound.

For completeness we point out that besides the $T^{1/2}$ -term we would be justified to include higher order terms in expression (1) to account for electron-electron interactions ($\rho_{e-e}(T)=\rho(0)-aT^{1/2}+bT-cT^{3/2}+...$) because our measurements extend up to room temperature. However, including higher order terms in expression (1) did not result in any significant improvement of the fitting error value (~0.6%). We speculate that this is indicative of the presence of strong electron-phonon coupling that completely dominates other interactions at high temperatures (T>100 K). In view of the above, equation (1) should be viewed as the best fitting expression with the minimum amount of physical parameters.

The logarithmic temperature dependence of the resistivity has been customarily associated with Kondo scattering. However, fitting the incremental resistivity data to the Appelbaum-Kondo relation [24] { $\Delta\rho(T)\sim[(T/T_K)\ln(T/T_K)]^2$ } resulted in an unphysical value for the fitted Kondo temperature, i.e. $T_K < 0$. Furthermore, the strong FM signal observed for x=0.4 indicates that this oxide cannot be treated as a dilute alloy. We point out that Kondo scattering is not the only source of a logarithmic-in-temperature resistivity. There have been several other theoretical suggestions such as the localized spin fluctuations [25] and the two-band scattering models [26], which contain a similar logarithmic functional dependence in temperature, and moreover, have been considered in explaining the electrical transport properties of concentrated, magnetically clustered, crystalline alloys [27]. The lnT-term has been certified to exist in other metallic members of the LaNi_xCo_{1-x}O₃ series as well, but the study of this, mostly unusual phenomenon, for a narrow band, non s-d exchange solid, extends beyond the scope of the present chapter [28].

We believe that the lnT-term plays a decisive role in determining the behavior of the magnetoresistance of the metallic phase. The inset of Fig. 5.4.2 depicts low-temperature ($T \le 50$ K) resistivity data taken under H=0 and 20 kOe as a function of lnT. The clear suppression of the observed linear part (decreasing slope with increasing field) is a strong indication that the main contribution to the magnetoresistance is the suppression of spin fluctuations.

The effect of the applied magnetic field on the resistivity of both compounds is depicted in Fig. 5.4.3. It is readily seen that both of them exhibit negative MR at 5 K. However, MR for x=0.8 reaches 60% at 65 kOe whereas the maximum MR value for x=0.4 does not exceed 6%. Notice also that for x=0.8 the MR values at low fields are positive; in the absence of any suitable theoretical model we do not further

discuss this effect. However, such a behavior certainly deserves further consideration and it would be useful to examine the magnetotransport properties by means of Hall effect as well as thermopower measurements under applied magnetic field.

5.5 Discussion

As we already mentioned in the introduction, the GMR phenomenon has emerged as a rich and extremely active topic of experimental research. The underlying mechanisms, which are responsible for the appearance of GMR in different systems, may be of completely different origin. In the manganites, for example, the subtle interplay of charge, spin and orbital degrees of freedom along with Zener's double exchange mechanism are widely considered responsible for the emerging GMR effect at and around the FM Curie temperature [2]. On the other hand, a large number of transition metal oxides, which exhibit large or giant negative MR, largely remain beyond our understanding. Regarding the investigated system, it has been previously suggested that it exhibits similar behavior to the magnetoresistive manganites [5]. However, our study reveals that there are distinct differences between the investigated system and the manganites. For example, the x=0.8 compound exhibits GMR which is enhanced with decreasing temperature without a temperature induced metal-to-insulator transition. Such effects are certainly worthy of further consideration.

As it was previously mentioned, the dominant transport mechanism in the temperature range of interest for the x=0.8 magnetoresistive compound is VRH. The random potential fluctuations needed for VRH are introduced by replacing Co with Ni. The introduction of Ni into the lattice strongly disorders the LaCoO₃ matrix as it introduces one extra e_g electron. In addition, it has been shown that Co cations, in LaCoO₃, can easily obtain higher spin states [intermediate spin (IS): $t_{2g}^{5}e_{g}^{1}$ and high spin (HS): $t_{2g}^{4}e_{g}^{2}$] in the presence of magnetic neighbors [29]. Regardless of the spin state of Co, we expect Ni-doping to introduce carriers, i.e., holes in the π^* (t_{2g}) band on nearest neighbor Co sites, consistent with thermopower data [30]. The energy difference between Ni and Co 3d-orbitals, which is of the order of ~1 eV [9], is most likely responsible for the localization of Co-related carriers around Ni and thus for the formation of bound magnetic polaron-like clusters. This mechanism would be enhanced both by charge disproportionation of Ni [5], which presumes two e_g electrons per Ni site, as well as by the coalescence of Ni ions.

The characteristic temperature T₀ appearing in Mott's VRH expression was calculated to be of the order of $\sim 10^5$ K, a value physically unjustifiable. However, similarly large T₀ values have also been previously reported for other lanthanum cobaltate perovskite oxides [31, 32]. The unusually high T₀ values are most likely related to the small bandwidth exhibited by this type of oxide-semiconductors. At sufficiently low temperatures, T \leq 20 K, a modified version of Mott's VRH can fit the data equally well (not shown here). Efros and Shklovskii showed that the Coulomb repulsion between carriers leads to a form of hopping for which $\rho = \rho_0 \exp\{-T_0'/T\}^{1/2}$ [33]. In this case, T_0' is related to the average localization length, ξ , through the relation $k_B T_0 = 1.5e^2/\kappa\xi$, where κ is the dielectric constant. Using this relation, we roughly estimate ξ to be ~3 Å. (For this estimation we used κ ~10, which is a typical value for semiconductors). It is worth mentioning that Gayathri et al. concluded that Co doping of La_{0.7}Ca_{0.3}MnO₃ suppresses both the metallicity and the magnetic long range ordering and leads to the formation of FM clusters, while the carriers exhibit an average localization length of 2.5-5 Å [32]. Therefore, the divergence of the magnetic susceptibility at T_C could be attributed to the confinement of induced carriers around magnetic Ni ions, which order ferromagnetically in order to minimize their energy upon lowering the temperature below T_C.

Next we present a plausible scenario within which we attempt to explain the magnetic as well as the transport data for both compounds. We propose that there are randomly dispersed Ni-based clusters and the intra-cluster exchange interactions between the Ni local moments and the induced carriers are FM. Furthermore, we attribute the observed metastable phenomena to the random distribution of the cluster moments in all directions. In the low Ni-doping regime, the magnitude of the localization length (~3 Å) indicates that the formed FM clusters most likely exhibit single domain-like behavior. In general, the magnetization of such a small cluster in the presence of an applied field should rotate as a whole, a process that usually requires large fields. Thus, we believe that the magnitude of the coercive field for x=0.8 reflects the small size of the cluster in the semiconducting matrix. On the other hand, the smaller coercive field for the metallic sample indicates that the size of the magnetic clusters is larger compared to that of the clusters in the semiconducting sample, and hence the rotation of the magnetization can be explained based on boundary displacement. The metallic nature of the resistivity suggests that these magnetic clusters should be treated as enhanced spin concentration regions which act as magnetic scattering centers in the σ^* delocalized conduction band formed by the extended overlap of Ni antibonding e_g orbitals. The appearance of the lnT-term in eq. (1) is thus consistent with the proposed spin fluctuation scattering mechanism.

The large negative values of MR for x=0.8 are typical of samples exhibiting hopping conduction involving cluster-like bound magnetic polarons [34]. The magnetic field strongly perturbs the relation $\Delta_{cf} \approx \Delta_{ex}$, which holds for LaCoO₃ [8, 35], and induces transitions of Co cations to higher spin state (IS or HS) configurations, thus magnetizing the Co³⁺ matrix (Δ_{cf} is the crystal field splitting energy and Δ_{ex} is the intra-atomic exchange energy for Co³⁺). The reduction of the difference in the magnetization between the matrix and the cluster polaron leads to a spatial expansion of the orbits of the trapped charge carriers, i.e. the hopping range increases, and this leads to the observed GMR. On the other hand, the MR values are not expected to drop significantly in the x=0.4 metallic sample, because the large mean free path due to percolative conduction of magnetic clusters is not significantly changed upon application of a magnetic field. Thus, small but still negative MR values most likely result due to the suppression of spin fluctuations by the magnetic field below the characteristic FM temperature (see inset of Fig. 5.4.2).

5.6 Conclusions

We have undertaken a comparative study between a semiconducting (x=0.8) and a metallic (x=0.4) member of the solid solution $LaNi_xCo_{1-x}O_3$. $LaNi_{0.6}Co_{0.4}O_3$ is a strongly correlated metal and exhibits small but negative MR, whereas $LaNi_{0.2}Co_{0.8}O_3$ exhibits semiconducting behavior and GMR at low temperatures. Both compounds exhibit strikingly similar magnetic properties, which are attributed to the formation of a cluster-glass-like magnetic phase with strong FM intra-cluster interactions. The existence of long range ferromagnetic ordering was excluded based on powder neutron diffraction performed on $LaNi_{0.5}Co_{0.5}O_3$.

Based on magnetotransport data, the negative but small MR of the metallic sample, x=0.4, is suggested to arise from the suppression of spin fluctuations while the GMR observed for x=0.8 is attributed to the formation of magnetic clusters which grow spatially inside the matrix with increasing applied magnetic field.

Nevertheless, the above observations are quite general in nature and lead to several reasonable questions like how is hole-conduction and/or electron-conduction

related to the observed magnitude of the MR? What is the nature of spin fluctuations and how can such interactions give rise to negative MR? The answer to the above as well as many additional useful observations can be supplied by the study of the Hall effect, which is a probe of current-carrying carriers at E_F and hence provides insight on the electronic structure of a material. Such a study has been performed for x=0.5.

[1] We should emphasize that the MIT in the investigated system is of complete different nature compared to the CMR perovskite manganites (see Refs. 2-4).

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Chapter 6

Hall effect on LaNi_{0.5}Co_{0.5}O₃: Two-band transport and ligand-hole assisted ferromagnetic interactions

In the previous chapter we have recognized the necessity for Hall effect measurements as a probe of current-carrying carriers in the vicinity of E_F that would eventually reveal significant information regarding the electronic structure of the solution. Since it is well known that the Hall signal of a specific material is heavily dependent on geometrical factors such as the thickness, it was decided the Hall effect study to be performed on thin films of LaNi_{1-x}Co_xO₃. This way we were able to measure a strong Hall signal that is particularly helpful in the analysis of the Hall data.

In this chapter we present such a study on thin films of $LaNi_{0.5}Co_{0.5}O_3$ grown on Si (100) substrates. Details about the growth, structural, electrical and magnetic characterization can be found in Appendix B.

The choice of the particular composition has been made based on several facts: (i) it shows the strongest ferromagnetic signal and thus its contribution can be easily subtracted (ii) it signifies the n-type low MR to p-type GMR transition in conduction (iii) it is metallic and (iv) it has been shown that all the bulk properties are very well reproduced in thin film structures (see Appendix B).

6.1 A few additional experimental details

Hall effect measurements were performed on high quality, polycrystalline, 100 nm thick films of LaNi_{0.5}Co_{0.5}O₃ deposited using pulsed laser ablation on Si (100) substrates. The film thickness was measured with the use of a step-profilometer, so an error in the reported values (\pm 10%) may be possible. Gold contacts were thermally evaporated in a 4 terminal Hall configuration and annealed in oxygen atmosphere in order to reduce the contact resistance to less than 2 Ω . The transverse resistance was measured by a dc technique and the Hall resistance, R_H , was determined from the half difference of two transverse resistance measurements taken in positive and negative applied magnetic fields respectively. The linear response of the investigated system could be verified by measuring current-voltage characteristics in the range 0-60 μ A for all temperature and field measurements. The Hall measurements taken at T=5 K were performed according to the following protocol in order to minimize noise and instabilities; after temperature stabilization, the magnetic field was slowly ramped up to +7 T and then reversed to -7 T with the same low ramp rate. The resistance was measured upon increasing the magnetic field in steps of 500 G within a period of 1.5 hours.

The temperature dependence (5<T<150 K) of the Hall resistivity was extracted from transverse resistance measurements both in fields of +H T and –H T (H=2 and 5 T) respectively, with the temperature increased in steps of 1 K allowing for temperature stabilization better than 50 mK. The data, both in +H and in –H, were interpolated with an excellent fitting accuracy (R²=0.9999, $\chi^2 \sim 10^{-11}$) in certain temperature regimes in order to subtract resistance values at exactly the same temperature and thus increase the reliability of the presented results. Note, that above 120 K, the extracted Hall resistivity was too noisy and thus reliable Hall measurements could not be recorded within the resolution of the electronic apparatus used. However, all physical effects, which are of interest in this study, appear below 90 K.

Finally, we mention that the study was performed on several films in order to check the reproducibility of our results.

6.2 Results and discussion

The temperature dependence of the saturation magnetization in μ_B per formula unit of the investigated film is shown in Fig. 6.2.1. The produced thin film exhibits a T_c=70.92 K, which was determined by differentiation of the static magnetization curve (*dM/dT*) in a field of 1.5 T. The inset of Fig. 6.2.1 presents a hysteresis loop obtained at 5 K. All presented data are corrected for the almost temperatureindependent Si (100) diamagnetic (linear in *H*) signal, which was measured independently under the same conditions of measurement that have been used for the film. Note that the magnetization at 5 K exhibits saturation (0.6 $\mu_B/f.u.$) above 1 T.



Fig. 6.2.1: Magnetization of the produced thin film as a function of temperature measured at a field of 1.5T. The diamagnetic signal of the substrate (Si) was subtracted as explained in the text. The inset depicts a magnetization isotherm as a function of the applied magnetic field obtained at 5K.

The saturation of the hysteresis loop indicates, possibly, the formation of a long-range ferromagnetic state in the film that has been predicted by theoretical calculations [1]. We attribute the latter effect to substrate strain effects since the X-ray diffraction pattern of the produced thin film has indicated increased texturing along the (012) direction of the rhombohedral ($R\overline{3}c$) lattice. However, since we are interested in the transport properties of the produced film we will not further discuss the above.

Fig. 6.2.2 presents the Hall resistivity, ρ_{yx} , as a function of temperature in two applied magnetic fields, H=2 and 5 T, respectively. We observe that ρ_{yx} is negative in the region 30<T<85 K which indicates a dominant electron conduction channel, in agreement with thermoelectric power measurements [2]. Notice that ρ_{yx} exhibits a minimum, which is strongly field dependent and shifts from ~28 K at 2 T to ~45 K in a field of 5 T. Furthermore ρ_{yx} values strongly decrease with increasing magnetic field and they exhibit a sign reversal at low temperatures. For high fields (5 T) there is an additional sign reversal from negative to positive values (it should be mentioned that the latter has been independently confirmed by Van der Pauw method measurements on a different LaNi_{0.5}Co_{0.5}O₃ film). The sign reversal of $\rho_{yx}(T)$ and its dependence on the applied magnetic field suggests a possible two carrier-type (holes and electrons) conduction mechanism [3]. Thus, it would be interesting to examine the field dependence of ρ_{yx} at a fixed temperature.

Fig. 6.2.3 shows ρ_{yx} as a function of the externally applied magnetic field at T=5K. We observe a steep hole-like increase up to 1 T and a subsequent electron dominant decrease of ρ_{yx} values with increasing applied magnetic field. A sign change occurs at ~7 T that further supports the argument for a possible two-type conduction mechanism along with an anomaly of the $\rho_{yx}(H)$ curve at 3.5 T (the two straight lines on Fig. 3 are guides to the eye). Assuming the Karplus and Luttinger theory [4] in which ρ_{yx} is expressed as the sum of two terms, the normal and the anomalous Hall parts, the Hall resistivity at a given temperature and in a magnetic induction B, is expressed as:

$$\rho_{vx}(B) = R_o B + R_A(4\pi\mu_o)M(B) \tag{1}$$

M(B) is the volume magnetization, R_o is the normal Hall coefficient related to the carrier density and R_A is the anomalous Hall coefficient that quantifies spin-orbit interactions between carriers and localized magnetic moments. Notice that the anomalous Hall scattering is an effect that takes place wherever there are large localized moments, like in super-paramagnets and/or in anti-ferromagnets [5], therefore even if there is no true long range FM order in the LaNi_{0.5}Co_{0.5}O₃ film the use of the above formula is justified. In addition, we should point out that R_A is field independent, i.e. it exists even in the absence of a magnetic field, which is merely used as a probe to make the anomalous contribution evident on a macroscopic scale. Therefore, for magnetic field values in the saturation magnetization regime ρ_{yx} should be linear in *B* and a subsequent linear fitting yields both R_o (slope) and R_A (intercept). On the other hand, any non-linear dependence of ρ_{yx} in the saturation magnetization magnetization field regime, as in the case of the film in consideration, arises solely from the normal part R_o , which in such a case should be considered as a functional coefficient depending on carrier concentration, mobility etc.

In the light of the above observations we analyzed the field dependence of the Hall resistivity at T=5K within a simple two-band (two carrier type) model as suggested by Chambers [6]. In the aforementioned model the Fermi surface is modeled assuming two independent closed spherical surfaces one containing electrons and the other holes. Consequently, the total conductivity of the system is the sum of the conductivities of the two bands $[1/\rho \approx \sigma = \sigma_1 + \sigma_2, \sigma_{1,2} = 1/(\rho_{1,2} - iR_{1,2}B)]$ so that the resultant ρ_{yx} and R_o are expressed in terms of contributions of the two bands:

$$\rho_{yx} = \frac{\rho_1 \rho_2 (\rho_1 + \rho_2) + (\rho_1 R_2^2 + \rho_2 R_1^2) B^2}{(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 B^2}$$
(2a)

$$\rho_{yx} = \frac{\sigma_2^2 R_2 - \sigma_1^2 R_1 - \sigma_2^2 \sigma_1^2 R_2 R_1 (R_2 - R_1) B^2}{(\sigma_1 + \sigma_2)^2 + \sigma_2^2 \sigma_1^2 (R_2 - R_1)^2 B^2} B \quad (2b)$$

$$R_o = \frac{\rho_1^2 R_2 + \rho_2^2 R_1 + R_1 R_2 (R_1 + R_2) B^2}{(\rho_1 + \rho_2)^2 + (R_1 + R_2)^2 B^2}$$
(3)



Fig. 6.2.2: Hall resistivity, ρ_{yx} , as a function of temperature in a field of 2 T (red filled circles) and 5 T (black filled circles). Notice the strong field and temperature dependence of ρ_{yx} . Solid lines are guides to the eye.



Fig. 6.2.3: Field dependence of the Hall resistivity, ρ_{yx} , at T=5K. Asymmetric magnetic scattering causes the low field hole-like steep increase. Notice the anomaly of the curve at 3.5T (the red straight lines have been used as a guide to the eye), which suggests that R_o is not a constant but rather a functional coefficient.



Fig. 6.2.4: Fitting of ρ_{xy}/H vs H^2 using equation (7) of the manuscript. The obtained fit (red solid line) is in a very good agreement with the two-band transport model.

In the above equations we have used subscripts 1, 2 for electrons and holes, respectively, while ρ_i , σ_i and R_i refer to the resistivity, conductivity and the Hall contribution of the i-th band respectively. In addition, $R_1 = (en)^{-1}$ and $R_2 = (ep)^{-1}$, where n and p are the concentration of electrons and holes, respectively. Equation (2b) is more useful in the sense that it allows for a direct incorporation of the Hall mobility, μ_i (vide infra). A similar σ -dependent relation can be reached for equation (3) as well but at this point it is not necessary for the analysis.

Assuming B^2 to be an independent variable, x, we may define three band parameter functions α , β , γ according to the following set of equations [13, 14]:

$$a = \frac{\sigma_2 \mu_2 - \sigma_1 \mu_1}{\sigma^2} \qquad (4)$$
$$\beta = \frac{R_1 R_2}{R_2 - R_1} \gamma \qquad (5)$$
$$\gamma = \left(\frac{\sigma_1}{\sigma} \mu_2\right)^2 \left(1 - \frac{R_1}{R_2}\right)^2 \qquad (6)$$

that help us to form a new functional form of equation (2b):

$$\frac{\rho_{yx}}{B} = y = \frac{\alpha - \beta x}{1 + \gamma x} \tag{7}$$

In the equations (4)-(6) the symbol μ_i refers to the Hall mobility of each of the two bands which is defined through the relations $\mu_i = \sigma_i R_i$ (i=1, 2).

Figure 6.2.4 shows a fitting of the ρ_{yx}/H vs H^2 data using equation (7) in the field range 1 to 7 T (we have assumed a simple linear relation between the applied magnetic field, H, and the magnetic induction, B since H>H_{sat}). The high quality fit (R²=0.985, χ^2 =2×10⁻¹⁰) implies that the essential physical mechanisms of the studied system can be well understood within the two-conduction bands model. Thus, it would be interesting to discuss the field dependence of the parameters used in the α , β , γ functions. We solved the above set of equations [(4)-(7)] numerically for magnetic field values between 0 and 7 T and obtained several possible sets of solutions of which only one gave physically accepted values (all positive quantities).

Figure 6.2.5 [(a) and (b)] presents our results for the Hall mobility and the conductivity for each of the two carrier bands. We note that the electron mobility is three orders of magnitude lower than that of the holes while the electron conductivity is two orders of magnitude greater than that of the hole band. The aforementioned results are not contradictory but rather suggest that the system exhibits an enhanced electron density, which eventually dominates most transport effects.

The increasing magnetic field results in significant modifications of the σ_i , μ_i values. Specifically, σ_i increases by ~14.6% while σ_2 increases only by ~0.46% at the highest applied magnetic field of 7 T. This result is rather surprising since the situation for μ_i is reversed. Our numerical solution suggests that μ_2 increases by almost 30% at 7 T, an effect that does not seem to have an analogous impact on σ_2 . If μ_2 was simply related to the concentration of holes, p, then an explanation through recombination effects would be clearly inconsistent and counterintuitive to what one normally expects, i.e. field-assisted higher spin state transition on Co cations that presumes hole generation in the π^* band. Thus, it is clear that holes in LaNi_{0.5}Co_{0.5}O₃ are mostly related to some different mechanism other than transport.

To date, the electronic structure of the investigated system has been discussed within the single electron, two orbital (e_g - t_{2g}) approximation of the crystal field theory. However, in time it has become clear that such a model is inadequate to account for strong e-e correlations [8]. A characteristic example of the above is the existence of an intermediate spin state of d^5 and d^6 cations, which although experimentally is well established [9] cannot be realized as the ground state of a simple crystal–field system [10]. Hence, many authors have extensively examined the O 2p-Co 3d electronic hybridization and have concluded that ligand holes play an important role in the stabilization of ferromagnetic interactions in perovskite cobaltites [10-12].



6.2.5: Electron and hole mobility (a) and conductivity (b) as a function of applied magnetic field at T=5K. The plotted data were obtained from a numerical solution of equations (4)-(7) with the restriction that $\rho = \rho_1 + \rho_2$.



Fig. 6.2.6: Magnetoresistance as a function of applied magnetic field at different temperatures. Notice a slight curvature around 35 kOe in the 5K data.

Therefore, it is highly possible that the holes present in the investigated compound participate/stabilize ferromagnetic interactions between neighboring Co cations. Actually, such a claim is further supported by several experimental observations: (i) the ferromagnetic correlations in LaCoO₃ have been attributed to ligand holes introduced through self-doping (La^{3+} and/or Co^{3+} vacancies) [12], (ii) a small amount of Ni doping LaCoO₃ causes the appearance of ferromagnetic interactions and hole-like conduction and (iii) ferromagnetic correlations are gradually vanishing with decreasing x (decreasing hole concentration) [13] suggesting that eg electrons do not participate in any type of short/long range collective magnetic behavior in agreement with experimental observations for LaNiO₃ [14]. It is important to notice that the mechanism of ligand-hole ferromagnetic stabilization is doubleexchange like, i.e. dynamic in nature [10]. This may well explain the fact that hole mobility is very much increased by the application of a magnetic field in the sense that magnetic field aligns nearby moments and thus hole hopping is greatly assisted. Note that in order to be consistent with theoretical predictions [10-12] an intermediate spin state (IS, $t_{2g}^{5}e_{g}^{1}$), on Co sites is almost a prerequisite. Indeed, assuming a completely delocalized electronic σ^* band which does not participate in the formation of local moments we calculate the ratio of IS to high spin (HS, $t_{2g}^{4}e_{g}^{2}$) Co cations, from magnetization measurements, to be 4/5, which means that 80% of Co sites are in an IS state at 5K.

Figure 6.2.6 shows MR measurements at several temperatures. It is interesting to point out that the observed negative MR at T=5K reaches ~12% which agrees quite well with the calculated change in the σ_1 value (~14.6%). For completeness we should mention that the two-band conduction model predicts saturation of MR according to $\gamma \gamma x/(1+\gamma x)$ [7], which was not observed in our case. This may be attributed to the oversimplifications employed in the model since the MR mechanism is actually a lot more complicated suggesting that holes and electrons are not totally independent but on the contrary interdependent as expected for a strongly correlated system. Nevertheless, a distinct break in the MR vs applied field curve at 3.5 T provides evidence for a saturation trend at high fields.

6.3 Conclusions

We have undertaken a Hall effect study of LaNi_{0.5}Co_{0.5}O₃ thin films grown on Si (100) substrates. The Hall data are fitted well by the two-carrier conduction mechanism suggested by Chambers showing that both electrons and holes are responsible for the observed transport properties. Within the framework of the Chambers model we have shown that MR in the metallic members of $LaNi_{1-x}Co_xO_3$ is merely an electronic mobility enhancement effect as opposed to carrier generation. Deviations from Chamber's model predictions for the behavior of the MR suggests MR is a rather complicated phenomenon in these type of oxides and involves strong correlation of electrons and holes. The interpretations of our results are consistent with ligand-hole stabilization of ferromagnetism which may serve as scattering centers for electrons and therefore give rise to MR as a spin fluctuation effect proposed in chapter 5. Furthermore, the formation of the two bands as well as the domination of one over the other in the electrical/thermal transport properties pertains to substitution effects of the B site (Ni) of the archetypal LaNiO₃ structure. Therefore, Seebeck coefficient measurements on the solid solution [2] may be viewed as the sum of two opposite type carrier currents, which almost cancel out at half filling.

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Chapter 7

Magnetoresistance of the metallic compositions and the study of the metalto-insulator transition

In this chapter we present a detailed study of the zero-field electrical resistivity and magnetoresistance for the metallic members of the LaNi_{1-x}Co_xO₃ solid solution with $0.3 \le x \le 0.6$. We study in detail the logarithmic temperature dependence of the resistivity that we have identified in chapter 5. Furthermore, an in depth analysis of the data for $x \rightarrow x_c$ reveals a plethora of interesting information for the occurrence of the chemically driven MIT as well as the MR for $x > x_c$.

7.1 Magnetoresistance in compounds with x=0.3, 0.4 and 0.5

Figure 7.1.1 shows the temperature dependence of the zero-field resistivity, $\rho(T)$, for the x=0.3, 0.4 and 0.5 compounds. The resistivity of the x=0.3 compound (Fig. 7.1.1a) exhibits a linear-in-T behavior for T > 140 K and a minimum at T_{min}~45 K followed by an upturn at lower temperatures. Upon increasing the Co-doping to x=0.4, we observe a dramatic change in the behavior of the $\rho(T)$ curve (Fig. 7.1.1b). The location of the minimum in $\rho(T)$ is shifted to T_{min}~160 K and the slope of the high-temperature linear part is strongly decreased. Upon further doping (x=0.5) the $\rho(T)$ curve exhibits semiconducting-like behavior and no minimum is visible up to 300 K (Fig. 7.1.1c). Nevertheless, according to the authors of Ref. [1] the x=0.5 compound is metallic since the derivative $\partial n\sigma/\partial nT$ tends to zero at T=0.

The solid lines in Fig. 7.1.1 represent the fitting of the experimental $\rho(T)$ data to the expression:

$$\rho(T) = \rho_0 + \alpha_1 T + \alpha_2 T^{1/2} + \alpha_3 \ln T \,. \tag{1}$$

This expression contains four terms as explained in chapter 5: the residual resistivity ρ_0 term [$\rho_0=\rho(T=0)$], which accounts for the scattering of conduction carriers by static defects such as grain boundaries; a linear term (~T) which accounts for scattering by phonons and is dominant at high temperatures; a T^{1/2}-term which arises from Coulomb interactions and is dominant at low temperatures; and an *-ln*T term which is characteristic of systems with spin fluctuations [2] and is observed over a limited range of low-temperatures below T_{min}.

The magnitude of ρ_0 (see Table I) obtained from the fitting procedure steadily diminishes with decreasing Co-doping and attains a value 1.12 m Ω ·cm for x=0.3. This behavior is consistent with the fact that $\rho_0 \sim 0.5 \text{ m}\Omega$ ·cm for the metallic end member of

the solid solution LaNiO₃ [3]. In addition, the magnitude of the coefficient α_3 decreases with decreasing Co-doping; this behavior can be attributed to the suppression of spin fluctuations with decreasing x (*vide infra*).

In earlier studies the low-temperature conductivity σ of the metallic members of the investigated solid solution (x ≤ 0.65) has been found to exhibit an almost $\sim T^{1/2}$ dependence and attributed to strong electronic correlations [1]. As was the case for x=0.4 in chapter 5, inclusion of higher order terms, other than the $\sim T^{1/2}$ one, of the electron-electron (e-e) interactions resistivity expansion formula ($\rho_{e-e}(T)=\rho(0)$ $aT^{1/2}+bT-cT^{3/2}+...$) did not result to any significant improvement of the fitting error value. We, therefore, conclude that electron-phonon interactions are mostly dominant at high temperatures for all x<x_e. Thus, equation (1) is the best fitting expression with the minimum number of physical parameters for x ≤ 0.5 . For completeness, we mention that the coefficient, a₂, of the e-e interaction term in Equation (1), $\rho_{e-e}(T)\sim a_2T^{1/2}$, is equal to a₂=-m_{\sigma} ρ_0^2 , where m_{\sigma} is the coefficient of the e-e conductivity expression, $\sigma(T)\sim m_\sigma T^{1/2}$, and contains the diffusion constant, D, and the screening constant for Coulomb interactions, F_{\sigma} [4]. It is also worth mentioning that for all x the fitting resulted in negative values for the coefficient a₂ in agreement with the transformed resistivity formula [4].

Figure 7.1.2 displays the resistivity-versus-lnT curve for the x=0.3 compound measured in various magnetic fields. The existence of a linear regime clearly demonstrates that the resistivity exhibits an lnT behavior over a limited range of low temperatures (the same holds true for x=0.4 and 0.5 and are shown as insets in Fig. 7.1.2).

Next we briefly discuss the possible origin of *-lnT*. The term "spin fluctuations" is quite general in its usage and may include several cases such as (i) the Kondo effect (ii) exchange enhanced systems (iii) localized spin fluctuations (LSF) and (iv) two band scattering [2]. The first two cases have been related to s-d exchange in *dilute* alloys of a non-magnetic host. However, the strong ferromagnetic signal observed in the investigated compositions as well as the unphysical values ($T_K < 0$) of the Kondo temperature, T_K , deduced from fitting the incremental resistivity data to the Appelbaum–Kondo relation [5], $\Delta \rho(T) \sim [(T/T_K) \ln(T/T_K)]^2$, suggest that the investigated system cannot be treated in the framework of the aforementioned models and thus cases (i) and (ii) will not be further discussed.



Figure 7.1.1: Temperature dependence of the resistivity in zero magnetic field for (a) x=0.3, (b) x=0.4 and (c) x=0.5. The solid lines are fittings to the data using equation (1). In order to make the fitting clearer we have removed some of the experimental data points from the figure.



Figure 7.1.2: Resistivity versus lnT plots for x=0.3 at different applied magnetic fields (indicated on the graph). The linear fittings provide concrete evidence for the lnT dependence. Notice that the higher the field the smaller the slope of the fitted line.

Table 7.1.1: Fitting parameters of the resistivity data in the temperature range $6 \le T \le 300$ K for the LaNi_{1-x}Co_xO₃ compounds with x=0.3, 0.4 and 0.5.

	Composition		
$ ho_0$ (m Ω .cm)	1.1 ± 0.0	2.1 ± 0.0	9.3 ± 0.0
$\alpha_1 (x \ 10^{-6})$	2.4 ± 0.0	2.8 ± 0.0	7.8 ± 0.0
$\alpha_2 (x \ 10^{-5})$	-3.01 ± 0.04	-8.0 ± 0.1	-3 ± 1
$\alpha_3 (x \ 10^{-6})$	-6.5±0.8	-9.8±0.3	-1690±3
Parameter	x=0.3	x=0.4	<i>x</i> =0.5
	Characteristics of the fit [*]		
N	978	327	856
χ^2	1.74×10^{-12}	1.13x10 ⁻¹¹	1.75x10 ⁻⁹
R^2	0.9998	0.9985	0.9983
Error (%)	0.3	0.24	2.5

*N is the total number of experimental data points, $\chi^2 = (1/N) \sum (\rho_{obs} - \rho_{fit})^2 / \rho_{fit}^2$, R^2 defines the goodness of the fit, Error(%) = 100 × $(\rho_{obs} - \rho_{fit}) / \rho_{obs}$

Cases (iii) and (iv) are two more typical examples of screening effects in s-d systems, that have been extensively discussed and applied in *concentrated* alloys [6]. Within the LSF model, the incremental resistivity, $\Delta\rho(T) = \rho_{alloy}-\rho_{host}$, is a logarithmic function of temperature according to the formula:

$$\Delta \rho(T) = A + B \ln[(T^2 + \theta^2)^{1/2}], \qquad (2)$$

where θ is the spin fluctuations temperature [6]. We have performed such an analysis for the normalized incremental resistivity of the x=0.3 compound:

$$\Delta \rho'(T) = \frac{\rho(T)}{\rho(290K)} \bigg|_{x=0.3} - \frac{\rho(T)}{\rho(290K)} \bigg|_{x=0}$$
(3)

The normalized incremental resistivity has been used (instead of the incremental resistivity) in order to account for possible differences regarding the grain boundary resistances due to different packing densities of the pellets for the "alloy" and the "host". Figure 7.1.3 shows the temperature dependence of $\Delta \rho'(T)$ for x=0.3 in the temperature range 8<T<30 K plotted as a function of $\ln[(T^2+\theta^2)^{1/2}]$ in various applied magnetic fields. The best fit for H=0 T was obtained for θ =13.02±0.52 K while this value drops to 9.76 K for H=5T and 8 K for H=3T. Similar fitting to $\Delta \rho'(T; H=0)$ for x=0.4 gave $\theta \sim 11.5$ K.

The LSF model results from a modification of the conventional Kondo model assuming an additional relaxation of the "impurity spin", which in our case should be viewed as the magnetic moment of the ferromagnetic cluster, because of multiple scattering events via for example spin-orbit effects [7]. The spin fluctuation temperature θ is actually a measure of the inverse LSF lifetime, thus the decrease of θ with increasing magnetic field implies that the effect of the magnetic field amounts to the reduction of the fluctuation rates of the cluster moments by stabilizing them parallel to its direction.



Figure 7.1.3: Inset shows the plot of normalized incremental resistivity $\Delta \rho'(T)$ vs $\ln[T^2+\theta^2]^{1/2}$ for x=0.3.

Another plausible explanation stems from the relation $\rho \sim \ln[(T^2 + \Delta^2)^{1/2}]$, which describes the low temperature resistivity of amorphous alloys, i.e. structural two level systems [2]. In this case Δ is related to the energy difference between the two tunnelling states. Crystalline magnetic spin glasses are known to exhibit several physical properties at low temperatures (e.g thermal conduction), which are similar to those of amorphous materials [8]. It was thus proposed that the low-temperature behavior of spin glasses could be described in terms of magnetic two level systems, in an analogy to the structural two-level systems [8]. We suggest that a similar intra- or inter-cluster effect may take place in the π^* - σ^* bands of the investigated system. If the latter is true, then Δ should be related to a magnetic energy barrier, e.g. the magnetic anisotropy energy of the clusters, which gives rise to a random spatial variation of cluster moments that is in turn viewed as "spin fluctuations". It seems natural that decreasing the tunnelling barrier by the application of a magnetic field will result in lower resistivity values, and hence in negative magnetoresistance.

The above models can both explain the evolution of the slope of the solid lines, which fit the linear part of the ρ vs. *In*T curves, as a function of the magnetic field in fig. 7.1.2. It is evident that the higher the magnetic field the smaller the observed slope that pertains to suppression of spin fluctuations. It is important to mention that the negative MR values are higher in the metallic members of the solid solution for which spin fluctuations are stronger, i.e., they exhibit higher magnetization values and the coefficient α_3 in Equation (1) is larger. We should emphasize that both models proposed here exhibit the same functional dependence, however, they are based on profoundly different physical backgrounds. An evident drawback of the second model is that the relation $\rho \sim \ln[(T^2+\Delta^2)^{1/2}]$ has been shown to be independent of the applied magnetic field for structurally amorphous alloys [2]. Therefore, one should consider it to be purely phenomenological. It is clear that further theoretical work is needed before one concludes on the validity of the second scenario although it is plausible.

To our knowledge, there have been thus far only three reports about oxides whose resistivity exhibits a logarithmic temperature dependence, which has been attributed to Kondo scattering [9-11]. In our opinion references [10] and [11], however, do not provide any conclusive data as to whether Kondo scattering is the origin of the logarithmic dependence of the resistivity. On the other hand, although the Kondo expression seems to fit quite well the data in reference [10], no accompanying measurements, like thermoelectric power, are reported which could elucidate the nature of the Kondo interaction in this oxide. It is important to note that regardless of which of the above cases may be responsible for the lnT dependence, all of the theoretical models have been developed for metallic s-d exchange systems, i.e. wide band metallic hosts, which are in marked contrast to 3d or 4d-O 2p hybridized oxide metals. Therefore, we believe that this physical effect deserves further theoretical as well as experimental investigations.

Furthermore, all of the aforementioned explanations are in agreement with results of chapter 6 which describe the observed MR in x=0.5 as an electron-mobility enhancement effect in contrast to the p-type conduction of semiconducting compositions. The electron-mobility enhancement occurs as a result of the alignment of the moments of the ligand-hole formed clusters, which suppresses spin scattering.

7.2 The metal-to-insulator transition as a percolation phenomenon and implications about the origin of GMR.

Figure 7.2.1 displays the temperature dependence of the resistivity for the x=0.6 compound. This member of the series is a case of special interest because even though its $\rho(T)$ curve exhibits semiconducting-like behavior and the resistivity values are enhanced almost 2 orders of magnitude in comparison to x=0.5 compound, it is considered to be metallic according to the authors of Ref. 5. In addition, it has been claimed that for this doping level (regime near the metal-to-insulator transition) there is no theory that can explain the data [1]. We show next that there is enough strong evidence, which can justify the application of the cluster percolation threshold (CPT) theory.



Fig. 7.2.1: Temperature dependence of the resistivity of the x=0.6 compound. The solid line is a fit to the data using equation (6) according to which the measured resistivity can be considered as a blend of a metallic and a semiconducting component.

CPT theory has been used over the years to describe a wide variety of phenomena, including conductivity of random resistor networks, gelation of polymers and smoke particle aggregation [12]. A new application of CPT theory, with significant impact is the explanation of metal-to-insulator transitions in transition metal oxides [13]. We claim that the CPT theory is applicable in the case of the LaNi_{1-x}Co_xO₃ system based on the following facts: (i) CPT theory applies to solid solutions and requires that one end member of the solution is metallic and the other one is insulating, and that the two phases interpenetrate each other randomly. This is indeed the case for the investigated solution as we have mentioned in the introduction part. In addition, we have shown in chapter 5 that a cluster glass phase exists throughout the whole compositional range. These clusters seem to remain fairly isolated at low Ni concentrations, while they exhibit a substantial overlap at x < 0.4. (iii) CPT theory predicts, for a cubic lattice, that a metal-to-insulator transition occurs at a critical concentration $x_c=0.69$ (or $x_c=0.31$ for transition from insulating to metallic state) [14]. Note that for the investigated system $x_c=0.65$. The small deviation in the value of x_c is attributed to the non-cubic structure of the members of the investigated solid solution. (iv) CPT theory predicts variable range hopping of charge carriers in the insulating regime above the percolation limit. Our resistivity data on LaNi_{0.2}Co_{0.8}O₃ and LaNi_{0.3}Co_{0.7}O₃ (see fig. 7.2.2) provide concrete experimental evidence for the occurrence of VRH for $x > x_c$. (v) Kirkpatrick has shown that the conductance in truly percolative systems scales as $G(x) \sim (x-x_c)^n$ with $1.5 \le n \le 1.6$ [15]. In fact, because the above relation was extracted for cubic systems, n rarely takes the above-predicted values and instead varies between 1.5 and 2.1 [15, 16]. A typical example is the case of Na_xWO₃ for which n=1.8 [14]. Regarding the investigated system, we have found that the zero point conductivity σ_0 scales as (x x_c ² (see inset Fig. 7.2.3). We conclude that the aforementioned arguments (i)-(v) constitute concrete evidence to classify the metal-to-insulator transition in the investigated solid solution as a percolative phenomenon, i.e. a purely geometrical effect.



Fig. 7.2.2: Resistivity data for x=0.7 compound in the temperature range $5 \le T \le 300$ K in zero applied magnetic field. The solid lines are fits to Mott's variable range hopping expression. The existence of two linear temperature regimes is obviously associated with strong temperature dependence of the density of states at E_F , which strongly modifies the electrical transport properties.



Fig. 7.2.3: Illustration of the zero point conductivity of the investigated solid solution scaling as $(x-x_c)^2$. Blue filled circles are our data while red open squares were taken from Table III of Ref. 5.
Therefore, compounds with x just below x_c can be considered as a blend of two components, a metallic and an insulating one, with conductivities σ_1 and σ_2 , respectively. In such a case the overall conductivity σ_{tot} (i.e., the measured conductivity), is a function of the relative volume fraction of the two phases as well as the shape and distribution of the cluster particles or domains of each phase [17]. Since the mean free path, ℓ , is sufficiently small compared to the relative size of the particles [18], one can assume that the cluster particles are immersed in a homogeneous medium of conductivity σ' and use the following expression, which holds for spherical clusters [19, 20]:

$$V_1 \frac{\sigma' - \sigma_1}{\sigma_1 + 2\sigma'} + V_2 \frac{\sigma' - \sigma_2}{\sigma_2 + 2\sigma'} = 0.$$
(4)

V₁ and V₂ are the volume fractions of the metallic and the insulating phases, respectively (V₁=1-V₂). In order to proceed with the calculation of the relative volume fraction of the two phases we consider $\sigma'=\sigma_{tot}$, i.e., we assume that the particles are embedded within a homogeneous effective medium of conductivity σ_{tot} which will be determined self-consistently. Another possibility would be to consider the case $\sigma'=\sigma_2$, but this is unsuitable since the relative concentration of the insulating phase (LaCoO₃) is comparable to that of the metallic phase. The calculation of $\sigma_1 = 1/\rho_1$ was based on a high-temperature fit (T>100 K) of the resistivity data shown in Fig. 3 to the following expression, which represents the metallic phase:

$$\rho_1 = 0.055 + 3x10^{-5} T - 0.011 \ln T.$$
 (5)

On the other hand, $\sigma_2=1/\rho_2$ was obtained by fitting the resistivity data in the low temperature regime (T<40 K) to the VRH expression, which represents the insulating phase:

$$\rho_2 = 38.855 \text{ x } \exp\{2.772/T^{1/4}\}.$$
 (6)



Fig. 7.2.3: Temperature dependence of the metallic volume fraction, V_1 , for the x=0.6 compound. It is noteworthy to mention that V_1 grows to almost 100% at high temperatures (T>100K), while its value at the lowest measured temperature (T=6 K) is slightly lower than the nominal concentration of Ni cations (40%). The red solid line corresponds to data taken in magnetic field of 45 kOe.

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In both cases the maximum fitting error does not exceed 1.1%. Replacing in equation (2): $\sigma' = \sigma_{tot}$, $V_2=1-V_1$ and $\sigma_1=1/\rho_1$, $\sigma_2=1/\rho_2$ with expressions (5) and (6), respectively, we obtained the volume fraction of the metallic phase, V_1 , as a function of temperature (shown in Fig. 7.2.3). Two important observations can be made: first that the low temperature value of the metallic volume roughly corresponds to the concentration of Ni cations in the matrix and second that V_1 grows to almost 100% at ~100K. As evident from fig. 7.2.1 for T>100K the resistivity for x=0.6 (nominal [Ni³⁺]=0.4) drops two orders of magnitude and thus the compound can be considered purely metallic. It is noteworthy to point out that a similar analysis of resistivity data taken in the presence of a magnetic field of 45 kOe shows that V_1 is enhanced by 3% relative to zero field values up to 80K (red solid line of fig. 7.2.3). Evidently, the increase of V_1 in the presence of the magnetic field lends further support to the proposed picture that spatial growth of magnetic clusters is primarily responsible for the observed phenomenon of GMR in $x \ge 0.6$ compounds [7].

In order to further check the validity of the above results, we considered a naive application of Matthiessen's rule in the sense that the random interpenetration of the aforementioned (metallic + non-metallic) phases can be expressed using the expression for a series connection of resistances:

$$\rho(T) = \rho_{metal} + \rho_{semiconductor}, \qquad (5)$$

where ρ_{metal} corresponds to equation (3) and $\rho_{semiconductor}$ to equation (4). Subsequently, we used the following equation:

$$\rho(T) = \rho_0 + \beta_1 T + \beta_2 ln T + \beta_3 exp(T_0/T)^{1/4}.$$
 (6)

The solid line in Fig. 7.2.1 is the result of fitting the data of x=0.6 compound using equation (6). The maximum fitting error of the curve is 2.8% while the calculated goodness of the fit is R²=0.9990. We should mention that compositions close to x=0.65 have been previously reported to obey for a limited temperature range the empirical equation $\rho(T) = \rho_0 exp(E_a/k_BT+\theta)$ which, nevertheless, is physically unjustifiable [21].

7.3 Conclusions

In conclusion, we have undertaken a detailed study of the resistivity of the LaNi_{1-x}Co_xO₃ solid solution for $0.3 \le x \le 0.6$ in the temperature range 6-300 K. For the compounds with $0.3 \le x \le 0.5$ we found the existence of a -lnT-dependence of the resistivity which has been attributed to the existence of spin fluctuations. In addition, we interpreted the decreasing contribution of the -lnT term to resistivity with increasing magnetic field as the suppression of spin fluctuations by the magnetic field and therefore, concluded that this mechanism is primarily responsible for the magnetoresistive behavior of these compounds. The existence of a logarithmic term in the resistivity expression of an oxide is mostly unusual as well as intriguing and warrants further in-depth perusal.

Furthermore, we provided concrete evidence that the metal-to-insulator transition in this solid solution is a percolation phenomenon. We applied the CPT theory to analyze the resistivity data for the x=0.6 member and found that the metallic volume of the matrix grows to 100% around 100 K while it decreases to almost the nominal [Ni] concentration (40%) at low temperatures. Also, we found that the metallic volume in the presence of a 45 kOe field increases by \sim 3% compared to the zero field value.

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Chapter 8 Concluding Remarks

The flood of interest on the benefits of giant, isotropic negative magnetoresistance has generated the study of this phenomenon in the $LaNi_{1-x}Co_xO_3$ solid solution. The present thesis has presented a complete analysis of the GMR effect and has provided a picture that explains the magnetic, electrical and thermal properties of the system in consideration in a consistent way.

The key idea for the interpretations given in chapters 4-7 has been the identification of *ferromagnetic clusters* that generate *holes* in the LaNiO₃ and *electrons* in the LaCoO₃ matrix, respectively. Neither LaNiO₃ nor LaCoO₃ are magnetic oxides, so the exchange interactions of Ni and Co cations mediated by oxygen atoms have been recognized as the source of the observed magnetism, which nevertheless, lacks a long-range order. Specifically, the interpretation of the Hall data has provided the essence of the aforementioned interactions, which is *ligand holes* (d-holes). The existence of ligand-hole assisted ferromagnetic interactions for all x can account for the apparent insensitivity of the magnetic properties of the solution with respect to doping in the compositional regime $0.15 \le x \le 0.85$.

In the case of the metallic compositions $x < x_c$ there is a sufficient concentration of Ni cations so that a delocalized σ^* band is formed and conduction is achieved through it. Holes are participating in the conduction processes to a very limited extend since they can be viewed as mainly trapped in the cluster regions in order to stabilize energetically favorable ferromagnetic interactions. The latter explains the logarithmicin-temperature dependence of the resistivity as arising from spin fluctuations, i.e. either a spatial variation of cluster moments that contribute to spin scattering (*magnetic two-level systems model*) or a time-dependent multiple scattering process of the conduction electrons on a cluster moment that causes it to change its direction in space (*localized spin fluctuations model*). The effect of the magnetic field in both of the above models would be to orient all of the cluster moment parallel to its direction therefore reducing spin scattering or time-dependent cluster movement and thus eliminate a source of resistance.

On the other hand for $x > x_c$ the σ^* band is completely destroyed and thus electrons are isolated inside a semiconducting crystal (*Anderson localization*). In

chapter 5 we have shown that in this case, hole-conduction is achieved as an effect of disorder due to Ni doping which introduces higher spin state Co sites. These holes form ferromagnetic droplets (*bound magnetic polaron-like states*), which are able to expand in size by the application of a magnetic field. Expansion of the orbits of the holes participating in the magnetic polaron-like states normally leads to *a giant resistance drop*.

Compositions near x_c have been shown to be a blend of two components a metallic and a semiconducting one. The *percolative* nature of the *metal to insulator transition* of the solid solution has greatly assisted in the interpretation of the transport properties for all x. Apart from the electrical transport properties, the thermoelectric power has been shown to arise from a sum of two opposite in sign currents, namely a p-type and an n-type. Electron doping of LaCoO₃ through Co substitution with Ni therefore naturally explains the reduction in thermopower values with increasing Ni concentration.

PART C

APPENDICES

Appendix A1

Powder x-ray diffraction and neutron spectra analysis

X-rays were discovered in 1895 by the German physicist Roentgen and were so named because their nature was unknown at the time. We know today that x-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength. The unit of measurement in the x-ray region is the angstrom (Å), equal to 10^{-8} cm, and x-rays used in diffraction have wavelengths lying approximately in the range 0.5-2.5 Å.

Nowadays, x-ray diffraction has become the most important and easily accessible technique in solid sate chemistry for the characterization and/or crystal structure determination of materials. This is mainly due to the advance in the technology of personal computers, which has made sophisticated programs widely available for the solution of unknown structures as well as their refinement.

The *Rietveld* analysis is a method for the analysis of powder diffraction spectra. Until recently, the standard procedure in the analysis of powder diffraction was the calculation of the integrated intensity of each Bragg reflection separatly (*pattern decomposition*). This technique is easy to use in highly symmetrical, simple

A1.1 The Rietveld Method

crystal structures that generate a few distinguishable reflections. However, in the case of lower symmetry, complex structures a pattern decomposition analysis is literally impossible owing to the unavoidable overlapping of Bragg reflections.

The Rietveld method, on the other hand, has bypassed the problem of the extended overlap of reflections by using the whole diffraction spectrum for the extraction of the maximum percentage of information regarding the crystal structure. In the Rietveld method least-squares refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models for the crystal structure, diffraction optics effects, instrumental factors, and other specimen characteristics such as the lattice parameters. Initially, the Rietveld method was used for the analysis of powder neutron diffraction spectra because the profile of such diffractions can be easily described with a simple gaussian function in contrast to that of x-rays where more complex functions are required. A key feature for a successful

Rietveld refinement is the choice of a good initial model being a close approximation of the actual structure.

The quantity minimized in the least square refinement is, S_y :

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

where $w_i = 1/y_i$, y_i is the observed (gross) intensity at the *i*-th step and y_{ci} is the calculated intensity at the *i*-th step. The sum is over all data points.

In a powder diffraction pattern each Bragg reflection is characterized by its intensity I_{hkl} , which is proportional to the square of the absolute value of the structure factor $|F_{hkl}|^2$, its 2θ position on the pattern, and finally by its width and height. Typically, many Bragg reflections contribute to the intensity, y_i , observed at any arbitrarily chosen point, *i*, in the pattern. The calculated intensities y_{ci} are then determined from the $|F_{hkl}|^2$ values calculated from the structural model by summing of the calculated contributions from neighbouring (i.e. within a specified range) Bragg reflections plus the background:

$$y_{ci} = s \sum_{K} L_{K} \left| F_{K} \right|^{2} \phi(2\theta_{i} - 2\theta_{K}) P_{K} A + y_{bi}$$
(2)

where

s it the scale factor,

K represents the Miller indices, h k l, for a Bragg reflection

 L_K contains the Lorentz, polarization, and multiplicity factors,

 ϕ is the reflection profile function,

 P_K is the preffered orientation function,

A is an absorption factor (usually taken to be constant),

 F_K is the structure factor for the K-th Bragg reflection, and

 y_{bi} is the background intensity at the i-th step.

The background of a pattern, which can be either fitted to a polynomial or may be estimated with a linear interpolation, may be due to several reasons. Usually fluorescence of the sample, thermally diffused scattering, a possible amorphous phase in the sample, or the sample holder itself contribute to the background scattering. In general when the background is not too complex and can be described by a simple polynomial it is better to be refined with the rest of the variables involved in the refinement procedure.

The exact knowledge of the intensity of the diffracted radiation from the atoms contains all the desired information for the positions of the atoms in the crystal structure since it is related to the structure factor through the relations:

$$I_{hkl} = sL_{p}F_{hkl}^{2}$$
(3)
$$F_{hkl}^{2} = \left|\sum_{n} f_{n} \exp 2\pi i (hx_{n} + ky_{n} + lz_{n})\right|^{2} e^{-2W(G)}$$
(4)

(2)

where L_p is the Lorentz polarization and f_n describes the atomic scattering cross section. The sum is over all atoms n present in the unit cell at x_n , y_n , z_n positions. The term e^{-2W} is known as the Debye-Waller coefficient and describes the thermal oscillations of atoms.

The Rietveld method gives us the potential to describe and model with appropriate functions all the factors that affect the intensity of a Bragg reflection. In addition proper mathematical functions are used to model the shape of the reflections which is heavily dependent on the crystallites shape and size and on factors which have to do with the specific diffractometer used (e.g. geometry of the measurement, slits used etc.). Mathematically the final function, which describes the peak shape of the reflections, is a convolution of two independent functions one of which describes specimen broadening and the other describes broadenings owing to the instrument used.

$$h(x) = \int g(x')f(x-x')dx'$$
(5)

where $x=2\theta_i-2\theta_K$.

A widely used function for the description of Bragg reflections from x-rays or neutron diffraction is the pseudo-Voigt. The pseudo-Voigt function is a linear combination of a Lorentzian and a Gaussian function.

$$\Omega(2\theta) = \eta L(2\theta) + (1 - \eta)G(2\theta)$$
(6)

where η , the statistical weight, can be refined. In the case of x-ray diffraction η depends on the scattering angle, at very low angles (regime where instrumental broadening is dominant) the peak shape is better described by the Gaussian function whereas at high angles the peak shape has more of a Lorentian shape.

Another important parameter in the profile analysis is the width of a reflection. This is determined by the FWHM (Full Width at Half Maximum) parameter, which depends on the function used to describe the peak shape. Thus the Gaussian part is described by the function:

$$FWHM^{2} = U\tan^{2}\theta + V\tan^{2}\theta + W$$
 (7)

while for the Lorentzian part the following relation is used:

$$FWHM = X \tan \theta + Y / \cos \theta \quad (8)$$

The parameters, which determine the FWHM, are preferably refined in a procedure, which does not contain data on the position of the various atoms in the crystal and it is called LeBail analysis. The LeBail analysis, thus, is a modified Rietveld method which is used to extract the initial profile parameter values that will be used in the Rietveld refinement procedure. Normally, the LeBail values of the refined parameters (e.g. lattice constants) do not undergo drastic changes upon the Rietveld refinement cycles. Thus the LeBail analysis has been known to be a quick, practical and reliable way to determine lattice constants, phase purity etc. of a sample of known crystal structure.

During a Rietveld refinement procedure we can judge the quality of the refinement as well as the reliability of the analysis. The reliability factors are summarized in the following:

A1.2 Reliability Factors

(a) 'Weighted profile'

$$R_{wp} = \left[\frac{\sum_{i} w_{i} |y_{i} - y_{bi}|^{2}}{\sum_{i} w_{i} y_{i}^{2}}\right]^{1/2}$$
(9)

(b) 'Profile'

$$R_p = \frac{\sum_{i} |y_i - y_{bi}|}{\sum_{i} y_i} \qquad (10)$$

(c) 'R-Bragg factor'

$$R_{B} = \frac{\sum \left| I_{K}('obs') - I_{K}('calc') \right|}{\sum I_{K}('obs')}$$
(11)

(d) 'Expected-Reliability factor'

$$R_{\text{exp}} = \left[\frac{(N-P+C)}{\sum_{i} w_{i} y_{i}^{2}}\right]^{1/2} (12)$$

where N is the number of the observed points, P is the number of the parameters that are refined during the refinement cycles and C is the number or restrictions imposed in the analysis.

(e) 'Goodness of fit GofF'

$$\chi^{2} = \left(\frac{R_{wp}}{R_{exp}}\right)^{2} = \frac{\sum_{i} w_{i} |y_{i} - y_{ci}|^{2}}{N - P + C}$$
(13)

The most important of the above is the R_{wp} factor because its numerator is being minimized during the refinement cycles and gives an estimate of the quality of the measurement since it includes all of the observed data points. Furthermore, χ^2 give an indication for the reliability of the analysis. Typically acceptable values of χ^2 are close to unity.

In this thesis we have used the FULLPROF program (*J. Rodriguez-Carvajal*, *FULLPROF*, *version 3.1 d-LLB-JRC*, *ILL*, *France*, *1998*) in order to perform Rietveld and LeBail analysis of powder neutron and powder x-ray diffraction on members of the LaNi_{1-x}Co_xO₃ solid solution.

References

The above description regarding techniques of powder diffraction analysis is far from complete. Following, are just a few representative samples for the reader who would like to expand his knowledge on the field:

- *The Rietveld Method*, edited by R. A. Young (Oxford University Press, 1995)
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Appendix A2 Static and dynamic magnetization measurements

A2.1 DC Extraction

DC magnetic measurements determine the equilibrium value of the magnetization in a sample. The sample is magnetized by a constant magnetic field and the magnetic moment of the sample is measured, producing a DC magnetization curve M(H). The moment is measured by force, torque or induction techniques, the last being the most common in modern instruments. Inductive measurements are performed by moving the sample relative to a set of pickup coils, either by vibration or one-shot extraction. In conventional inductive magnetometers, as the one used in the experiments described in this thesis, one measures the voltage induced by the moving magnetic moment of the sample in a set of copper pickup coils. The voltage induced in the coils is given by:

$$V = -\frac{d\Phi}{dt}$$

so that

$$\Phi = -\int V dt$$

and the measured magnetic moment, m, is

$$m=a\Phi$$

where *a* is a calibration factor and Φ is the magnetic flux sensed by the coil. Inductive magnetometers can also be used to perform AC magnetic measurements.

A2.2 AC Susceptibility

The ac technique for the measurement of a magnetic moment provides a direct measurement of $\chi_{ac}=dM/dH$ using a sinusoidally varying field applied to the primary coil of typically ~1 Oe. Therefore no sample movement is required. The technique complements that of dc extraction by providing additional frequency dependent information.

The coil system (see fig. A2.1) is designed such that when an ac current is driven through the primary coil, the two secondary coils balance exactly (without a sample in position) since an identical signal is induced in both, and when one is subtracted from the other the resultant is zero. When a sample is introduced into one of the secondary coils, the inductance of this coil is changed due to the intrinsic

Appendix A: Experimental TechniquesA2. Static & Dynamic MagnetizationMeasurements

magnetic properties of the sample. This in turn changes the impedance of the coil, such that the voltage induced in this coil will differ from the perfectly balanced empty coil. When one is subtracted from the other the resultant voltage is no longer zero, and it is this resultant voltage that is related to the ac susceptibility χ_{ac} .



An ac field applied by the primary coil to a sample in the pick up coil will produce an out of balance voltage across the balancing coil given by:

V=V'+iV''

with the in phase (real part) and out of phase (imaginary part) voltages:

$$V' = \frac{fD\chi'h}{a}$$
$$V'' = \frac{fD\chi''h}{a}$$

where h is the amplitude and f is the frequency of the ac field, D is the volume of the sample, α is the calibration constant determined by coil geometry and χ' , χ'' the real and imaginary parts of the ac susceptibility.

A2.3 MagLab Exa Magnetometer

The MagLab Exa 2000 Magnetometer from Oxford Instruments is a multifunctional experimental platform designed to perform a set of experiments in the temperature range 1.8 to 400 K and in magnetic fields up to 7 T. During the experiments

required for this thesis, we have made extensive use of the Oxford Instruments Magnetic Properties (MP) probe (fig. A2.2) which is capable of performing both dc extraction and ac susceptibility measurements. The MagLab system provides these functions as part of a general purpose Integrated Signal Processor, controlled from a computer. The following schematic illustrates the MP probe.



Fig. A2.3: MP probe from Oxford Instruments used to perform dc extraction and ac susceptibility measurements.

Appendix A3 Resistivity measurements

All resistivity measurements were performed on bar-shaped dense polycrystalline pellets using a conventional four-probe technique in which the current is supplied uniformly across the sample while the voltage is being measured by a set of two Au wires ($\emptyset = 30\mu m$), which are used as pick-up probes and are attached to the samples with silver-paste (DUPONT, 4929). In order to reduce the resistance of the contacts we annealed the samples with the attached Au probes at 400 °C for 2 hours in flowing oxygen. The I-V characteristics were linear at the lowest and highest temperature of measurement both in zero and nonzero applied magnetic fields.

Four probe measurements of the samples with x=0.7, 0.6 and 0.5 were performed with a dc technique in which a Keithley 224 current source was used in series with the sample while a Keithley 181 nano-voltmeter was used to measure the voltage drop across the sample. The polarity of the dc current was reversed and a series of voltage measurements were taken across the sample at each point of measurement.

Samples with x=0.4 and 0.3 were measured with the use of an ac technique in which a 5210 EG&G Princeton Applied Research lock-in amplifier was used as the current source and another one as a voltmeter respectively. The amplitude of the ac current was determined through a standard reference resistance at room temperature. The use of a low frequency (\sim 18.3 Hz) ac technique in metallic samples prevents accuracy problems arising from thermal electromotive force due to overheating of the samples.

The sample with x=0.8 for T<70 K exhibited a very high resistance and thus was measured with the use of a two-probe technique through a Keithley 617 electrometer. For T>80 K the resistance of the sample was determined with the four-probe dc method.

In the following we show the schematics of the experimental set-ups used.



Fig. A3.1: Four probe dc resistivity experimental set-up.



Fig. A3.2: Four probe ac resistivity experimental set-up.



Fig. A3.3: Two probe resistivity experimental set up.

Appendix A4 The Hall effect

In 1879 while Edwin Hall was studying transport phenomena of conductors immersed in a magnetic field, he discovered that when the field was perpendicular to the applied current, there was an electric field set up in the sample perpendicular to both the applied magnetic field and the current. It was then realized that this electric field was caused due to pilling up of charge carriers (see figure A4.1) to a certain face of the sample as a result of the Lorentz force:

$$\vec{F} = \frac{e}{c} \vec{v} \times \vec{H} \qquad (1)$$

where e is the electron charge, c is the speed of light, v is the velocity of the charge carrier and H is the applied magnetic field. Furthermore, it was quickly realized that the direction of the built-up electric field was depending on the charge of the carriers. Therefore, this new effect, which is now known as the *Hall effect*, offered a quick and reliable way to identify the type of carriers (holes or electrons) in a material.



Fig. A4.1: Electrons are deflected to the edges of the sample as a result of the Lorentz force acting on them in a direction perpendicular to the

In the following we consider the two most common phenomena studied in $H\neq 0$, i.e. magnetoresistance and the Hall effect. We define a vector **d** that points towards the direction of an electric field **E** which is applied in order to create a current

density J. If d is collinear with x axis and H lies in the xy plane then the magnetoresistance is defined as

$$\frac{\Delta\rho}{\rho(0)} = \frac{\rho(H) - \rho(0)}{\rho(0)} \tag{2}.$$

In the case where H//x then the above relation defines the *longitudinal* MR while for H//z it describes the *transverse* MR.

Taking the transverse geometry (H//z) then we can express the Hall field E_H with the following relation

$$E_H = (1/2)[E_d(H) - E_d(-H)]$$
 (3).

In most cases, the Hall field is varying linearly with the product JH and this has led to the proportionality constant R, which is known as the Hall constant, according to the relation :



Fig A4.2: Illustration of the arrangements of externally applied fields on a given sample; (a) is the general case, (b) is the longitudinal magnetoresistance, (c) is the transverse magnetoresistance, (d) the transverse electromotive force.

The Hall field per unit longitudinal current density, E_H/J_x in terms of Fig. A4.2, is known as the *Hall resisitivity* ρ_H :

$$\rho_H = \frac{E_H}{J_x} = RH \tag{5}$$

However, if ρ is written as a tensor then we can come up with pretty useful relations regarding the experimental set up to be used in a Hall experiment. Thus for

$$\rho = \begin{vmatrix} \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zx} & \rho_{zy} & \rho_{zz} \end{vmatrix}$$
(6)

the transverse MR is given by:

$$\frac{\Delta \rho}{\rho(0)} = \frac{\rho_{xx}(H) - \rho_{xx}(0)}{\rho_{xx}(0)}$$
(7).

the longitudinal MR is given by:

$$\frac{\Delta\rho}{\rho(0)} = \frac{\rho_{zz}(H) - \rho_{zz}(0)}{\rho_{zz}(0)}$$
(8).

and the Hall coefficient is given by:

$$R = \frac{\rho_{yx}(H) - \rho_{yx}(-H)}{2H}$$
(9).

Using the above analysis we have chosen to perform the Hall effect study using the geometry illustrated in fig. A4.3. The transverse resistance was measured by a dc bipolar technique and the Hall resistance, R_H , was determined from the half difference of two transverse resistance measurements in the same values of positive and negative applied magnetic fields respectively.



Fig. A4.3: The geometry used for the Hall effect measurements on laser ablated $LaNi_{0.5}Co_{0.5}O_3$ thin films. The yellowish parts represent thermally evaporated golden contacts used to create E_d and measuring the Hall Voltage.

B. Growth of polycrystalline LaNi_{1-x}Co_xO₃ (x=0.3, 0.5) thin films on Si(100) by pulsed laser deposition

B1. Introduction

The measurement of the Hall effect is known to be greatly affected by the shape of the sample [1]. In particular reduction of the sample thickness usually results in an increase of the Hall voltage, and hence its accuracy [2]. Thus, growth of high quality polycrystalline thin films was of great help in order to achieve accurate Hall measurements. However, the growth of metallic oxides such as LaNi_{1-x}Co_xO₃ in thin film structures is of particular interest for a whole different number of reasons.

The metallic conductivity in LaNiO₃ has attracted a lot of attention due to potential technological applications, e.g. as a thin film electrode in ferroelectric memory elements [3] and superconducting devices [4]. Unfortunately, LaNiO₃ is particularly difficult to be prepared in a single phase with conventional ceramic procedures; the combined use of high pressure and high temperature methods is required. Furthermore, it decomposes in air at T>860 °C which results in the appearance of insulating oxide by-products (e.g. $La_{n+1}Ni_nO_{3n+1}$, and NiO) [5]. Therefore, it is difficult to prepare single-phase materials to be used as targets in pulsed laser deposition and/or sputtering. However, the random introduction of Co at Ni sites results in compounds, which can be prepared employing the usual ceramic synthesis techniques, they are very stable with respect to temperature and most importantly, they retain the desired property of metallic conductivity. Because of these properties, LaNi_{0.6}Co_{0.4}O₃ thick films have been proposed as candidates for solid oxide fuel cell cathodes [6]. In addition, the LaNi_{1-x}Co_xO₃ solid solution exhibits a transition from n to p type conduction at $x \sim 0.5$, which makes the particular system a strong candidate to be used as an electrode or buffer-layer in thin film technology [7].

Thus far selected members of the solid solution under consideration have been grown in thin film structures using chemical solution decomposition [7], metalorganic decomposition [6] and DC reactive sputtering [8]. In order to grow thin films of LaNi_{1-x}Co_xO₃ we have used Pulsed Laser Deposition (PLD), which is a very efficient technique due to high deposition rates and exhibits many advantages like the absence of any corrosive or hazardous chemicals during growth. In this appendix we report the PLD growth and characterization (including structural, magnetic and electrical properties) of polycrystalline thin-films of $LaNi_{0.5}Co_{0.5}O_3$ and $LaNi_{0.7}Co_{0.3}O_3$ on polished Si (100) substrates.

B2. Experimental

LaNi_{1-x}Co_xO₃ thin films were grown by the conventional PLD method in an oxygen atmosphere of 0.4 mbar using targets produced with the method described in chapter 1. The base pressure of the vacuum chamber was $5x10^{-6}$ mbar. A KrF excimer laser (λ =248 nm, τ =34 ns pulse duration, 600 mJ/ pulse maximum) was used, delivering a series of 5000-25000 pulses at a repetition rate of 10 Hz. The beam was incident onto the rotating target at an angle of 45° with respect to the target surface and was focused by a spherical lens to yield an energy fluence of 1.5 J/cm². The ablated material was collected on polished Si (100) substrates, placed parallel to the target at a distance of 40 mm. The substrate was heated at 650 °C using a resistive heater. After the end of deposition the films were cooled to room temperature at a rate of 5-10 °C/ min under 10 mbar pressure of oxygen. We were able to produce films of thickness, t, in the range $100 \le t \le 400$ nm. Here we report on the 100 nm thick films, which exhibited the best surfaces (i.e. they were smooth and crack-free).

The crystallographic structure of the grown films was determined by X-ray diffraction measurements using the same diffractometer as for the target materials with a thin film attachment. The morphology of the films was investigated using scanning electron microscopy (SEM). Magnetic measurements were performed in a MagLab EXA extraction magnetometer from Oxford Instruments. The electrical properties of the films were examined in the temperature range $40 \le T \le 300$ K using the conventional 4-probe method. In order to improve the electrical contact between the film and the measuring probes, we deposited gold contacts on the films using thermal evaporation and then annealed the samples at 450 °C for 2 hours in an oxygen flow. As probes we used 30µm Au wires, which were attached to the Au contacts with silver-paste (DUPONT, 4929).



Fig. B3.1.1: X-ray θ -2 θ scans (points) for thin films of LaNi_{1-x}Co_xO₃ with x=0.5 and 0.3. Both x=0.5 (a) and x=0.3 (b) thin films reproduce the expected reflection lines in the $R\overline{3}c$ space group (red solid line). The vertical bar signs indicate the positions of the expected Bragg reflections. We have denoted only major peaks and removed the contribution of the Si (100)-peak from the difference plots for clarity.

B3. Results and discussion

B3.1 Structural characteristics

The points in Figs. B3.1.1a and B3.1.1b are the obtained X-ray θ -2 θ scans for the LaNi_{0.5}Co_{0.5}O₃ and LaNi_{0.7}Co_{0.3}O₃ thin films, respectively. Using the FULLPROF program [10] all peaks were successfully indexed in the rhombohedrally distorted crystallographic space group, $R\overline{3}c$. (The red solid lines in Figs. B3.1.1a and B3.1.1b) represent the fit of the obtained x-ray spectra.) At the bottom of each graph we show the difference between the calculated and the observed diffraction patterns of the thin films (blue solid lines). Arrows indicate the Si(100) peak, which has been removed from the difference plot for clarity. Profile refinement of the obtained spectra using the LeBail method yielded lattice parameter values that are slightly larger than those of the target materials (see Table B3.1.1 for details). In addition, a careful comparison of the bulk versus the thin film x-ray diffraction patterns revealed a weak texturing in the (012) direction for all films regardless of their thickness. It is worth noting that the pseudo-cubic lattice parameter is 0.3863 nm for x=0.3 and 0.3864 nm for x=0.5, which is suitable for epitaxial heterostructures with the perovskites of enormous technological potential such as high-temperature superconductors, colossal magnetoresistive and ferroelectric materials.

Composition	$LaNi_{0.5}Co_{0.5}O3$		$LaNi_{0.7}Co_{0.3}O3$	
Lattice parameter	a=b	с	a=b	С
Target	5.4600	13.1210	5.4600	13.1380
Thin film on	5.4630	13.1740	5.4631	13.1790
Si(100)				
% Deviation	0.050	0.404	0.057	0.311

Table B3.1.1: Lattice parameters (in Å) of LaNi_{1-x}Co_xO₃ powders and 100 nm thick films.



(a)



(b)



Fig. B3.1.2: SEM images of the x=0.5 (a, b, e, f) and x=0.3 (c, d) films. The films with thickness of 100 nm (a, b, c, d) are crack-free and smooth with a low density of isolated particulates of $\sim 2\mu m$ in lateral size. On the other hand, the films with thickness of 400 nm (e, f) exhibit severe cracking.

The surface morphology of the grown films (with different thicknesses) was examined by SEM and is depicted in Fig. B3.1.2. Films of both compounds a few tens of nm thick have a smooth surface with no visible cracks (see Figs. B3.1.2a-d). Furthermore, we observe sparsely dispersed particulates of ~1-3 μ m lateral size, which have been previously reported to exist in similar oxide materials [11]. It is noteworthy to mention that deposition of thicker films (~400 nm) usually resulted in cracked surfaces (see Fig. B3.1.2e-f) regardless of the tuning in parameters like oxygen pressure, substrate temperature and cooling rate. This indicates that the lattice mismatch between the substrate and the deposited oxide film is probably of high importance and needs to be further investigated if thick films are desired.

B3.2 Magnetic properties

The investigated solid solution exhibits interesting magnetic properties at low temperatures (T<60 K) [12]. In order to check the reproducibility of the magnetic properties of the bulk materials in thin film structures, we performed dc magnetization, M, measurements as a function of dc magnetic field, H, in the temperature range 5<T<150 K. Here, we report magnetization hysteresis loops, which were recorded with the applied field, H, parallel to the plane of the films in order to eliminate demagnetization effects. Separate M(H) measurements, employing the same geometrical configuration, were carried out on polished Si (100) substrates in order to subtract the diamagnetic background signal from the measured signal of the films have been corrected for the diamagnetic signal coming from the Si substrate.

In Figs. B3.2.1a and B3.2.1b, we present hysteresis loops M(H) obtained at T=5 K for powders (filled symbols) and thin films (open symbols) of x=0.5 and x=0.3, respectively. The values of the coercive field, H_c , for both films (H_c=5 kOe for x=0.5 and H_c=2.3 kOe for x=0.3) are significantly enhanced compared to the ones of the powder samples. On the other hand, these H_c values of the as grown films are similar to previously reported values for polycrystalline materials of the same composition [13]. The observed difference in the H_c values is most likely related to the different size of the grains in the films and the powders used in our study. It is well known that as the size of the grain approaches that of the single domain the coercive force increases and then as it becomes less than that of the single domain the



Fig. B3.2.1: Magnetization hysteresis loops for both powders (black lines and symbols) and thin films (colored lines and symbols) of (a) x=0.5 and (b) x=0.3 compounds collected at T=5 K. The M(H) data of the films have been corrected for the diamagnetic background signal of the Si substrate.

coercive force decreases. In addition, the magnitude of the measured moment is enhanced for both films. The M(H) curve for the x=0.3 film (Fig. 3b) is not saturated even at the highest field applied (30 kG) and it follows a linear increase in agreement with the bulk behavior. In contrast, the M(H) curve for x=0.5 reaches saturation around ~10 kOe and exhibits a maximum of 0.6 µ_B per formula unit in agreement with local spin density approximation calculations for long range ferromagnetically ordered LaNi_{0.5}Co_{0.5}O₃ [14].

The temperature dependence of the magnetization (not shown here) agrees qualitatively with that of the powders although there seems to be a noticeable increase (~15 K) in the value of the Curie temperature, T_C . We speculate that the aforementioned phenomena (qualitative and quantitative differences in hysteresis loops as well as enhanced T_C) could be a strain effect due to the lattice mismatch of the film with the used Si substrate.

B3.3 Electrical Properties

As mentioned in the introduction of this appendix the investigated solid solution system is particularly attractive because of its metallic electrical behavior for compositions below x=0.65. The temperature dependence of the resistivity $(40 \le T \le 300 \text{ K})$ is depicted in Figs. B3.3.1 and B3.3.2 for x=0.5 and 0.3 samples, respectively. It is important to mention that the presented data were independently confirmed by two different measurement techniques, namely dc and low frequency (18.3 Hz) ac resistivity methods.

The x=0.5 film exhibits a room temperature resistivity of ~1 m Ω cm, which agrees well with the reported value for the bulk polycrystalline samples [15]. As the temperature decreases the resistivity is rapidly enhanced and reaches ~11 m Ω cm at T=40 K. Figure B3.3.1 presents a direct comparison the $\rho(T)$ curve for the thin film with that of the bulk. The two curves are in qualitative agreement. Thus we find that the x=0.5 thin film retains its metallic conductivity and bulk characteristics although it exhibits enhanced resistivity at low temperatures (more than 3 times that of the bulk bar-shaped polycrystalline samples).



Fig. B3.3.1: Temperature dependence of the resistivity (in $[m\Omega \text{ cm}]$) in zero magnetic field for the x=0.5 thin film (red line) and polycrystalline pellet (blue line).



Fig. B3.3.2: Temperature dependence of the resistivity (in [$\mu\Omega$ cm]) in zero magnetic field for the x=0.3 thin film (red circles). Notice that ρ is almost temperature-independent and less than 50 $\mu\Omega$ cm for T>200K. Inset: $\rho(T)$ for the polycrystalline pellet; notice the scale change in the ordinate axis.
Figure B3.3.2 presents the dramatic differences in the temperature dependence of the resistivity of the x=0.3 film compared to that of the bulk. The resistivity of a bar shaped polycrystalline sample exhibits a linear-in-T metallic high-temperature behavior and a slight upturn below 50 K due to electronic localization (see inset of Fig. 5) [15]. On the other hand, the resistivity of the film is almost temperature independent above 200 K, while below 100 K rises rapidly and is qualitatively similar to a temperature-induced metal-to-insulator transition. We should point out that such a behavior is not unusual in perovskite nickelates. For example, it has been shown that the temperature induced metal-to-insulator transition observed in bulk samples is strongly affected in PrNiO3 films and in fact it is completely suppressed or enhanced by strain interface effects [16]. Thus, we attribute the observed behavior in our films to the lattice mismatch between the substrates and the investigated oxide film. It is noteworthy to point out the magnitude of the resistivity values. As it is evident in Fig. 5, above 200 K the measured resistivity is below 50 $\mu\Omega$ cm and specifically at room temperature is 30 $\mu\Omega$ cm (note the scale change of the inset of Fig. 5), which is lower by a factor of three than the lowest ever reported value for LaNiO₃ thin films [17]. The low-resistivity of the x=0.3 film combined with the phase stability and ease of synthesis of bulk Co-doped LaNiO₃ makes the present material particularly attractive for low-resistance electrode applications, for example, in ferroelectric memory devices as well as in solid oxide fuel cells for power generation.

B4. Conclusions

We have successfully grown thin films of metallic members of the LaNi_xCo_{1-x}O₃ solid solution using the conventional pulsed laser deposition technique on polished Si (100) substrates. The deposited films have the same structure as the target materials with slightly higher (0.05%-0.4%) lattice parameters. The magnetic properties of the films are enhanced compared to those of the bulk. Furthermore, the LaNi_{0.7}Co_{0.3}O₃ thin film compound exhibits a very low room-temperature resistivity (~50 $\mu\Omega$ cm). This fact makes it a potential candidate for low-resistive thin film electrode applications. Most importantly, the x=0.5 thin films were shown to reproduce well most of the bulk properties and thus they are suitable to be used for Hall effect measurements to extract useful information regarding the electronic structure of the bulk.

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List of abbreviations used in this thesis

AO Atomic orbital

AMR Anisotropic MagnetoResistance

	A B			
CF	Crystal Field			
CG	Cluster Glass			
CMR	Colossal MagnetoResistance			
СРТ	Cluster percolation threshold			
EDX	Energy Dispersive X-Rays			
FC	Field Cooled			
GMR	Giant MagnetoResistance			
LSF	Localized Spin Fluctuations			
MO	Molecular Orbital			
MR	MagnetoResistance			
MIT	Metal Insulator Transition			
SEM	Scanning Electron Microscopy			
SG	Spin Glass			
TMI	ThermoMagnetic Irreversibility			
VRH	Variable Range Hopping			
ZFC	Zero Field Cooled			

UNITS FOR MAGNETIC PROPERTIES

Quantity	Symbol	Gaussian & cgs emu units	Conversion factor	Si & rationalized mks
Magnetic flux density, magnetic induction	В	gauss (G)	10 ⁴	Tesla(T), Wb/m ²
Magnetic flux	Φ	maxwell (Mx), G•cm ²	10 ⁻⁸	Weber (Wb), volt second (V•s)
Magnetic field strength, magnetizing force	Н	oersted (Oe)	$10^{3}/4\pi$	A/m
Magnetic moment	m	emu, erg/G	10 ⁻³	A•m ² , joule per tesla (J/T)
Volume magnetization	$M_{\rm V}$	emu/cm ³	10 ³	A/m
Volume magnetization	$M_{\rm V}$	G	$10^{3}/4\pi$	A/m
Mass Magnetization	σ, Μ	emu/g	$1 4\pi \Box 10^{-7}$	A•m²/kg Wb•m/kg
Molar susceptibility	$\chi_{ m mol}$	cm ³ /mol, emu/mol	$4\pi\Box 10^{-6}$ $(4\pi)^2\Box 10^{-13}$	m ³ /mol H•m ² /mol