

The effect of pressure on transport and magnetic properties of layered manganites

Dmitriy A. Sokolov



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Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless stated otherwise.

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Abstract

The bilayered manganites with general formula $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ (where Ln is a rare-earth ion) have recently attracted a great deal of interest due to the ability of some of these compounds to demonstrate colossal magnetoresistance (CMR).

The samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) and $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ were prepared using the solid state reaction and floating zone technique. The structure and magnetic properties of manganites have been studied using powder neutron diffraction technique. The effect of pressure on transport and magnetic properties of bilayered manganites has been studied using a piston-cylinder pressure cell and a diamond anvil pressure cell in the temperature range of 16-300 K and at pressures up to 75 kbar. In the course of the project a new method of laminating the gasket was developed.

In a novel $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ manganite, three different magnetic phases have been found below room temperature. Below ~ 75 K, the Mn^{4+} sublattice is antiferromagnetically (AF) ordered with an antiparallel alignment between all the nearest-neighbour manganese ions. Between ~ 75 and ~ 150 K extensive quasi two-dimensional magnetic clusters are present. At temperatures above ~ 150 K, we have observed correlations related to intradimer spin pairing.

Samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) experience a transition into a spin-glass state at ambient pressure. Analysis of neutron diffraction data revealed that in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) the key Mn-O bonds, which control the magnetic exchange, are longer than those in the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series, which demonstrates the CMR effect. Magnetic susceptibility data showed that application of pressure larger than 64 kbar resulted in the weakening of the spin-glass state and the development of long-range magnetic order. The electrical resistivity data suggested that this order was of antiferromagnetic origin.

A pressure induced local maximum on the temperature profile of the electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ was observed. The evolution of the maximum is explained in terms of competing ferromagnetic (FM) and AF short-range interactions.

Preface

In this preface, the core of the research is presented in chronological order to help the reader better understand the reasoning and motivation behind the studies reported in the following chapters.

This work has been primarily focused on studies of magnetic and structural properties of a Pr-based series of manganese oxides with a bilayered structure (general formula $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$). Initially it has been motivated by much recent interest in a similar group of La-based materials (general formula $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$), which exhibit a number of interesting properties, including the colossal magnetoresistance (CMR). Interestingly, despite the large number of various studies of the La-based bilayered manganites, there have been virtually no publications on crystallographically similar compounds based on other rare-earths, like $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ or $\text{Nd}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. This was even more surprising since $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ manganese oxides, also exhibiting the CMR effect but all having a perovskite-type structure, have been equally extensively studied in the recent past.

Therefore, it was decided to prepare several Pr-based compounds and study the effect of the substitution of La with the slightly smaller Pr ion on the physical properties of these manganites. Single crystals of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) were prepared and the magnetic susceptibility measured as a function of temperature. These measurements have revealed a rich magnetic phase diagram with three features appearing in the collected data between 4 K and 340 K. The observed magnitude of the susceptibility signal was lower than theoretically predicted. However, it was also clear from the magnetic susceptibility measurements that the samples were highly anisotropic, exhibiting different features along different directions in the crystals. Such anisotropy was expected for the bilayered structure and it has been assumed that the observed features in the magnetic susceptibility originate from magnetic phase transitions within the bilayered manganese structure.

Since there were several such transitions in each of the studied compositions, the magnetic susceptibility data were not sufficient to tell what each feature corresponds to in terms of magnetic phase transitions. Therefore, in order to clarify the nature of those features and to explain why we observed rather low susceptibility

values, a series of neutron diffraction experiments was performed. To our surprise, these measurements did not reveal any dramatic changes in the magnetic order of the Pr-based bilayered manganites. Combined analysis of the neutron diffraction and the magnetic susceptibility data has shown that apart from the majority $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ phase there was a small amount (2 - 4%) of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ intergrowth phase with perovskite-type structure in the studied samples. Two out of three of the magnetic phase transitions observed in the magnetic susceptibility data belong to the intergrowth phase, while the third transition originates from the majority phase. After analysing the magnetic phase diagram of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$, the intergrowth has been identified as $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. It experiences two phase transitions into the antiferromagnetic and into the ferromagnetic phase on cooling. The majority phase undergoes a phase transition into a spin-glass state at a low temperature.

It has been found in a number of studies conducted on bilayered manganites that perovskite intergrowths are by-products of the bilayered structure formation and are practically always present in the majority phase. In some materials like $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, for example, which show long-range magnetic order, their presence can be ignored, because the magnetic signal generated by the majority phase in the measurements is several orders of magnitude higher than the magnetic signal from the intergrowth phase. In the case of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ however, the majority phase orders into a short-range spin-glass, producing a magnetic susceptibility signal comparable with the signal produced by the 2 - 4% intergrowth phase, which displays long range magnetic order.

The presence of the intergrowth phase is clearly undesirable whenever the properties of the majority phase are considered. And, indeed, in this study it has made it quite difficult to extract the information about the majority phase from the experimental data. However, it is worth remembering that intergrowths are not merely impurities. The intergrowth material grows into the structure of the majority phase, matching its lattice parameters and aligning itself along the crystallographic axes of the majority phase (although the symmetry of the intergrowth can be different from the symmetry group of the majority phase, as was indeed observed in the case of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series). This is exactly the reason why the overall anisotropic behaviour of the sample has been observed in the magnetic susceptibility data. Interestingly, bulk samples of pure perovskite-type manganese oxides do not

show any anisotropy, although it is predicted theoretically. The reason for this is because their structure always consists of twins, which occur as a result of the structural phase transition from cubic para-phase into a structure with lower symmetry during the crystallisation at sub-melting temperatures. Because of the twinning, the bulk properties of the perovskite-type manganites always appear to be isotropic. However, it has been theoretically predicted that structural, magnetic and electronic anisotropy plays an important role in explaining the CMR effect. Therefore, finding anisotropic perovskite-type intergrowth in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ suggests a method of growing perovskite-type manganites inside non-magnetic layered manganites in a controlled way for future studies of their anisotropic properties.

The intergrowth phase has a tiny volume fraction and, therefore, does not appear in the electrical resistivity measurements, which have been conducted as the next step. The resistivity data show only a broad feature at low temperatures, characteristic of the insulating spin-glass behaviour. The analysis of the neutron diffraction data has shown that the spin-glass state occurs in the majority phase because the Pr-substitution takes Mn atoms further apart along some directions in the crystal, making it difficult to establish long-range magnetic order. It was then decided to apply external pressure to shorten those distances and bring atoms in the Mn sublattice closer to each other.

The magnetisation and electrical resistivity of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ were first measured at pressures of up to 10 kbar using a piston-cylinder pressure cell, during which no development of the long-range magnetic order was detected. The applied pressure only slightly increased the temperature of the transition into the spin-glass state. It was clear that pressure of up to 10 kbar was not high enough to induce a long-range magnetic order in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. Therefore, a diamond anvil cell capable of reaching higher pressure was used to study electrical resistivity and magnetic susceptibility. In order to conduct these studies, a new method of the laminating the metallic gasket was developed. The new method allows multiple measurements of electrical resistance at low temperatures and high pressures. Pressure generated in a diamond anvil cell was sufficient to compensate for the effect introduced by rare-earth substitution and to enhance the long-range magnetic correlations in the majority phase. The following chapters describe the studies in detail.

Thesis outline

Chapter 1 provides an introduction and gives an insight into the following subjects relevant to the studies described in the thesis:

- perovskite and layered manganese oxides and their magnetic, electronic and structural properties (colossal magnetoresistance, metal-insulator transition, Jahn-Teller distortions etc.);
- theoretical models developed to explain these properties;
- pressure effects on various manganites.

Chapter 1 ends with an outline of the objectives for the research project.

Chapter 2 is dedicated to the preparation of the samples used in the project. It provides a description of the solid state reaction and single crystal growth using the floating zone technique in a two-mirror infra-red image furnace.

Chapter 3 describes the results of the neutron diffraction studies conducted on the samples of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) series at ambient pressure. It has been found that the substitution of La ions with smaller Pr ones results in the following changes in the *crystal structure*:

- an increase of Mn-O(1) and Mn-O(2) linkages and decrease of Mn-O(3) distance;
- a decrease in the interbilayer spacing, i.e. the adjacent bilayers are brought closer to each other with higher Pr-doping level.

The *magnetic refinement* has shown that there is no long-range magnetic order in the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials in the temperature range of 1.8 K – 300 K. This is in contrast to $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ materials, which have rich magnetic phase diagrams. The analysis of the neutron diffraction data made it

possible to conclude that the absence of long-range magnetic order in the Pr-based materials can be attributed to the elongation of the MnO_6 octahedra along the c -axis. This results in a greater separation between the magnetic Mn atoms in the lattice and leads to a lesser degree of exchange interaction between them.

Chapter 4 begins with the outline of the experimental setup used in the in-house laboratory. Special attention is paid to the following issues:

- A description of the electrical resistivity measurements in the LC-10 piston-cylinder pressure cell, including a procedure for attaching the electrical leads to the samples and a method for calculating the resistivity of highly anisotropic samples;
- A technique for measuring very high resistances.

The Chapter then describes the *transport* properties of the Pr-base bilayered manganites measured at the pressure of up to 10 kbar. It was found that the behaviour of the electrical resistivity can be attributed to the thermally activated hopping of the charge carriers and that the resistivity decreases with applied pressure, which is typical for this type of conductivity. The Chapter continues with the description of the *magnetic susceptibility* measurements on $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) samples. The phase composition of the samples is analysed based on these, and previously described, measurements. It has been found that all samples contain a small amount of the perovskite impurity phase (2 - 4%) in the form of intergrowths, which is common for the layered manganese oxides. Based on the critical temperatures of the susceptibility curves, the composition of the intergrowth has been identified as being close to $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. Interestingly, the intergrowth phase “picks up” the symmetry of the majority phase, and exhibits an anisotropic magnetic behaviour which has been predicted for the perovskite manganites but has never been experimentally observed due to the twinning of the perovskite crystals. The majority phase shows a phase transition into a spin-glass state at about 50 K for all $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ samples. Pressure of up to 10 kbar did not significantly affect the magnetic properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) and no transition into the long-range ordered state was observed.

Chapter 5 begins with a description of the technique for measurements of the electrical resistance in a diamond anvil cell. A new method of laminating the gasket, developed in the course of the project, is outlined in detail.

The effect of pressures of up to 70 kbar on the transport properties of the majority phase in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is then reported. A pressure-induced transition from an insulator to a metallic-like behaviour in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ has been observed at 13 kbar. A transition developed with increasing pressure becomes more prominent at 33 kbar and disappears beyond 37 kbar leaving only an inflection point. It was also observed that the resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ below the transition temperature begins to increase at pressures above 20 kbar.

These results are analysed along with the magnetic susceptibility data collected at pressures of up to 86 kbar. The analysis shows that applied pressure weakens the spin-glass state by reducing the temperature hysteresis of the magnetisation. It has also been observed that the magnetisation considerably enlarges with increasing pressure. This fact, combined with the observed increase in the resistivity at temperatures below ~ 30 K, suggests that applied external pressure enhances the *antiferromagnetic* correlations between the bilayers in the system.

A similar transition from an insulator to a metallic-like behaviour was also observed in $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ in the pressure range between 15 and 28 kbar. However, no such transition was observed for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under pressures of up to 60 kbar. The analysis conducted in Chapter 2 shows that even though the MnO_6 octahedra in this compound are less distorted than in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, the interbilayer spacing is considerably larger, leading to the weakening of the magnetic interaction across the bilayers. The electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ decreases with pressure which is characteristic for the activated type of conductivity. It seems that pressures higher than 60 kbar are needed to induce the transition from an insulator to a metal-like behaviour in this compound.

Chapter 6 presents the structural and magnetic studies of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ - a layered manganite of a different type. The magnetic and structural properties of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ have been studied by neutron powder diffraction and magnetic susceptibility techniques between 5 and 300 K. The structure consists of pairs of face sharing MnO_6 octahedra to form Mn_2O_9 dimers. Three different magnetic phases can be

distinguished in the temperature region studied. Below ~ 75 K, the Mn^{4+} sublattice is antiferromagnetically ordered with an antiparallel alignment between all nearest-neighbour manganese ions. Between ~ 75 and ~ 150 K, extensive quasi two-dimensional magnetic clusters are present. At temperatures above ~ 150 K, one can observe correlations related to intradimer spin pairing. Truly paramagnetic behaviour is not observed at any temperature below 300 K.

Chapter 7 concludes the thesis, summarises the achievements to date and discusses potential future studies.

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Chapter 1

Introduction

1.1 Manganese oxides

Manganese oxides have attracted a great deal of interest because they demonstrate the colossal magnetoresistance (CMR) effect - a drastic increase in electrical conductivity when they order ferromagnetically (FM) (Jin *et al.* (1994)). Ramirez (1997) has reviewed recent experimental work on colossal magnetoresistance in manganites based on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ manganite is a CMR material and it is derived from the parent compound, perovskite LaMnO_3 . The LaMnO_3 ground state is antiferromagnetic (AF) (Wollan and Koehler (1955)), however, when doped at a concentration of 20 – 40% holes per Mn ion by Ca or Sr substitution for La, the material displays a transition from a high-temperature paramagnetic insulator to a low-temperature ferromagnetic metal (Jonker and Van Santen (1950)).

The relationship between magnetism and transport properties in manganese oxides can be explained using the double exchange theory (DE) (Zener (1951) and Anderson and Hasegawa (1955)). In this model the magnetic exchange is mediated by itinerant electrons, which hop between the Mn^{4+} and Mn^{3+} ions.

The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ manganite is the $n = \infty$ member of the $(\text{Ln}, \text{A})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ Ruddlesden-Popper family, where Ln is a trivalent lanthanide cation, and A is a divalent alkaline earth cation. In these compounds n two-dimensional layers of MnO_6 corner-sharing octahedra are joined along the z -direction, with the neighbouring n -layer thick perovskite blocks separated by rock-salt LnO layers (Ruddlesden and Popper (1958)). The structure of the $(\text{Ln}, \text{A})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($n = \infty$) perovskite is presented in Figure 1.1.

A bilayered manganite $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ can be considered a product of the structural modification of the perovskite type structure $(\text{Ln}, \text{Sr})\text{MnO}_3$. In this modification, a rock-salt-type layer $(\text{Ln}, \text{Sr})_2\text{O}_2$ is inserted between every two MnO_2 sheets, see Figure 1.2. The concentration of holes is controlled by the substitution of Ln ions with Sr. A reduced dimensionality, which enhances the charge and spin

fluctuation in bilayered manganites with general formula $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, makes these systems a very interesting object of study.

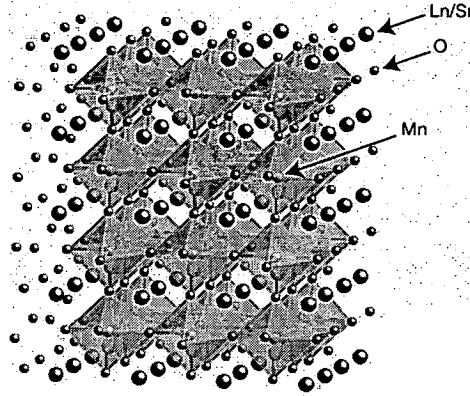


Figure 1.1: Structure of $\text{Ln}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($n = \infty$) perovskite.

The manganites $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$), were found to be ferromagnetic (FM) metals below 75 K (Kimura *et al.* (1996)) and 126 K (Moritomo *et al.* (1996)) respectively. It was found that two-dimensional (2-D) FM short-range correlations are present within the bilayer even at ambient temperature. On cooling, such correlations grow, which eventually leads to the development of long-range magnetic order in the materials (Kimura *et al.* (1996)).

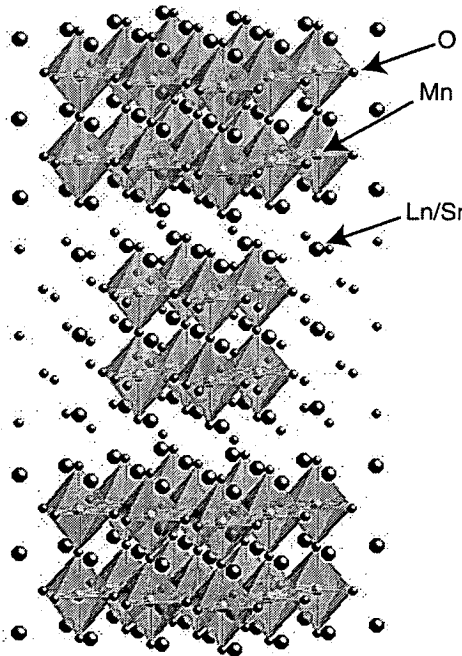


Figure 1.2: Bilayered structure of $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ manganite.

1.2 Magnetoresistance

The term magnetoresistance is used for the change in resistance measured in a magnetic field and defined by magnetoresistance ratio (MR) as:

$$MR = [R(H) - R(0)] / R(0), \quad (1.1)$$

where $R(H)$ is the resistance measured in the presence of a magnetic field, and $R(0)$ is the resistance measured in zero magnetic field.

Since the electron has a charge, the external magnetic field affects electron motion. This results in an effective decrease of the mean free path (because the cyclotron orbits of electrons shrink as magnetic field increases) and, hence an increase in resistance. In metals the change in resistance is about 2 - 3 %.

The term negative magnetoresistance is used for a decrease in resistance in a presence of a magnetic field. Searle and Wang (1969) first reported giant negative magnetoresistance in the perovskite manganites near the Curie temperature (T_c) for a crystal of $La_{1-x}Pb_xMnO_3$. Kubo and Ohata (1972) explained the phenomenon using the double exchange theory.

The Giant Magnetoresistive (GMR) behaviour has captured much attention since GMR multilayers displayed much larger magnetoresistance than any simple metal or an alloy at room temperature. Novel structures comprising magnetic layers separated by non-magnetic metallic spacer layers can exhibit GMR in which there is up to 100% change in resistance upon the application of an appropriate magnetic field, resulting from the non-parallel spin alignment of the magnetic layers at zero field. The change in resistance is caused by the spin-polarised tunnelling, Figure 1.3. The electrical current flows through the magnetic layers. Electrons with spins parallel to the magnetisation are called "spin-up"; those with antiparallel spins are called "spin-down". An electron does not meet with much resistance when its spin axis is aligned with the magnetisation in the layer it is passing through. If the next magnetic layer is magnetised in the same direction, the resistance stays low, but if it points in the opposite direction, the resistance rises. So if the fields in every magnetic layer of a multilayer point in the same direction, the resistance for the spin-up electrons is low in every layer, while the resistance for the spin-down electrons is

high. The spin-up and spin-down electrons can be thought of as forming two separate currents, flowing in parallel. When a low and a high resistance are connected in parallel, the result is a low resistance. But if the multilayers fields align in opposite directions, then both resistances are fairly large, and the combined resistance in parallel is also large. This is the origin of giant magnetoresistance. In simple terms, GMR compounds are insulators, which become conductors when there is an external magnetic field. Read heads using the GMR effect outperformed conventional ones, those based on magnetic inductance. More sensitive GMR materials allow data to be stored even more densely and read more quickly, and GMR technology is now used in most modern hard drives.

The Colossal Magnetoresistance (CMR) materials demonstrate a thousandfold change in resistance in the presence of a magnetic field. The mechanism for magnetoresistance is effectively very similar to the case of the GMR, but in the case of manganites the spin-tunnelling occurs on every Mn atom, rather than on a layer of thin film. The discovery of colossal magnetoresistance in certain oxides of manganese has stimulated intense research into the properties of manganese perovskites and may lead to a new generation of electronic devices.

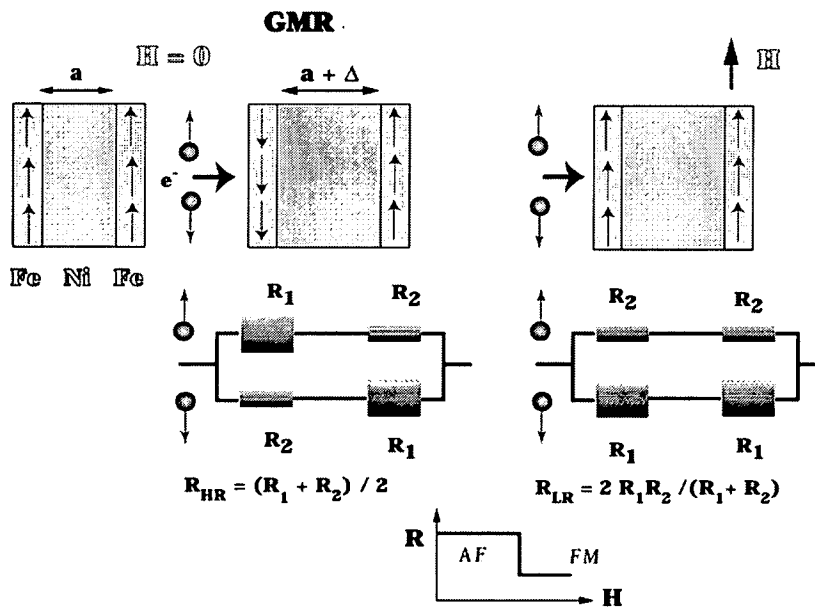


Figure 1.3: GMR model. R_1 (R_2) is the resistance of the layer with antiparallel (parallel) orientation of magnetic moments within the layer to the spin of electron. R_{HR} (R_{LR}) represents the situation where two magnetic layers have antiparallel (parallel) spin alignment with magnetic field off (on).

1.3 Colossal Magnetoresistance in manganites

1.3.1 Experimental results

The interest in manganites was stimulated after the discovery of the CMR effect in La-Ca-Mn-O films. Jin *et al.* (1994) first reported that thin films of La-Ca-Mn-O (1000 to 2000 Å thick) exhibit magnetoresistance values as high as 127000% near 77 K in a magnetic field of 6 T.

The temperature dependence of the resistivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ manganites was studied by Urushibara *et al.* (1995). They found that the resistivity of compounds with $x > 0.175$ became metallic-like below the T_c , Figure 1.4. The resistivity of materials with $x = 0.1$ and $x = 0.15$ showed a local maximum at the Curie temperature, with a transition to metallic behaviour. On further cooling, the resistivity of materials with $x = 0.1$ and $x = 0.15$ increased. Materials with x between 0.1 and 0.17 are ferromagnetic insulators.

They have also studied the effect of magnetic field on the transport properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15, 0.175, 0.2$) and found large negative magnetoresistivity around the ferromagnetic transition temperature T_c . The commonly used term magnetoresistivity is defined as $[\rho(H) - \rho(0)] / \rho(0)$, where $\rho(H)$ is the resistivity measured in a magnetic field, and $\rho(0)$ is the resistivity measured in a zero magnetic field. Therefore, the magnetoresistivity is essentially the same quantity as magnetoresistance (see 1.2).

It was shown that the application of a magnetic field shifts the resistivity maximum to higher temperatures because the magnetic field suppresses the spin scattering of the charge carriers, Figure 1.5. When the magnetisation is small, the reduction in resistivity is scaled with the change in the magnetisation:

$$-\Delta\rho / \rho = C(M / M_s)^2, \quad (1.2)$$

where $\Delta\rho$ is the reduction in resistivity and M_s is the saturation magnetisation. The coefficient C strongly depends on x in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15, 0.175, 0.2$) (Urushibara *et al.* (1995)).

The effect of magnetic field on the transport properties of $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was studied by Tokura *et al.* (1996). They have found that a first order metal-insulator transition in $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ can be caused by an

external magnetic field. The resistivity of $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($y = 0$) shows a decrease at ~ 255 K, which corresponds to the onset of the ferromagnetic state (Tokura *et al.* (1996)). With a further decrease in temperature, the resistivity shows an abrupt jump at ~ 150 K, Figure 1.6. Such a jump corresponds to a phase transition from the ferromagnetic metal to an antiferromagnetic insulator. Application of an external magnetic field reduces the resistivity around the Curie temperature due to a reduced spin scattering by field induced alignment of the local spins. The most striking effect of the magnetic field is the extension of the ferromagnetic metallic region to lower temperatures. It has also been found by the authors of the previous work that the antiferromagnetic insulating state disappears under a magnetic field above 7 T.

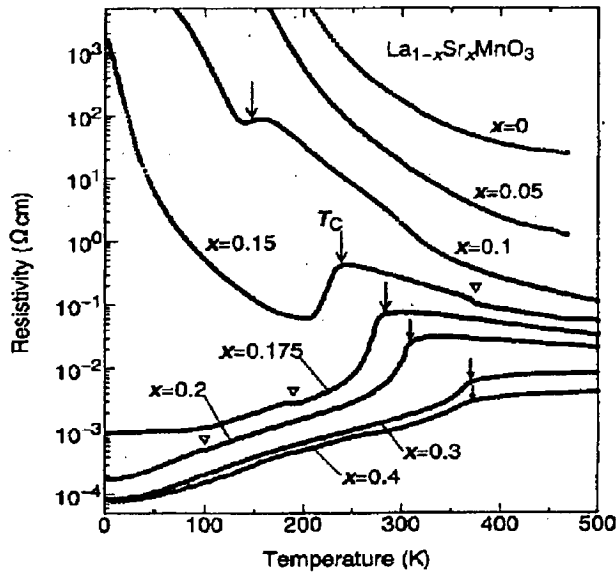


Figure 1.4: Temperature dependence of resistivity for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ crystals. Arrows indicate the critical temperature for the ferromagnetic transition. Anomalies indicated by open triangles are due to the structural transition (After Urushibara *et al.* (1995)). Copyright of the American Physical Society (1995).

Kuwahara *et al.* (1995) have also observed a hysteresis on the resistivity of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ during the increase and decrease of the external magnetic field at a fixed temperature. They also found that the hysteresis region depended critically on temperature and expanded drastically with a decrease of temperature, perhaps as a

result of suppression of the effect of thermal fluctuations on the first-order phase transition.

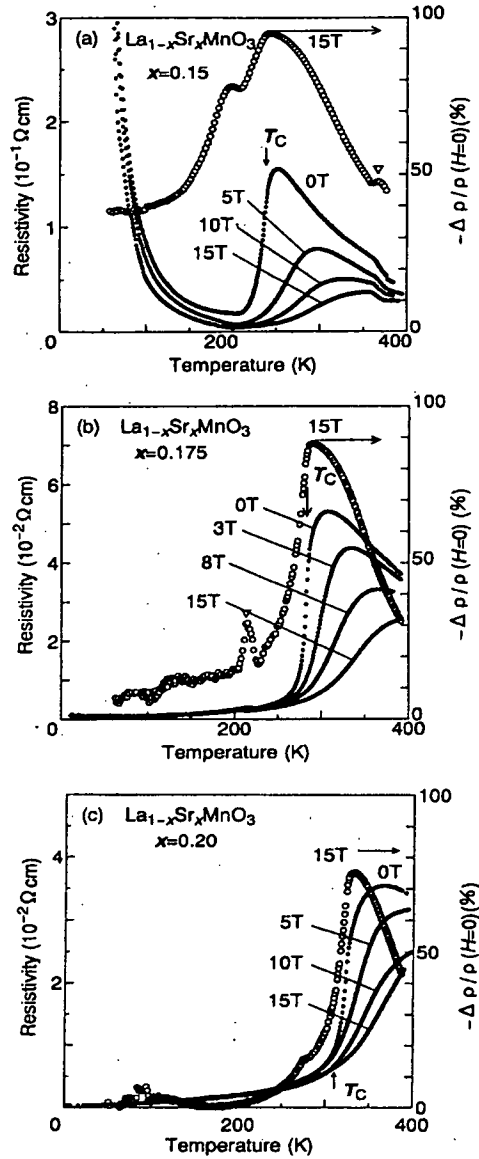


Figure 1.5: Temperature dependence of resistivity for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15$) crystal under various magnetic fields. Open circles represent the magnitude of negative magnetoresistance $-\left[\rho(H) - \rho(0)\right] / \rho(0)$ with the magnetic field of 15 T. Open triangles represent the structural transitions (After Urushibara *et al.* (1995)). Copyright of the American Physical Society (1995).

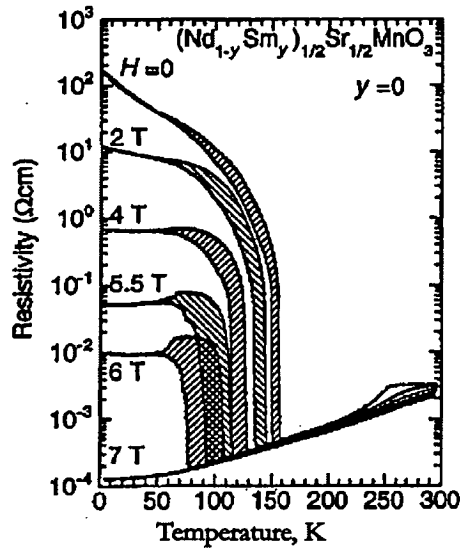


Figure 1.6: Temperature dependence of resistivity of $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($y = 0$) under various magnetic fields. A pair of curves allotted to each magnetic field corresponds to the cooling and warming runs. The hatched area represents a thermal hysteresis (After Tokura *et al.* (1996)). Copyright of the American Physical Society (1996).

A similar effect of an external magnetic field on the resistivity of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was observed by Tomioka *et al.* (1995). They reported that $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ becomes a ferromagnetic metal at ~ 280 K. The magnetisation of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in the ferromagnetic state increases on cooling and at ~ 170 K $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ transforms into an antiferromagnetic nonmetal. The authors of the previous work also found that the temperature of a nonmetal to metal transition was decreased to near 0 K with a magnetic field of 7 T.

Tomioka *et al.* (1996) have studied the metal-insulator phase diagram of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, ($0.3 \leq x \leq 0.5$). They have found field induced metal-insulator transitions in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, ($0.3 \leq x \leq 0.5$). The magnetic field of 6 T was needed to induce the metal-insulator transition in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, ($0.3 \leq x \leq 0.5$). The magnetic field of 12 T was needed to destroy the insulating state in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.35, 0.4$) at all temperatures.

$\text{La}_2\text{SrMn}_2\text{O}_7$ ($x = 0$) was found to be a Mott insulator (T. Hayashi *et al.* (1998)). In $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, x stands for the number of holes per Mn site. Temperature dependence of c -axis resistivity of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3$)

demonstrates a sharp peak at $T \sim 100$ K with metallic-like behaviour below 100 K and semiconducting behaviour above 100 K (Kimura *et al.* (1996)). They associated the drop of c -axis resistivity with the three-dimensional (3-D) weak antiferromagnetic coupling between bilayers. However, the inplane measured resistivity showed a broad maximum at $T \sim 270$ K where the magnetisation deviates from the Curie-Weiss law. This indicates that two-dimensional (2-D) ferromagnetic correlations are present in the system in the temperature interval between 270 K and 100 K. In this temperature interval the material can be considered as a 2-D ferromagnetic metal. It was found that applied magnetic fields shift the temperature of the metal-insulator transition into higher temperatures and suppress the value of the resistivity maximum, Figure 1.7.

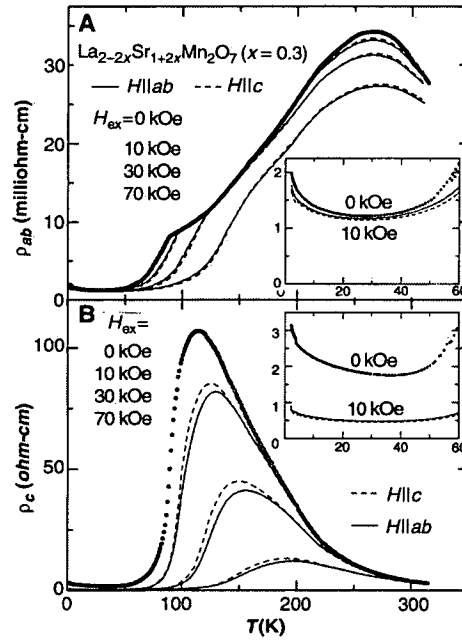


Figure 1.7: Temperature dependence of resistivity with (A) current parallel to the MnO_2 bilayer (ρ_{ab}) and (B) perpendicular to the MnO_2 bilayer (ρ_c) in various magnetic field orientations, in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3$) crystal. Inset: Expanded view of the low-temperature region, which shows the much greater magnetoresistance effect in ρ_c than in ρ_{ab} at the field of 10 kOe. The axis labels in the main panels also apply to the inset (After Kimura *et al.* (1996)).

Moritomo *et al.* (1996) have studied the temperature dependence of the inplane and c -axis resistivity of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4$) under various magnetic fields. They reported that in contrast to the $x = 0.3$ compound, both resistivities showed the

activated behaviour with a decrease in temperature down to the Curie temperature. At around 126 K both resistivities demonstrated a steep decrease by more than two orders of magnitude. The authors have observed a metallic behaviour in the temperature interval between ~ 126 K and ~ 20 K. Application of a magnetic field suppresses the magnitude of the step in electrical resistivity and increases the temperature of the metal-insulator transition. Battle *et al.* (1996) have studied $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ ($x = 0.0, 0.1$) and found that both materials demonstrated the CMR effect; however neither compound showed a transition into the ferromagnetic state. The resistivities of these materials remained high ($\rho > 10^3 \Omega\cdot\text{cm}$) for $4.2 < T/\text{K} < 100$.

1.3.2 Theoretical models

Double-exchange and super-exchange

The magnetic ordering in manganites can be explained within the framework of the double exchange theory (Zener (1951) and Anderson and Hasegawa (1955)). Ln and Sr ions do not contribute to the long-range order magnetism. The magnetic order in the system is created by the exchange coupling between ions of Mn.

The electronic configuration of the $3d$ shell in the Mn atoms consists of a t_{2g} triplet and an e_g doublet, Figure 1.8. The $3d_{x^2-y^2}$ or $3d_{z^2}$ dumbbell of the e_g orbital is aligned along the Mn–O bond, while the electronic density in any of the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, orbitals is concentrated between the bonds. Oxygen's $2p$ electronic shell also has two types of orbitals: p_σ , along the Mn–O bond, and p_π , perpendicular to the bond. Therefore, the p_σ orbital is orthogonal to the t_{2g} orbital, while the p_π is orthogonal to the e_g . Electron transfer can only take place between non-orthogonal orbitals, i.e. between a p_σ and e_g orbitals as well as between the p_π and t_{2g} orbitals. The overlap between p_σ and e_g orbitals is greater than the overlap between p_π and t_{2g} orbitals because the former two are aligned along the Mn–O bond. Since the orbital overlap along the bond is greater, and because the t_{2g} electrons are more localised than the e_g electrons due to the lower energy of the triplet with respect to the doublet, $p_\sigma - e_g$ transfer is stronger than $p_\pi - t_{2g}$, (Goodenough (1963)).

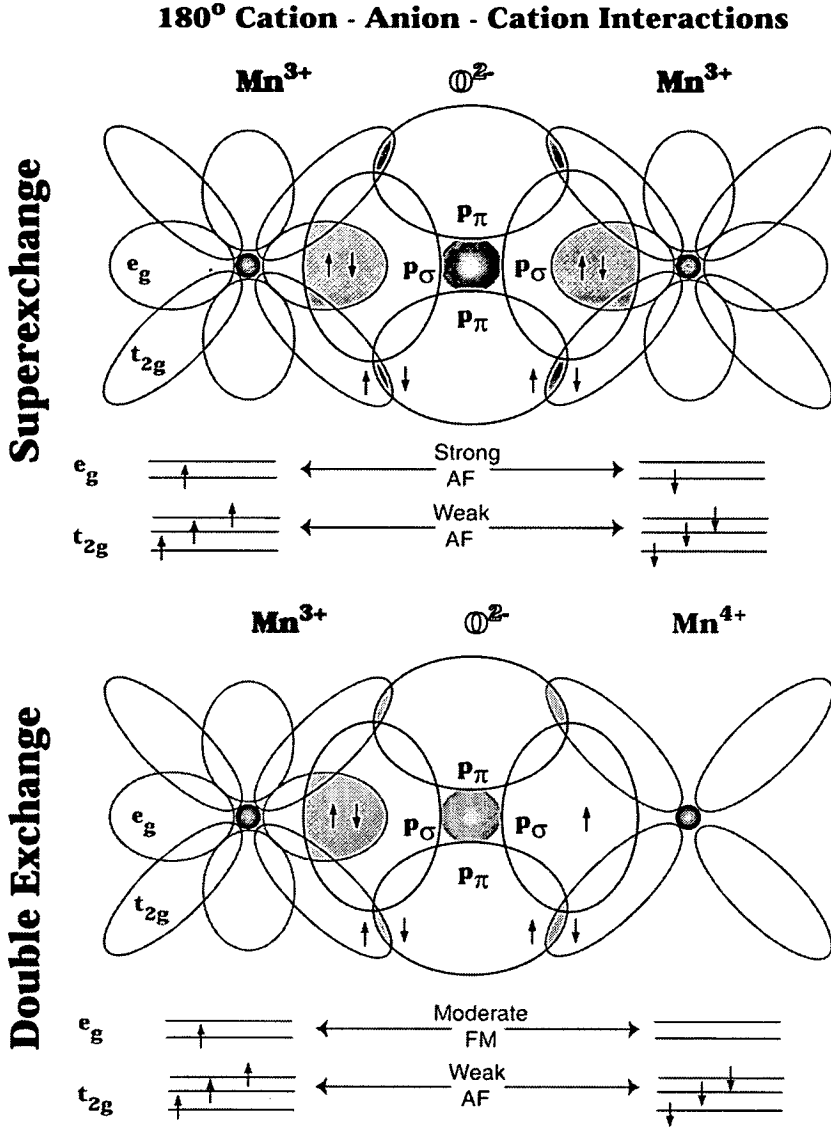


Figure 1.8: Antiferromagnetic 180° cation-anion-cation Super-Exchange between 3d-electrons and ferromagnetic 180° Double-Exchange between 3d-electrons.

In undoped manganese oxides ($x = 0$) all Mn ions have four 3d-electrons of which three occupy the t_{2g} triplet and the other occupies an e_g orbit. The Pauli exclusion principle constrains the number of electrons of each spin in the $p_\sigma - e_g$ and $p_\pi - t_{2g}$ overlap regions to one. Therefore, only antiparallel coupling of spins is allowed on both ends of the cation–anion–cation bond, giving rise to an antiferromagnetic (AF) order of the magnetic moments. This AF coupling is called *super-exchange* (Anderson (1950)).

When the rare-earth ion Ln, in $(\text{Ln}_{1-x}\text{A}_x)_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($x = 0$), is substituted by a divalent ion, A, some Mn^{3+} ions become Mn^{4+} ions after transferring their e_g electron

to the divalent ions. In this instance the p_σ orbital overlaps with empty e_g orbital on one side of the $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$ bond, Figure 1.8. Therefore, the transferred p_σ orbitals are antiparallel to the cation spin on one side and parallel on the other, resulting in ferromagnetic (FM) coupling. The $p_\pi - t_{2g}$ overlap still favours AF coupling but it is now weaker than the FM coupling from $p_\sigma - e_g$ overlap and so the net interaction is FM. This FM coupling between the Mn atoms of different valence is called *double-exchange* (DE) (Zener (1951) and Anderson and Hasegawa (1955)).

Zener (1951) defined wavefunctions representing the configuration of the system before and after electron transfer as follows:

$$\begin{aligned} \Psi_1: & \text{Mn}^{3+} \text{O}^{2-} \text{Mn}^{4+} \\ \Psi_2: & \text{Mn}^{4+} \text{O}^{2-} \text{Mn}^{3+} \end{aligned} \quad (1.3)$$

A B C

The exchange energy is given as:

$$E = \int \Psi_1^* (H - \epsilon_0) \Psi_2 d\tau, \quad (1.4)$$

where H is a hamiltonian, of the whole system, ϵ_0 is the energy associated with the initial states, Ψ_1 and Ψ_2 and the integral is extends over coordinates and spins of all electrons. The dominant term in the intergrand involves the following product of the wavefunctions:

$$(A|1)^*(B|1)^* (B|2)^* (C|2). \quad (1.5)$$

Here (A|) and (C|) are the wavefunctions of Mn^{3+} and Mn^{4+} ions respectfully, while (B|) is the wavefunction of the O^{2-} ion. Therefore, the electron transfer form the left Mn ion to O^{2-} and from O^{2-} to the right Mn ion can be visualised simultaneously. This electron transfer is called *double exchange*.

Polarons

Millis *et al.* (1995) solved a double-exchange model for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, ($0.2 < x < 0.4$) and predicted several experimental consequences which disagreed

with actual experimental data by an order of magnitude or more. They reported that the DE theory alone can not explain the resistivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, ($0.2 < x < 0.4$). The authors have proposed an addition to the DE theory, which takes into account polaron effects due to a very strong electron-phonon coupling, coming from the Jahn-Teller splitting of the Mn^{3+} ion. Jahn and Teller (1937) found that if the lowest energy level for an ion is degenerate, a spontaneous or dynamic distortion occurs, which splits the energy level and produces a lower ground state. Millis *et al.* (1995, 1996) have also reported that the electron-phonon coupling constant λ was large in a high temperature state, and, therefore the charge carriers were polarons. On cooling, the growing ferromagnetic order increases the bandwidth and hence reduces the λ enough to enable the metallic behaviour below the Curie temperature (T_c). The polaronic nature of the charge carriers was confirmed by a giant isotope effect (Zhao *et al.* (1996)), sign anomaly of the Hall effect, and the Arrhenius behaviour ($\ln\{\sigma T = A/T\}$, where σ is a conductivity, T is a temperature and A is a constant) of the drift and Hall mobilities over a temperature range from $2T_c$ to $4T_c$ (Jaime *et al.* (1997)). However, it was suggested that even below T_c the polaronic hopping was a dominant conduction mechanism (Hundley *et al.* (1995)). There are also published results on electron energy loss spectroscopy (EELS) showing that the manganites have p holes as the current carriers rather than $\text{Mn}^{3+} d$ electrons (Ju *et al.* (1997)).

The photoemission and O 1s X-ray absorption spectroscopy of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ showed that the itinerant holes doped into LaMnO_3 are of oxygen p character, and their coupling with d^4 local moments on Mn^{3+} ions align the moments ferromagnetically (Saitoh *et al.* (1995)). The calculated resistivity is in poor agreement with the data and the characteristic theoretical field (the magnetic field H that destroys an insulating state); $H \sim 15$ T for CMR is too high compared to the experimental one ($H \sim 4$ T) (Millis *et al.* (1995, 1996)). As a result, self-trapping above T_c and the idea of metallization below T_c alone do not explain CMR either. Charge carriers retain their polaronic character well below T_c , as also manifested in the measurements of resistivity under pressure (Zhou *et al.* (1997)).

An electron in a localised state, in either a crystalline or a non-crystalline material, will always distort its surroundings to some extent. A significant distortion of the surroundings can also occur if a free electron possesses a large effective mass. A quasi-particle, which consists of the electron and the distortion that the electron

produces, can travel as a whole. This quasi-particle is called a polaron (Mott and Davis (1979)).

The concept of the polaron can be illustrated on a system where a bound electron's energy depends on a general coordinate q (Mott and Davis (1979)). The coordinate q can be a change in the distance between ions in a crystal lattice, caused by the presence of a localised electron. The energy of the lattice is $A q^2$, while the energy of the bound electron is $-B q$. Therefore, the total energy is

$$E = A q^2 - B q, \quad (1.6)$$

where A and B are some constants. Such a function has a minimum at $q_0 = B / 2A$. This means that the energy of the bound electron is lowered by Bq_0 . The energy of the whole system is lowered by

$$A q_0^2 = 1 / 2 B q_0 = B^2 / 4A \quad (1.7)$$

The polaron behaves like a particle with enhanced effective mass, and a mean free path tending to infinity at low temperature. The polaron is strongly scattered by the phonons. The mean free path l of the polaron becomes comparable with the distance between the possible sites at the temperature $\sim 1 / 2\Theta$, where Θ is the Debye temperature. At higher temperatures the thermally activated hopping sets in, while the mobility μ obeys the relation:

$$\mu \sim \exp (-W_H / k_B T), \quad (1.8)$$

where W_H is the hopping energy. The resistivity of a semiconductor, in which the principal mechanism of conduction is polaron hopping, has a maximum (Mott and Davis (1979)). At low temperature electrons are bound to donors. On heating, at $T < 1 / 2\Theta$ when all electrons are free and $k_B T \ll \hbar \nu / 2$, they work as charge carriers scattered by phonons, and the resistivity raises with the temperature increase. At $T > 1 / 2\Theta$ the conduction is due to hopping, and the resistivity decreases with the increase of temperature.

Alexandrov and Bratkovsky (1999) have proposed a model in which colossal magnetoresistance and ferromagnetism in doped manganites are explained by

exchange interactions of the polaron carriers with localised spins. The strength of the interaction determines whether the transition is first or second order. A large drop in the number of current carriers during the transition, a consequence of bound pair (polarons tend to form bound pairs) formation in a paramagnetic phase close to the transition, is extremely sensitive to the strength of an external magnetic field. This carrier density collapse describes the resistivity peak and the colossal magnetoresistance of doped manganites (Alexandrov and Bratkovsky (1999)). The strong electron-phonon interaction binds two holes into a pair (bipolaron) (Alexandrov and Mott (1995))

It is the localisation of p holes into immobile bound pairs, combined with their exchange interaction with the Mn d^4 local moments, that is responsible for CMR (Alexandrov and Bratkovsky (1999)). The density of these pairs has a sharp peak at a ferromagnetic transition when the system is cooled down through the critical temperature T_c . Below T_c , the binding of polarons into pairs competes with the ferromagnetic exchange. This tends to align the polaron moments, and therefore breaks those pairs apart. These competing interactions lead to unusual behaviour of the CMR materials and a huge sensitivity of their transport to the external field. The remarkable observation is that there is a sharp increase of the polaron density at temperatures below T_c . The physical origin of the unusual minimum of the current carrier density at T_c lies in the instability of bipolarons below T_c , which is due to the exchange interaction of polarons with d electrons (Alexandrov and Bratkovsky (1999)).

1.4 Manganites with short-range magnetic order

Since the discovery of the CMR phenomenon in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ manganites, there were attempts to detect the CMR effect in other $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ materials. Battle *et al.* (1997a) have studied the effect of lanthanide size on magnetic properties of polycrystalline $\text{LnSr}_2\text{Mn}_2\text{O}_7$ ($\text{Ln} = \text{Nd}, \text{Pr}, \text{Gd-Er}, \text{Y}$) materials. They have discovered that samples with a larger lanthanide cation like Pr and Nd demonstrate the co-existence of the antiferromagnetic phase with small ferromagnetic clusters. In samples containing smaller cations ($\text{Ln} = \text{Gd-Er}, \text{Y}$), the authors of the above mentioned work have found spin-glass magnetic ordering. They have explained the magnetic properties using the variation in the relative strength of *super-exchange* and *double-exchange* interactions as a function of the lanthanide cation. Later, Battle *et al.* (1997b) carried out neutron diffraction studies of polycrystalline $\text{Sr}_2\text{HoMn}_2\text{O}_7$ and $\text{Sr}_2\text{YMn}_2\text{O}_7$ and confirmed that these materials do not show any long-range magnetic ordering. Instead both compounds undergo a transition into a spin-glass state.

Moritomo *et al.* (1997b) have investigated the lattice effect on the anisotropic magnetic and transport properties of single crystals of $(\text{Ln}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. They reported that the ferromagnetic transition temperature T_c is suppressed from $T_c = 130$ K for $z = 0.0$ to 80 K for $z = 0.2$. The transition eventually disappears beyond $z = 0.4$. Samples with $z \geq 0.4$ undergo a transition into a spin-glass state. They attributed the suppression of the long-range magnetic order to an increase of $d_{3z^2-r^2}$ character in the occupied e_g state due to the Jahn-Teller distortion of the MnO_6 octahedra.

Therefore, it seems that there is a number of bilayered manganese oxides which do not show any long-range magnetic order, while their counterparts with the perovskite type structure and the same $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio develop long-range magnetic correlations.

1.5 Effect of pressure on structural, magnetic and transport properties of manganese oxides

Hwang *et al.* (1995b) have studied the effect of pressure on the magnetoresistance in doped manganese perovskites. They found that the application of external pressure monotonically increases the Curie temperature in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, Figure 1.9. The application of external pressure, and a chemical one (the substitution of La with other rare earth ions), leads to a modification of the Mn-Mn electronic transfer integral (Hwang *et al.* (1995a), Hwang *et al.* (1995b)).

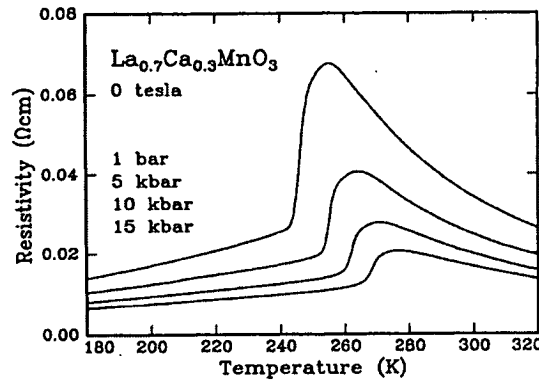


Figure 1.9: The pressure dependence of the resistivity for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (After H. Hwang *et al.* (1995b)). Copyright of the American Physical Society (1995).

Moritomo *et al.* (1997a) have studied the effect of chemical and external pressures on $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$. The doped manganites often undergo a phase transition into a charge-ordered state (CO), where Mn^{3+} and Mn^{4+} show a real space ordering in the crystal (Kuwahara *et al.* (1995) and Tokura *et al.* (1996)).

Moritomo *et al.* (1997a) distinguished 2 types of the charge-ordering transitions. In type 1, the charge-ordered state emerges with the concomitant antiferromagnetic (AF) ordering in the metallic ferromagnetic phase below the Curie temperature ($T_{\text{co}} < T_c$, where T_{co} is the temperature of a transition into the charge-ordered state). Kuwahara *et al.* (1995) reported that $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ belongs to this type of CO. They established that $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ becomes a conducting ferromagnet below $T_c = 250$ K and then an antiferromagnetic charge ordered insulator below 158 K. In type 2 of the CO systems, the charge-ordering phase occurs at higher

temperatures and no ferromagnetic metallic (FM) phase is present (Moritomo *et al.* (1997a)). $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 < x < 0.7$) belong to type 2 of the CO systems.

In $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, the Nd ions were partially substituted with larger La ones, leading to an increase of the 3d-electron hopping interaction (Moritomo *et al.* (1997a)). It was found that with an increase in concentration of bigger La ions in $(\text{Nd}_{1-z}\text{La}_z)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, the one-electron bandwidth (W) increases. They also reported that with an increase of the one-electron bandwidth, the enhanced ferromagnetic double-exchange interaction increases the Curie temperature (T_c) and suppresses the charge-ordered state with a concomitant antiferromagnetic charge-exchange (CE) type spin ordering. The charge-ordering temperature decreases from $T_{co} = 158$ K at $z = 0$ to $T_{co} = 120$ K at $z = 0.4$, and the charge-ordered state disappears above $z = 0.6$. Application of an external pressure also increases the value of W and induces the transition from AF-CE to AF-A (layered) type for $z = 0.4$.

For $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, the application of external pressure induces the metallic state from the low temperature region in the charge-ordered insulating phase (Moritomo *et al.* (1997a)). The temperature dependence of the resistivity of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.3$) was measured under hydrostatic pressures of up to 1.5 GPa (15 kbar). $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is a CMR material and shows a metal-insulator transition at low temperatures under a magnetic field (Hwang *et al.* (1995b)). At a pressure of 0.5 GPa, a steep drop in the resistivity of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ by more than eight orders of magnitude was observed, Figure 1.10. At a pressure of 1.5 GPa the temperature of this transition increases to ~ 120 K, Figure 1.10. Pressure also decreases the value of the resistivity drop, Figure 1.10. Moritomo *et al.* (1997a) have found a scaling relation between the field- and pressure-induced shifts in the temperature of the metal-insulator transition; the effect of the magnetic field of ~ 6 T is almost equivalent to that of pressure of 1 GPa. Such a scaling relation suggests that the basic mechanisms for the pressure- and field-induced metal-insulator transitions are similar to each other.

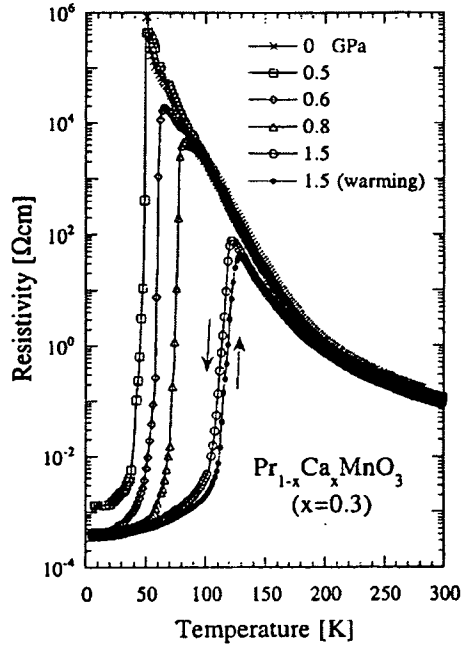


Figure 1.10: Temperature dependence of resistivity for a $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.3$) (After Moritomo *et al.* (1997a)). Copyright of the American Physical Society (1997).

Hwang *et al.* (1995b) have studied the impact of chemical pressure (Pr doping) on the crystal structure of LaMnO_3 and found that variations in the size of Ln ions, or external pressure, affect the overlap between the manganese d , and the oxygen p , orbitals. The Pr ions are too small to fill the space in the 3-D network of the MnO_6 octahedra. The smaller Ln ion causes the octahedra to rotate which reduces the excess of space around the Ln site. This results in $\Theta < 180^\circ$, where Θ is the Mn-O-Mn bond angle, which is 180° in LaMnO_3 . The application of external pressure decreases the rotation of the MnO_6 octahedra through the reduction of the ionic size mismatch. This can also be viewed as the result of more dense packing of the oxygen ions around the Ln ion. Therefore, both applying the external pressure and introducing the larger Ln ions leads to an increase of the transfer integral as these two factors cause the same geometrical changes.

Moritomo and Itoh (1999) have studied the effect of chemical pressure on the magnetoresistance of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. The La ions were substituted with smaller Nd ones. They reported that in a $(\text{La}_{1-z}\text{Nd}_z)_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ crystal with bilayered structure, Nd doping changes the ferromagnetic ground state to the antiferromagnetic one. In the parent compound $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, a metal-insulator transition is observed at ~ 100 K. With an increase of z , the metal-insulator transition becomes blurred. The

value of the resistivity measured along the bilayer increases with an increase of z . A prominent upturn of resistivity occurs in the AF state.

Kamenev *et al.* (2000) have reported that $(\text{La}_{0.6}\text{Nd}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ shows a transition into a spin-glass state at low temperature. The amplitude of the peak on the magnetisation curve increases with the applied pressure and reaches a maximum at 1.9 GPa. On further increasing the pressure, the amplitude of the peak starts to decrease. However, pressures of up to 7.1 GPa shift the spin-glass transition to higher temperatures monotonically. At ambient pressure the Mn atoms in the $(\text{La}_{0.6}\text{Nd}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ are brought closer to the centre of each bilayer and the O(3)-Mn-O(3) angle is about 178.8° . The MnO_6 octahedra are elongated towards the outer ends of each bilayer along the c -axis. Three different O positions in a MnO_6 octahedron are shown in Figure 1.11. When external pressure is applied, the length of the Mn-O(1) bond increases, while the length of the Mn-O(2) bond decreases. This change is caused by a shift of the Mn atoms towards the outer edges of the bilayer along the c -axis. The change is continuous up to about 1.2 GPa. At this pressure a discontinuous change in the bond lengths is observed. The interchange in the inter-atomic bonds is accompanied by further distortion of the O(3)-Mn-O(3) angle and by a decrease in the Mn-O(3) bond length.

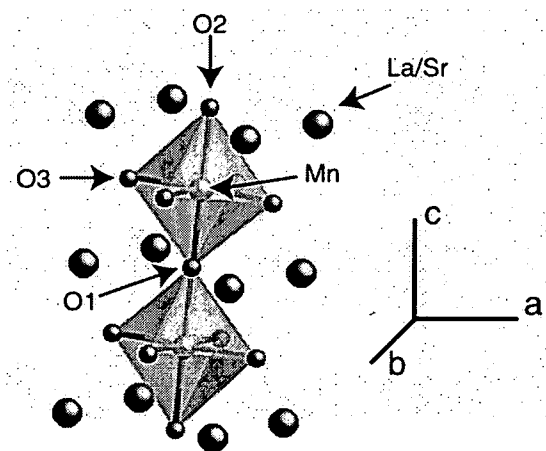


Figure 1.11: Three different O positions in MnO_6 octahedron in bilayered manganites. Axis c is the four-fold axis.

Despite the dramatic change in the individual axial Mn-O bond lengths, the mean bond length $[\text{Mn-O}(1) + \text{Mn-O}(2)]/2$ is almost unchanged in the pressure range from 0 to 3 GPa (Kamenev *et al.* (2000)). In other words, the spacing between the O(1) and O(2) atoms, representing effectively the “thickness” of the bilayer, remains constant. The application of pressure results mainly in a shift of the manganese atom along the O(2)-Mn-O(1) linkage towards the O(2) atom, due to a rather high in-plane compressibility as discussed above.

Argyriou *et al.* (1997) have observed a similar effect in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, at pressures of up to 0.63 GPa. They found that in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ the Mn-O(1) bond length decreases and Mn-O(2) bond length increases under pressure. Since the Mn-O(2) bond is not part of the Mn-O-Mn linkages, the Mn-O(2) bond adjusts to the changes in length of the Mn-O(1) and the Mn-O(3) bonds to conserve the mean equilibrium bond length sum for the Mn valences (Kamenev *et al.* (2000)). The applied pressure does not change the thickness of the bilayer, but it affects the interbilayer spacings and brings rigid bilayers closer to each other. Therefore it is possible to describe the effect of pressure as a twofold one. It shifts the manganese atoms away from the centre of each bilayer and brings bilayers closer together.

It is well known that in manganites with the three-dimensional perovskite structure the e_g electron in the Mn^{3+} ion has orbital degrees of freedom in addition to the charge and spin (Ishihara *et al.* (1997)). They found that the orbital plays an important role in the spin and charge dynamics in manganites. Orbital degrees of freedom strongly couple with the lattice, therefore, the structural change due to applied pressure results in a modification of the orbital state.

Ishihara *et al.* (1997) confirmed the change of the orbital state having calculated the Madelung potential for the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals and showed that the $d_{x^2-y^2}$ orbital is relatively stabilised with an increase of pressure. They reported that the spin and charge dynamics are restricted within the ab -plane under the $d_{x^2-y^2}$ orbital state. As a result, the three-dimensional ferromagnetic state in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ is replaced by the two-dimensional state with a weak interplane spin coupling. Such a magnetic structure can be understood with the $d_{x^2-y^2}$ state, which causes the ferromagnetic double-exchange interactions within the MnO_2 sheet, and the antiferromagnetic super-exchange coupling between the adjacent sheets. Mitchell *et al.* (1997) have investigated the temperature

dependence of the MnO_6 octahedra of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ by means of neutron diffraction measurements. They have found that the magnitude of the Jahn-Teller distortion is enhanced in the ferromagnetic metallic state. This means that the enhanced distortion of the MnO_6 octahedron stabilises the $d_{3z^2-r^2}$ state rather than the $d_{x^2-y^2}$.

Argyriou *et al.* (1997) studied the crystal structure of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under hydrostatic pressure of up to 6.3 kbar by means of powder neutron diffraction. They reported that the absolute value of the c -axis compressibility is almost three times larger than that in the ab -plane in the entire temperature range. In $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ the application of pressure results in a charge transfer from $d_{x^2-y^2}$ to $d_{3z^2-r^2}$ orbital in the metallic state, i.e. at temperatures below 120 K (Zhou *et al.* (1998)).

Akimoto *et al.* (1999) have investigated the stability of the $d_{3z^2-r^2}$ orbital at room temperature by means of a Madelung potential calculation based on structural data of $(\text{La}_{1-z}\text{Nd}_z)_{1.2}(\text{Sr}_{1-y}\text{Ca}_y)_{1.8}\text{Mn}_2\text{O}_7$. They found a strong inter-relation between the orbital stability and magnetic structure: with an increase in stability of the $d_{3z^2-r^2}$ orbital, the magnetic structure changes from layered-type antiferromagnetic to ferromagnetic.

Akimoto *et al.* (2000) have also reported studies of the relative stability of the e_g orbital by means of a Madelung potential calculation for ferromagnetic $\text{La}(\text{Sr}_{1.8}\text{Ca}_{0.2})_2\text{Mn}_2\text{O}_7$ and antiferromagnetic $\text{NdSr}_2\text{Mn}_2\text{O}_7$. They have found that the orbital state of the ferromagnetic state is a linear combination of the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals, whereas $d_{x^2-y^2}$ corresponds to the antiferromagnetic spin-ordered phase. Thus, the orbital state is strongly coupled with the spin-state in bilayered manganites.

1.6 Concluding notes

The panorama of magnetic properties demonstrated by manganese oxides makes them very attractive object for studies. One needs to explore both transport and magnetic properties of manganese oxides because these properties are ultimately bound. High magnetic fields, compositional variation or external pressure can be used to induce the metal-insulator transition in manganese oxides. The external pressure directly affects the crystal structure of the studied material. The effect of pressure is purely mechanical and therefore the results are easier to interpret in comparison with the effect of chemical doping and the magnetic field, which can multiply the number of charge carriers, or in the case of magnetic field set the preferred direction of the magnetisation. A reduced dimensionality and, therefore strong anisotropy of the magnetic and transport properties of the bilayered manganites, makes these materials especially interesting for high pressure studies.

$\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($\text{Ln} = \text{La}$) series of bilayered manganites are relatively well studied (Moritomo *et al.* (1996), Kimura *et al.* (1996)). However, there are virtually no publications on $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series of manganites, though $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ materials are extensively studied (Tomioka *et al.* (1995), Kimura *et al.* (1997), Jirak *et al.* (2001)). This is probably because no long-range magnetic ordering was ever found in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ compositions.

The primary goals of this PhD project were:

1. To study the structural changes resulting from the substitution of La ions with smaller Pr ones, and to investigate the effect of such changes in crystal structure on the magnetic and transport properties of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) series of manganites.
2. To study the effect of external pressure on the transport and magnetic properties of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) series of manganites.
3. To study the structural, magnetic and transport properties of the novel $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ material.

Chapter 2

Sample preparation

2.1 Introduction

The single crystal samples of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series ($x = 0.25, 0.3, 0.4$) have been grown using the floating zone technique, which employs a two-mirror infra red image furnace NEC SC-N35HD (Warwick University).

The floating zone method was first used for single crystal growth of Si (Keck and Golay (1953)). A thermal imaging technique was developed and used to characterise new materials of various categories (Little (1962)). The combination of the floating zone technique and the thermal imaging is necessary for effective crystal growth procedures (Kimura and Kitamura (1992)). A technique using a complete ellipsoidal mirror is probably the most advanced method in terms of simplicity and energy efficiency (Akashi *et al.* (1969)). The authors of this work first used the complete ellipsoidal mirror technique for the study of ferrite materials.

2.2 Crystal growth procedure

An infra-red image furnace has a number of significant advantages over the more conventional types of apparatus that are used to prepare single crystals. In an infra-red image furnace, uniform illumination and temperature profile can be achieved. Therefore, floating zone methods can be used, the doping levels can be kept uniform and well defined and nonmetallic materials can be grown (Balakrishnan *et al.* (1993)). The compositions that are grown are noncontaminated due to the use of an isolated growth chamber. A schematic of the furnace is shown on Figure 2.1. Light from two halogen bulbs is focused using the semi-ellipsoidal mirrors onto a central zone. The mirrors are gold-coated (for high reflectivity), water-cooled, aluminium blocks. A temperature of up to 2423 K can be achieved in this system. The two counter rotating shafts are used to support the polycrystalline feed rod (upper shaft) and the single

crystal/seed rod (lower shaft). Both the feed and seed shafts are counter rotated to ensure efficient mixing and a uniform temperature gradient in a molten zone. The molten zone is established between the feed and seed rods. The liquid forming the molten zone is held in place by surface tension. The feed and seed rods are slowly moved downwards. The growth rates vary between 0.25 and 10 mm/hour. New material is introduced into the molten zone from the feed rod and deposited in the form of a single crystal onto the seed rod. The growth takes place inside a quartz tube, which can be over pressured with up to 3 atmospheres of certain gases that can be selected to suit the materials being prepared. Choices include a reducing atmosphere such as an argon/hydrogen mixture, an inert gas such as argon or nitrogen, or an oxidising atmosphere of air or oxygen. Sample boules of up to 80 mm in length and 8 mm diameter can be grown. Single crystals are extracted and prepared for further studies using a range of crystal cutting and polishing tools.

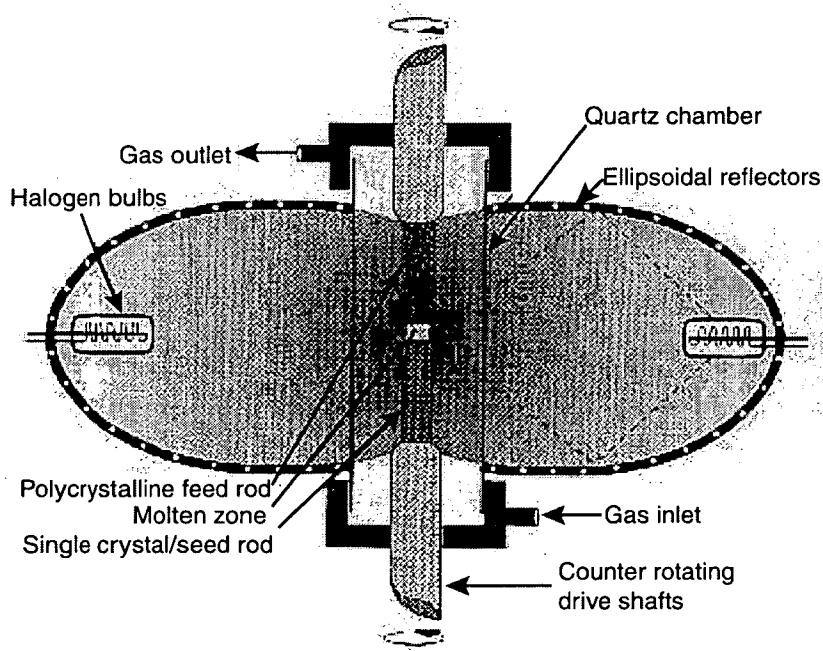


Figure 2.1: Infra-red image furnace NEC SC-N35HD.

Polycrystalline powders of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) were prepared from the high-purity precursors SrCO_3 (98+%), Pr_6O_{11} (99.9%), and MnO_2 (99+%),

which are commercially available, using the solid state reaction method. The thoroughly mixed oxide precursors were first fired at 1523 K for 12 hours and then at 1623 K for 12 hours with intermediate grinding. The powder was isostatically pressed into the form of rods and sintered at 1623 K for 24 hours. The growth rate used was 7 to 8 mm/h with feed and seed rods rotated in opposite directions at 30 rpm. A large single-crystalline boule with an approximate length of 50 mm and a diameter of 8 mm was obtained.

The as-grown crystal was cut off the boule using a diamond saw and subsequently cleaved parallel to the growth direction yielding the (001) surface. A piece was cut parallel to the symmetry directions in order to perform the magnetic and transport characterisation in the temperature range $1.8 \text{ K} < T < 300 \text{ K}$. X-ray Laue tests were performed on each of the grown single crystals in order to confirm their orientation.

2.3 Preparation of samples for diamond anvil cell and piston-cylinder pressure cells

For measurements of the electrical resistivity in a piston-cylinder pressure cell, single crystals with a shape of a parallelepiped were cut from the bulk crystal. Then a smaller crystal was cut in pieces using a surgical blade. Of those pieces, a crystal with a typical size of $2 \times 1 \times 1 \text{ mm}^3$ was chosen. The smaller the crystal, the better, as a smaller size allows a crystal with two parallel crystallographic *ab*-planes to be obtained.

It is very important to use the core part of the boule because it contains less perovskite ((Pr,Sr)MnO₃) intergrowths. Sloan *et al.* (1998) reported that such intergrowths are quite common in layered manganese oxides. They showed that the concentration of the perovskite intergrowths is higher on the outer edges of the single crystal material.

Therefore, to get rid of the (Pr,Sr)MnO₃ intergrowths one needs to cut the crystal with the aim of obtaining a sample with a minimal thickness. However, the surface containing the *ab*-plane should be large enough to accommodate 4 electrical probes sitting next to each other (see part 4.4). The wire, of which the probes are made, should be at least 50 μm in diameter to sustain the mechanical stress (the sample is not attached to anything- it is hung on probes in a pressure transmitting medium which becomes

frozen at low temperature). For wire with a smaller diameter, it is also difficult to remove the 5 μm thick electrical insulation without also removing part of the wire itself

For measurements of the magnetisation, samples with a typical size of $2 \times 2 \times 1 \text{ mm}^3$ and mass of about 50 mg were used because a Superconducting Quantum Interference Device (SQUID) magnetometer has a sensitivity of 10^{-9} emu . A special sample holder made of non-magnetic material (gelatine) was used to orient crystals so the magnetic field would be parallel to the crystallographic *c*-axis or parallel to the *ab*-plane. For measurements of magnetisation in a Diamond Anvil Cell (DAC), a small crystal with a size of $50 \times 50 \times 40 \mu\text{m}^3$ was chosen from the crushed bulk single crystal.

For measurements of the electrical resistance in a Diamond Anvil Cell (DAC), a powder made of ground single crystal was used because the concentration of the (Pr,Sr) MnO_3 intergrowths is smaller in single crystals than in powder samples prepared by using the solid state reaction method. For neutron diffraction experiments, a powder was prepared using ground single crystals of each composition.

A polycrystalline sample of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ was prepared by Vente (Cinvestav-IPN Unidad Merida, Departamento de Fisica Aplicada, Mexico). The synthesis of 8 g of polycrystalline sample of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ was started by heating a stoichiometric mixture of high purity SrCO_3 and MnO_2 for one day in an alumina crucible in air at 1073 K. Subsequently, the mixture was reground, pelletised, and fired at 1273 K (1 day), 1473 K (1 day) and 1573 K (10 days) with further grindings. After the last firing the sample was furnace cooled to 1273 K and subsequently air quenched to room temperature.

2.4 Conclusions

Single crystals of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25, 0.3, 0.4$) have been grown using the floating zone technique. Samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) for transport, magnetic and neutron diffraction measurements were prepared from grown single crystals of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$).

The presence of a (Pr,Sr) MnO_3 intergrowth phase is an unfortunate, but inevitable, part of the crystal growth because of the complex crystal structure of the

$\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ phase. Using the floating zone technique decreases the concentration of the intergrowths in comparison to using the solid state reaction method.

Chapter 3

Powder neutron diffraction studies of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series

3.1 Introduction

The difference between the magnetic properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ manganites will be described in Chapter 4. This difference results from the substitution of the bigger La ion with a smaller Pr one. The ionic radius of La^{3+} is 130 pm, while ionic radius of Pr^{3+} is 113 pm (Shannon (1976)). The $x = 0.3$ and the $x = 0.4$ members of the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ family demonstrate different magnetic and transport properties and it was found that such dissimilarity comes from the difference in the crystalline structure. Therefore, to discover the changes in crystal and magnetic structure caused by the substitution of La ions with Pr ones, it is necessary to study $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials using a neutron powder diffraction techniques.

3.2 Neutron diffraction

Neutron diffraction provides information on the location of atoms within a sample which may be a single crystal or polycrystalline powder. Single crystal diffraction and powder diffraction may be used to reveal the position of atoms within the unit cell of a crystalline material. Neutron diffraction also provides information on the location and orientation of the magnetic moments in a magnetic material.

Neutrons have wavelike properties, which give rise to diffraction phenomena. When a beam of radiation is incident on a crystalline sample, interference effects between wavefronts scattered from the regular array of atoms in the material, produce a diffraction pattern characteristic to that material. Measurement of the positions and intensities of the reflections in the diffraction pattern allows the locations of the atoms

in the material to be determined. Bragg's law (1) is used in a diffraction measurement, which treats the scattering process in terms of reflection from planes of atoms, Figure 3.1.

$$n \lambda = 2 d \sin \theta, \quad (3.1)$$

where λ is a neutron's wavelength, d is the distance between atomic planes, 2θ is the angle between incident and scattered beam directions, and n is the integer that refers to the order of the diffraction.

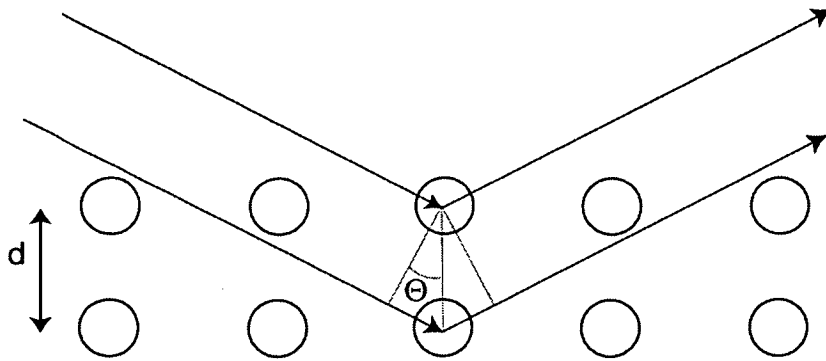


Figure 3.1: Bragg's law- constructive interference occurs when $n\lambda = 2d \sin\theta$.

Depending on the wavelength of the neutrons, the incident angle of the incoming radiation and the repeat distances between atoms, constructive interference between reflected rays gives rise to Bragg reflections only in certain well-defined directions: the interference maximum only occurs when the path length difference between waves scattered from the successive layers is a whole number of wavelengths (Bragg condition). The angle between the incident and diffracted beams is 2θ (Bragg angle). If a single crystal is placed in the beam then a scattered beam is observed in any direction for which Bragg's law is satisfied by some set of Bragg planes. Therefore, knowing the wavelength, λ , and the angle between the incident and scattered beam directions, 2θ , it is possible to calculate the interplanar d -spacings and hence determine the dimensions and symmetry of the unit cell.

If a set of planes hkl in an appropriately oriented single crystal satisfy the Bragg condition, the scattered radiation will emerge from the crystal in a well-defined direction. By placing a detector in the path of the scattered beam it is possible to measure the intensity of that reflection. Moving the crystal will then cause other sets of planes to satisfy the Bragg condition, allowing one to measure the intensities of any number of Bragg reflections. In the case of a polycrystalline material, the sample can be considered to be a very large number of small, randomly oriented single crystals, such that for any reflection hkl there will always be a finite number of planes inclined at the correct Bragg angle. However, because the orientation of these crystallites around the incident beam is not fixed, the scattered radiation emerges not as a single, narrow beam, but as a continuous cone of intensity, the axis of which lies along the incident beam direction, Figure 3.2. Because the crystallites are oriented randomly, discrete cones of scattered radiation will be produced simultaneously for all reflections hkl . A powder diffraction pattern, containing information on the intensities of a large number of reflections, can be recorded by measuring the scattering over a range in 2θ .

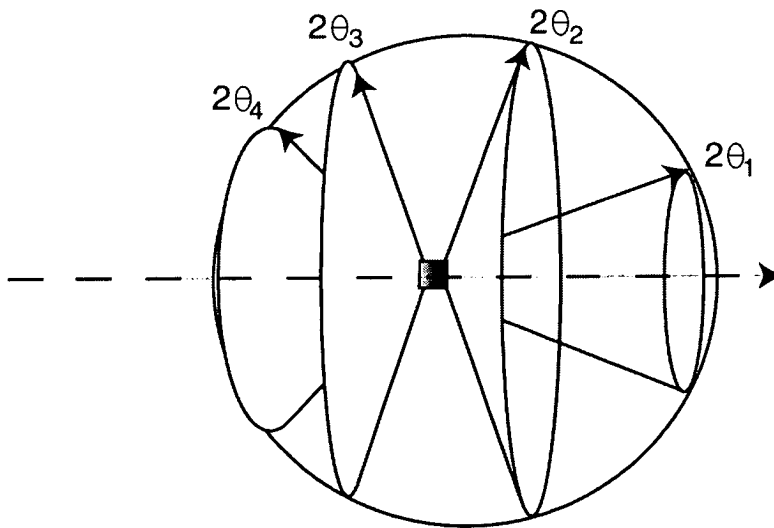


Figure 3.2: Diffraction from a powder sample forms cones of scattered intensity of half angles $2\theta_1$, $2\theta_2$, $2\theta_3$, $2\theta_4$. A suitable detector can measure the intensities.

The positions of the Bragg reflections allow one to determine the dimensions of the unit cell in a crystalline material, i.e. the size of the basic building block, which makes up the structure. However, in order to describe the crystal structure fully, i.e. determine atomic positions, the reflection intensities have to be measured. The measured intensity of a Bragg reflection I_{hkl} is proportional to the square of the structure factor, where the structure factor F_{hkl} is calculated from the positions (x_i, y_i, z_i) of all the i atoms in the unit cell as follows (Bacon (1975)):

$$F_{hkl} = \sum_i n_i f_i \exp\{2\pi i(hx_i + ky_i + lz_i)\} \exp\{-(B_i \sin^2 \theta)/\lambda^2\}, \quad (3.2)$$

f_i is the atomic scattering factor of atom i , and is different for neutron scattering than for X-ray diffraction. In X-ray diffraction measurements the radiation is scattered by electrons in orbitals surrounding the nucleus. Because the distances between the electrons are of a similar magnitude to X-ray wavelengths, the scattering power of an atom is strongly dependent on the scattering angle. The nature of this interaction also means that the X-ray scattering power of an atom is related to its number of electrons. This means that the light atoms have scattering powers very much smaller than those of the heavier ones. With neutron diffraction however, the scattering process involves an interaction between the neutron and the atomic nucleus over a distance very much shorter than the wavelength of the neutron. This means that the scattering power depends on properties of the nucleus itself. In neutron diffraction there is an almost random variation in scattering power (termed the scattering length), with atomic number. B_i , in (2), is the Debye-Waller (temperature) factor, which accounts for the thermal motion of an atom. Vibration of the atoms around their mean positions produces a slight mismatch between the scattered wavefronts and causes a reduction in the intensities of all Bragg reflections. The effect is most noticeable at larger values of $\sin\theta/\lambda$ (smaller d -spacing). Several other factors can affect the measured intensity of a Bragg reflection in a powder diffraction pattern, including absorption, extinction and preferred orientation (Bacon (1975)).

A neutron has a spin. Therefore, as well as the scattering from atomic nuclei, the neutron can interact with electron spins and induced orbital moments. Because the

magnetic scattering process involves an interaction with electrons over distances comparable to neutron wavelengths, magnetic neutron scattering is attenuated by a form factor, f_m . The scattering lengths for the nuclear and magnetic processes are additive. For an unpolarised incident neutron beam, the total scattered intensity is the sum of the nuclear and magnetic scattering:

$$F^2 = F_{nuc}^2 + F_{mag}^2 \quad (3.3)$$

The structure factor for magnetic scattering, F_{mag} , for the reflections whose scattering vector is $\mathbf{h}$, depends on the magnitude of the magnetic scattering length p , and the magnetic interaction vector, $\mathbf{q}$ (Bacon (1975)).

$$F_{mag} = \sum_i q_i p_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i), \quad (3.4)$$

where the sum is over all the magnetic atoms in the unit cell and the $\mathbf{x}_i$ are the position vectors of the magnetic atoms. The magnetic scattering length p_i is calculated from the magnitude of the magnetic moment on an atom, S , and the magnetic form factor, f_m .

$$p = (S f_m) 0.54 \times 10^{-12} \text{ cm} \quad (3.5)$$

The magnetic interaction vector, $\mathbf{q}$, for an atom depends on both the scattering vector and the magnetic moment on that atom.

$$\mathbf{q}_i = \boldsymbol{\varepsilon} \cdot (\boldsymbol{\varepsilon} \cdot \mathbf{K}_i) - \mathbf{K}_i, \quad (3.6)$$

where $\boldsymbol{\varepsilon}$ is the unit vector in the direction of the scattering vector $\mathbf{h}$; and $\mathbf{K}$ is the unit vector in the direction of the magnetic moment.

Therefore, in order for an atom to make a magnetic contribution to the scattered intensity, it must have a component of its magnetic moment perpendicular to the scattering vector. Because of this complex nature of magnetic interactions,

crystallographically identical atoms or ions in adjacent unit cells may have different magnetic properties. The result of this is that the nuclear and magnetic unit cells in a material can be of different dimensions. Often magnetic neutron diffraction measurements are characterised by the appearance of Bragg reflections and changes in intensities of existing reflections as the material undergoes a magnetic transition.

3.3 The Rietveld method

In conventional crystal structure analysis, a single crystal diffraction experiment (X-ray or neutron) is carried out and the structure factors calculated from the measured intensities. Provided with structure factor information, a large number of techniques are available for structure solution and structure refinement.

The Rietveld method (Rietveld (1969)) is an analysis procedure that addresses the problems associated with peak overlap in a powder diffraction pattern by treating each point in the pattern as an individually observed intensity. Through knowledge of certain diffractometer parameters describing the reflection shape and width, and sample parameters describing the positions and intensities of the reflections, a powder diffraction profile can be modelled. This model is then refined against the experimentally observed data by the least square method to obtain a best fit. During the Rietveld refinement the intensity of each point in the diffraction pattern is calculated using the expression:

$$Y_{ic} = Y_{ib} + \sum_k G_{ik} I_k, \quad (3.7)$$

where Y_{ic} is the calculated intensity at point i in the diffraction pattern, Y_{ib} is the background intensity at point i in the diffraction pattern, G_{ik} is the value of normalised peak profile function at point i for reflection k , I_k is the Bragg intensity of reflection k , k is a reflection contributing to point i .

This method allows a large amount of structural information to be extracted from the intensities of overlapping reflections whether it is partial or complete overlap. However, the Rietveld method is a structural *refinement* method and not a structure

solution method. The experimentalist must have sufficient information about the crystal structure of the material to calculate the expected diffraction pattern first.

3.4 $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$

Powder neutron diffraction studies of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) were performed using the D2B (mean wavelength 1.59432 Å, $5 \leq 2\Theta/^\circ \leq 165$) diffractometer at the Institute Laue Langevin (ILL).

The schematic diagram of the diffractometer D2B is shown in Figure 3.3. A complete diffraction pattern is obtained after about 100 steps of 0.025° in 2Θ , since the 64 detectors are spaced at 2.5° intervals. D2B is particularly well suited for the Rietveld refinement of relatively large structures (Hewat (1986)).

D2B was also designed for work on magnetism and high resolution measurements of very large d -spacings using wavelengths of between 2.4 Å and 6.0 Å (Hewat (1986)). Wavelengths can easily be changed under computer control, since they are all obtained by a simple rotation within the Ge [hkl] plane. A large graphite filter can be used to provide a very clean beam at 2.4 Å, and a cold Be-filter can be used for longer wavelengths. Neutron diffraction patterns were collected at 1.8, 40, 100, 150, 200 and 300 K using a standard cryostat ($T = 1.6 - 300$ K). Data were collected on samples contained in cylindrical vanadium cans with diameter of 7 mm (vanadium does not produce Bragg reflection). All diffraction patterns were analysed with the Rietveld technique (Rietveld (1969)) using the program packages GSAS (von Dreele and Larson (1986)).

The structure was refined using the published (see Argyriou *et al.* (1999)) description of the $n = 2$ Ruddlesden-Popper structure with space group $I4/mmm$, Table 3.1. The background was fitted with a twelve order shifted Chebychev polynomial. The constraints were applied for pairs of atoms of Pr and Sr, occupying the same crystallographic positions, to keep their coordinates and isotropic temperature factors (UIO) the same. Constraints were also applied for fractional occupancy variables (OCC) for the Pr and Sr atoms in order to keep the total occupancy of the positions they

occupied equal to 1. The shape of the Bragg peaks was described by a pseudo-Voigt function.

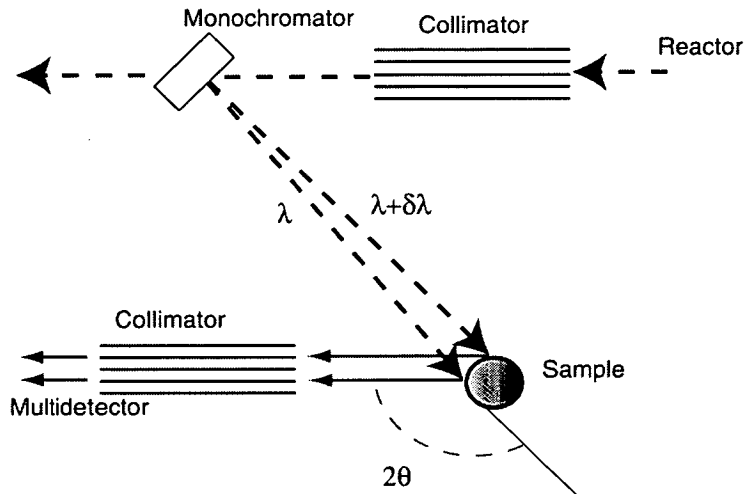


Figure 3.3: D2B high-resolution two-axis diffractometer.

Attempts to refine the structure resulted in a fit with $\chi^2 = 10.256$, $R_{wp} = 7.94\%$, $R_p = 5.28\%$, and the peak observed at $2\Theta \sim 42^\circ$, at 300 K, was not fitted at all, Figure 3.4 (A).

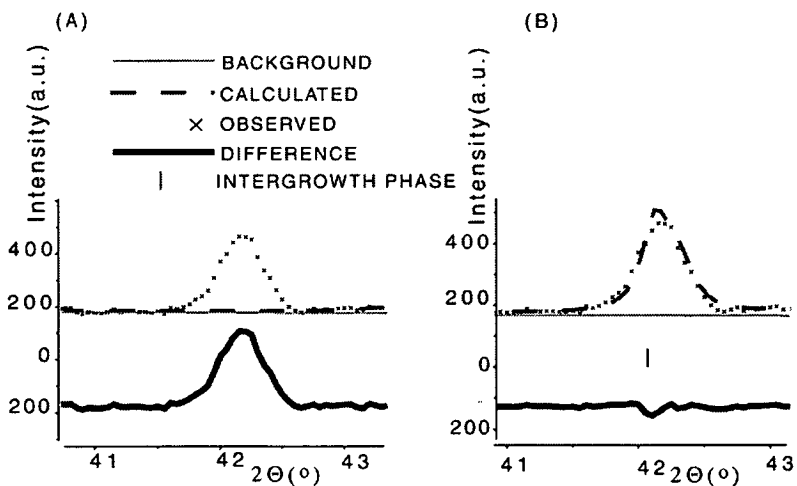


Figure 3.4: (A) The peak profile at $2\Theta \sim 42^\circ$ (300 K). (B) The fitted peak after the second, $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase was included in the refinement.

Atom	X	Y	Z	OCC	UIISO (Å ²)
Pr(1)	0	0	0.5	0.41(3)	0.0093(8)
Sr(1)	0	0	0.5	0.59(3)	0.0093(8)
Pr(2)	0	0	0.31705(9)	0.37(2)	0.0083(5)
Sr(2)	0	0	0.31705(9)	0.63(2)	0.0083(5)
Mn	0	0	0.0974(2)	1	0.0044(4)
O(1)	0	0	0	1	0.0166(6)
O(2)	0	0	0.1976(1)	1	0.0194(5)
O(3)	0	0.5	0.09622(7)	1	0.0116(3)

Table 3.1: Structural parameters of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ at 300 K.

Space group $I4/mmm$; $a = 3.8478(1)$ Å, $c = 20.1343(5)$ Å.

The data were modelled in a more convincing way by assuming that the sample consisted of two phases i.e. the majority phase $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ with space group $I4/mmm$ and the intergrowth phase $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ with space group $I4/mcm$. Jirak *et al.* (2001) have reported the magnetic phase diagram of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$. They have shown that above room temperature $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.48 \leq x \leq 0.75$) is pseudocubic, with possibly a weak tetragonal lattice distortion due to the MnO_6 octahedral tilt (space group symmetry $I4/mcm$). At low temperatures the symmetry becomes orthorhombic (Damay *et al.* (1998)). The magnetic phase diagram reported by Jirak *et al.* (2001) shows that $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ undergoes a transition into a ferromagnetic state at temperature about 280 K, and on further cooling it becomes an antiferromagnet at temperature about 150 K.

The presence of such a perovskite intergrowth phase is quite common in layered manganites of $\text{A}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ formulae (Sloan *et al.* (1998)). The two-phase model considerably improved the fit (Agreement indices are: $\chi^2 = 3.999$, $R_{wp} = 6.17$ %, $R_p = 4.41$ %, for 42 variables), Figure 3.4(B). The phase fractions were refined to the ratio of 100:2.018(8). As the intergrowth phase amounts only to 2% of the sample, it was not possible to refine either the fractional occupancies or the isotropic temperature factors of the atoms in the intergrowth phase. Figure 3.5 shows the final observed and

calculated diffraction patterns at 300 K. The structural parameters for the intergrowth phase are given in Table 3.2.

Atom	X	Y	Z	OCC	UIISO, ($\text{\AA}^2$)
Pr	0	0.5	0.25	0.5	0.008
Sr	0	0.5	0.25	0.5	0.008
Mn	0	0	0	1	0.003
O(1)	0	0	0.25	1	0.015
O(2)	0.779(2)	0.279(2)	0.277(6)	1	0.015

Table 3.2: Structural parameters of intergrowth phase at 300 K.

Space group $I4/mcm$; $a = 5.386(1) \text{ \AA}$, $b = 5.386(1) \text{ \AA}$, $c = 7.7909(2) \text{ \AA}$.

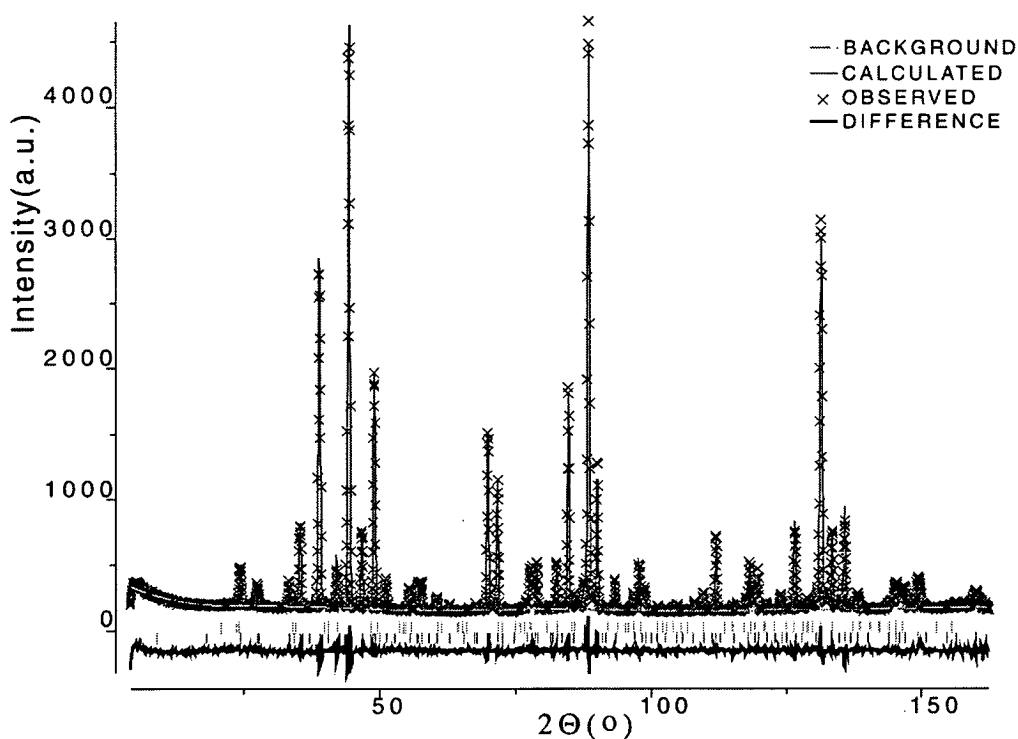


Figure 3.5: Observed and calculated pattern for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ collected at 300 K. Reflection positions are marked for the majority phase (lower) and the intergrowth phase (upper).

The interpretation of the diffraction patterns collected at $T = 1.8$ K was made more difficult by the presence of an additional magnetic peak at $2\Theta \sim 12^\circ$, Figure 3.6. The presence of this additional magnetic peak corresponds to a doubling of the length of the unit cell. Therefore, this peak was attributed to an antiferromagnetic transition (ferromagnetic contribution appears on the nuclear peaks). The magnetic peak was observed in the neutron diffraction data below 150 K, while it disappeared at 200 K; this corresponds to the transition temperature for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (Damay *et al.* (1998)). On cooling, $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ undergoes a transition from the ferromagnetic to antiferromagnetic state at ~ 150 K. The magnetic structure of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was reported by Kawano *et al.* (1997), who found that $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ shows an A-type layered antiferromagnetic structure in the low temperature phase. The magnetic moments of the Mn atoms are aligned along the longest b -axis, Figure 3.7.

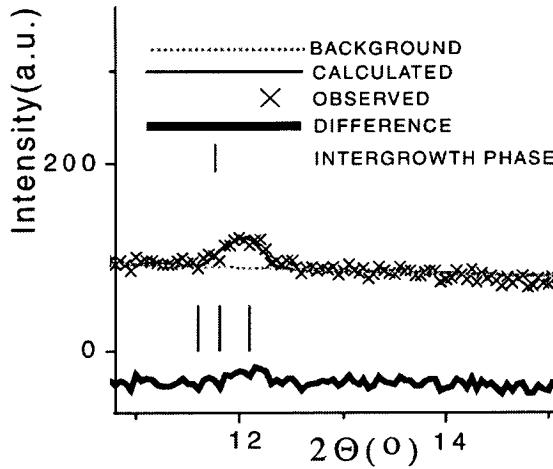


Figure 3.6: Magnetic peak from $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase at 1.8 K.

Damay *et al.* (1998) reported that the antiferromagnetic structure of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ has the $Fmmm$ space group. The structure was refined using the published (see Damay *et al.* (1998)) description of the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ structure with space group $Fmmm$ for the intergrowth phase, Table 3.3. Fractional occupancies and isotropic temperature factors for atoms in this phase were not refined. The magnetic moment refined to 2.9(2) Bohr magneton (at 1.8 K).

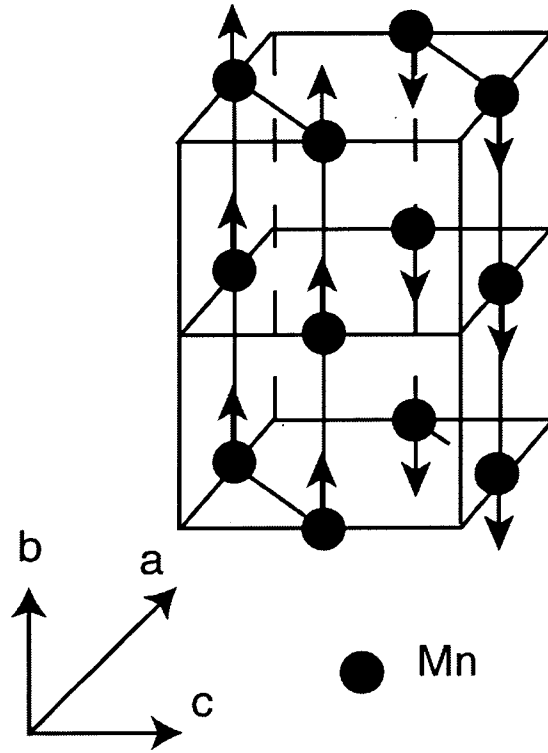


Figure 3.7. Layered antiferromagnetic structure of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

The final observed and calculated diffraction patterns at $T = 1.8$ K are shown in Figure 3.8. The structural parameters and bond lengths derived from the experiments performed at $T = 1.8$ K are presented in Tables 3.3 and 3.4. Agreement indices are: $\chi^2 = 3.365$, $w_{\text{Rp}} = 10.50$ %, $R_{\text{p}} = 7.92$ %, for 46 variables.

Atom	X	Y	Z	OCC	UIISO, ($\text{\AA}^2$)
Pr	0	0.247(6)	0	0.5	0.00428
Sr	0	0.247(6)	0	0.5	0.00428
Mn	0.25	0	0.25	1	0.003
O(1)	0.167(6)	0	0	1	0.01372
O(2)	0	0	0.286(6)	1	0.01372
O(3)	0.25	0.25	0.25	1	0.00724

Table 3.3: Structural parameters of intergrowth phase at 1.8 K.

Space group $Fmmm$; $a = 7.492(3)$ $\text{\AA}$, $b = 7.81(2)$, $c = 7.673(3)$ $\text{\AA}$.

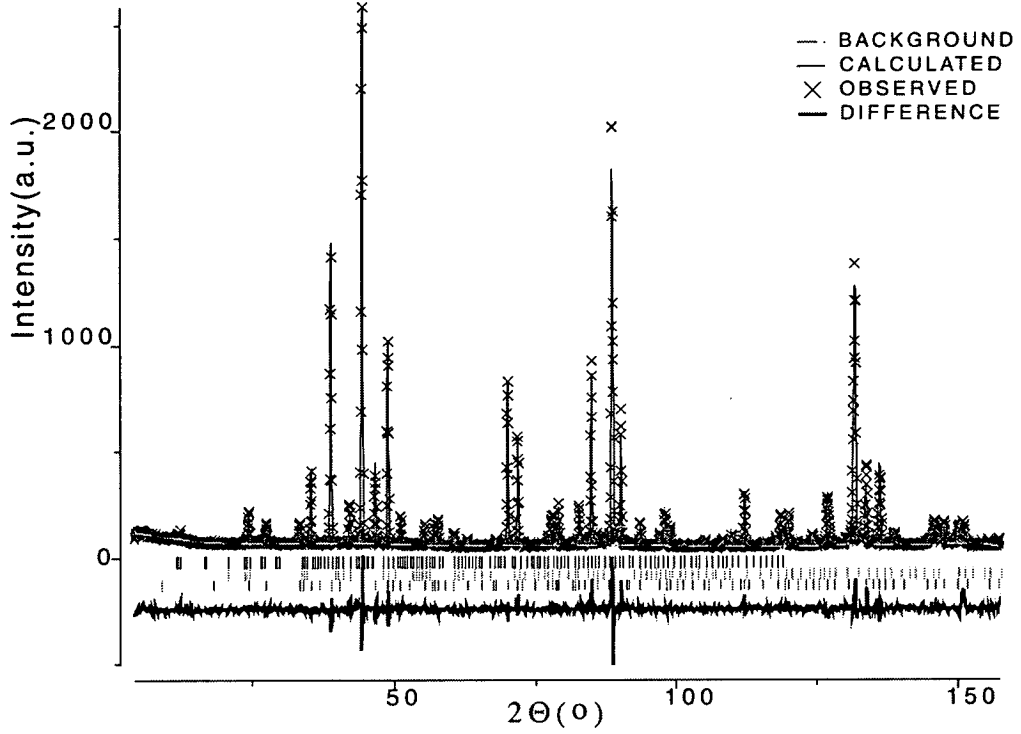


Figure 3.8: Observed and calculated pattern for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ collected at 1.8 K. Reflection positions are marked for the majority phase (lower), the intergrowth phase (middle), and the magnetic phase (upper).

Atom	X	Y	Z	OCC	UIISO, ($\text{\AA}^2$)
Pr(1)	0	0	0.5	0.41(4)	0.0050(1)
Sr(1)	0	0	0.5	0.59(4)	0.0050(1)
Pr(2)	0	0	0.3174(1)	0.31(3)	0.0062(1)
Sr(2)	0	0	0.3174(1)	0.69(3)	0.0062(1)
Mn	0	0	0.0959(2)	1	0.0029(6)
O(1)	0	0	0	1	0.0143(9)
O(2)	0	0	0.1978(2)	1	0.0132(8)
O(3)	0	0.5	0.0964(1)	1	0.0079(4)

Table 3.4: Structural parameters of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ at 1.8 K. Space group $I4/mmm$; $a = 3.84335(11) \text{ \AA}$, $c = 20.09679(59) \text{ \AA}$.

3.5 $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$

D1B is a two-axis spectrometer dedicated to diffraction experiments requiring a high neutron flux, Figure 3.9. A great number of experiments performed on D1B are concerned with the determination of magnetic structures. However, compared to D2B, D1B is a low-resolution instrument. D1B does not facilitate detailed crystal structure analysis and is best used to collect diffraction patterns rapidly as a function of temperature. Three pyrolytic graphite monochromators, focusing onto the sample position, provide a flux of $6.5 \times 10^6 \text{ n cm}^{-2}\text{s}^{-1}$. D1B is equipped with a $^3\text{He/Xe}$ position-sensitive detector composed of a system of multi-electrodes with 400 cells which span a 2Θ range of 80° . The detector can be moved so that an angular range of $2 \leq 2\Theta/^\circ \leq 160$ can be covered. D1B is now controlled by a Silicon graphic workstation on which data reduction and treatment programs are also available. The raw data are corrected on-line for the efficiencies of the detector cells. During the experiment Rietveld analysis was done using the FULLPROF software package (Rodriguez-Carvajal (1993)).

The structure refinement was carried out on the assumption that both samples, $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, contained a small amount of the intergrowth phase ($\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$) as it had already been found in $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ using a higher-resolution diffractometer. Indeed, refinements showed that the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase amounts to about 4% in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$.

The data collected at $T = 2 \text{ K}$ for both $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, show clear evidence of magnetic order coming from the intergrowth ($\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$) phase, see Figure 3.10 and Figure 3.11. The broad magnetic peak is observed at $2\Theta \sim 19^\circ$, Figure 3.10 and Figure 3.11.

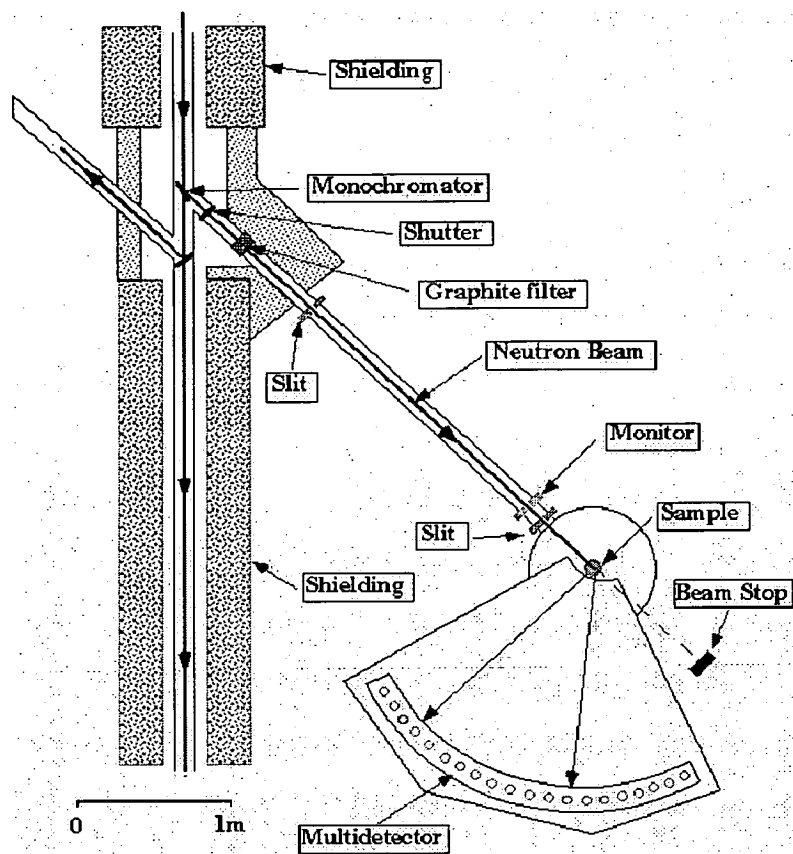


Figure 3.9: D1B two-axis diffractometer (courtesy of ILL, France).

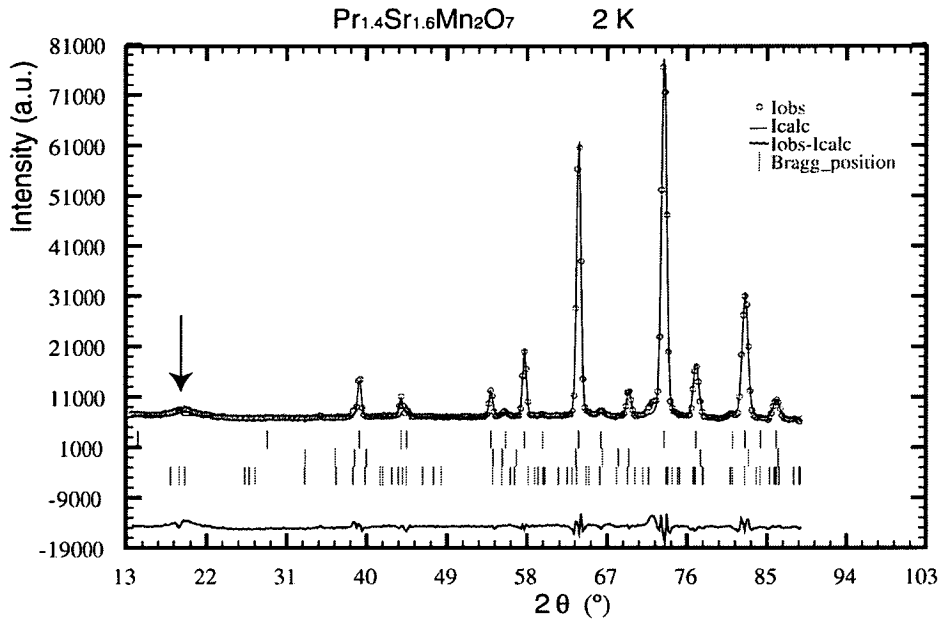


Figure 3.10: Observed and calculated pattern for $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ collected at 2 K. Reflection positions are marked for the majority phase (lower), the intergrowth phase (middle), and the magnetic phase (upper). The arrow points at the magnetic peak.

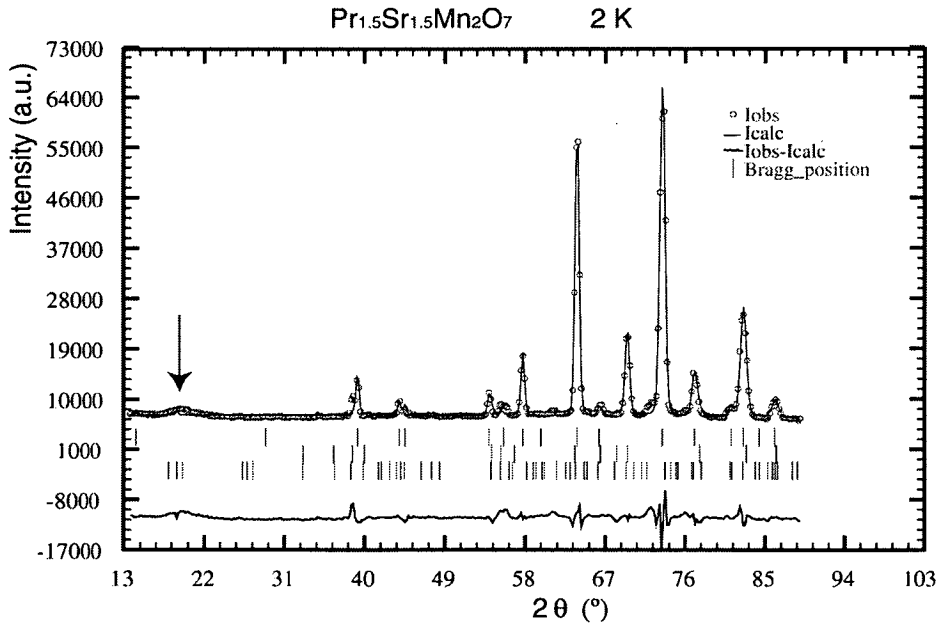


Figure 3.11: Observed and calculated pattern for $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ collected at 2 K. Reflection positions are marked for the majority phase (lower), the intergrowth phase (middle), and the magnetic phase (upper). The arrow points at the magnetic peak.

The magnetic peak disappears at temperatures above 150 K for both compositions. It was found that the coordinate of the magnetic peak in d -spacing for all $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) samples was 7.67 Å. The majority phase does not produce the Bragg reflections at this position. This means that the magnetic peak comes from the intergrowth phase only. The magnetic peak on Figures 3.10 and 3.11 is broad; this is because compared to D2B, D1B is a low-resolution diffractometer.

The small peak observed at $2\Theta \sim 72^\circ$, in Figures 3.10 and 3.11, originates from the vanadium wall of the cryostat.

Structure parameters, bond lengths and bond angles of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) series of manganites at ambient temperature are shown in Table 3.5. The $a(b)$ lattice parameter decreases slightly with the decrease of x , and the Mn-O(3) bond length along the $a(b)$ axis also decreases with the decrease of x . The Mn-O(2) bond length along the c axis increases considerably with the decrease of x . However, the c lattice parameter generally increases with the decrease of x and reaches the maximum at $x = 0.3$.

Structure parameter	$\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	$\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$	$\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$
a , (Å)	3.8478(1)	3.8381(7)	3.837(1)
c , (Å)	20.13429(53)	20.311(3)	20.309(6)
Mn-O(1), (Å)	1.9611(31)	2.023(96)	1.999(47)
Mn-O(2), (Å)	2.017(4)	2.034(113)	2.147(55)
Mn-O(3), (Å)	1.92405(7)	1.917(28)	1.9184(7)
Mn-O-Mn, ($^\circ$)	178.59(22)	178.08(57)	179.26(5)

Table 3.5: Structure parameters, bond lengths and bond angles of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ series of manganites at ambient temperature.

The Mn-O(1) bond length obeys the same pattern as the c lattice parameter, i.e. the largest Mn-O(1) distance is for the $x = 0.3$ composition while the smallest one is for $x = 0.4$. The effect of Sr doping in the Pr-based bilayered manganites on the Mn-O bond lengths is therefore similar to the one in La-based manganites (Kimura *et al.* (1998)).

However, the behaviour of the Mn-O(1) bond length makes it a little different. The $2\{\text{Mn-O}(1) + \text{Mn-O}(2)\}$ is the thickness of the bilayer and the O(2)-O(3) is the distance between the bilayers, Table 3.6. The O(2)-O(3) is the distance between the bilayers, i.e. the distance between O(2) and O(3) in the neighbouring bilayers. These ions are not to be confused with O(2) and O(3) ions within the octahedra, Figure 3.12.

The thickness of the bilayer decreases with the increase in x , despite the fluctuation of the Mn-O(1) distance. The interbilayer spacing increases monotonically with the increase in x . The effect of Sr doping on the structural properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) is a two-fold one. It squeezes the MnO_6 octahedra and, therefore, brings the Mn ions within the bilayer closer to each other and spaces the adjacent bilayers out.

Composition	$2\{\text{Mn-O}(2)+\text{Mn-O}(1)\}$ thickness of the bilayer, (Å)	O(2)-O(3) interbilayer spacing, (Å)
$\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	7.9562(51)	4.576(3)
$\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$	8.094(148)	4.534(113)
$\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$	8.292(72)	4.377(82)

Table 3.6: Thickness of the bilayer and the interbilayer spacing of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) manganites at ambient temperature.

The data in Tables 3.7 and 3.8 for $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$) have been extracted from the papers published by Argyriou *et al.* (1999) and Argyriou *et al.* (1997) correspondingly. The data in Tables 3.7 and 3.8 for $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ have been extracted from the work published by Battle *et al.* (1997c).

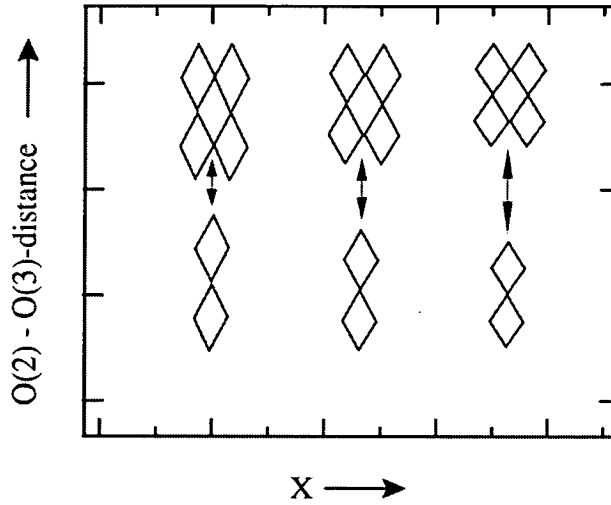


Figure 3.12: Schematic diagram of the change in the thickness of the bilayer and the interbilayer spacing with an increase of x in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ (shown exaggerated).

Composition	Mn-O(1), (Å)	Mn-O(2), (Å)	Mn-O(3), (Å)	Mn-O-Mn, (°)
$\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	1.958(2)	2.029(3)	1.92000(4)	179.960(1)
$\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$	1.946(5)	1.989(8)	1.93611(1)	178.8(5)
$\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$	1.9716(28)	2.045(4)	1.93110(4)	178.8(5)

Table 3.7: Bond lengths and bond angles of $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$) manganites at ambient temperature.

Unfortunately, the information on structure parameters and bond lengths for $\text{La}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ was not available, perhaps because it is difficult to grow a single crystal material of this composition and the powder-grown samples usually contain a lot of impurities. The analysis of bond lengths for compositions with $x = 0.3$ reveal that the substitution of La ions with smaller Pr ones result in an increase of the Mn-O(1) and Mn-O(2) distances, and a decrease in the Mn-O(3) distance. In $x = 0.4$ compositions the Mn-O(1) distance is also larger than in Pr-based compounds, while Mn-O(2) and Mn-O(3) are larger in La-based compositions. The thickness of the bilayer, and the distance between the bilayers for La-based manganites are listed in Table 3.8.

Composition	2{Mn-O(1)+Mn-O(2)} thickness of the bilayer, (Å)	O(2)-O(3) interbilayer spacing, (Å)
Nd _{1.2} Sr _{1.8} Mn ₂ O ₇	7.974(4)	4.540(8)
La _{1.2} Sr _{1.8} Mn ₂ O ₇	7.870(9)	4.629(4)
La _{1.4} Sr _{1.6} Mn ₂ O ₇	8.033(5)	4.629(3)

Table 3.8: Thickness of the bilayer and the interbilayer spacing of Ln_{2-2x}Sr_{1+2x}Mn₂O₇ (x = 0.4, 0.3) manganites at ambient temperature.

Comparing the data in Tables 3.8 and 3.6 one can see that the substitution of the smaller Pr ions for the larger Ln ions leads to:

1. A decrease of the interbilayer spacing, i.e. the adjacent bilayers are brought closer to each other in Pr-based compositions.
2. An elongation of the bilayers in Pr-based compositions. This includes simultaneous elongation of both the Mn-O(1) and Mn-O(2) distances, shortening of the Mn-O(3) distance, and enlargement of the Mn-O-Mn angle within the MnO₆ octahedra.

Moritomo *et al.* (1997b) have reported magnetic and transport properties of (La_{1-z}Nd_z)_{1.2}Sr_{1.8}Mn₂O₇. They have found that the partial substitution of the smaller Nd ions for the larger Ln ions results in the suppression of the FM state, which eventually disappears beyond z = 0.4. They have ascribed the suppression of the FM state to a variation of the *e_g*-electron character from $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ state and a resultant reduction of the transfer integral of the *e_g* electrons. The *e_g* orbitals in bilayered manganites are split into the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states (Moritomo *et al.* (1997b). The $d_{x^2-y^2}$ extends along the sheet direction and has a large transfer integral (*t*) while the $d_{3z^2-r^2}$ has a small *t* (Moritomo *et al.* (1997b).

Dessau *et al.* (1998) performed X-ray absorption spectroscopy and angle-resolved photoemission spectroscopy on a single crystal of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and found that the $d_{x^2-y^2}$ character dominates the occupied e_g state even though it is located slightly above $d_{3z^2-r^2}$ the state. Therefore, the relatively large t can cause the FM state at low

temperatures. With increasing z in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, however, the MnO_6 octahedra elongate along the c -axis (Moritomo *et al.* (1997b)). Such a distortion modifies the crystal field around the e_g state and stabilises the $d_{3z^2-r^2}$ state. Reduction of the transfer integral causes a metal-insulator transition.

The absence of a long-range magnetic order in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) manganites can be explained in a similar manner, i.e. elongation of the Mn-O(1) and Mn-O(2) distances within the MnO_6 octahedra stabilises the $d_{3z^2-r^2}$ state and reduces the transfer integral, changing a FM metal into PM insulator.

It is quite natural, therefore, to try to reduce the Mn-O(1) and Mn-O(2) bond lengths and to enlarge the Mn-O(3) bond length to make a material a FM metal again. This can be done by the application of chemical pressure, i.e. by doping of La, or by the application of an external pressure. Studies of the effect of the external pressure on the magnetic and transport properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) manganites are described in the following chapter.

3.6 Concluding notes

Crystal and magnetic structures of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) manganites were studied using the neutron powder diffraction technique at ambient pressure.

It was found that substitution of La ions with smaller Pr ones results in the following changes in the crystal structure:

- An increase of the Mn-O(1) and Mn-O(2) linkages and a decrease of the Mn-O(3) distance;

- A decrease in the interbilayer spacing, i.e. the adjacent bilayers are brought closer to each other with a higher Pr-doping level.

The magnetic refinement has shown that there is no long-range magnetic order in the majority bilayered phase in either of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials in the temperature range of 1.8 K – 300 K. The analysis of the neutron diffraction data makes it possible to conclude that the absence of the long-range magnetic order in the Pr-based materials can be attributed to the elongation of the MnO_6 octahedra along the c -axis. This results in a greater separation between the magnetic Mn atoms in the lattice and leads to a lesser degree of the exchange interaction between them. It was also found that samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.4, 0.3, 0.25$) contain a small (2 - 4%) amount of (Pr,Sr) MnO_3 phase.

Chapter 4

Measurements of electrical resistivity and magnetic susceptibility of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) and $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ using piston cylinder pressure cells

4.1 Introduction

Electrical resistivity of Pr-based bilayered manganites needs to be measured in order to find out whether or not these materials undergo a metal-insulator transition, and to study the type of conductivity inherent to these manganites at different temperatures. Because of the anisotropic nature of these manganites, the resistivity has to be measured within the *ab*-plane (along the bilayer) and along the *c*-axis (across the bilayer). External pressure has been shown to be an effective tool for inducing the metal-insulator transition in manganese oxides (Hwang *et al.* (1995b)). Magnetic susceptibility of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) needs to be measured to study their magnetic properties and the anisotropy of these properties. It is also necessary to measure the magnetic susceptibility of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) to identify the composition of the intergrowth phase by comparing these results with neutron diffraction data. External pressure can significantly affect the magnetic properties of bilayered manganites. Studies of the effect of pressure on magnetic properties are also needed because the magnetic and transport properties of the bilayered manganites are related (Moritomo *et al.* (1996) and Kimura *et al.* (1996)).

4.2 Experimental setup

The experimental hardware used for these studies includes the following items, some of which are shown in Figure 4.1:

- The self-clamped high-pressure LC-10 cell from Unipress. It consists of an open-ended cylinder (the body of the cell), the plug with 12 lead-in electrical feedthroughs, and the piston. Commercially available mineral oil, Fluorinert FC-77, was used as a pressure transmitting media. It is important that the Fluorinert FC-77 is a non-reactive material. The LC-10 can generate hydrostatic pressure of up to 11 kbar (1.1 GPa). The cell is made from a non-magnetic CuBe alloy and is, therefore, suitable for magnetic measurements such as magnetic susceptibility.
- The hydraulic press is used to apply pressure to the pressure cell. The pressure inside the LC-10 cell is monitored by a pressure gauge. The pressure gauge is made of manganin wire wound as a cylindrical coil in two rows separated by a layer of PTFE tape. The sensor was “aged” before use: the coil was annealed in the induction oven and quenched to the liquid nitrogen temperature several times to make its resistivity stable.
- The LC-10 cell is used with the two-stage cryogenic closed-cycle refrigerator (CCR) in order to study properties of solids at low-temperatures. The CCR uses helium gas from a helium compressor to produce temperatures down to approximately 10 K. The system includes interconnecting gas lines to carry helium gas to and from the components.

A set of miniature coils was built and wired to the plug provided with the LC-10 pressure cell to measure the magnetic *ac* susceptibility (see part 4.8) under pressure. The setup utilises an inductance method and consists of two copper wire coils – a primary and a pick-up. The *ac* current goes through the primary coil and induces current in the pick-up coil, which is then monitored.

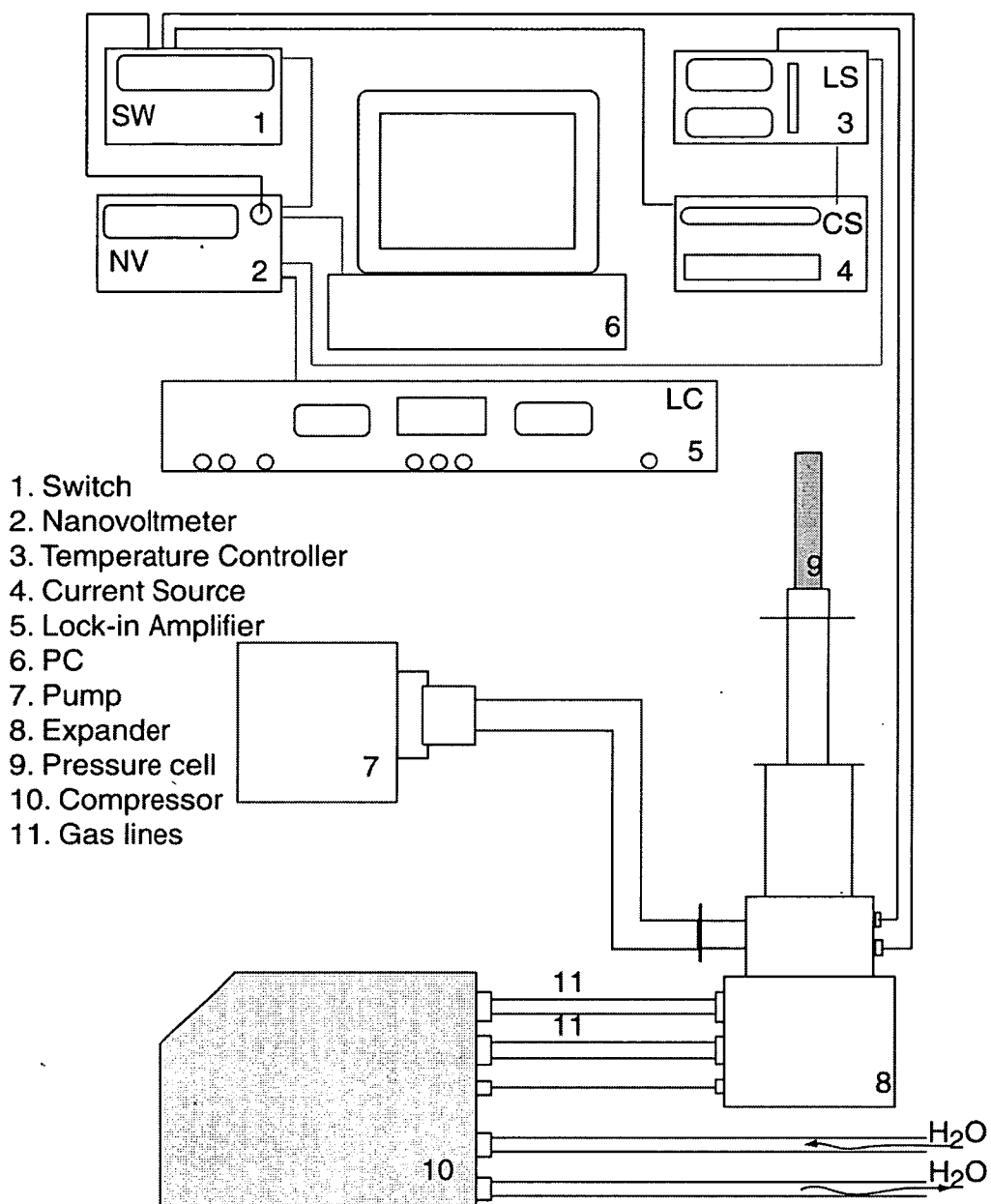


Figure 4.1: Experimental setup for measurement of transport and magnetic properties under pressure at low temperature.

The pick-up coil consists of the two coils with an equal number of turns wired towards each other, thus compensating for the magnetic response from the coil itself. Therefore, the current in the pick-up depends on the degree of the magnetic order in the studied material.

To acquire the data, a programmable current source, a nanovoltmeter and a multichannel switch system were used. Using the multichannel switch system makes it possible to measure several resistances almost simultaneously. To control and monitor the temperature an auto-tuning temperature controller was utilised. The lock-in amplifier and a current calibrator were used for sensitive *ac* susceptibility measurements. All the instruments have programmable interface cards and are connected to a PC via an IEEE/GPIB interface. In order to run the experiments and to collect the data, a series of the data acquisition subroutines based on the “IGOR Pro” software package were written. The programs are designed to:

- monitor the pressure during the pressure adjustments in the LC-10 pressure cell;
- carry out the measurements of electrical resistivity with the six-probe technique (see part 4.4) and magnetic *ac* susceptibility during temperature variations (on both, cooling and warming);

The program continuously displays the data as they are collected and stores them in the data file.

4.3 LC-10 pressure cell

The LC-10 liquid pressure cell was adapted for measurements of electrical resistivity and *ac* susceptibility of the $\text{Ln}_{2-2x}\text{A}_{1+2x}\text{Mn}_2\text{O}_7$. The LC-10 cell is shown in Figure 4.2. The pressure is measured by the pressure gauge (a manganin wire), which has a linear pressure dependence of its electrical resistivity:

$$\rho(P) = \rho(P = 0)\{1 + \alpha P\}, \quad (4.1)$$

where $\alpha = 0.002465$, P is the pressure in kbar (Bridgeman (1952)). It is therefore possible to calibrate the pressure gauge knowing the $\rho(P = 0)$, i.e. the temperature dependence of the resistivity of the pressure gauge measured at zero pressure.

The pressure is applied at room temperature using the hydraulic press, which brings the load on the piston. The value of the applied pressure is monitored during the procedure so the pressure limit for this cell is not exceeded, and the pressure is increased as smoothly as possible. Without this monitoring there is a real chance of damaging either the metal or rubber piston seal. Normally, when studying the effect on pressure one needs to do several temperature variations at different pressures. It is recommended to go to a maximum pressure first, and then subsequently to lower it in fine steps. When a certain pressure is applied, and the set screw of the piston is tightened to fix the pressure, the metallic piston seal locks the pressure cell. It is virtually impossible to enhance and fix the value of pressure after the set screw of the piston is tightened as the pressure can only be lowered. Although one could reload the cell before each run and use new piston seals this is less desirable because in order to reload the cell, the pressure must be fully released. Each procedure of reloading the cell inevitably results in pulling the electrical leads off the sample (if electrical resistivity is measured). Therefore, changing seals during the measurement considerably lowers the lifetime of the electrical probes and should be avoided. Pressure should be lowered as smoothly and slowly as possible as the metallic piston seal becomes thinner and could easily break which could lead to an abrupt pressure drop. Such a drop usually breaks the electrical probes of the sample and, even worse, can break the contact on the plug of the pressure cell. The break is fatal and a new plug needs to be used. Therefore, the time used to lower the pressure from 11 kbar to 0 kbar cannot be less than half an hour. The electrical leads are stacked at the generatrix of a cone, which goes inside of a plug, Figure 4.3. The wires are covered with pyrophyllite, which serves as an insulator and a gasket. The pyrophyllite is a solid substance and in the event that some, or all, of the electrical probes are broken inside of a plug it is impossible to open it and replace the wires.

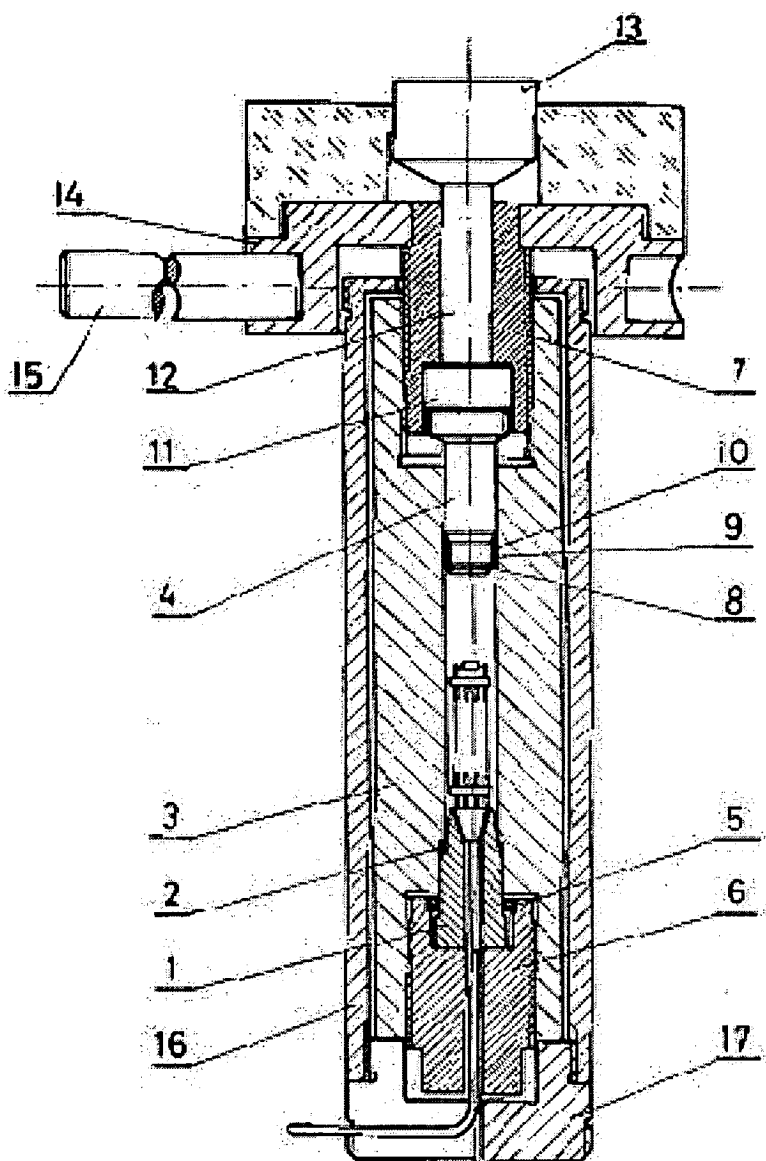


Figure 4.2: LC-10 pressure cell.

- | | | |
|--------------------------------------|--------------------------|--------------------|
| 1. Plug with electrical feedthroughs | 8. Retaining ring | 15. Rod for wrench |
| 2. Metal seal for plug | 9. Rubber seal | 16. Base |
| 3. Cell body | 10. Metal seal | 17. Safety sleeve |
| 4. Piston | 11. CuBe anvil | |
| 5. Retaining nut | 12. Push rod | |
| 6. Plug screw | 13. Steel anvil | |
| 7. Set screw of the piston | 14. Wrench for set screw | |

If one of the wires is broken inside the plug it is usually only a short time before the others get broken because the pyrophyllite gasket is damaged and will break on cooling.

The piston seals, as well as the seals for the plug, can be made of copper and subsequently plated with silver. The use of silver, which has a greater plasticity than copper, gives the rings a better sealing quality.

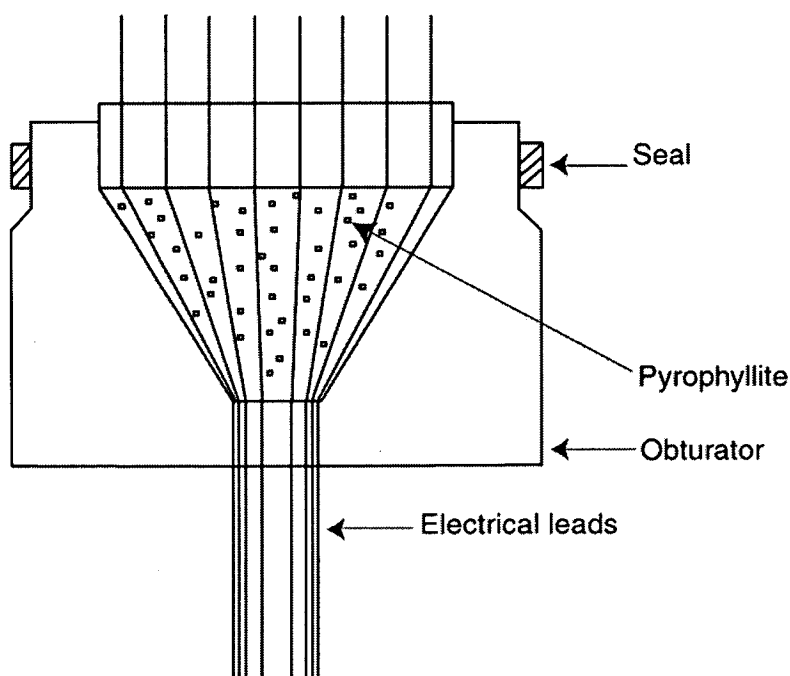


Figure 4.3: Sealing of the electrical leads into a plug.

4.4 Configuration of the electrical probes

The electrical resistivity of isotropic or weakly anisotropic materials is conventionally measured by the four-probe technique. The four-probe technique is normally used to remove the resistance of the electrical leads when the resistance of the leads is comparable with the resistance of the material under investigation. Since the layered manganites are highly anisotropic, and the in-plane and out-of-plane resistivities can differ by 2 to 3 orders of magnitude, the recently developed six-probe method for the resistivity measurements (Levin (1997)) needs to be used.

In the Montgomery method for calculating the resistivity from current-voltage measurements, the current-voltage contacts are assumed to be small in size compared to the sample (Montgomery (1971)). In the current experiments electrical probes cover a considerable part of a sample. Therefore, another method for calculating the resistivity needs to be used.

Levin (1997) proposed a new method of calculating the electrical resistivity for six-probe resistivity measurements, which takes into account the finite size of the electrical probes. Figure 4.4 shows the geometry of the sample and the configuration of the current and voltage probes. The current runs through the contacts 1 and 4, while the voltage is measured on the upper, V_{top} (through the contacts 2 and 3) and the lower, V_{bot} (through the contacts 5 and 6) faces of the sample. The distribution of the current and the potential is considered to be two-dimensional. The z direction is along the c axis and the x coordinate is along the ab plane. The respective components of the resistivity tensor are ρ_c and ρ_{ab} .

$$V_{top} = \frac{4j}{\pi} \sqrt{\rho_c \rho_{ab}} \ln \tan \left(\frac{\pi}{4} + \frac{\pi l}{4L} \right), \quad (4.2)$$

$$V_{bot} = \frac{8j}{\pi} \sqrt{\rho_c \rho_{ab}} \frac{\sin \left(\frac{\pi l}{2L} \right)}{\sinh \left(\frac{\zeta \pi D}{L} \right)}, \quad (4.3)$$

where $\zeta = \sqrt{\rho_c \rho_{ab}}$, j - is the density of the current, D - is the thickness of the sample, L - is the distance between current probes, l - is the distance between voltage probes.

The contacts for the electrical resistivity measurements are made of copper wire with a diameter of 61 μm . A combination of low-resistivity silver paint and a very strong low-temperature silver epoxy was used to attach the electrical contacts to the surface of the sample. One should aim to attach all the contacts to a certain surface of the sample at one time. The surface of the sample is cleaned using ethanol, and the

insulation of the copper wire is removed. A small amount of the low-resistivity silver paint is put directly on the segment of wire to be attached, and the probes are then attached to the sample. Once all the probes are attached, their position should be fixed until they become dry.

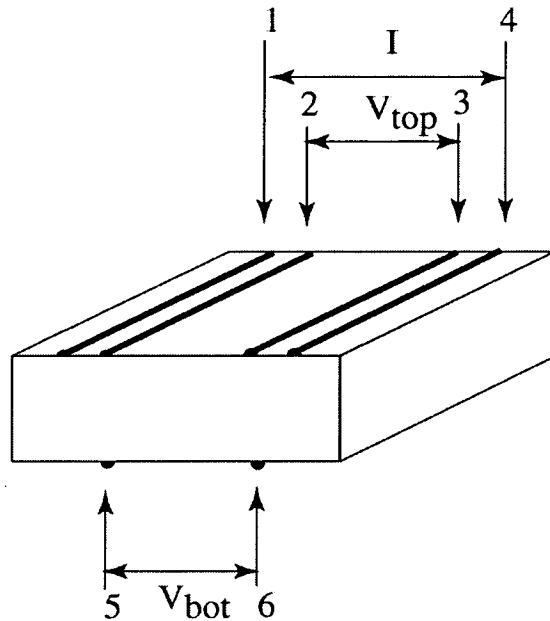


Figure 4.4: Configuration of the electrical probes. Electrical current runs through probes 1 and 4. The voltage on the upper surface (V_{top}) is measured using probes 2 and 3. The voltage on the bottom surface (V_{bot}) is measured using probes 5 and 6.

The thermal treatment (using a hot tip of a soldering iron) allows one to reduce the hardening time for the paint. However, the low-resistivity silver paint does not provide a reliable grasp for the contacts, therefore a thin layer of the strong low-temperature silver epoxy is used to firmly attach the probes to the sample surface. A thermal treatment (using a soldering iron) is highly recommended ($T \sim 450 \text{ K}$). If the contacts prove to be firmly attached to the sample surface on one side of the sample, the same procedure is repeated for the other sample surface. The attached probes are then soldered to the plug of the pressure cell. Insulating the probes using, for instance, nail varnish to reduce the risk of contact touching each other or parts of the pressure cell is recommended. In order to monitor the pressure inside of the pressure cell the pressure gauge is also soldered to the plug.

4.5 Measurements of high resistances using an electrometer

The electrical resistance of layered manganites can easily exceed $10^6 \Omega$. A model 6517A Keithley electrometer was therefore used to measure samples with very high resistance. An electrometer is essentially a highly refined DC multimeter. The special input characteristics and high sensitivity of the electrometer allow measurements of voltage, current, resistance, and charge to be carried out far beyond the realm of conventional digital multimeters (Low Level Measurements, Keithley, 5th Edition, 2001). An electrometer must be used when any of the following conditions exist:

1. Extended range is needed over that of conventional instruments, such as for measuring:
 - currents below 10^{-10} A
 - resistance above $10^9 \Omega$
2. Circuit loading must be minimised, such as when:
 - measuring voltage across a source resistance of $10^6 \Omega$ or higher
 - measuring the current if an input voltage drop of less than a few hundred millivolts is required (when measuring currents from sources of a few volts or less)
3. Functions not available on general purpose equipment are needed, including:
 - charge measurement
 - sensitive current measurement

The input resistance of an electrometer voltmeter is extremely high, typically above $10^{14} \Omega$ and may be as high as $10^{16} \Omega$. Furthermore, the input offset current is less than $5 \times 10^{-15} \text{ A}$ and may be as low as $5 \times 10^{-17} \text{ A}$. These characteristics describe a device that can measure voltages with a very small amount of circuit loading. Because of the very high input resistance and low offset current, the electrometer voltmeter has a

minimal effect on a circuit being measured. As a result, the electrometer can be used to measure voltage in situations where an ordinary multimeter would be unusable. For instance, the electrometer can measure the voltage on a 5×10^{-10} F capacitor without significantly discharging the device.

As an ammeter, the electrometer is capable of measuring extremely low currents, limited only by theoretical limits or by the instrument's input offset current. It also has a much lower voltage burden than conventional digital multimeters. With its extremely low input, offset current, and minimal input voltage burden, it can measure currents as low as 10^{-15} A. Because of this high sensitivity, it is suitable for measuring very low currents in semiconductors. An electrometer may measure resistance by using either a constant current or a constant voltage method. If using the constant current method, the electrometer's high input resistance and low offset current enables measurements up to $2 \times 10^{11} \Omega$. When using the constant voltage method, the electrometer applies a constant voltage to the unknown resistance, measures the current, and then calculates the resistance. This is a preferred method and it was realised in the experimental setup because it allows the unknown resistor to be tested at a known voltage. The electrometer can measure resistances up to $10^{16} \Omega$ using this method. Since the electrometer was used to measure very high resistances and it was possible to neglect the resistance of electrical probes ($\sim 2 \Omega$), the two-probe scheme of measurement was used. A desirable voltage value can be chosen and set up manually in the range of 5×10^{-3} V to 400 V. It is therefore possible to measure quite low resistances of order of 100Ω . If an electrometer is used as a voltmeter, and the four-probe method is realised, then it is possible to measure even low resistances $\sim 1 \Omega$ without an additional shielding of the wires.

The electrometer was used for measurements of the resistance of the powder samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, and $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ in a Diamond Anvil Cell (two-probe method). Measurements of the resistivity of single crystals of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ in the LC-10 pressure cell were performed using a setup for the six-probe method that includes a nanovoltmeter and a current source. While resistance and resistivity are related properties, they are not the same. Resistivity is an intrinsic property of a material, so it is independent of the geometry of a particular sample. In contrast, resistance depends not only on the material, but also on the length and cross-

sectional area of the sample being measured. When making volume resistivity measurements, the measured resistance is multiplied by the cross-sectional area of the sample perpendicular to the current flow, and divided by the path length of the current. The results are expressed in $\Omega\cdot\text{cm}$. Effective area and thickness values must be used in calculations when working with samples with complex geometry. For surface resistivity measurements, the measured resistance is multiplied by the width of the surface across which the current flows, this value is then divided by the path length of the current along the surface. The results are expressed in $\Omega\cdot\text{cm}$.

When using the constant voltage method, it is important to realise that the measured current is a combination of the background currents from many sources, the *dc* resistive current, and the current charging the capacitance of the material. Background currents can be produced by many different phenomena, such as piezoelectric effects, temperature induced pole relaxation, or discharging of the internal capacitance elements. The background currents decay over time at different rates depending on their individual time constants. Sometimes the stimulated current can be completely masked by the background current. Such measurements produce erroneous results. Any sample has a capacitance as well as a resistance. Therefore, any sample can be modelled as a collection of the resistances and the capacitance. That is why when measuring very high resistances it is important to consider the characteristic frequency at which the sample is to be measured. A 15 second delay (3.3×10^{-2} Hz) is often a very good approximation of *dc* response.

4.6 Measurements of the electrical resistivity of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$

The electrical resistivity of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ was measured as a function of temperature under pressures of up to 9.4 kbar, Figure 4.5. At high temperatures, both the resistivities measured within the *ab*-plane (ρ_{ab}) and along the *c*-axis (ρ_c) show an increase on cooling which corresponds to thermally activated behaviour, characteristic for semiconductors and insulators. A sharp peak on ρ_{ab} is associated with a metal-insulator transition, has been observed at a temperature of ~ 80 K under ambient pressure. Under applied pressure the temperature of the transition shifts to higher

temperatures. At a pressure of 9.4 kbar, $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ undergoes a metal-insulator transition at ~ 100 K. It has also been found that pressure suppresses a peak in the resistivity.

The value of ρ_c demonstrates a transition from an insulating into a metallic-like state at ~ 95 K. A pressure of 9.4 kbar increases the temperature of the transition to ~ 105 K and suppresses the peak. It has been reported that the applied pressure extends the region of long-range magnetic ordering in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ (Kamenev *et al.* (2001)). An increase in the temperature of the metal-insulator transition corresponds to an increase in a temperature of the long-range magnetic ordering. Due to the anisotropic nature of the electronic transport in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, resistivity across the bilayers is 3 orders of magnitude higher than along the bilayers.

When hydrostatic pressure is applied, the temperature of the metal-insulator transition (T_{MI}) increases. It reflects the fact that the metal-insulator transition is ultimately bound to magnetic ordering in the manganese sublattice. Under a pressure of 9.4 kbar the peak at T_{MI} is suppressed, and the resistivity at T_{MI} drops by a factor of about 35 along the bilayers, and by a factor of about 15 across the bilayers. This considerable drop can be explained by an increase in the overlap of the Mn-O-Mn linkages, controlling the conductivity in manganites. This leads to an increase in the transfer integral and leads to a decrease in the electrical resistivity (Goodenough (1963)).

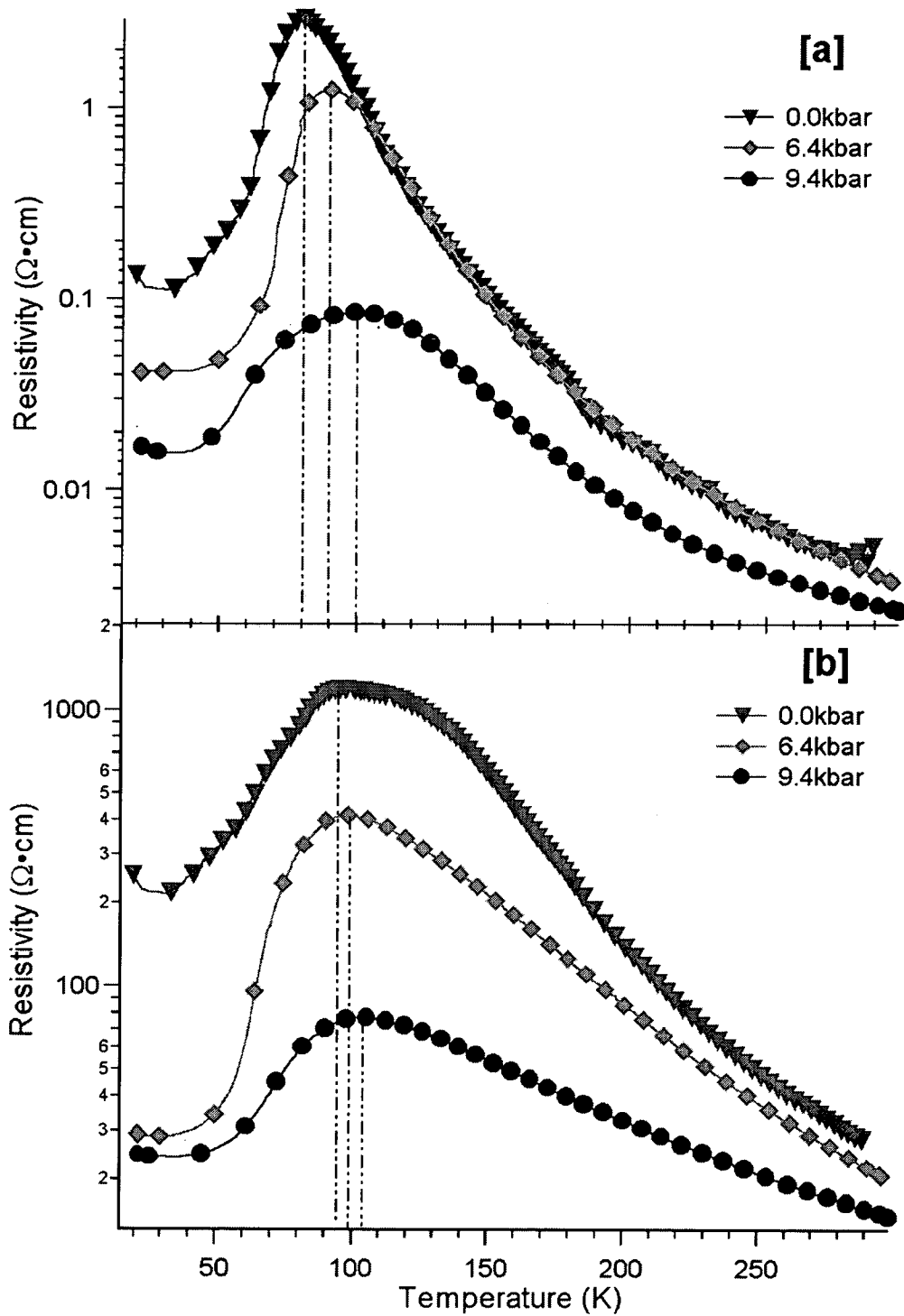


Figure 4.4: Electrical resistivity of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ [a] within the ab -plane and [b] parallel to the c -axis under different hydrostatic pressures.

4.7 Measurements of the electrical resistivity of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$

The electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ has been measured as a function of temperature under pressures of up to 10 kbar. The electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured within the *ab*-plane (ρ_{ab}) and along the *c*-axis (ρ_c) at different pressures is shown in Figure 4.6 and Figure 4.7 respectively.

The values of the resistivity measured within the *ab*-plane and along the *c*-axis at the same temperature were quite different. Moreover, ρ_c changed more than a thousandfold in the temperature interval between 120 and 20 K (Figure 4.7), while ρ_{ab} changed only tenfold between 120 and 20 K, Figure 4.6. However, to calculate the correct values of ρ_{ab} and ρ_c , both values had to be measured simultaneously using the constant current method. The electrical current within the *ab*-plane and along the *c*-axis had to be the same in order to calculate the correct values of resistivity (see part 4.4). Because of the instrumental limits of the nanovoltmeter Keithley 2182 and the current source Keithley 224, the temperature range for collecting the data is considerably restricted. This is why the ρ_c and ρ_{ab} were measured only in the temperature interval between 120 and 20 K.

Unlike the resistivity of $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, the resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ did not demonstrate a metal-insulator transition in the studied pressure range. The electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured within the *ab*-plane (ρ_{ab}) at ambient pressure increased monotonically until ~ 60 K, Figure 4.6. Below ~ 60 K, ρ_{ab} became saturated.

A pressure of 6 kbar expanded the regime of saturation on the resistivity curve to ~ 70 K, Figure 4.6. At a pressure of 9 kbar the saturation regime began at ~ 80 K, Figure 4.6. At 10 kbar (the maximum pressure that can be reached in LC-10), the saturation started at 85 K. The external pressure also considerably lowered the value of ρ_{ab} . A pressure of 10 kbar changed the value of ρ_{ab} by 4 orders of magnitude. The saturation regime of the electrical resistivity was typical for non-metallic spin-glasses (Mott (1990)). This was due to the scattering of the charge carriers on the short-range magnetic order (i.e. on magnetic clusters) (Mott (1990)).

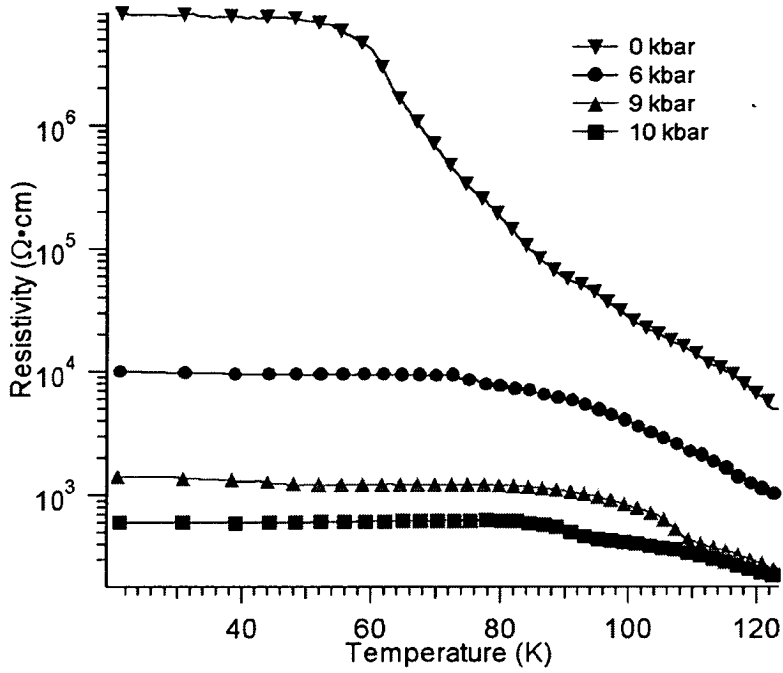


Figure 4.6: Electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under different hydrostatic pressures measured along the ab -plane.

At higher temperatures (above the saturation temperature), the ρ_{ab} measured at ambient pressure was well described by $\ln(\rho/\rho_0) = 1/(T_0/T)^{1/4}$ (Mott (1979)), Figure 4.8. Such behaviour of the resistivity curve can be attributed to hopping of the charge carriers localised by the magnetic disorder (Mott (1979)). Higher pressure enhances the short-range magnetic correlations in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ (see part 5.7). This leads to a change in the type of the conductivity, which can be seen as a deviation from $\ln(\rho/\rho_0) = 1/(T_0/T)^{1/4}$ law, Figure 4.8.

The electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured along the c -axis (ρ_c) at ambient pressure monotonically increased on cooling down to ~ 55 K, where it became saturated, Figure 4.7. Unlike ρ_{ab} , ρ_c did not show considerable change in the pressure range below 10 kbar, Figure 4.7. The saturation regime started at ~ 55 K at pressures below 10 kbar, Figure 4.7. A small decrease of the absolute value of ρ_c with applied pressure was observed at temperatures above 60 K (see the insert in Figure 4.7).

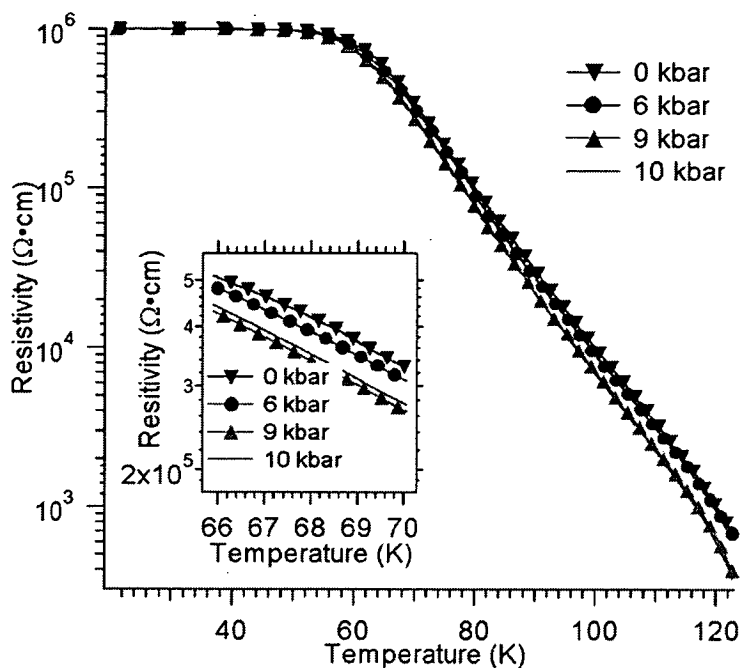


Figure 4.7: Electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under different hydrostatic pressures measured along the c -axis.

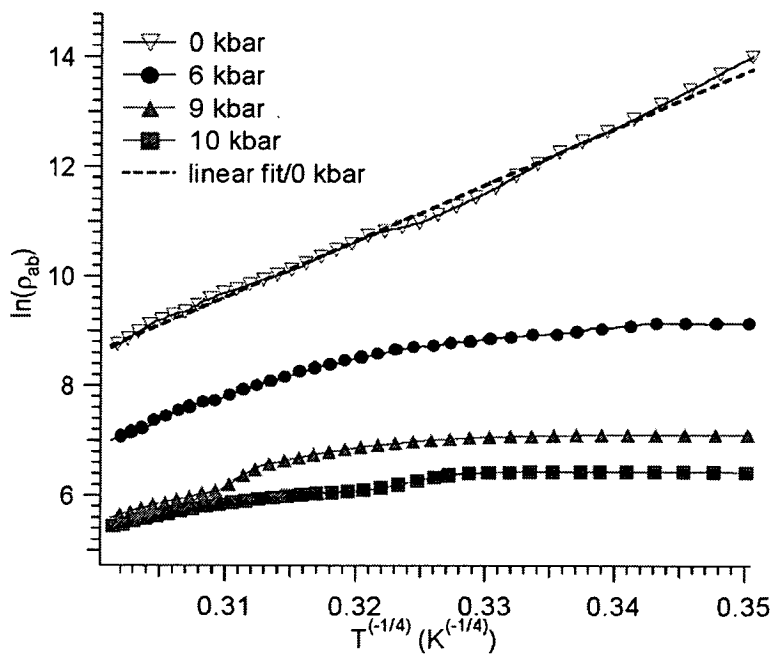


Figure 4.8: $\ln(\rho_{ab})$ vs $T^{-1/4}$ plot for $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. The straight line is the best fit for the data points. The temperature (T) shown is from 66 to 123 K.

The electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ has been measured as a function of temperature at pressures of up to 10 kbar. The temperature profiles of the electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured within the ab -plane (ρ_{ab}) in the pressure range 0-10 kbar are shown in Figure 4.9. At ambient pressure, ρ_{ab} of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ increased monotonically with temperature decrease, and did not show a metal-insulator transition or a tendency to saturation. The resistivity was well fitted using a $\ln(\rho / \rho_0) = 1 / (T_0 / T)^{1/4}$ law, (Mott (1979)). This means that the conductivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ within bilayers can be attributed to thermally activated hopping in a temperature interval between 300 and 108 K, Figure 4.10.

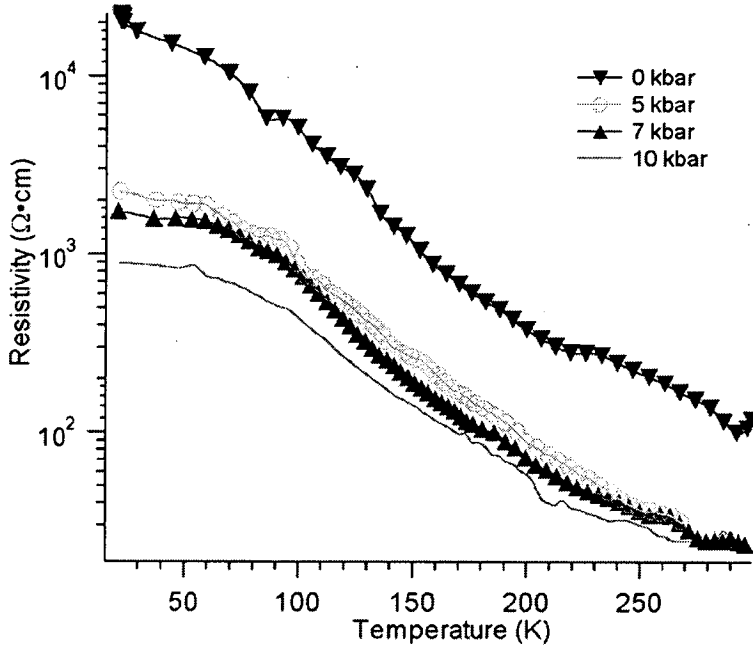


Figure 4.9: Electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under different hydrostatic pressures measured within the ab -plane.

The applied pressure decreased the absolute value of the resistivity without changing the general profile of ρ_{ab} , Figure 4.9. It was possible to fit a resistivity curve collected at a pressure of 10 kbar using a $\ln(\rho / \rho_0) = 1 / (T_0 / T)^{1/4}$ law. This probably means that a pressure of 10 kbar is not large enough to enhance the magnetic correlations in $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and hence considerably change the mechanism of conductivity. Again no metal-insulator transition was found.

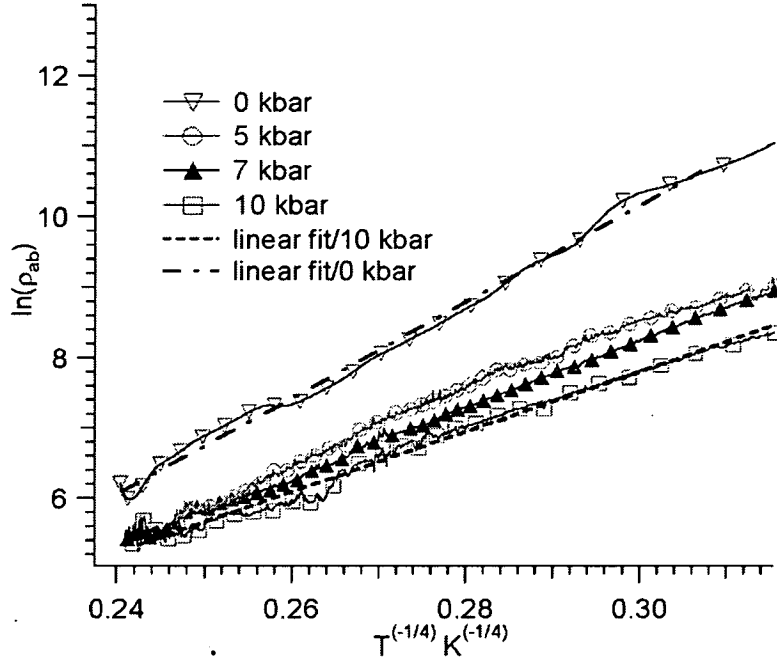


Figure 4.10: $\ln(\rho_{ab})$ vs $T^{-1/4}$ plot for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. The temperature (T) shown is from 101 to 301 K.

The electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured along the c -axis (ρ_c) at ambient pressure increased monotonically with a temperature decrease until ~ 75 K, reaching $\sim 10^7 \Omega\cdot\text{cm}$, which is the maximum resistivity that can be measured using the nanovoltmeter Keithley 2182 and the current source Keithley 224 (constant current method and six-probe scheme is utilised), Figure 4.11. The applied pressure lowered the absolute value of the resistivity. The resistivity ρ_c was well described by $\ln(\rho/\rho_0) = 1/(T_0/T)^{1/4}$ law above ~ 132 K at all pressures, Figure 4.12. Thus it is possible to ascribe the conductivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ across bilayers to thermally activated hopping in the temperature interval from 273 to ~ 132 K.

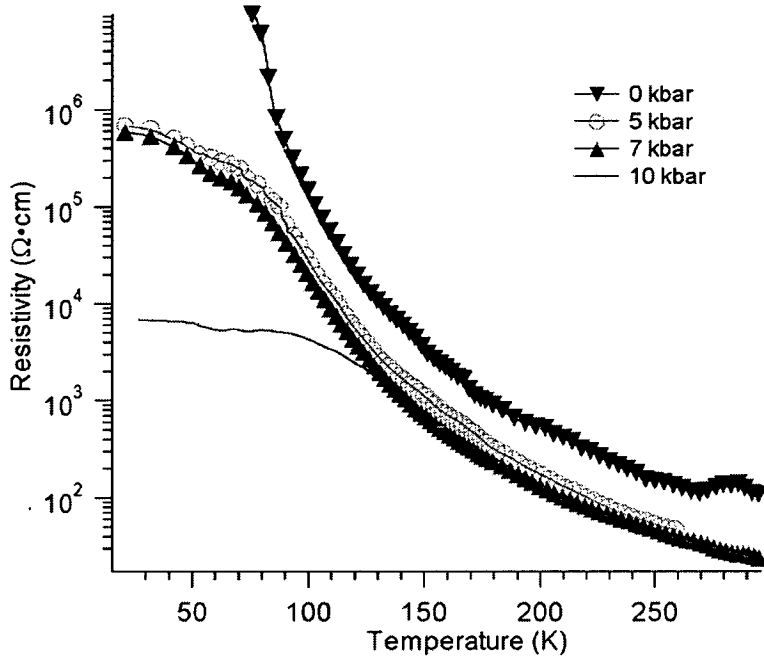


Figure 4.11: Electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under different hydrostatic pressures measured along the c -axis.

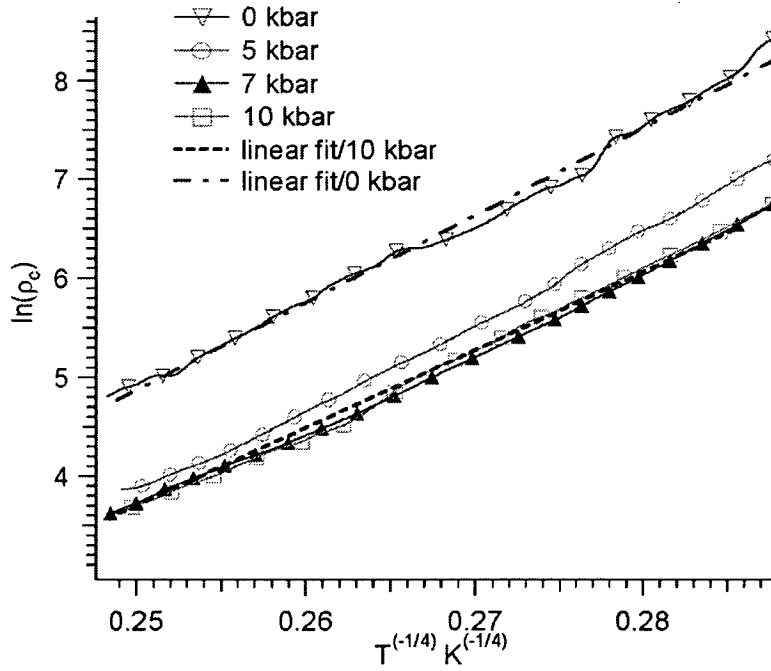


Figure 4.12: $\ln(\rho_c)$ vs $T^{-1/4}$ plot for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. The temperature (T) shown is from 132 to 273 K.

The general profiles of the resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ were quite similar. They both demonstrated an increase in the value of the resistivity on cooling, which was well described by thermally activated hopping (Mott (1979)). No drastic changes in the behaviour of the resistivity curves of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under applied pressure were observed. The absolute value of the resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ monotonically decreased under applied pressure. Application of pressure increases the overlap of the Mn-O-Mn linkages, which control the conductivity in manganites. This leads to an increase in the transfer integral and, therefore, to a decrease in the electrical resistivity (Goodenough (1963)).

It is important to realise that the four (six)- probe method does not allow the experimentalist to remove the resistance of the electrical contact. It simply allows for the elimination of the resistance of the electrical feedthroughs, which in this case are made of copper. All of the feedthroughs that go through the closed-cycle refrigerator, switch, voltmeter and electrical leads on a sample have a total resistance of $\sim 2 \Omega$. However, the resistance of the contact, which is essentially a “sandwich” consisting of sample surface-silver epoxy-copper wire, is much larger ($\sim 10^3 \Omega$). Therefore, one always measures the resistance of the sample as well as the resistance of the sample surface-silver epoxy-copper wire. However, it is still preferable to use the four (six)-probe method, when looking for metal-insulator transition. During the procedure of attaching the electrical leads to the sample special care must be taken to bring the wire and the sample as close together as possible. However, as the contacts dry, they get lifted under the surface of the sample or shifted even if a counterbalance is used. Even relatively small changes in the geometry of electrical contacts may result in large changes of measured resistance. Therefore, even with the four-probe technique it is imperative to make the resistance of the contact as low as possible.

To fully investigate the effect of external pressure on the transport properties of Pr-based bilayer manganites, a pressure cell capable of exceeding pressure of 10 kbar is required, and a new method of measuring the resistivity between ~ 20 to 300 K is needed.

4.8 Measurements of the magnetic susceptibility of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$)

The usual way to determine the magnetic susceptibility χ , is when a static magnetisation M is measured and divided by the applied field H . However, when χ is a function of applied field, this method fails. A different technique is to apply a small *ac*-field, called the driving field h , and measure χ by taking the derivative dM / dh at some frequency ω and even with some *dc* magnetic field. This *ac* susceptibility is especially important for spin-glasses since h can be made very small ~ 0.1 Oe and ω can be varied over a rather large frequency range, therefore permitting a full determination of the real $\chi'(\omega)$ and the imaginary $\chi''(\omega)$ parts (Mydosh (1993)).

Sharp cusps were discovered in the susceptibility of AuFe (Cannella and Mydosh (1972)), which is now one of the model spin-glass materials. This material was studied for many years before but only in large magnetic fields. A few hundred gauss of applied *dc*-field smeared out the cusp into a broad maximum. This is why the spin-glasses were not identified a decade or two sooner (J. Mydosh (1993)).

The real part of susceptibility $\chi'(\omega)$ is called the dispersion, and imaginary part, the $\chi''(\omega)$, is called the absorption. $\chi'(\omega)$ and $\chi''(\omega)$ are related through the relaxation time by the Casimir-du Pre equations (4.4 and 4.5) (J. Mydosh (1993)). $\chi''(\omega)$ is smaller than $\chi'(\omega)$. In spin-glasses, the peak on $\chi'(\omega)$ usually corresponds to the peak on $d\chi''(\omega) / d\omega$. The appearance of the imaginary component means that relaxation processes are affecting the measurement, and by decoupling the spins from the lattice they can cause the absorption.

To measure field cooled (FC) magnetic susceptibility, one needs to apply the field far above the temperature of a transition into a spin-glass state T_s , and cool the sample in a field to a $T < T_s$. The sample is then heated while measuring the magnetisation to a $T > T_s$ with a constant field. In the second method, the sample is cooled in a zero magnetic field to a $T < T_s$. At this low temperature, the field is then applied. The sample is then heated while measuring the magnetisation to a $T > T_s$ with a constant field. This procedure is called zero-field cooling (ZFC). In AuFe, the FC χ becomes constant at T_s (Cannella and Mydosh (1972)). The FC procedure is reversible, i.e. if the spin-glass

material is cooled or heated, the FC susceptibility curve traces the same path. When a magnetic field is on and at a constant temperature, the ZFC χ jumps to a value comparable with that of the FC χ . However, the ZFC χ for a spin-glass is never equal to 0 at the lowest temperatures provided the magnetic field is on. On heating, the ZFC χ curve arrives to the T_s , where it meets the FC χ .

$$\chi' = \chi_s + (\chi_T - \chi_s) / (1 + \omega^2 \tau^2) \quad (4.4)$$

and

$$\chi'' = \omega \tau (\chi_T - \chi_s) / (1 + \omega^2 \tau^2), \quad (4.5)$$

where τ is the single relaxation time, χ_T is the isothermal susceptibility in the limit $\omega \rightarrow 0$, and the χ_s is the adiabatic susceptibility in the limit $\omega \rightarrow \infty$.

If $\chi'' = 0$, then there are two possibilities: either $\omega\tau \rightarrow 0$, and one measures an equilibrium isothermal χ_T , or $\omega\tau \rightarrow \infty$ and one measures non-equilibrium adiabatic χ_s . At $\omega = 1 / \tau$ the dispersion $\chi'(\omega)$ will have an inflection point, whereas the absorption $\chi''(\omega)$ will show a maximum. This maximum provides a way for determining an average relaxation time for each temperature.

The magnetic *ac* and *dc* susceptibilities of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4, 0.5$) manganites were measured using a superconducting quantum interference device (SQUID). A SQUID consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions, (Jaclevic *et al.* (1964)). The device is configured as a magnetometer to detect incredibly small magnetic moments. The great sensitivity of the SQUID devices is associated with measuring changes in magnetic field, associated with one flux quantum. If a constant biasing current is maintained in the SQUID, the measured voltage oscillates with the changes in phase at the two junctions. These changes depend upon the change in the magnetic flux. Counting the oscillations allows one to evaluate the flux change which has occurred (Rohlf (1994)).

A special sample holder made of gelatine was used in order to orient the single crystal material to the magnetic field. All the data were collected on heating after cooling in the zero field (ZFC) and in the field of measurements (FC). The *ac* susceptibility χ is represented as:

$$\chi = \sqrt{\chi'^2 + \chi''^2} \quad (4.6)$$

The magnetic susceptibility of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) reflects their rich magnetic behaviour, Figures 4.13, 4.14, and 4.15. However, the analysis of the neutron diffraction data (parts 3.4 and 3.5) shows that there is no long-range magnetic order in the main tetragonal phase in any of the samples. The analysis of the neutron diffraction data also shows that each sample contains a small amount of perovskite-type intergrowth phase $(\text{Pr,Sr})\text{MnO}_3$. The refinement of the neutron diffraction data also shows that all samples undergo a magnetic transition at ~ 150 K which can only be attributed to the intergrowth phase. Therefore, the majority and intergrowth phase transitions have to be looked at separately.

$\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ becomes a ferromagnetic metal at ~ 270 K (Jirak *et al.* (2001)). The magnetisation of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in a ferromagnetic state increases on cooling and at ~ 150 K $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ transforms into an antiferromagnetic nonmetal (Jirak *et al.* (2001)). Tomioka *et al.* (1995) reported that $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ undergoes a transition into an antiferromagnetic state at 140 K. Knizek *et al.* (1992) reported 160 K as the temperature of antiferromagnetic transition in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in ceramic samples. Tomioka *et al.* (1995) reported that such a difference in temperatures of the antiferromagnetic transition in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is probably due to a slight difference in the composition of the samples.

The analysis of the neutron diffraction data shows that the sample of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ contains $\sim 4\%$ of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth. The magnetic susceptibility of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured along the c -crystallographic axis demonstrates the first magnetic transition at ~ 280 K, which corresponds to the Curie temperature for $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, Figure 4.13 (b, c). Kimura *et al.* (1997) have found that in $\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ magnetic moments within the bilayer order ferromagnetically at ~ 270 K in the magnetic field of 2 Oe. It is quite possible that such quasi-two-dimensional ferromagnetism takes place in Pr-based bilayered manganites. However it is difficult to comment on the contribution of this ordering. Therefore, this transition should be attributed to the establishment of ferromagnetism in the intergrowth phase.

On further cooling, one can see the magnetic transition at ~ 170 K, which corresponds to an antiferromagnetic transition in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. The 4% of the absolute magnitude of the magnetisation of the floating-grown sample of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ reported by Tomioka *et al.* (1995) at 150 K is $\sim 21 \times 10^{-3} \mu_B/\text{Mn site}$, and $\sim 4 \times 10^{-3} \mu_B/\text{Mn site}$ at ~ 280 K, which is fairly close to what is observed in Figure 4.13 (b). The magnetic transition at ~ 55 K should be attributed to the majority $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ phase because $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ does not show any transition or anomaly at this temperature.

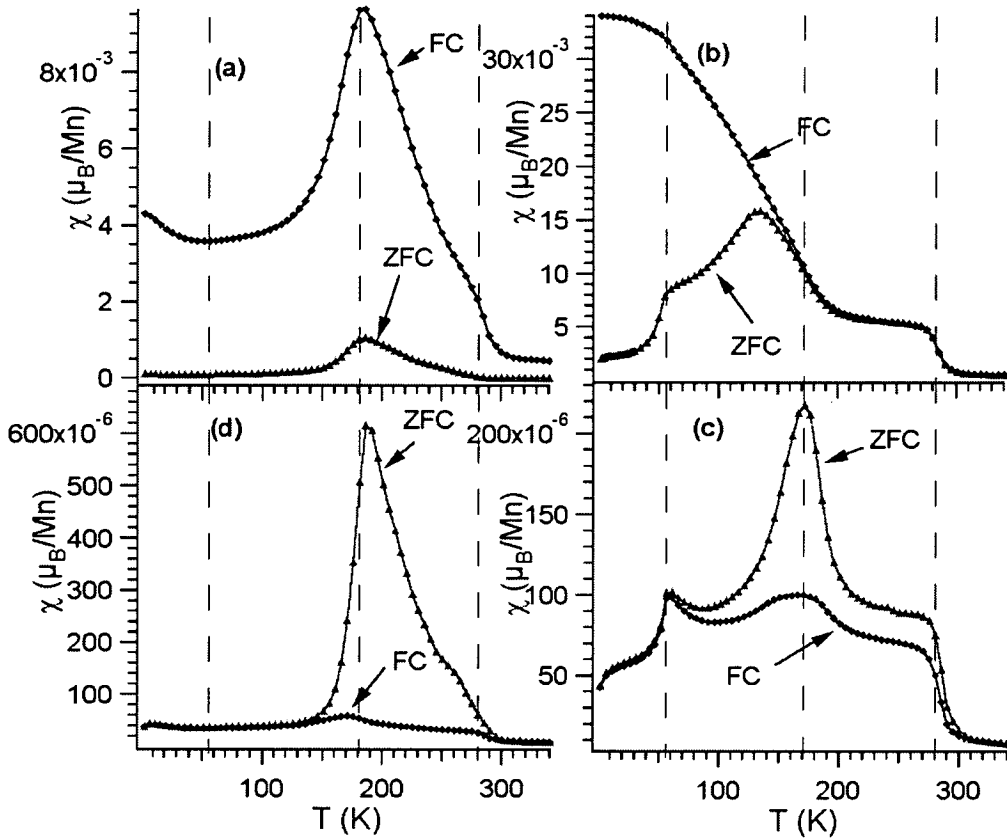


Figure 4.13: Magnetic susceptibility of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured at ambient pressure, $H = 100$ Oe:

- (a) *dc* magnetic susceptibility $H \parallel ab$ plane.
- (b) *dc* magnetic susceptibility $H \parallel c$ axis.
- (c) *ac* magnetic susceptibility $H \parallel c$ axis, $f = 113\text{Hz}$.
- (d) *ac* magnetic susceptibility $H \parallel ab$ plane, $f = 113\text{Hz}$.

The magnitude of the magnetisation measured at ~ 55 K suggests that this is a transition into a spin-glass state. The characteristic for spin-glass temperature hysteresis, starting from the transition point, is not observed because the intergrowth phase orders at a higher temperature of ~ 170 K and has a higher magnetisation than the $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ phase.

The magnetic susceptibility of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ is shown in Figure 4.14.

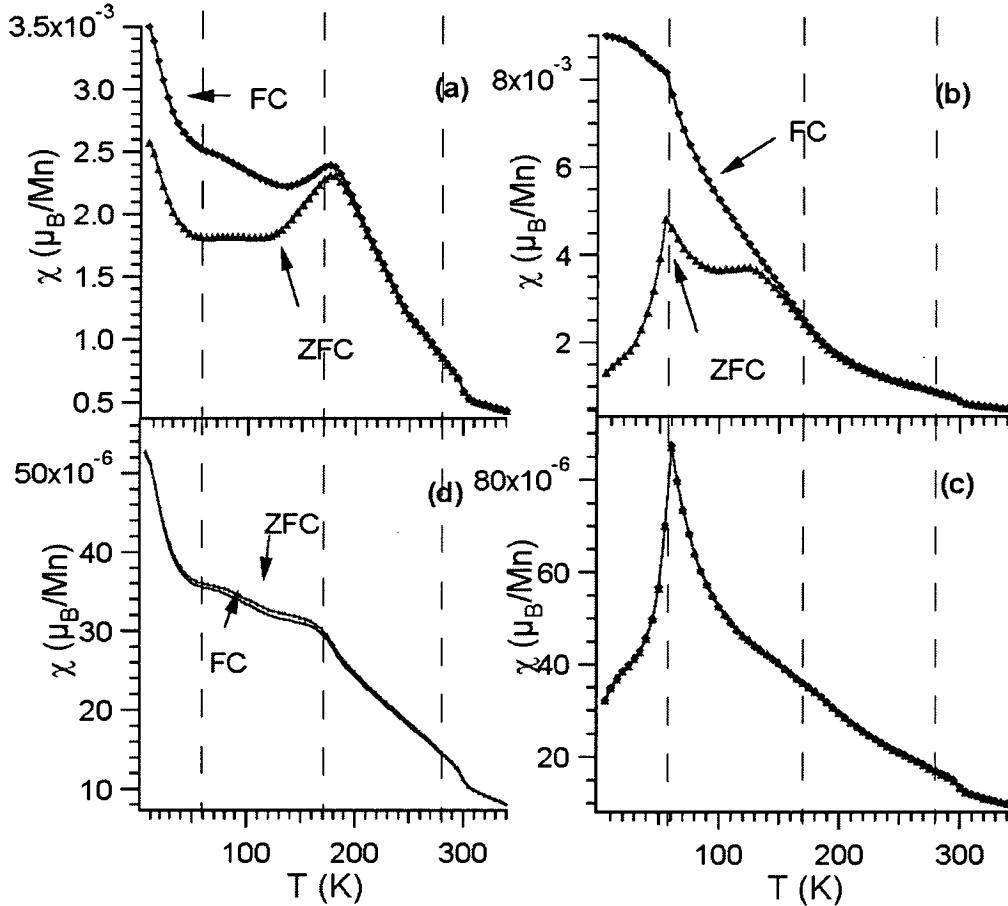


Figure 4.14: Magnetic susceptibility of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ measured at ambient pressure, $H = 100$ Oe:

(a) *dc* magnetic susceptibility $H \parallel ab$ plane.

(b) *dc* magnetic susceptibility $H \parallel c$ axis.

(c) *ac* magnetic susceptibility $H \parallel c$ axis, $f = 113$ Hz. ZFC and FC coincide.

(d) *ac* magnetic susceptibility $H \parallel ab$ plane, $f = 113$ Hz.

The transitions were again observed at ~ 56 K, ~ 170 K, and ~ 280 K. The last two come from the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth phase. The transition from the $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ phase, occurs at ~ 56 K, Figure 4.14 (a,b). No characteristic for spin-glass temperature hysteresis, starting from the transition point, is observed because the intergrowth phase orders at a higher temperature of ~ 170 K, and its magnetisation increases faster than the magnetisation of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ phase.

A peak in the ZFC *ac* susceptibility occurs at the temperature of transition into a spin-glass state on the *dc* susceptibility curve Figure 4.14(c). The *ac* susceptibility measured with a magnetic field parallel to the *c*-crystallographic axis does not show the temperature hysteresis in a studied temperature region. However the temperature hysteresis on the *ac* susceptibility measured with a magnetic field parallel to the *ab*-crystallographic plane can be seen, though it is small.

The magnetic susceptibility of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured along the *ab*-crystallographic plane also shows a transition at ~ 170 K, which is attributed to the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth phase, Figure 4.15 (a, d). The *dc* magnetic susceptibility of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured along the *c*-crystallographic axis increases with a decrease in temperature and demonstrates a clear transition into a spin-glass state at ~ 42 K, Figure 4.15 (b). A peak in the ZFC *ac* susceptibility occurs at the transition temperature into a spin-glass state on *dc* susceptibility curve, Figure 4.15 (c). However, no transition into a ferromagnetic state in the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase is observed. Analysis of the neutron diffraction data shows that in this composition, the perovskite intergrowth amounts to $\sim 2\%$, compared to $\sim 4\%$ in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$. Therefore, in $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ one can expect less contribution from ferromagnetism in the intergrowth phase. The magnitude of the *dc* susceptibility (which probes the degree of the magnetic order in a system) of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ varies from 2×10^{-3} to $5 \times 10^{-3} \mu_B/\text{Mn}$ site at 280 K (the transition temperature) depending on the orientation of the sample to the magnetic field. In $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ the *dc* susceptibility at 280 K is smaller than $1 \times 10^{-3} \mu_B/\text{Mn}$ site. Therefore, it is possible that the magnitude of the ferromagnetic transition in the intergrowth phase in $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ was too small to be detected.

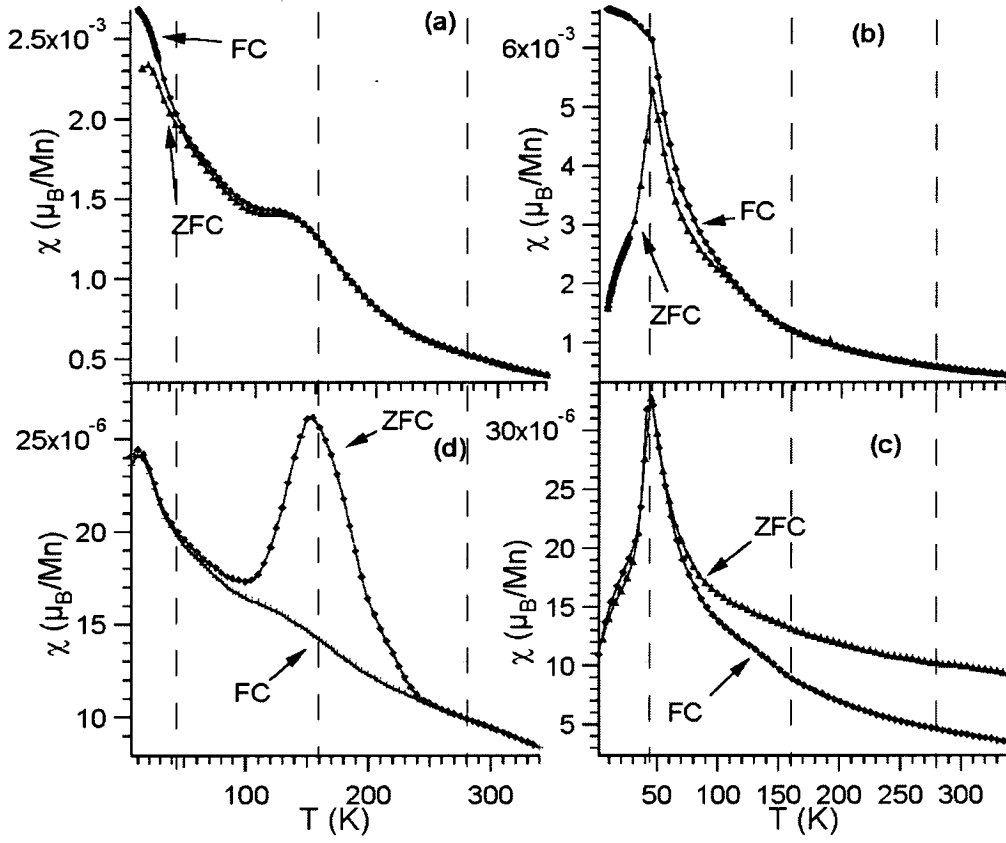


Figure 4.15: Magnetic susceptibility of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured at ambient pressure, $H = 100 \text{ Oe}$:

- (a) *dc* magnetic susceptibility $H \parallel ab$ plane.
- (b) *dc* magnetic susceptibility $H \parallel c$ axis.
- (c) *ac* magnetic susceptibility $H \parallel c$ axis, $f = 113 \text{ Hz}$.
- (d) *ac* magnetic susceptibility $H \parallel ab$ plane, $f = 113 \text{ Hz}$.

Berger *et al.* (1999) have investigated the structural and magnetic properties of single crystals of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$). They reported that both samples showed a non-vanishing magnetisation in an extended temperature range above the Curie temperature. They attributed the magnetisation in this temperature range to the intergrowths. The intergrowths were observed in transmission electron micrographs as missing or extra layers of SrO. They have observed the magnetic ordering in both compositions above the Curie temperature and attributed this to the contribution from the intergrowth phase. However, later Kimura *et al.* (1997) have found that in

$\text{La}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ the magnetic moments within the bilayer order ferromagnetically at ~ 270 K in the magnetic field of 2 Oe.

Sloan *et al.* (1998) have reported high-resolution transmission electron microscopy (HRTEM) studies of $\text{Sr}_2\text{LnMn}_2\text{O}_7$ (Y, La, Nd, Eu, Ho). They have found that the intergrowth phase is present in the majority phase and the density of the perovskite intergrowths is greater near the edges of the thin samples. The formation of the intergrowth phase in the bilayered manganites is probably inevitable, as the majority (tetragonal) phase has a larger strain in it, and needs to be “relaxed” occasionally by means of forming the intergrowths of the Ruddlesden-Popper phase $\text{Ln}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ with $n > 2$. During the formation of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ crystal, the intergrowth grows in the layered structure adjusting its lattice parameters to match those of the majority $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ phase, Figure 4.16. The intergrowth can be envisioned as an occasional stacking fault with missing SrO layers.

The behaviour of the magnetisation of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and other perovskite-type manganites was predicted to be anisotropic (Kawano *et al.* (1997)). However, this anisotropy has never been observed experimentally because the structure of $(\text{Ln},\text{Sr})\text{MnO}_3$ manganites prepared by conventional methods consists of twins (Rodriguez-Carvajal *et al.* (1998), Zvyagin *et al.* (2000)). Twinning keeps one characteristic axis unchanged and forms the domains by rotation around that axis, (Rodriguez-Carvajal *et al.* (1998)). Shklyarevskiy *et al.* (2002) have reported the domain structure of the antiferromagnetic insulating state in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. They have confirmed that the antiferromagnetic domains in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ are crystal twins. The formation of the domains makes the magnetic properties of the bulk samples look isotropic.

In this work, however, a clear anisotropy of magnetic properties of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, which is present as intergrowths in the main $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ phase, was observed. The presence of the perovskite intergrowths in the majority bilayered phase was reported in almost every work concerned studies of the single crystals of bilayered manganites (the concentration of the perovskite phase in the polycrystalline samples is even higher). However, in studies of the La-based bilayered manganites, which were found to be ferromagnetic, the contribution from the intergrowth phase was

vanishingly small in comparison with the fully ordered majority phase, and the magnetic properties of the intergrowth phase were never studied. The Pr-based manganites undergo a transition into a spin-glass state and, therefore, the magnetism from the majority phase does not mask the magnetism of the intergrowth phase. The process of the formation of the intergrowth within the majority bilayered phase also prevents the perovskite phase from twinning. This provides an excellent opportunity for studies of the magnetic properties of (Pr,Sr)MnO₃ and their predicted (but never observed) anisotropy.

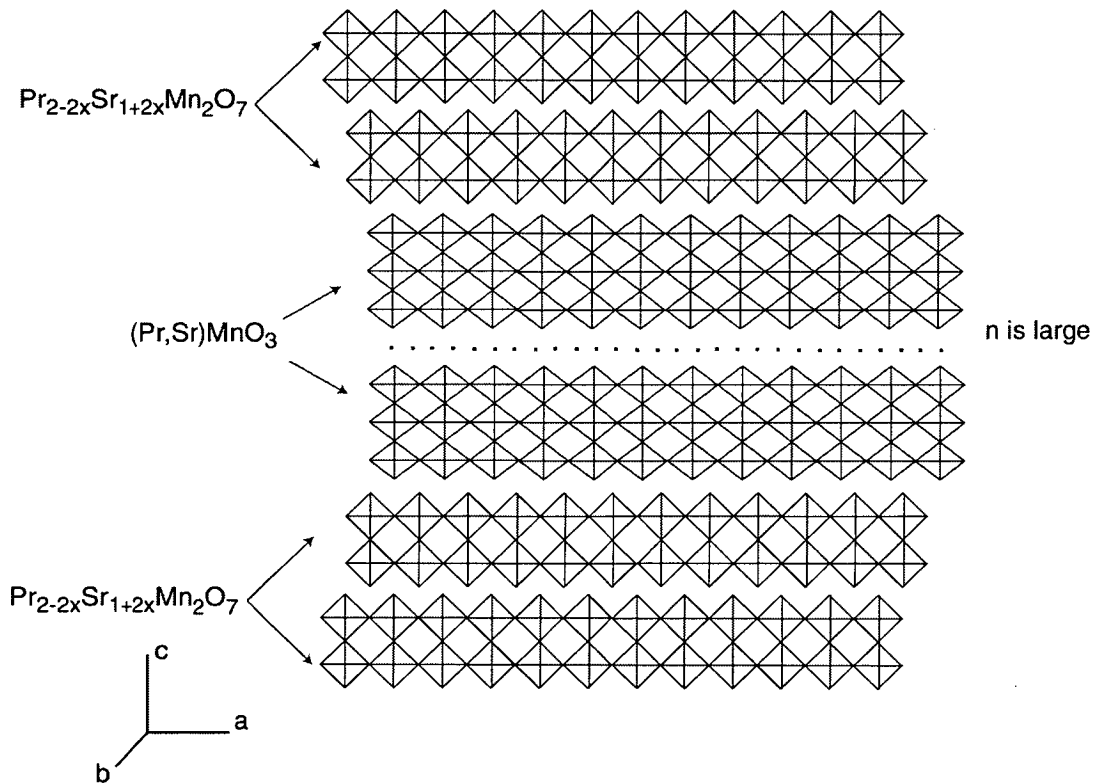


Figure 4.16: (Pr,Sr)MnO₃ intergrowth in Pr_{2-2x}Sr_{1+2x}Mn₂O₇ phase. Note, that the lattice parameters of the majority and the intergrowth phases match along the *a*-axis.

4.9 Measurements of the magnetisation of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) under pressure.

To study the effect of pressure on the magnetic properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) a miniature pressure cell of the piston-cylinder type made of CuBe alloy was used, Figure 4.17. It is capable of reaching a pressure of 11 kbar. The design of the pressure cell is similar to that of the LC-10.

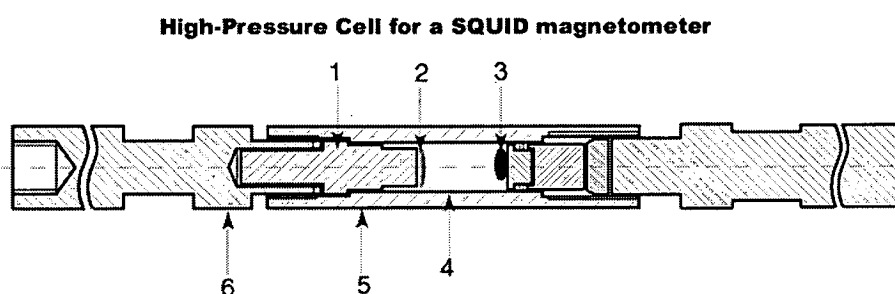


Figure 4.17: High-pressure cell for a SQUID magnetometer.

- | | |
|--------------------------|---------------------|
| 1. Piston | 4. Teflon container |
| 2. Sample | 5. Body of the cell |
| 3. Pressure gauge (lead) | 6. Backing screw |

The sample is put in a cylindrical container made of Teflon. The container is filled in with Fluorinert FC-77, which is used as a pressure transmitting medium. Pressure is changed at room temperature and measured at low temperature using the superconducting transition of lead, a small amount of which is located near the sample inside the container. However, when the cell is cooled down, the pressure inside the cell drops because of the different coefficients of thermal expansion of cell material and pressure transmitting medium. The value of drop for this particular cell is ~ 3 kbar. The values of pressure listed below were calculated at the temperature of the superconducting transition in the lead, which has a known pressure dependence (Swenson (1960)):

$$P = (T_0 - T) / 0.0405, \quad (4.7)$$

where P is the pressure in kbar, T_0 is the temperature of superconductive transition in the lead at ambient pressure, and T is the temperature of the transition at higher pressure. The superconductive transition was observed as a discontinuity in the magnetisation, Figure 4.18. Measurements of the *dc* magnetisation were performed using a SQUID magnetometer.

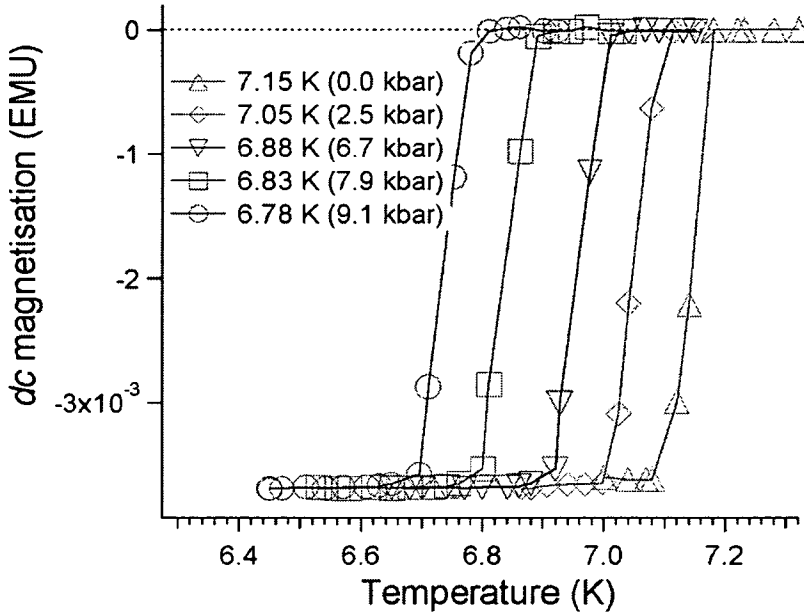


Figure 4.18: Pressure dependence of the superconducting transition in lead.

A magnetic field of 1 T was used, as no considerable magnetic response from the samples of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ was detected in a studied temperature region at lower fields. However, a magnetic field of such strength inevitably smears the sharp cusp of the magnetisation into a broad maximum if the studied material remains a spin-glass (Mydosh (1993)). All samples were oriented so that the magnetic field would be parallel to the c crystallographic axis of the majority phase. It was impossible to stabilise the magnetic response at a temperature above 150 K because the diamagnetic contribution, which comes from the material the pressure cell is made of, effectively cancels the weak paramagnetic signal from the sample of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$.

The magnetisation of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures is shown in Figure 4.19. The material experiences a transition into the spin-glass state at ~ 50 K, however in such a strong magnetic field the peak on the magnetisation curve is smeared and is slightly different from the position of the peak at 100 Oe (~ 55 K, see Figure 4.13). The applied pressure lowers the absolute value of the magnetisation, and shifts the temperature of the development of the short-range order T_{sg} into higher temperatures with a rate of 0.12 K / kbar, Figure 4.20(a).

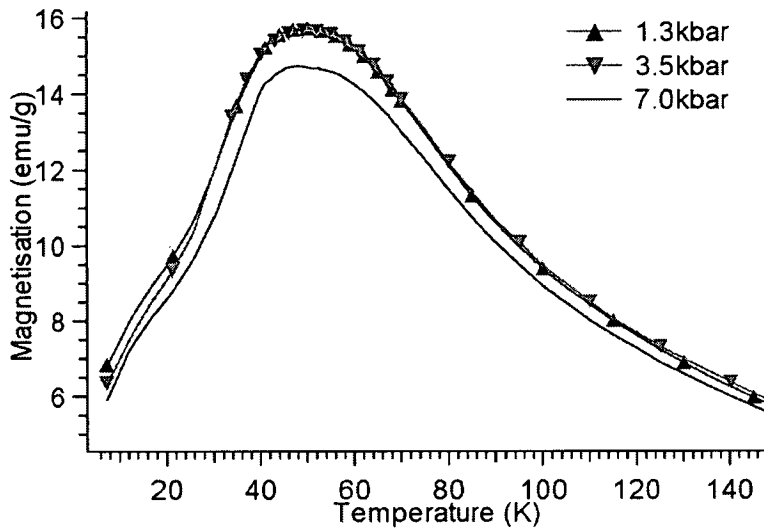


Figure 4.19: Magnetisation of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures, $H = 1$ T, $H \parallel c$.

The magnetisation of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures is shown in Figure 4.21. A shift of the transition temperature into a higher temperature region with the application of pressure with a rate of 0.27 K / kbar is observed, Figure 4.20(b). Applied pressure also decreases the absolute value of magnetisation.

The magnetisation of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures is shown on Figure 4.22. At ambient pressure, and in the field of 100 Oe, the material undergoes a transition into a spin-glass state at ~ 42 K. In a field of 1 T the transition was also observed at ~ 43 K. An applied pressure of 6.6 kbar increases the temperature of the spin-glass transition (T_{sg}) to ~ 45 K, Figure 4.20(c). Increasing the pressure shifts the temperature of the development of the short-range order T_{sg} to higher temperatures

with a rate of 0.22 K / kbar, Figure 4.20(c). The applied pressure also lowers the absolute value of the magnetisation.

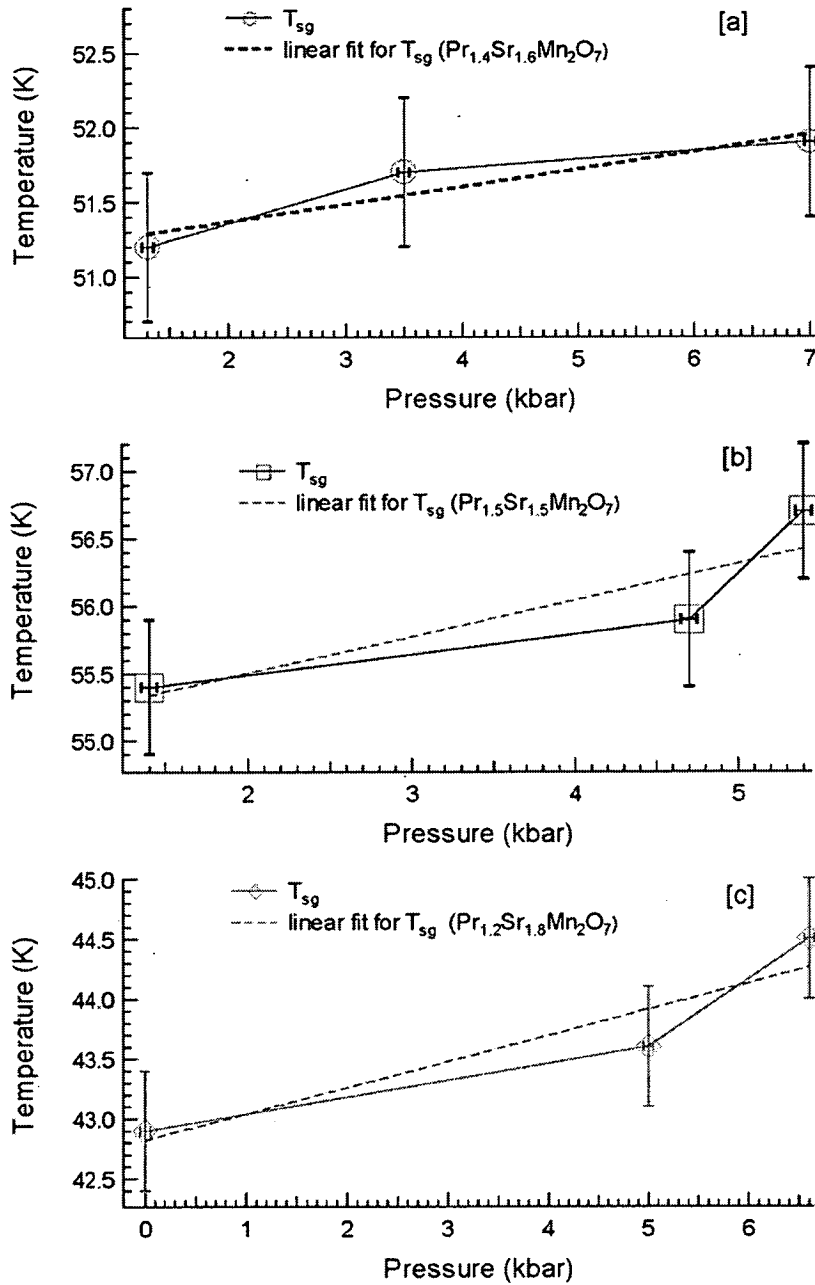


Figure 4.20: Effect of pressure on the temperature of the transition into a spin-glass state in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) manganites.

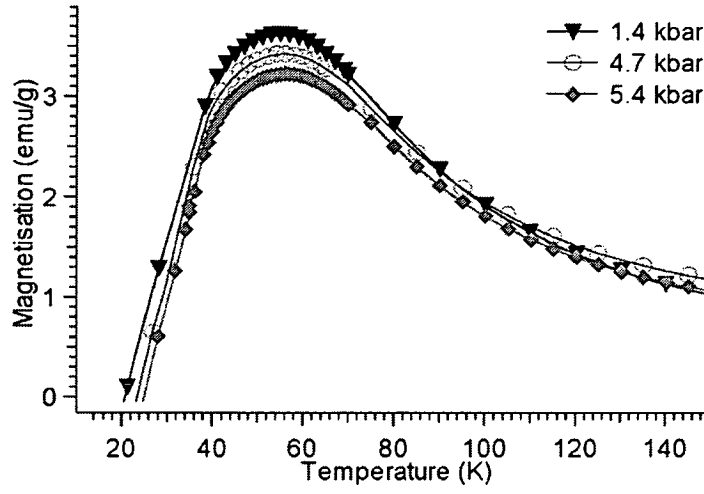


Figure 4.21: Magnetisation of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures, $H = 1 \text{ T}$, $H \parallel c$.

While a weakening of the short-range magnetic order by applied pressure is observed, no development of the long-range magnetic ordering down to 4 K in any of the studied materials was detected and it is clear that the pressure range needs to be extended. Since the pressure cells of piston-cylinder type operate in a pressure range of up to 11 kbar, another type of a pressure cell capable of reaching pressures above 11 kbar should be used.

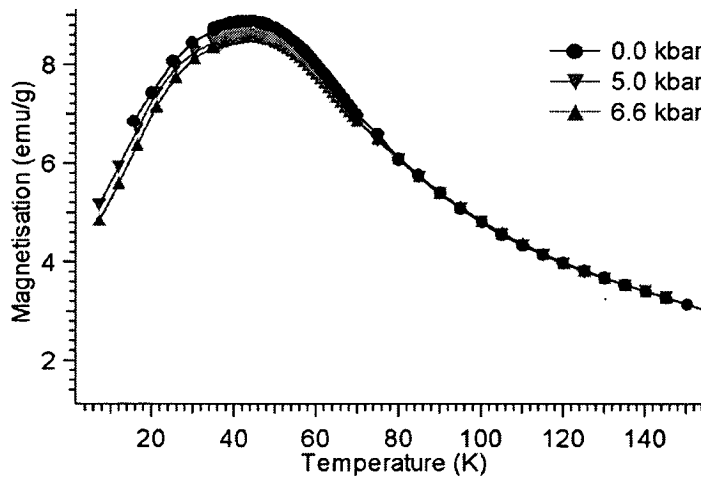


Figure 4.22: Magnetisation of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured at different hydrostatic pressures, $H = 1 \text{ T}$, $H \parallel c$.

4.10 Concluding notes

It was found that the behaviour of the electrical resistivity of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ manganites can be attributed to the thermally activated hopping of the charge carriers, and that the resistivity decreases with applied pressure which is typical for this type of conductivity. No metal-insulator transition was detected at a pressure below 10 kbar.

The phase composition of the samples is analysed based on measurements of magnetic susceptibility. Analysis of neutron diffraction data shows that all samples contain a tiny amount of the perovskite intergrowth phase (2 - 4%), which is common for the layered manganese oxides. Based on the critical temperatures on the susceptibility curves, the composition of the intergrowth has been identified as being close to $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. It was found that the symmetry of the intergrowth phase matches the symmetry of the majority phase and exhibits an anisotropic magnetic behaviour. This behaviour has been predicted for the perovskite manganites but has never been experimentally observed due to the twinning of the perovskite crystals.

The majority phase shows a phase transition into a spin-glass state at ~ 50 K for all $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ samples. Pressures of up to 10 kbar did not significantly affect the magnetic properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, and no transition into the long-range ordered state was observed at a pressure below 10 kbar.

Chapter 5

Measurements of electrical resistance of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ in a diamond anvil pressure cell DXR-6C.

5.1 Introduction

To fully investigate the transport properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ materials, a pressure cell capable of exceeding 11 kbar needs to be used. The pressure cell must be of a compact size to fit into the CCR and be cooled to at least 20 K. The maximum static pressures are now reached using diamond anvil cells (DAC), which are also compact and safer to use than a piston-cylinder pressure cell. However, introducing electrical leads into a diamond anvil cell is not an easy task due to the small size of the sample space inside the pressure cell. It will be shown below that even in the DAC with relatively large anvils of 800 μm , the sample space is smaller than 300 μm . There is also a probability that the electrical probes will be cut off by the diamond anvils or gasket. Such difficulties make the task of developing a technique to measure the electrical resistivity of the material a real challenge.

5.2 General remarks on resistivity measurements in a DAC

There is a number of reports in the scientific literature of experiments in which electrical leads have been taken into a DAC (Mao and Bell (1981), Grzybowski and Ruoff (1984), Tozer and King (1985), Gonzalez and Besson (1986), Eremets *et al.* (2000)). However, there does not seem to be an accepted general approach to the problem of introducing electrical leads through the gasket into a DAC. Since all pressures from ambient to the maximum experimental pressure must be experienced by the electrical lead, it is essential that the materials of the lead and insulation are well behaved over this whole pressure range. Many materials exhibit very low shear strengths as they pass through pressure-induced phase changes. Such an effect, within an electrical lead, would cause it either to lose continuity if it occurred within

the conductor, or to short-circuit the electrical lead to the gasket if this occurs within the insulating layer. Bringing the diamond anvils together, thereby compressing the sample, the pressure transmitting medium and the central part of the gasket, increases the sample pressure within a DAC. A certain minimum friction between the materials of the electrical feedthroughs and the gasket material is essential to the maintenance of the pressure gradient. Therefore, when the gasket material is extruded as the pressure is raised, it will inevitably drag the material of the electrical feedthroughs with it. It is essential that the feedthrough material can extrude with the gasket whilst retaining the appropriate conducting and/or insulating properties. An adequate match between the properties of the gasket, feedthrough conductor and feedthrough insulator must be maintained at all studied pressures and temperatures.

Mao and Bell (1981) have reported measurements of the electrical resistivity of conducting materials in a DAC. They proposed a configuration in which a pressed disk of MgO was placed on the culet of the lower diamond anvil. The wires were pressed into the MgO disk and remained within the disk as pressure was increased. To reduce the gradient of pressure a small hole was drilled in the MgO disk and filled with a compressed NaCl, which has larger compressibility. The authors stated that the method works at pressures of up to 130 kbar, and that no metal gasket was used. This method is certainly not safe at low temperature as cooling of the cell can result in an increase of pressure and can break the gasket made of MgO, which leads to a failure of the diamonds. It is also difficult to drill a hole in a pressed MgO disk without making radial cracks in it. The authors did not report the gasket thickness, making it difficult to reproduce their method. Besides, it is not clear whether or not this method will work for several temperature variations in a range from 20 to 300 K with a monotonic increase of pressure.

Sakai *et al.* (1982) have proposed a technique for electrical resistivity measurements at high pressure and low temperature. The resistivity measurements were carried out at pressures of up to 25 GPa (250 kbar) and temperatures down to 1.7 K using a diamond-anvil cell driven by helium gas. A polymer film was inserted between the copper leads and the lower anvil face. A sample was put in the centre of the anvil, bridging the copper probes. The other diamond anvil was also covered with two layers of a polymer film. The total thickness of the polymer film surrounding the sample was about 50 μm . In this method, a sample was compressed between polymer films which worked as a pressure transmitting medium. The measurement of

electrical resistivity was performed using a two-probe technique. The assembly had a leakage resistance of about $10^{11} \Omega$. The main component of the polymer film was polyvinylidene chloride. Polyethylene film proved to be too soft to maintain the electrical leads.

Knittle and Jeanloz (1991) have reported measurements of electrical resistivity of $\text{Fe}_{0.94}\text{O}$ at pressures of up to 83 GPa in a temperature range between 300 and 4300 K. Although they operated in a different temperature interval, the configuration of probes and the setup of the DAC are quite interesting and worth considering. They used a pseudo-four-lead configuration of the electrical probes. That is to say, the sample resistance is measured between two leads, each of which consists of a wire going through the high-pressure cell. They used a gasket made of spring-steel, which was coated with a mixture of the MgO or Al_2O_3 and an epoxy in a proportion of 3:1 by volume to prevent the leads from making an electrical contact with the metal gasket. A hole was drilled in a coated gasket and the sample material was precompressed into the gasket before the leads were attached. Leads, made of 10 - 25 μm platinum or tungsten wire, were placed across the sample and connected to external leads in such a way that there was no electrical contact between the body of the pressure cell and the leads. A small amount of the ruby powder was pressed onto the sample and the pressure was measured using the ruby fluorescence technique. They also proposed a second method in which a spring-steel gasket was coated with a mixture of epoxy and MgO and then indented between diamonds. A hole nearly as large as the culet diameter was drilled in the indented region i.e. the entire indentation was drilled out. MgO was pressed into this hole and the gasket was compressed between the anvils. MgO served as the insulating layer between the metal gasket and the leads as well as supporting the gasket between the diamonds. They reported that the leads were less likely to be cut off at the sharp corner around the edge of the diamond culet than with the first technique.

More recently, Morris and Williams (1997) measured the electrical resistivity of Fe_3O_4 at pressures of up to 48 GPa at temperatures between 258 and 300 K, using a very similar procedure to that of Knittle and Jeanloz (1991). A modified Mao-Bell type diamond cell with 350 μm culets was used to generate pressure. A gasket with a 250 μm hole was electrically insulated with a mixture of MgO and epoxy mixed in a 3:1 ratio. The gasket was filled with MgO powder and compressed, providing extra

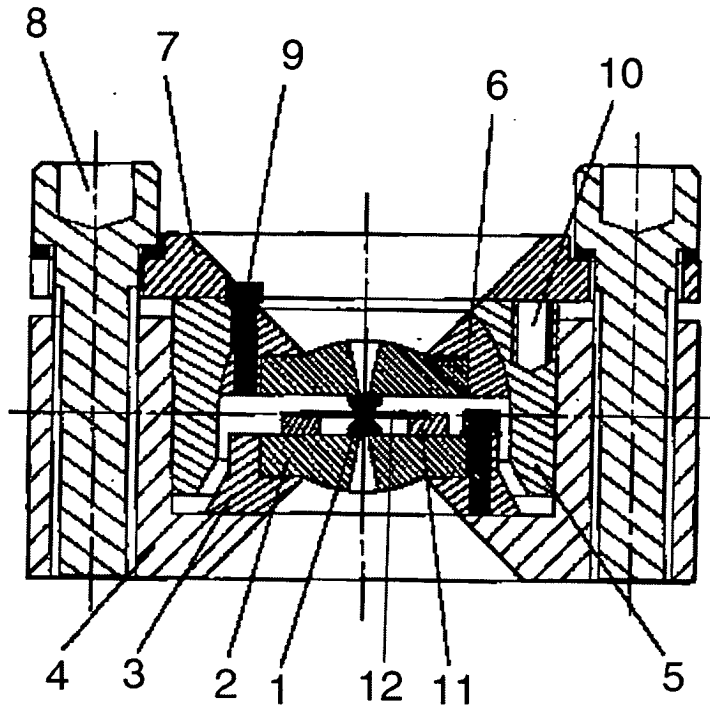
insulation between the gasket and the sample. A layer of Fe_3O_4 was placed on top of MgO , and two 25 μm platinum leads were put on the top of the powder sample.

Eremets *et al.* (1998) have reported measurements of electrical resistivity in a DAC at pressures of up to 206 GPa and temperatures from 50 mK to 300 K. They used 300 μm diamond anvils with bevelled (10°) tips. The gasket was made of rhenium and was preindented with its thinnest part removed. In its place Al_2O_3 powder was pressed to form a transparent insulating gasket. A 20 μm hole was drilled in the centre of the insulating gasket and the 15 - 20 μm sample of CsI was placed inside. The thickness of the Al_2O_3 gasket was $\sim 7 - 10 \mu\text{m}$. The electrodes made of platinum foil were placed onto the Al_2O_3 layer. In some experiments the probes were sputtered on the surface of the diamond.

A new method of measurement of the electrical resistivity of materials in a DAC was developed during this project. The difficulty in developing such a technique was to position several electrical contacts with a size of 25 μm on the sample with the size of $\sim 250 \mu\text{m}$ and to ensure there was no electrical circuit to the metal gasket. There should be no electrical contact between probes under high pressure, which deforms the contacts severely. The insulation should also work reliably during several temperature variations in the interval between 20 and 300 K. In the insulating regime, the resistance of the manganites can grow a thousandfold or more, starting from already high values of the order of several $\text{k}\Omega$. Therefore, to detect the effect of pressure in the low-temperature region, one needs to use different regimes of the current/voltage stabilisation, as the sensitivity of the voltmeter depends on the measured resistivity.

5.3 Construction and principles of operation of a diamond anvil cell

The pressure range for measuring the electrical conductivity and magnetic susceptibility of $\text{R}_{2-2x}\text{A}_{1+2x}\text{Mn}_2\text{O}_7$ materials can be extended using a DXR-6C diamond-anvil cell manufactured by the Diacell Company, Figure 5.1.



- | | |
|----------------------------|-----------------------------------|
| 1. Diamond anvil | 7. Top plate |
| 2. Berillium support plate | 8. Bolt -UNF 1/4"-28 LH/RH |
| 3. Support ring | 9. Tilt adjustment screws |
| 4. Cell body | 10. Piston extraction screw holes |
| 5. Piston | 11. Gasket support ring |
| 6. Hemisphere | 12. Gasket |

Figure 5.1: DXR-6C diamond anvil cell.

A DAC consists of two main parts: the anvils and a gasket. When a material is compressed between the anvils, a much higher pressure can be achieved than in a piston-cylinder cell. This is mainly due to the following reasons:

1. Diamond is a very hard material; its compression yield strength is more than 3 times greater than its tensile yield strength, σ_y .
2. Pressures much greater than σ_y can be generated with the anvils made in the form of a truncated cone because the surrounding material supports the loaded area. The larger the angle of the cone, the greater the support. In the situation when the compressed volume of the material is supported by the half space of the

compressing media, the average pressure under the indenter is $H \sim 3 \sigma_y$, where σ_y is the compression yield strength.

3. The pressure between the anvils is not uniform and the maximum pressure in the centre of the anvils may be much higher than the mean pressure over the anvil $P = F / S$, where F is the applied force and S is the contact area (M. Eremets (1996)).

The gasket contains the sample, supports the edges of the anvils and determines the pressure distribution on them. The gasket has a hole, where a sample under hydrostatic pressure is located. Thus the pressure distribution over the gasket has a flat part in the region of the hole. Transformation of the pressure distribution under a load in a gasket containing a hydrostatic medium is not trivial. Problems of the stability of a gasket with the hole were thoroughly studied by Dunsten (1989) and Moss and Goettel (1987).

The gasket is loaded with a pressure transmitting medium (gas or liquid) which makes the pressure inside the hole hydrostatic, and is sealed. It can be sealed with a small force when the anvils create normal stress over an area exceeding the initial pressure. The gasket starts to extrude outside the anvils, and inside the hole, compressing the pressure transmitting medium. Thus pressure is applied to the sample achieving a maximum value of the pressure over the gasket. Under further loading, the pressure in the hole increases and the hole expands. The experiment has to be stopped when the hole expands significantly, otherwise the gasket can be broken, leading to the failure of the diamond. Experimental results show that the initial radius of the hole has to be $\sim 1/3$ of the radius of the flat anvil tip (Eremets (1996)). The initial thickness of the gasket must be only slightly greater than the final thickness to provide the maximum pressure on the sample.

Anvils with flat culets can generate pressures of up to 100 GPa (Eremets (1996)). The smaller the culet size, the higher the pressure that can be generated with the anvils. Large anvils need a larger force, and high pressure (3-5 GPa) can be generated at the table of the anvil, leading to the plastic deformation of the seats and a possible failure of the diamond (Eremets (1996)). Bevelled anvils (Figure 5.2) are used for studies above 100 GPa (Mao and Bell (1978)).

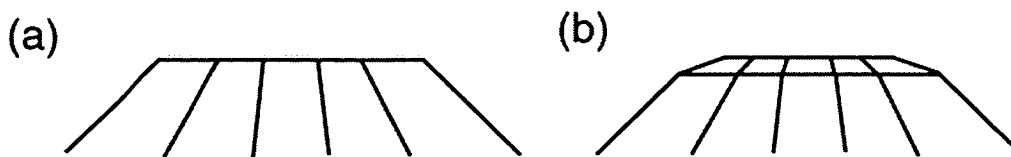


Figure 5.2: Types of culets (a) standard culet, (b) bevelled culet.

To achieve the highest pressure the shape of the tip approaches the shape of a cone. A pressure of 400 GPa was achieved using bevelled anvils (Ruoff *et al.* (1990)). The tip can also be produced in the form of a sphere, cylinder, or cone (Timofeev *et al.* (1991)). The difference in the diameters of the tips of the two anvils used in one cell has to be no larger than $\sim 1\%$ of the smallest diameter (Eremets (1996)). The flat culet and the diamond table have to be parallel with a precision of $\sim 0.1\%$ of the culet size (Eremets (1996)).

Anvils with a diameter of the culets of 800 μm were chosen for the measurements of electrical resistance reported in this chapter because they provide a larger sample space. A larger sample space makes it easier to introduce and position electrical leads in it.

5.3.1 Alignment of the anvils

Maintaining the alignment of the diamond culets is a crucial factor in achieving the highest possible stable pressure in a DAC. The alignment is usually checked using a microscope. To observe deviations from alignment, the anvils must be gently pushed together to bring the culet faces into contact. For the DXR-6C a pair of 16-sided Drukker standard cut diamonds with flat tips was used, Figure 5.3. First, the diamonds had to be glued to the diamond seats, which were made of stainless steel. Holes were drilled in the centres of the seats to enable the alignment procedure and to visually control the stress distribution during the application of pressure. The seats were treated on a flat-grinding machine, however to ensure that the surfaces were as flat as possible, and did not contain any microscopic scratches, they were polished using SiC sandpaper. The anvils were put directly on the seats, however Eremets (1996) reported using aluminium, tantalum, or indium foil to smooth the roughness of the seat's surface and make the pressure distribution under the table of the anvil

more favourable. However, this was not essential for the work described in this thesis as the maximum pressure in the studies described here did not exceed 75 kbar.

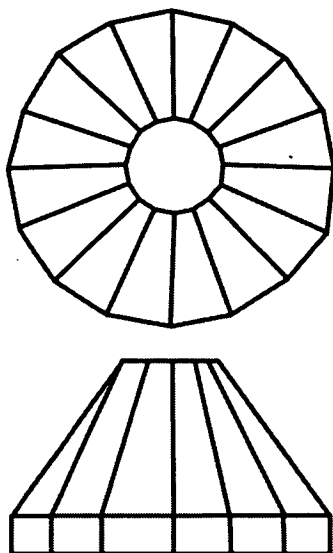


Figure 5.3: 16-sided Drukker standard cut diamond anvil.

The touching surfaces of the diamond and seat were cleaned using ethanol to make sure there were no dust particles between them. The anvil was aligned so that the hole in the seat and the tip of the anvil were sitting on the common vertical axis. Then, the anvil was glued to the diamond seat using Rapid Araldite epoxy resin. A small quantity of glue was put around the perimeter of the anvil. One should avoid the penetration of glue under the diamond. The Rapid Araldite epoxy has proved to be a reliable glue for temperature cycling. In the experiments described here, the diamond anvil cell was cooled many times down to low temperatures. However, it is advisable to check the condition of Rapid Araldite for any cracks after several temperature variations.

During the procedure of alignment, the anvils were observed through the holes in the diamond seats and the side windows of the body of the pressure cell. Both diamond tips were cleaned using ethanol so the interference fringes could be observed. The side surface of the piston should be cleaned to eliminate the possibility of jamming the piston in the body of the cell. For alignment, the diamond tips were brought very close together. The touching of anvils must be done very carefully, as there is nothing between them and consequently there is a high risk of breaking the diamonds. Sometimes diamonds are not exactly of the same size, and therefore it is

advisable to check the facet alignment from all of the side windows. A very powerful side illumination is needed to ensure correct alignment.

The anvils should be brought gently into contact, whereupon a set of linear interference fringes will be seen. If the anvil culets are quite far out of parallel, the fringes will be seen as a closely spaced set of lines at one side of the field of view. The fringe pattern is removed by adjusting the three screws on the piston containing the upper anvil. Using 3 adjustable screws, one can change the orientation of the flat tip of the upper anvil and keep it fixed simultaneously, as the 3 points of touch always control the orientation of plane.

During the procedure of the alignment, the observed interference fringes should get broader and their number should decrease. Finally one should be able to observe just one fringe. The absence of fringes indicates the absolute parallelism of the culet faces.

After the vertical alignment, the horizontal alignment should be carried out. This can be achieved by adjusting screws that move the lower diamond seat within the horizontal plane. The alignment of the recently glued diamonds should be checked during the process of indentation. Small corrections need to be done should any multiple interference fringes appear. However, once the correct alignment is achieved, there is no need to repeat the procedure before each experiment.

5.3.2 Gasket preparation

After the alignment, the gasket was loaded between the anvils. Gaskets made of stainless steel with a thickness of 0.25 mm were used. Before drilling the hole for the sample, the gasket should be pre-indented to avoid a large deformation and instability of the hole. A support ring for the gasket was glued to the diamond seat. The height of the ring was equal to the height of the diamond, so the gasket could lie flat on the tip of the anvil and could be easily centred with respect to a diamond anvil. Marks were made on the surface of the gasket and on the support ring to provide a reproducible placement. The gasket was fixed to the ring using Blu-Tack. For the first load, a small force was applied to the piston, the cell was then unloaded and the thickness of the gasket was subsequently measured using a micrometer. Simultaneously the alignment of the diamonds was checked each time. The stress

distribution picture was drawn for each thickness of the gasket during the indentation process. The stress picture was observed in polarised light, Figure 5.4. The evolution of the stress picture, with the thickness of the gasket, enables one to make the indentation in one attempt and to be certain about the thickness of the gasket without the actual measurements of its thickness. This means there was no need to unload the pressure cell and displace the gasket, as even with the marks it was difficult to reproduce the exact placement of the gasket.

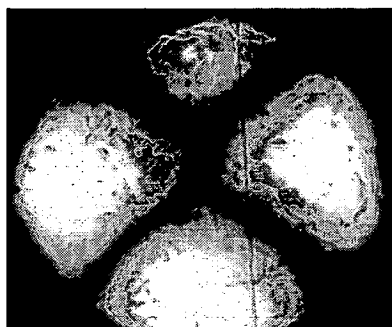


Figure 5.4: Stress pattern observed during the procedure of indentation (in polarised light).

The thickness of the indentation depends on the size of the flat tips of the anvils and the design of the pressure cell. For a DXR-6C pressure cell, diamonds with culets of 800 μm an indentation of 80-90 μm was made.

After the indentation procedure, a hole was drilled in the centre of the indented area using an electro-erosion machine. In such a machine a tungsten carbide wire works as a cathode and the gasket as an anode. Electrical sparks are produced when the gasket and the wire are brought near each other. A 270 μm tungsten wire was used as a drill because the diameter of the hole should be $\sim 1/3$ of the diameter of the indentation. The electro-erosion machine allows the precise centering of the drill and produces fine holes, Figure 5.5. After drilling the hole, the cell can be assembled.

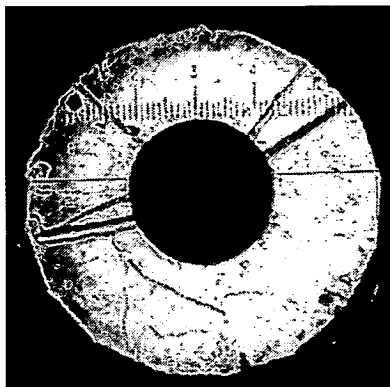


Figure 5.5: Gasket with a hole. Bright ring is the indented part of the gasket. The dark circle in the centre is the hole.

5.3.3 Gasket lamination

To measure the electrical resistance of materials in a DAC there should be no electrical contact between the metal gasket and the electrical probes. It was impossible to use only insulated probes and a non-insulated gasket for the following reasons:

1. The insulation was removed from the tips of the probes to enable the electrical contact between the probes and the studied material. Applied pressure tended to rip the insulation starting from the area where insulation was already removed.
2. Applied pressure deformed the material the probes were made of. Deformed probes expanded and so electrical contact between the probe and the edge of the hole of the gasket often occurred.

Therefore, it was decided to use insulated probes and an insulated gasket. Probes should be insulated to avoid electrical contact between them and the conductive body of the cell. Commercially available copper wire with a diameter of 25 μm laminated with a 5 μm layer of PVC insulation was used.

Three different materials were used to laminate the gasket. There have been reports describing the use of MgO powder for insulation of a gasket (Knittle and Jeanloz (1991), Morris and Williams (1997)). However, it was impossible to isolate the stainless steel gasket reliably by using the MgO alone. Instead a combination of

non-conducting low temperature varnish (Oxford Instruments) and MgO powder was chosen for the gasket lamination. Under applied pressure, the electrical leads were often short-circuited through the gasket.

Therefore, a new method of a gasket lamination was developed. A mixture of Rapid Araldite and MgO proved to be a reliable working insulator. MgO powder tends to absorb the CO₂ from the atmosphere and coagulate into particles with a size of 20 - 40 μm . This is unacceptable because the thickness of the insulating layer within the indented area should be smaller than 10 μm otherwise it is not possible to reach maximum pressure. Therefore, MgO powder was ground in a mortar and then quickly and thoroughly mixed with prepared Rapid Araldite. The mixture was spread over the indented area, making sure that the edges of the hole were also covered, Figure 5.6. The thickness of the spread should be as homogeneous as possible to avoid the expansion of the mixture into the sample region and extra side pressure on the anvil. Then, ground MgO powder was pressed into the hole, using the piston with the upper anvil, in order to:

1. Add extra insulation to the potentially “dangerous” region of the inner surface of the hole.
2. Provide a quasi-hydrostatic pressure transmitting medium.

Next, a small indentation was made in the hole filled with MgO powder using a sharpened needle. The powder sample to be measured was loaded into that indented region. Again, the cell was loaded and the powder was compressed.

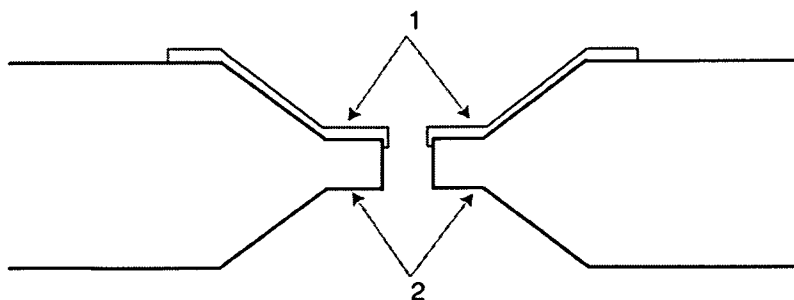


Figure 5.6: Laminated gasket.

1. Insulating layer
2. Preindented gasket with a hole

The insulation was removed from the tips of the copper wires using a surgical blade. Two wires were inserted into the sample area and positioned so that they did not touch each other, Figures 5.7.

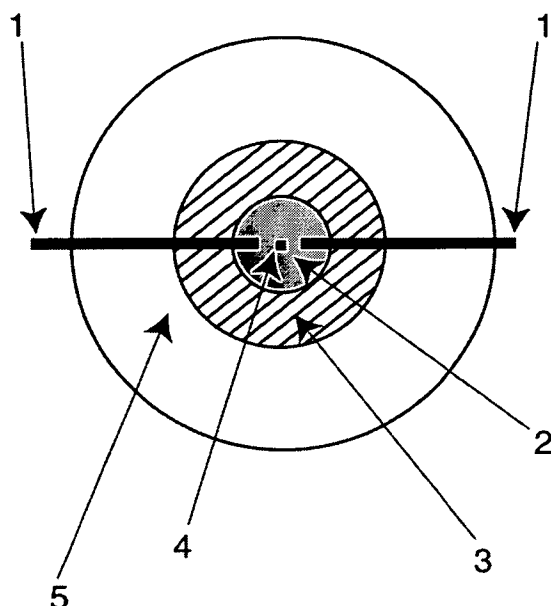


Figure 5.7: Gasket loaded with a sample and electrical leads.

- | | |
|---------------------|---------------------------------|
| 1. Electrical leads | 4. Ruby chip |
| 2. Sample | 5. Laminated part of the gasket |
| 3. MgO layer | |

In some experiments, three wires were introduced into the sample area. Two of the wires served as electrical leads for measurement of resistance. The other was inserted in the event that the diamonds cut one of the wires, Figure 5.8. Then, the wires were fixed to the gasket using Rapid Araldite. The ruby chip was attached to the upper anvil using grease to ensure its exact position. The cell was then ready for the measurements, Figure 5.7.

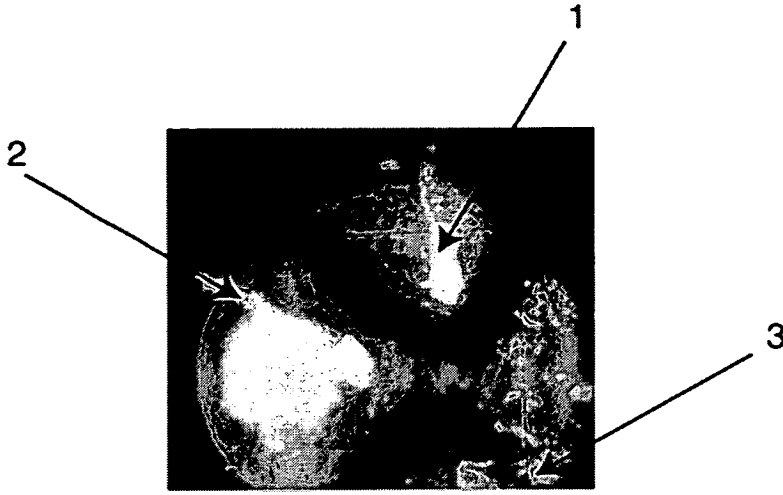


Figure 5.8: Electrical leads in a DAC (shown in polarised light). Leads 1 and 2 were used for the measurements. Lead 3 was meant to be used in case one of the leads 1 or 2 fails.

5.3.4 Measurements of pressure

A ruby gauge is commonly used for pressure determination. The use of ruby gauges for measuring pressure was first introduced by Barnett (1973) and Piermarini (1975), who calibrated the ruby gauge up to 19.5 GPa. Ruby has a very strong luminescence doublet of peaks R_1 at 6942 Å and R_2 at 6928 Å under ambient conditions. It was also found that the R_1 lines shifted approximately linearly with the pressure $d\lambda / dP = 0.364$ Å/kbar (Barnett (1973), Piermarini (1975)). Mao *et al.* (1978) calibrated the ruby up to 100 GPa using Cu as a reference material. The calibration was described by:

$$P = 1904[(1 + \delta\lambda / 694.24)^B - 1] / B, \quad (5.1)$$

where P is the pressure in GPa and $\delta\lambda$ is the ruby R_1 line wavelength shift in nm. Parameter $B = 7.665$ for quasi-hydrostatic conditions and $B = 5$ for non-hydrostatic conditions. Equation (1) gives a higher pressure under quasi-hydrostatic conditions at the same line shift.

The positions of the ruby luminescence lines shift with the temperature at a rate of $0.068 \text{ \AA/K}$ (Vos and Schouten (1991)). This means that $\Delta T = 5 \text{ K}$ produces the same shift as $\Delta P = 1 \text{ kbar}$.

It is possible to insert several chips of the ruby into the sample area to monitor the pressure distribution in the measured region. The ruby fluorescence system, which includes the laser to stimulate the ruby luminescence and a spectrometer to measure the wavelength shift, was used for the measurements of pressure. The spectrum is recorded and displayed on a PC, where the wavelength of the R_1 line is measured. Pressure is deduced using the value of the wavelength shift (1).

5.4 Electrical resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$

The temperature dependence of the electrical resistance of a powder sample of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ in the temperature range of $20 \leq T/\text{K} \leq 120$ is shown in Figure 5.9. All data were collected on heating, as it was much easier to keep the temperature change rate steady in the lowest temperature region. The value of pressure was checked after each temperature run and found to be unchanged. Eremets (1996) reported that the pressure in a diamond anvil cell usually increases on cooling, however no technique for measuring pressure at low temperature was available and, therefore, it was not checked at low temperatures. It is advisable to start from low pressures and go to higher ones. Such an approach gives more experimental data in case of a diamond, Rapid Araldite or probes failure, which is much more likely to occur at higher pressure.

Measurements of the electrical resistance began at a pressure of 13 kbar. It is important to realise that the electrical leads are not attached to the powder sample, in fact they need to be pressed into a sample's surface to provide the necessary grip for electrical contact. If the leads are not sufficiently pressed into the sample's surface, they can make the resistance too large to be measured due to large resistance of the electrical contact between the leads and the sample's surface. High contact electrical resistance was due to a small surface of the contact between the sample and the electrical lead. On a further pressure increase, the leads can change their positions because the tips of the leads are not fixed to the sample's surface.

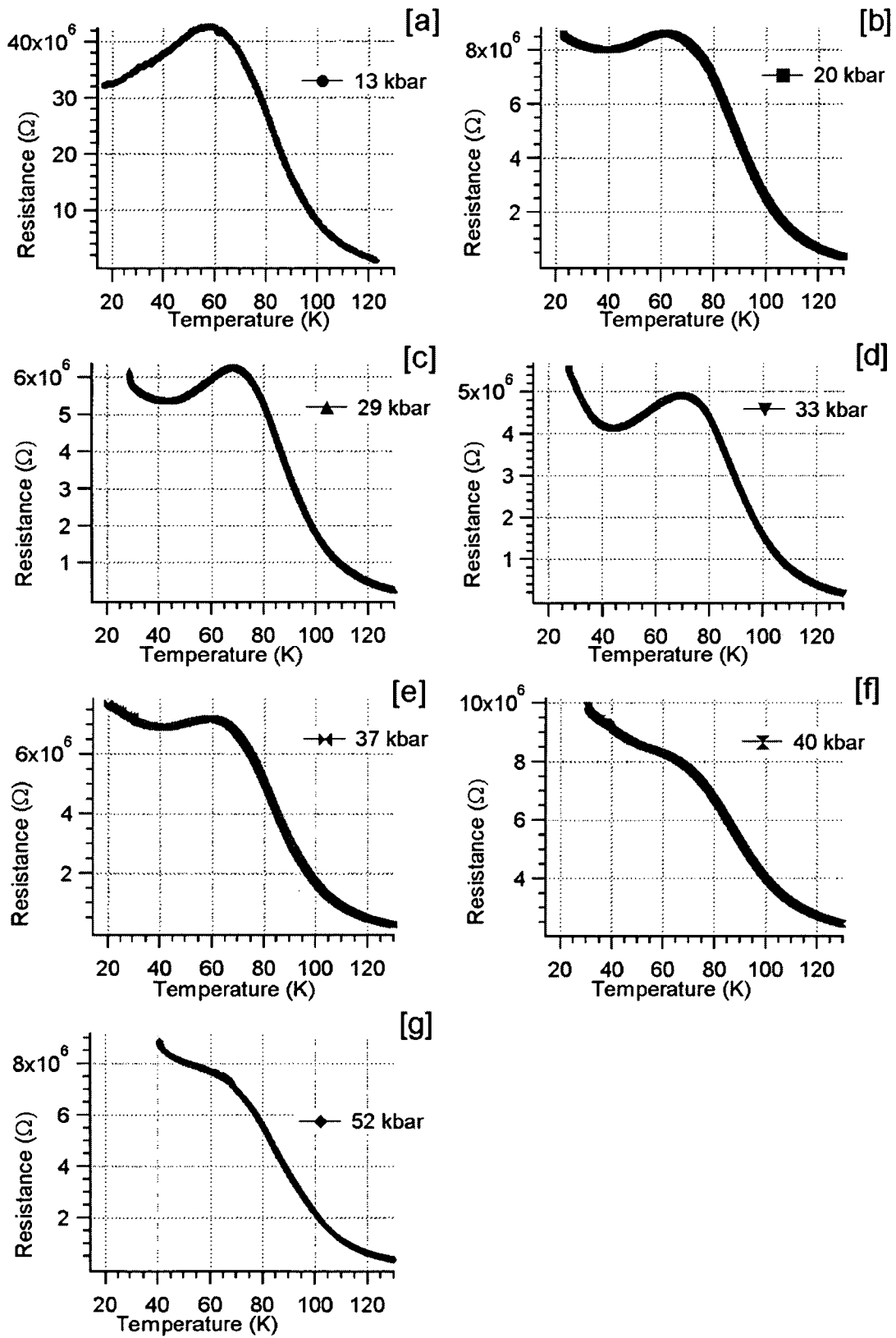


Figure 5.9: The electrical resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ at different pressures.

The application of a small initial pressure fixed the position of the electrical leads on the sample's surface and reduced the contact resistance. The value of this initial pressure was approximately 10 - 15 kbar. The error for the pressure determination in this experimental setup was 1 kbar.

The absolute value of the resistances measured at different pressures must be treated with caution. The applied pressure severely deforms the electrical probes and therefore, changes the geometry of the measurement. This is the reason why the resistances measured at different pressures are all plotted separately. However, the data can still be analysed and some useful information can be extracted, i.e. the shift of critical temperatures, relative magnitudes of resistance within each temperature variation, profile shape etc. The resistivity of the material has not been calculated because it was not possible to measure the changes in the size and position of the electrical leads under pressure.

The resistance measured at 13 kbar increased with the decreasing temperature (which is characteristic for semiconductors) and developed a maximum at $T \sim 58$ K, Figure 5.9 (a). Below ~ 58 K the resistance showed a metallic-like behaviour, i.e. it decreased with decreasing temperature. The resistivity of a single crystal sample measured in a hydrostatic pressure cell at pressures below 10 kbar showed a behaviour typical for materials with activated type of conductivity (see part 4.7, Figures 4.6, 4.7). However, it was found that the application of pressure began to change the type of conductivity. The application of higher pressure (13 kbar) resulted in a considerable change in the mechanism of conductivity, Figure 5.9 (a).

A pressure of 20 kbar shifted the maximum on the resistance curve to ~ 62 K, Figure 5.9 (b). The resistance reached its minimum at $T \sim 39$ K and then began to rise, Figure 5.9 (b). At 29 kbar, the resistance showed a maximum at ~ 68 K, and on further cooling, a minimum at ~ 43.5 K, Figure 5.9 (c). At 29 kbar the local maximum and minimum on the resistance curve became clearer. At 33 kbar the resistance demonstrated a maximum at ~ 69 K, and reached a minimum at ~ 45 K, Figure 5.9 (d). At 33 kbar the local maximum on the resistance curve was the most prominent.

Resistance was measured at higher pressures showing a maximum at ~ 59 K, and a minimum at ~ 42 K, at pressure of 37 kbar, Figure 5.9 (e). The temperature of the transition from activated to a metallic-like behaviour increases with an increase of pressure up to 33 kbar.

At 40 kbar, no change from activated to metallic-like behaviour was observed, although the behaviour of the resistance curve was somewhat different from activated below 62 K, Figure 5.9 (f). On resistance data collected at 52 kbar, no change from activated to a metallic-like behaviour was observed, though the inflection point is clearly seen at ~ 63 K, Figure 5.9 (g).

The application of chemical pressure resulted in similar changes in the transport properties of bilayered $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, Moritomo *et al.* (1997b). It was found that the materials with $z = 0.0, 0.2$ showed a metal-insulator transition at low temperatures. $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0$) undergoes a transition into a ferromagnetic state at a temperature of about 130 K. The transition into the ferromagnetic state is accompanied by a decrease in resistivity as predicted by the double-exchange theory. With an increase of z , the Curie temperature is suppressed to 80 K for $z = 0.2$. The ferromagnetic phase disappears at $z = 0.4$. The resistivity of the $z = 0.4$ sample slightly decreased at 50 K, demonstrating a broad maximum, which was attributed to the growth of short-range ferromagnetic correlations. The $z = 0.4$ sample was found to be a spin-glass material below ~ 40 K. The samples with $z = 0.6, 1.0$ were insulators down to the lowest temperatures.

A metal-insulator transition in these compositions was associated with a transition from a ferromagnetic state into a paramagnetic phase. The sample with $z = 0.4$ showed a transition from an insulator to a metallic-like state, i.e. below 50 K the resistivity decreased with a temperature decrease, however the magnitude of the resistivity remained large. The samples with $z = 0.6, 1.0$ demonstrated insulating behaviour down to the lowest measured temperature (~ 95 K).

In Chapter 4 it was established that $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ becomes an insulating spin-glass material as a result of the substitution of La with Pr (the Pr ion has a smaller radius than the La, but bigger than the Nd). The electrical resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ demonstrated behaviour typical for materials with activated-type conductivity at temperatures above 60 K. The substitution of La ions (chemical pressure) in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0.4$) and in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ resulted in similar changes in the magnetic and transport properties of studied materials, i.e. a weakening of the long-range magnetic order and the concomitant metallic behaviour. By applying external pressure it was possible to induce a maximum on the resistance curve for $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. Similar changes in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ can be achieved by lowering z from 1.0 to 0.4. This means that the application of external pressure,

and a chemical pressure, can result in similar changes to the crystal structure, which leads to corresponding changes in the magnetic and transport properties of the materials.

The broad peak on the electrical resistance curves of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ was caused by the presence of short-range magnetic correlations, which were enhanced under applied pressure. Moritomo *et al.* (1997b) reported that the broad peak on the resistivity curve of $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0.4$) was due to the growth of the short-range ferromagnetic correlations. It is believed that the pressure-induced short-range magnetic correlations in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ were also of ferromagnetic origin because the decrease in resistance is characteristic for a ferromagnetic state in both perovskite and layered manganites. For instance, Kawano *et al.* (1997) have investigated magnetic and transport properties of $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, ($\text{Ln} = \text{Pr}, \text{Nd}$). They found that on cooling, both materials showed transitions, first into a ferromagnetic phase, and then into an antiferromagnetic one. The resistivity in the ferromagnetic phase showed metallic behaviour, i.e. it decreased on cooling. In the antiferromagnetic phase, the resistivity increased with a temperature decrease.

The analysis of the neutron diffraction data (Chapter 3) showed that the majority $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ phase contained a small amount of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth phase. However, the maximum on the resistance curve should be attributed to the majority $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ phase and not to the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth phase because the latter remained an insulator at low temperature (see for instance Kawano *et al.* (1997)). Besides, it is unlikely that 4% intergrowth phase in a powder sample could cause the maximum on the resistance.

The application of pressure ≥ 40 kbar in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ resulted in the disappearance of the maximum in the resistance curve. This means that an increase of pressure above 40 kbar suppressed ferromagnetic correlations. However, the resistance began to increase below 50 K. This suggested that pressure enhances antiferromagnetic correlations in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ (see part 5.7). The short-range antiferromagnetic correlations between the neighbouring bilayers are always present in $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ manganites.

Moritomo *et al.* (1997b) reported that in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, MnO_6 octahedra elongated along the c -axis with an increase of z . This means that the average out-of-plane Mn-O bondlengths $[\text{Mn-O}(1) + \text{Mn-O}(2)]/2$ increased with an increase of z , Figure 5.10. Such a distortion of MnO_6 octahedra stabilised the

$d_{3z^2-r^2}$ state and deformed the long-range magnetic order. Analysis of the neutron diffraction data (see parts 3.4, 3.5) showed that in $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials the average out-of-plane Mn-O bond lengths $[\text{Mn-O}(1) + \text{Mn-O}(2)] / 2$ are also larger than in the corresponding $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ compounds. This means that the chemical pressure affected the crystal structure of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ materials in a way similar to $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, which then resulted in similar changes in magnetic and transport properties.

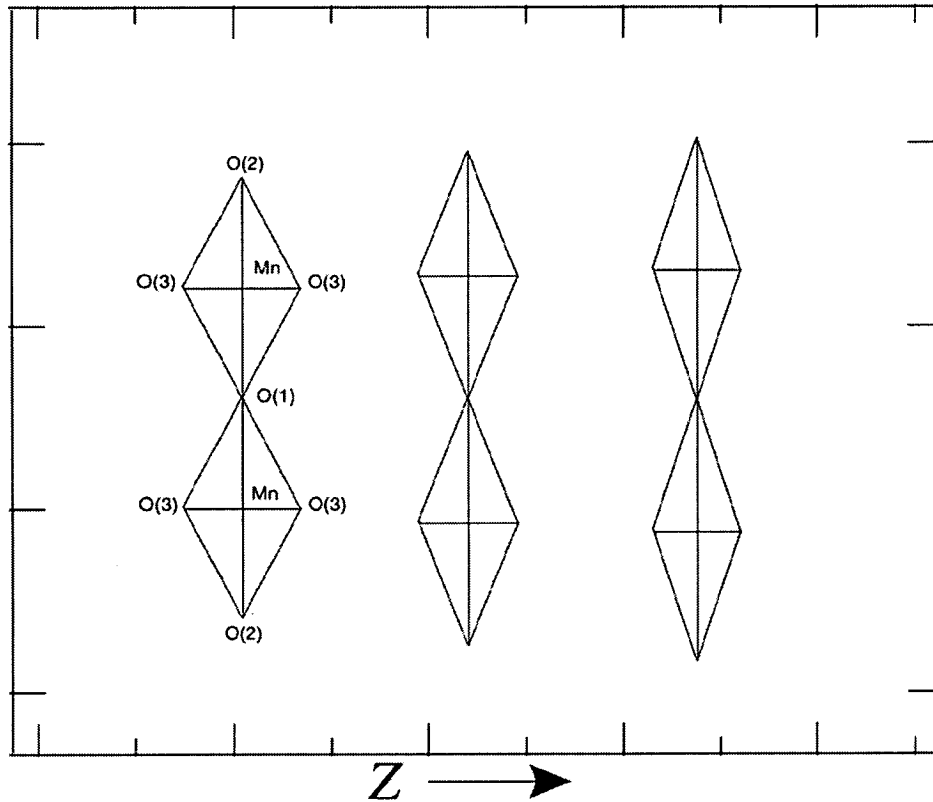


Figure 5.10: Schematic diagram of the distortion of MnO_6 octahedra under chemical pressure (increase of z) in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ manganites. The abscissa is not quantitative.

Kamenev *et al.* (2000) have reported that the application of external pressure in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0.4$) resulted in the following changes in crystal structure:

- A decrease of the interbilayer spacings (Figure 5.11),
- A shift of the manganese atoms along the O(1)-Mn-O(2) linkages (not shown).

If the application of external pressure in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ resulted in similar changes in crystal structure as in the case of $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0.4$), i.e. pressure brought the bilayers closer to each other, then it would enhance the antiferromagnetic correlations between the neighbouring bilayers. The growth of the pressure-enhanced antiferromagnetic correlations would lead to an increase of the electrical resistance on cooling.

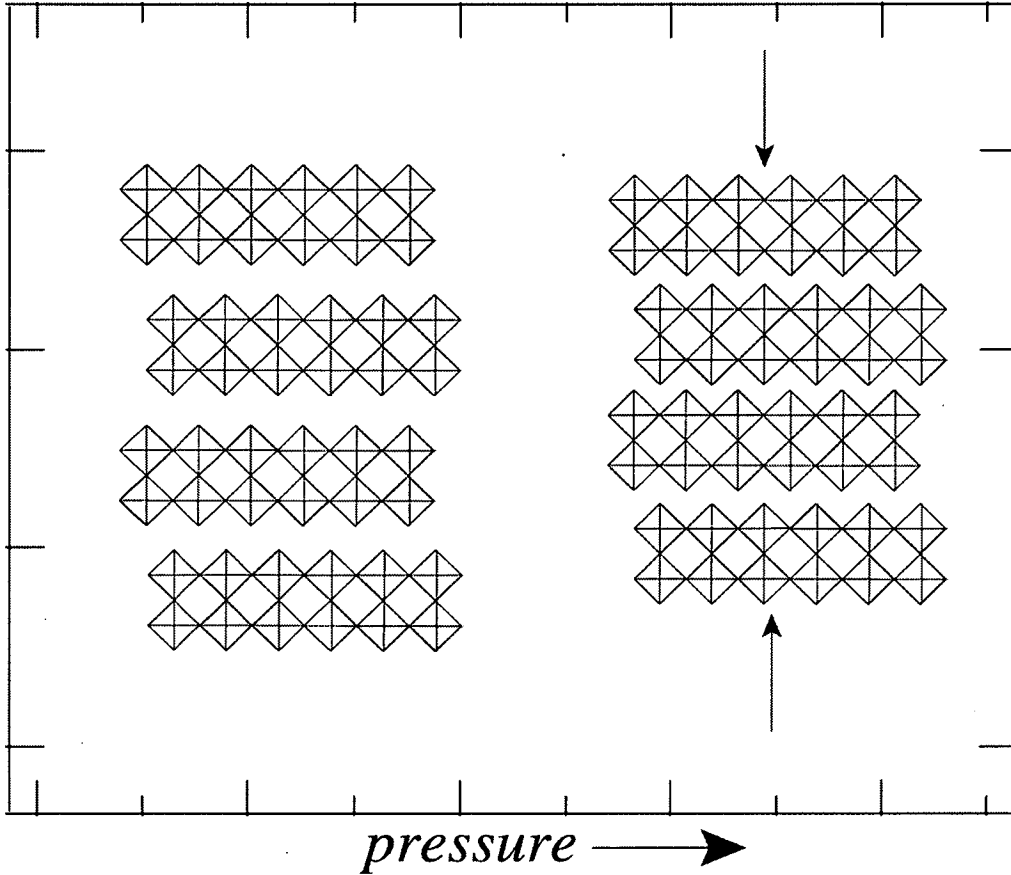


Figure 5.11: Schematic diagram of the effect of external pressure on a distance between bilayers in $(\text{La}_{1-z}\text{Nd}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0.4$). The abscissa is not quantitative.

Figure 5.12 shows the pressure dependence of the temperature of the maximum on the resistance curve (T_m), where the maximum exists, or the position of the inflection point on the resistance curve where such a maximum is suppressed by the pressure, Figure 5.9 (f, g). The temperature at which the maximum occurs increases with an increase of pressure from 13 kbar almost linearly up to 33 kbar, Figure 5.12. However, at 37 kbar it suddenly drops and continues to decrease at 40 kbar. Although at 40 kbar no maximum itself was observed, a trace of the maximum as an inflection point was observed. T_m at 52 kbar is slightly larger than T_m at 40 kbar.

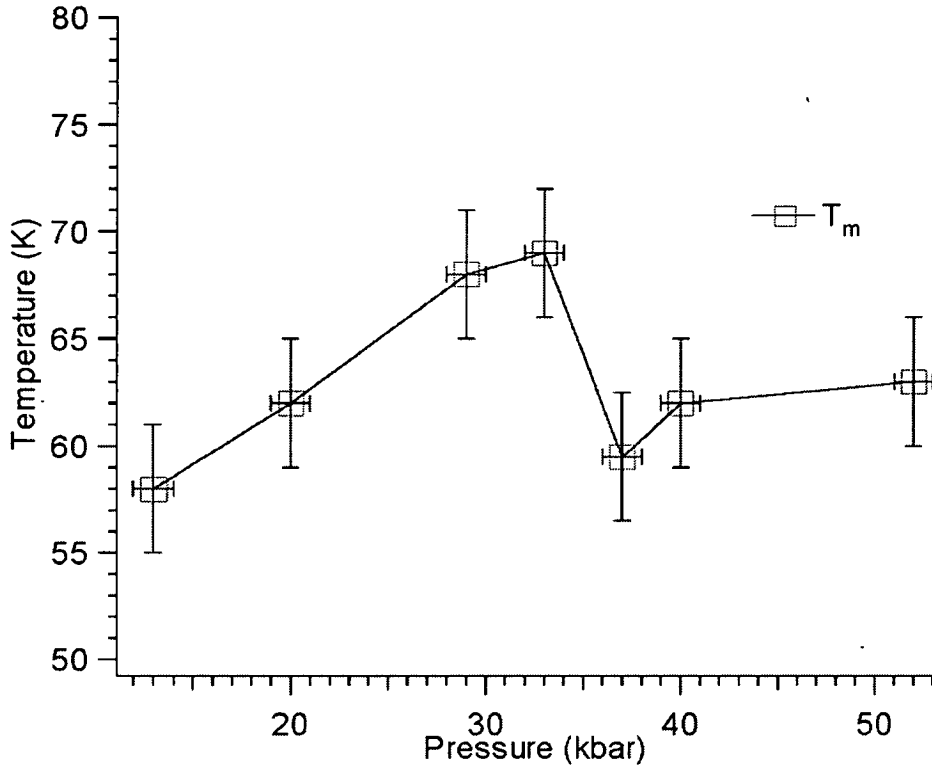


Figure 5.12: Pressure dependence of the temperature T_m of the maximum on the resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$.

Such a pressure dependence of the temperature of the maximum on the resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ can be explained in terms of competition between short-range ferromagnetic (FM) and short-range antiferromagnetic (AF) correlations. The application of pressure enhances the FM correlations, which results in the presence of a maximum on the resistance curve and a metallic-like behaviour below the temperature of the maximum. Higher pressures further enhance the FM correlations, therefore the temperature of the maximum increases. However, at the pressure of 20 kbar, below the temperature of maximum, the resistance begins to rise again. This means that the AF correlations between the neighbouring bilayers start to dominate at this temperature. AF correlations are of a three-dimensional character, which means that they become stronger when pressure brings the bilayers closer to each other. At a pressure of 40 kbar the maximum disappears, which means that the AF correlations became strong enough to dominate the FM ones. Higher pressures

further enhance the AF correlations, therefore the temperature of the inflection point increases.

5.5 Electrical resistance of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$

The temperature dependence of the electrical resistance of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ is shown in Figure 5.13. Because the resistance drops dramatically on heating, it was not possible to measure the resistance at a larger voltage at higher temperatures as the maximum current is limited to 20 mA. Therefore, it is quite a delicate job to find the correct value of voltage in order to measure the resistance in the most extended temperature range, or in the most crucial one.

The measurements of the electrical resistance of this composition were started from 10 kbar. At a pressure of 10 kbar, the resistance increased with a temperature decrease down to 20 K, demonstrating behaviour typical for materials with activated type of conductivity, Figure 5.13 (a). However, at 15 kbar a broad maximum on the resistance curve was observed at ~ 57 K, Figure 5.13 (b). The maximum still existed at 21 kbar at ~ 49 K, Figure 5.13 (c), however, it disappeared at 28 kbar, Figure 5.13 (d). The maximum on the resistance of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ could be attributed to the presence of the pressure-enhanced ferromagnetic correlations in the majority $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ phase. In comparison with the $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, the maximum on the resistance of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ existed in a much shorter pressure and temperature range. Therefore, it was much more difficult to detect and study the evolution of this maximum.

It is reasonable to believe that the short-range ferromagnetic correlations in $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ are weaker than in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. This is why the maximum on the resistance curve is smaller and less prominent than the one on the resistance curve of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. No upturn on the resistance curve below the temperature of the maximum was observed, therefore, one can only speculate whether or not pressure enhances the antiferromagnetic correlations in this material.

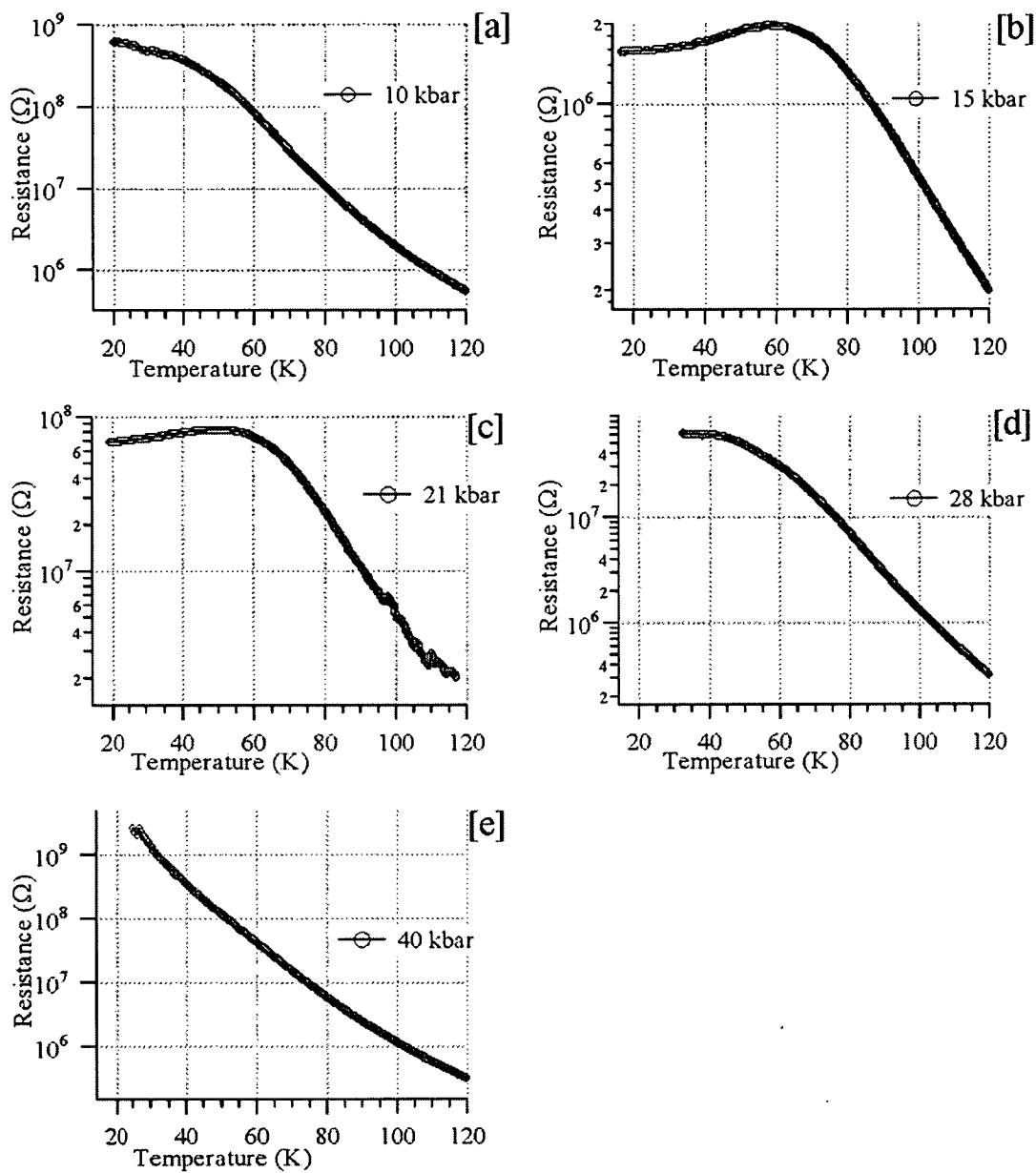


Figure 5.13: The electrical resistance of $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ at different pressures.

5.6 Electrical resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$

The temperature dependence of the resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is shown in Figure 5.14. The electrical resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ increases with a temperature decrease, which is characteristic for the activated type of conductivity (Mott and Davis (1979)).

At 7 kbar the resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ increased exponentially, with a temperature decrease down to 78 K, reaching the value of 4×10^9 Ohm, which is close to the maximum resistance that can be reliably measured using the experimental setup. At 14 kbar, the resistance value was lowered, therefore it was possible to measure the resistance at lower temperature. The temperature profile is very similar to the one collected at 7 kbar, i.e. the resistance increases with the temperature decrease. The pressure of 27 kbar continues to lower the absolute value of the resistance without changing its behaviour. Higher pressures, 41 and 60 kbar, produced a very similar picture. The analysis of the neutron diffraction data shows that even though the MnO_6 octahedra in this compound are less distorted than in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, the interbilayer spacings are considerably larger, leading to the weakening of the magnetic interaction across the bilayers (see part 3.5).

Kamenev *et al.* (2000) reported that in $(\text{La}_{0.6}\text{Nd}_{0.4})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, the external pressure first brings the adjacent bilayers closer together and only then squeezes the MnO_6 octahedra. It is possible that in $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, the pressure of 60 kbar only does the first part of the job, leaving MnO_6 octahedra unaffected. Therefore, pressure higher than 60 kbar is needed to induce the transition from insulator to metal-like behaviour in this composition.

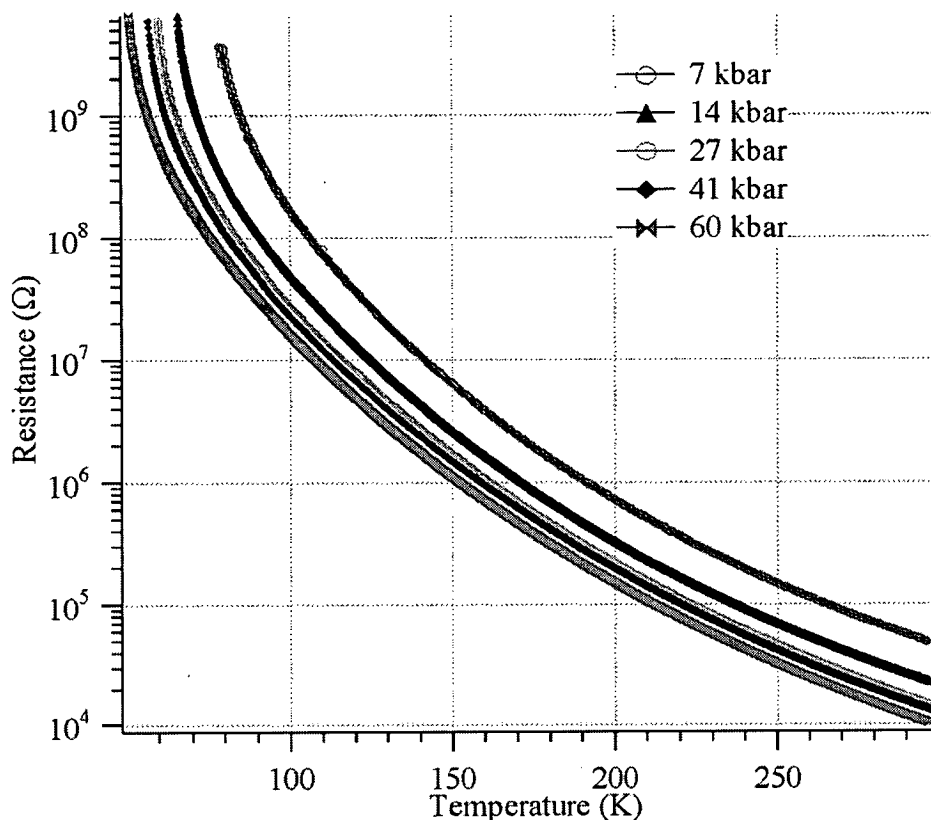


Figure 5.14: Electrical resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under different pressures.

5.7 Magnetic properties of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under pressure of up to 86 kbar

The resistivity data alone cannot provide enough information about the magnetic properties of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under pressure. Therefore, it is necessary to study the effect of external pressure on magnetisation at low temperatures. Attempts to study the effect of pressure on magnetisation at pressures below 10 kbar showed that $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ remained a spin-glass material at temperatures below 55 K. It was found that applied pressure lowered the absolute value of the magnetisation, and shifted the temperature of development of the short-range magnetic order T_{sg} into higher temperatures with the rate of 0.12 K / kbar. No development of the long-range magnetic order was detected at a pressure of below 10 kbar. Therefore, the magnetisation had to be studied at pressures above 10 kbar.

5.7.1 Setup for magnetic measurements

The measurements of the *dc* magnetisation under different pressures were carried out in Osaka University, Japan. A diamond anvil cell was used to generate pressure. The experimental setup for the measurement of the *dc* magnetisation consists of a Position Differentiating Detection (PDD) and a SQUID magnetometer (Ishizuka *et al.* (1995)). The PDD works as a vibrating coil magnetometer, and the detection coil is wound close to the diamond tips (Smith (1956)). The gradient of the magnetic flux is detected along the axis of the detection coil of the SQUID magnetometer. PDD allows the location of the detection coil to be adjusted, in order to obtain maximum sensitivity above the gasket of the DAC as the magnetic flux threading the detection coil has a maximum gradient at a position 0.5 - 1.0 mm away from the sample. Phase sensitive detection of the SQUID is synchronised with the phase of the vibration of the detection coil. This improves the signal to noise ratio. By subtracting the background from the PDD signal, it is possible to obtain a sample magnetisation.

Due to the design, the setup operates in the temperature range between 1.4 and 70 K. The sensitivity of the apparatus is 10^{-9} emu.

The pressure was determined by shift in the temperature of a superconducting transition in Pb (Swenson (1960)).

5.7.2 The *dc* magnetisation of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$

The magnetisation data collected under different pressures support the proposed scenario for the explanation of the development of the local maximum on the resistance curve, Figure 5.9. Under ambient pressure the typical spin-glass behaviour, i.e. the temperature hysteresis below a temperature of transition into a spin-glass state, is observed, Figure 5.15 (a). Under a pressure of 14 kbar the field cooling (FC) and the zero-field cooling (ZFC) curves are brought closer to each other indicating that the spin-glass ordering is deformed in the material, Figure 5.15 (b). A further increase of pressure up to 64 kbar results in a significant increase in the magnetic response at temperatures below 20 K, which corresponds to the development of the long-range magnetic order, Figure 5.15 (c). A pressure of 86 kbar

further enhances the magnetic response below ~ 20 K and continues to weaken the spin-glass ordering at higher temperatures, Figure 5.15 (d).

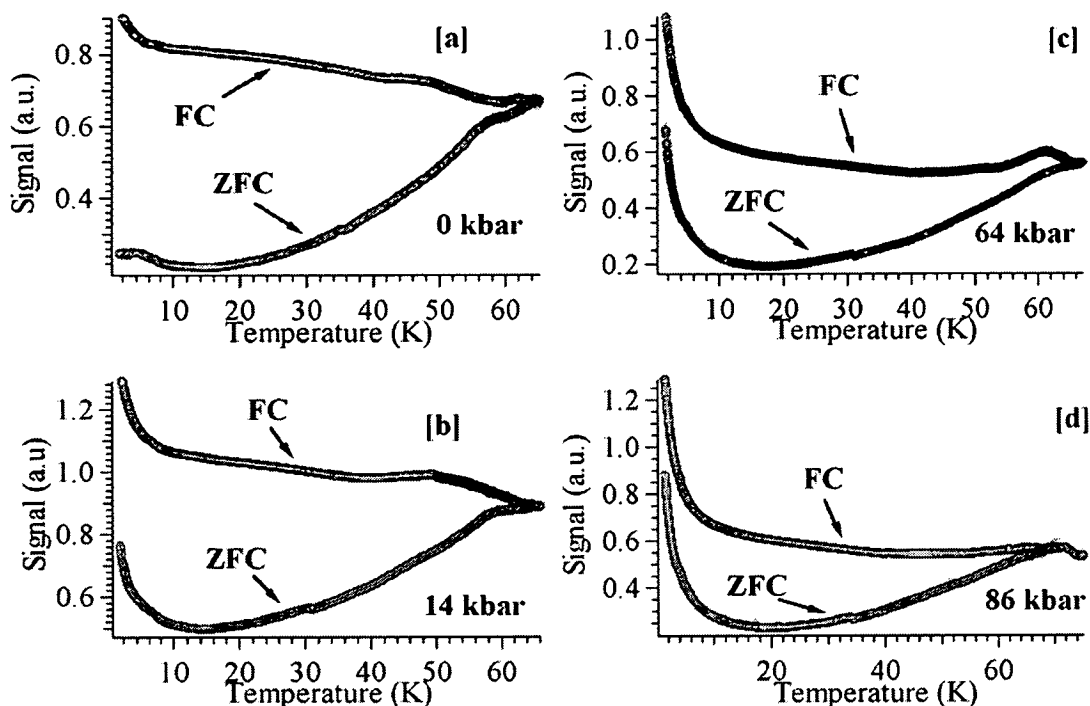


Figure 5.15: The *dc* magnetisation of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ under different pressures.

The transition into the antiferromagnetic phase was not observed, however the resistivity data suggested that the order is of AF origin as the increase of resistance is observed at lower temperatures.

Figure 5.16 (a) shows the decrease of temperature hysteresis with an increase of pressure, which indicates the weakening of the spin-glass state. The relative increase of the measured magnetisation with an increase of pressure suggests the formation of long-range magnetic order, Figure 5.16 (b).

Measurements of the *dc* magnetisation of a single crystal of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ were carried out using the SQUID magnetometer in order to compare the behaviour of the magnetisation with the signal measured in DAC. Measurements were carried out at ambient pressure in temperature interval between 4 and 75 K, Figure 5.17.

A temperature profile of the *dc* magnetisation is identical to the temperature behaviour of the signal measured in DAC. Such a likeness proves that the setup for the magnetic measurements was properly calibrated at ambient pressure.

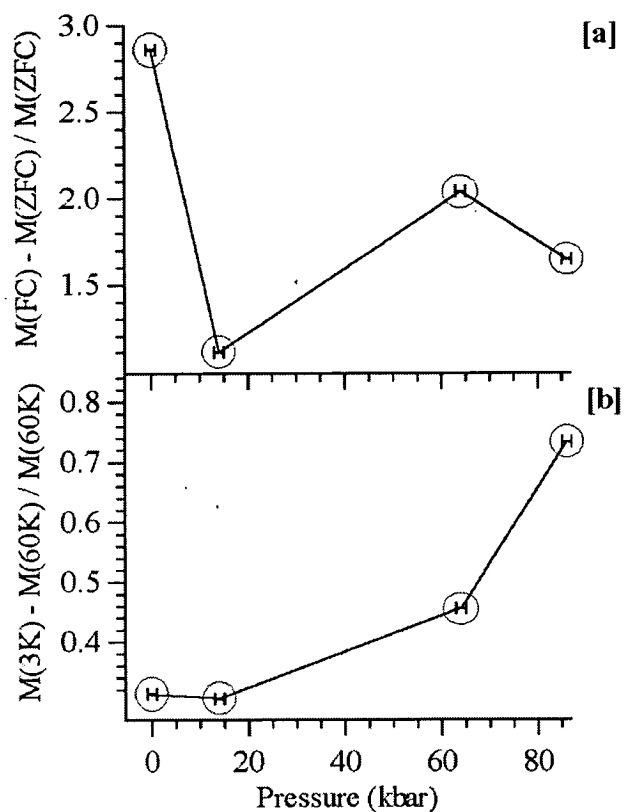


Figure 5.16: [a] $\{M(FC) - M(ZFC)\} / M(ZFC)$ as a function of pressure at 15 K. [b] Relative FC magnetisation $\{M(3K) - M(60K)\} / M(60K)$ as a function of pressure.

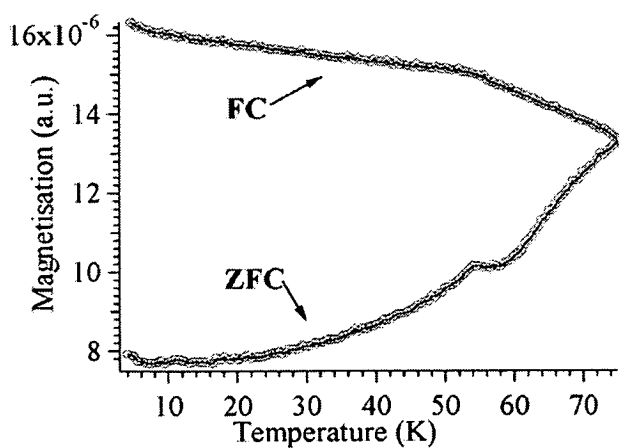


Figure 5.17: Magnetisation of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ measured in a SQUID without DAC.

5.8 Conclusions

A relatively simple technique of measuring the electrical resistance in a DAC under pressure below 70 kbar was developed. A new method of laminating the gasket, developed in the course of the project, is outlined in detail. The effect of pressure up to 70 kbar on the transport properties of the majority phase in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$, $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is reported. A pressure-induced transition from an insulator to a metallic-like behaviour in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ has been observed at ~ 58 K at 13 kbar. As the transition develops with increasing pressure, it becomes more prominent at 33 kbar and disappears at pressures above 37 kbar, leaving only the inflection point on the temperature profile of the resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. It is observed that the resistance of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ below the transition temperature begins to increase at pressures above 20 kbar.

The analysis of the magnetisation data shows that applying pressure weakens the spin-glass state by reducing the temperature hysteresis of the magnetisation. It has also been observed that the magnetisation increases considerably with increasing pressure. This fact, combined with the observed increase in the resistivity at a temperature below ~ 30 K, allows one to suggest that the application of external pressure enhances the antiferromagnetic correlations between the bilayers in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$. A similar transition from an insulator to a metallic-like behaviour was also observed in $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ in the pressure range between 15 and 28 kbar. However, no such transition was observed for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under pressures of up to 60 kbar. The analysis of the neutron diffraction data shows that even though the MnO_6 octahedra in this compound are less distorted than in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, the interbilayer spacing is considerably larger, leading to the weakening of the magnetic interaction across the bilayers. The electrical resistance of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ decreases with pressure, which is characteristic for the activated type of conductivity. It seems that pressures higher than 60 kbar are needed to induce the transition from the insulator to a metal-like behaviour in this compound.

Chapter 6

Studies of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$

6.1 Introduction

The structural, magnetic and transport properties of layered manganites have been studied extensively since the discovery of the CMR phenomenon in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ (Moritomo *et al.* (1996)). In $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ compounds as well as in other layered members of $\text{Ln}_{n+1}\text{Mn}_n\text{O}_{3n+1}$, MnO_6 octahedra share corners, which are separated by rock-salt-like $\text{Ln}(\text{Sr})\text{O}$ layers. It has been shown in the previous chapters of this thesis that structural, magnetic and transport properties of $\text{Ln}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ materials strongly depend on the dopant level and on the size of the Ln ion. In this chapter, a novel manganese oxide will be considered. $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ also has a layered structure, but unlike the case of $\text{Ln}_{n+1}\text{Mn}_n\text{O}_{3n+1}$, MnO_6 octahedra in this material share not only corners, but also faces. As a result, the Mn-O-Mn super-exchange pathways are not restricted to 180° , but allow for competition with 90° interactions (Goodenough (1963)).

The main objective of the research described in this chapter was to investigate structural, magnetic and transport properties of this manganese oxide.

6.2 Structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$

$\text{Sr}_7\text{Mn}_4\text{O}_{15}$ was synthesized and analysed for the first time by Kriegel, *et al.* (1992), but perhaps because it was before the CMR effect was rediscovered in perovskite manganites, there were no further studies of this material until the current one.

The structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is presented in Figure 6.1. Manganese is present as Mn^{4+} and is located solely in pairs of face sharing octahedra, which are similar to those found in SrMnO_3 (Battle *et al.* (1988)). The Mn_2O_9 groups are linked to six analogous groups in SrMnO_3 , but only to three in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. The Mn_2O_9 dimer is shown in Figure 6.2. Two crystallographically distinct Mn cations can be distinguished in this structure. Mn(1) shares two oxide ions with two neighbouring

dimers, whereas Mn(2) shares only one oxide ion with a neighbouring dimer. The Mn(1)-O-Mn(2) coupling creates columns which are joined by Mn(1)-O-Mn(1) linkages every ~ 10.3 Å to form layers. In this way a 2D compound with a strong in-plane anisotropy is formed. The structure can thus be considered a combination of the $n = 1$ Ruddlesden-Popper phase of Sr_2MnO_4 (Bouloux *et al.* (1981)) and the perovskite SrMnO_3 (Battle *et al.* (1988)), a single layer compound with Mn_2O_9 dimers as principal building blocks. The structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is flexible, and up to $\sim 30\%$ of the Sr ions can be replaced by Ba and Ca ions without any significant change in the crystal structure. The application of chemical pressure does cause the cell parameters to change in an anisotropic fashion, thus reflecting the cation ordering that occurs between the different alkaline earth metal ions (Vente *et al.* (2000)).

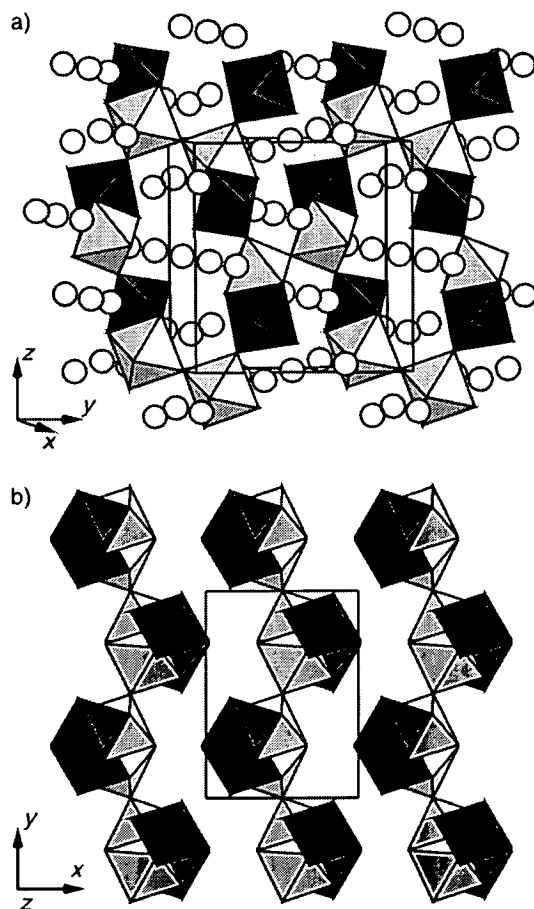


Figure 6.1: Structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. Light octahedra are those enclosing Mn(1) and dark ones are those enclosing Mn(2). Sr is shown as circles. Part (a) emphasises the linking within planes, while (b) shows the columns and stacking of the planes.

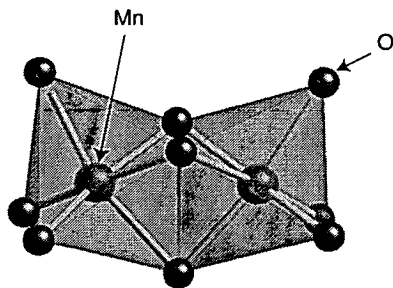


Figure 6.2: Two MnO_6 octahedra sharing faces.

6.3 Magnetic susceptibility of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$

A polycrystalline sample was used for the measurements of magnetisation (sample preparation is described in Chapter 2). Measurements of the *dc* magnetisation were performed using a SQUID magnetometer in a temperature range from 5 to 300 K, and in a magnetic field of 100 Oe. The data were collected on warming after cooling in zero field (ZFC), and after cooling in the field of the measurement (FC). The *ac* susceptibility was measured in the temperature range 5 - 300 K in a *dc*-bias field of 1 kOe with an amplitude of the oscillating field of 1 or 2 Oe at frequencies of 1, 10, and 113 Hz.

The *dc* molar susceptibility of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is shown in Figure 6.3(a). A clear maximum is observed at ~ 90 K which indicates the onset of co-operative effects. However, the maximum is quite broad, so it is not a transition from a high temperature paramagnetic state to a low temperature 3D- magnetically ordered state. Figure 6.3 (b) shows the central part of the magnetic hysteresis loops measured at 5, 75, and 150 K after cooling the sample in a field of 2 kOe. The temperature hysteresis at lower temperature (Figure 6.3 (a)) along with the small displacement of the centre of the FC hysteresis loop at 5 K away from the origin (Figure 6.3 (b)), is a characteristic of a spin-glass behaviour. Attempts to model the high temperature part of the susceptibility using the Curie-Weiss law:

$$\chi \sim 1 / (T - \Theta), \quad (6.1)$$

where Θ is the Weiss temperature, resulted in $\Theta = -490$ K and $\mu_{\text{eff}} = 4.47 \mu_B$, which

does not make sense because manganese is present as Mn^{4+} and cannot have a magnetic moment larger than $3.87 \mu_B$. Therefore, the interatomic magnetic interactions are significant throughout the measured temperature range.

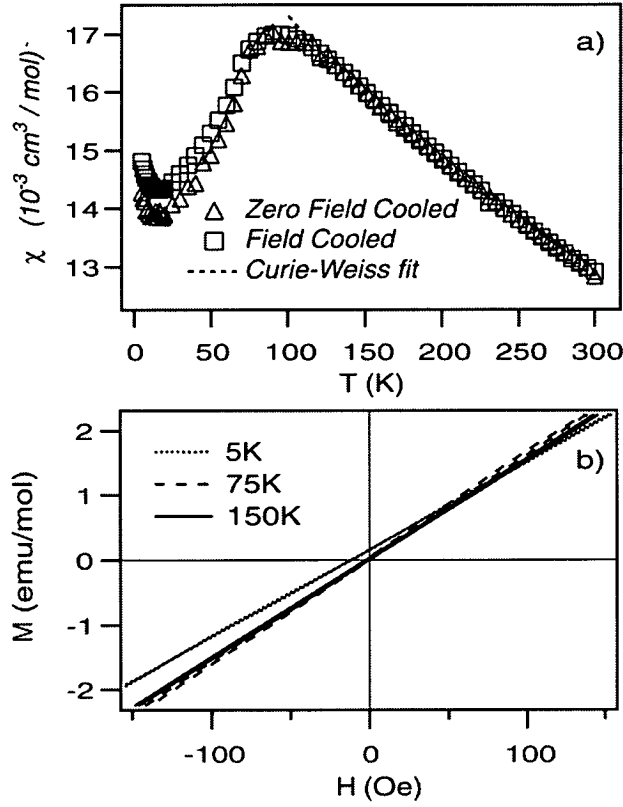


Figure 6.3: The ZFC and FC molar magnetic susceptibilities of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ measured in the dc field of 100 Oe (a), and the central part of the hysteresis loops after cooling the sample in 2 kOe (b).

The ac magnetic susceptibility (χ_{ac}) of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is shown in Figure 6.4 (a). The χ_{ac} did not demonstrate any interesting features in the studied temperature region. No frequency dependence of χ_{ac} was detected. However, a slight upturn of susceptibility was observed on both dc and ac curves. The differential $d\chi_{ac} / dT$ was fitted to a four-term polynomial which showed a peak at $T \sim 70$ K. The peak represents a transition from concave to convex behaviour, Figure 6.4 (b).

However, analysis of the dc and ac magnetic susceptibilities did not provide enough information about either presence or absence of a long-range magnetic order. Therefore, to study the structure and magnetic properties of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$, powder neutron diffraction experiments had to be carried out.

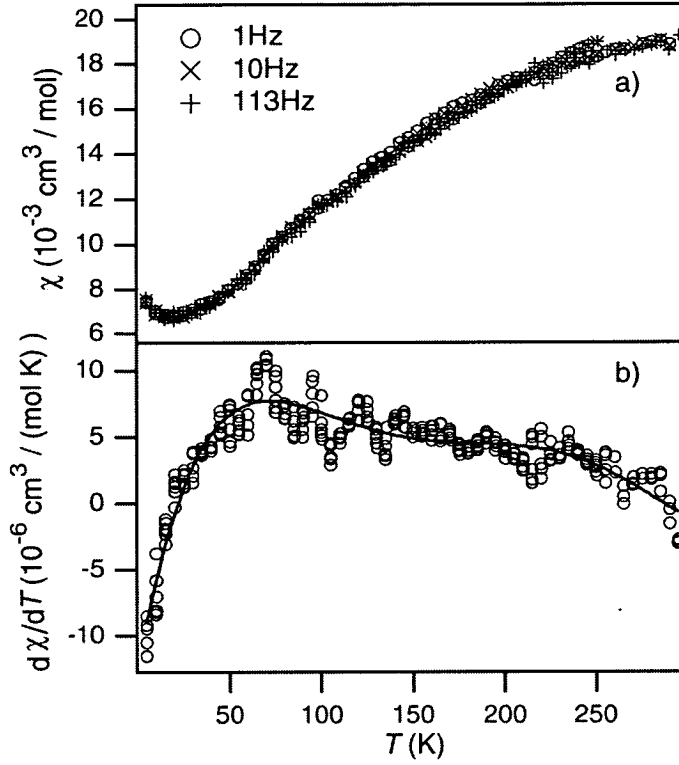


Figure 6.4: The *ac* magnetic susceptibility of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ as a function of temperature at three different frequencies, measured at zero bias field with an amplitude of 2 Oe (a), and the partial differential $d\chi_{ac}/dT$ (b).

6.4 Powder neutron diffraction studies of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$

The time-of-flight neutron diffraction technique involves measuring the time of flight t taken for a neutron to travel the total flight path L from the moderator to the detector, via the sample. The use of the time-of-flight technique removes the need to use a monochromatic neutron beam. Therefore, even though the raw flux produced initially by an accelerator-based source is much less than that produced by a reactor source, the final flux available for scattering experiments is of a comparable order of magnitude. The moderator at an accelerator-based neutron source is used to slow the neutrons down so that they have suitable wavelengths for neutron scattering, in the same way as for a reactor neutron source. In time-of-flight diffraction, the sample is irradiated with a pulsed beam containing neutrons of different wavelengths. The neutron travels a known distance, L , from the source to the sample, and then to the detector, which is positioned at an angle 2θ . Their arrival times at the detector are

then recorded. As wavelength λ is related to momentum (mv) through the de Broglie relationship ($\lambda = h / mv$, h is the Planck's constant), it is then possible to calculate the d -spacing (Bacon (1975)):

$$d = h / \{2mv (\sin\theta)\}, \text{ or } d = 1.977 \times 10^{-3} t (L \sin\theta)^{-1}, \quad (6.2)$$

where time-of-flight (t) is measured in microseconds, flight path (L) in metres and d -spacing in Å units.

A fundamental feature of the time-of-flight technique is its ability to measure a complete diffraction pattern using a single, fixed detector. In practice, in order to reduce counting times, time-of-flight diffractometers typically contain large numbers of detectors arranged into a series of different banks. Each bank has its own characteristic resolution, d -spacing range and count rate. During an experiment, data are accumulated over a sufficient number of neutron pulses from the source until the diffraction pattern is of a desired statistical accuracy.

The neutron source at the ISIS facility, Rutherford Appleton Laboratory, produces a flux that is rich in a much higher energy than is possible at reactor sources. This allows diffractometers to measure very small d -spacings without reaching the $\sin\theta$ limit. According to the Bragg's law ($\lambda = 2 d \sin\theta$), the smallest d -spacing that can be measured on a constant wavelength diffractometer is:

$$d_{min} = \lambda / 2. \quad (6.3)$$

On a spallation source such as ISIS, very small d -spacings are measured using the highest energy, shortest wavelength neutrons emerging from the moderator. Spallation is an interaction between the proton, fired at a heavy metal target, and the target nucleus, which results primarily in the emission of neutrons and light nuclear fragments.

Variable temperature time-of-flight powder neutron diffraction data (PND) were obtained on the OSIRIS instrument at the ISIS facility, Rutherford Appleton Laboratory. Data were collected in a temperature interval between 5 and 290 K with $\Delta T = 14.25$ K using an orange ILL cryostat in the d -spacing range $0.96 \text{ Å} < d < 7.11 \text{ Å}$ on the sample contained in a cylindrical vanadium can. A small part of the detector bank (10%) was used to obtain the highest resolution possible at a cost of reduced

counter statistics. All neutron diffraction data were analysed by the Rietveld method (Rietveld (1969)) as implemented in the GSAS program suite (von Dreele and Larson (1986)). Scattering lengths and the magnetic form factor for Mn^{4+} were provided by this software package. The peak shape was described using a convolution of the Ikeda-Carpenter and pseudo-Voigt functions after David (David (1986)) (three refineable parameters). Also, a wavelength-dependent absorption correction according to an empirical formula after Hewat (Hewat (1979)) was included. The refined structural parameters of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ at 290 K are presented in Table 6.1. The positions of the atoms in crystal structure are shown in Figure 6.5. The diffraction profile at 290 K is shown in Figure 6.6.

Atom	Name	x	y	z
Sr(1)	s1	0.9974(9)	0.1861(6)	0.4621(5)
Sr(2)	s2	0.351(1)	0.1540(5)	0.1936(5)
Sr(3)*	s3	0.500(3)	0.021(1)	0.510(1)
Sr(4)	s4	0.1828(9)	-0.019(5)	0.8345(7)
Mn(1)	m1	0.589(1)	0.165(1)	0.9246(9)
Mn(2)	m2	0.781(1)	0.1701(9)	0.7199(8)
O(1)	o1	0.512(1)	0.1038(7)	0.7525(7)
O(2)	o2	0.682(1)	0.1758(7)	0.3389(7)
O(3)	o3	0.331(1)	0.2528(8)	0.9532(7)
O(4)	o4	0.839(1)	0.0845(7)	0.8852(7)
O(5)	o5	0.682(1)	0.2220(7)	0.0839(8)
O(6)*	o6	0.503(3)	0.005(3)	-0.024(2)
O(7)	o7	0.839(1)	0.0148(7)	0.6221(6)
O(8)	o8	0.026(1)	0.2492(6)	0.7110(7)

Table 6.1: Structural parameters of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ at 290 K. Space group $P2_1/c$; $a = 6.81825(9)$, $b = 9.6228(1)$, $c = 10.3801(1)$ Å, $\beta = 91.8771(9)^\circ$, $V = 680.68(1)$ Å³. For all Sr $U_{iso} = 0.007(1)$ Å², for all Mn $U_{iso} = 0.001(1)$ Å², for all O $U_{iso} = 0.012(7)$ Å². Agreement indices: $R_{wp} = 7.66\%$, $R_p = 9.95\%$, $\chi^2 = 1.91$ for 59 variables. *Fractional occupancy of Sr(3) and O(6) is 0.5.

In comparison with the data collected at 290 K, the data set collected at 5 K contained a considerable number of additional magnetic Bragg peaks at d values larger than 3 Å, Figure 6.7. All the additional peaks could be indexed using the crystallographic cell, and no cell multiplication was required. The presence of the $\{1\ 0\ 0\}$ and $\{0\ 0\ 2\}$ reflections indicated that the moments were aligned along the y direction.

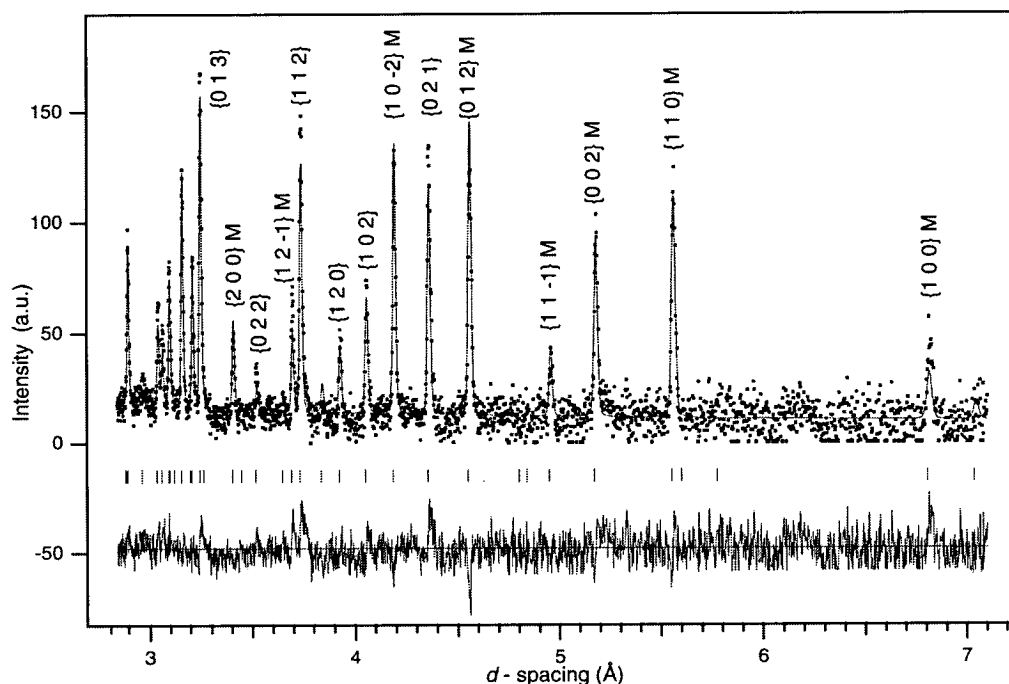


Figure 6.7: Diffraction pattern collected at 5 K. Observed (dots), calculated (top line), and difference (bottom). Reflection positions where nuclear and/or magnetic Bragg intensities may be observed are marked. The main peaks are indexed and those with a predominant magnetic contribution are labelled M.

A model in which each manganese atom couples antiferromagnetically to the nearest neighbour provided the best fit to the observed data, Figure 6.8. The ordered moment refined to a value of $2.83(2) \mu_B$ per Mn. No crystallographic phase transition was observed and the cell parameters at 5 K refined to the following values: $a = 6.80928(8)$, $b = 9.5999(1)$, $c = 10.3492(1)$ Å, and $\beta = 91.922(1)^\circ$. The intensities of the magnetic Bragg reflections decrease with increasing temperature to the noise level at ~ 75 K. This provides an estimation for the Neel temperature (T_N).

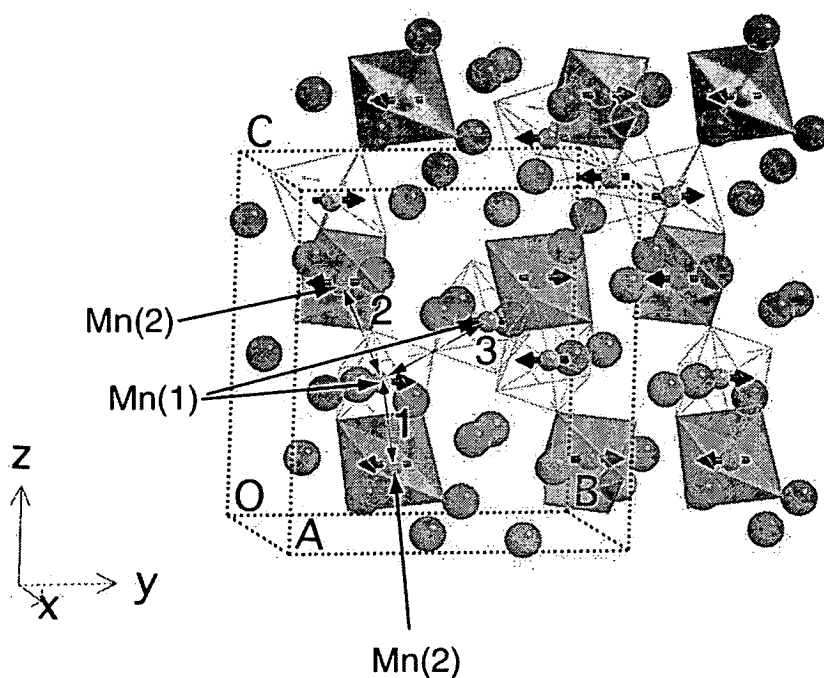


Figure 6.8: Magnetic structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. (1) intradimer Mn(1)-Mn(2) distance, (2) interdimer Mn(1)-Mn(2) distance, (2) interdimer Mn(1)-Mn(1) distance.

The relative cell parameters $\sim l / l_{290\text{K}}$ ($l = a, b$, and c) change smoothly with temperature. The a axis shows the smallest reduction (0.15%) on cooling and the c axis the largest (0.3%), Figure 6.9. Little variation was observed below 50 K and there were no indications of discontinuities.

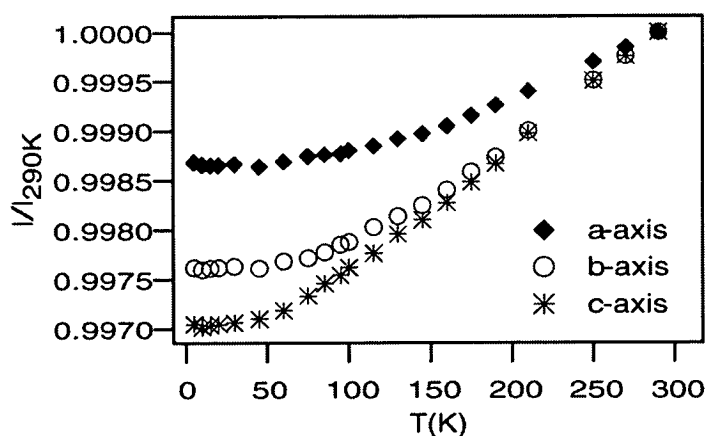


Figure 6.9: The relative cell parameters for $l = a, b$, and c , as a function of temperature. The estimated standard deviation is considerably smaller than the size of a marker.

The three different characteristic Mn-Mn distances present in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ (see Figure 6.8) are shown in Figure 6.10 as a function of temperature. Clear discontinuities are seen despite the relatively large error bars in these graphs. Above 130 K, the intradimer Mn(1)-Mn(2) distance is roughly constant at ~ 2.54 Å, but it becomes somewhat smaller in the interval $75 \text{ K} < T < 115 \text{ K}$ (~ 2.51 Å). On further cooling, the Mn(1)-Mn(2) distance increases again and becomes almost constant at 2.58 Å, $T \sim 30 \text{ K}$. The behaviour of the interdimer Mn(1)-Mn(2) bond length is very different. Above 85 K , this distance is constant within the error bars at ~ 3.64 Å. On further cooling, it decreases to ~ 3.58 Å below 30 K . This shortening might be related to exchange-striction effects (Greenwald and Smart (1950)) caused by the onset of long range magnetic ordering. The interdimer Mn(1)-Mn(1) distance is not very well established, but the values for $T < 30 \text{ K}$ appear to be larger than those at higher temperatures.

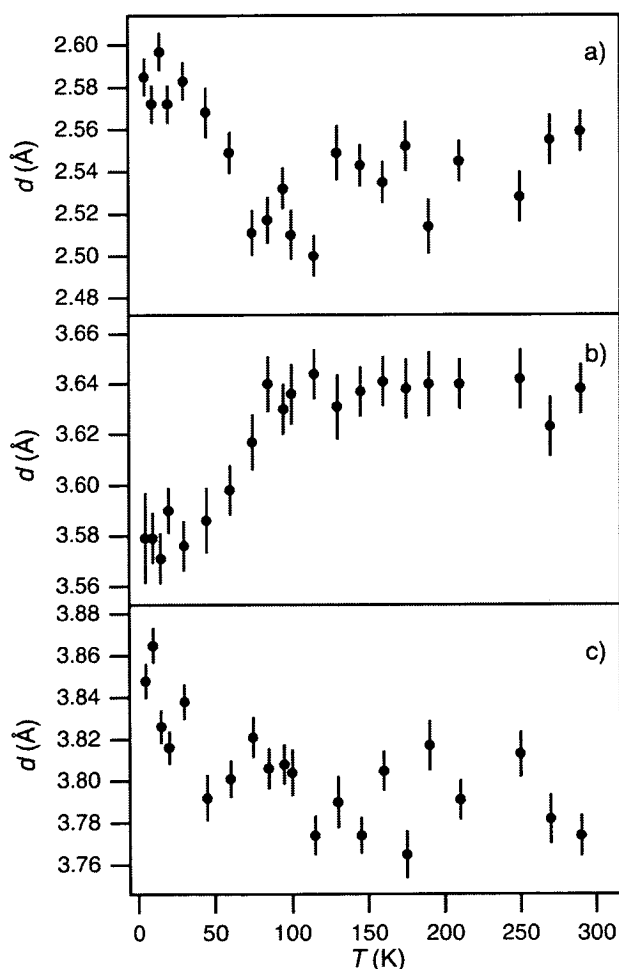


Figure 6.10: The intradimer Mn(1)-Mn(2) (a), the interdimer Mn(1)-Mn(2) (b), and the interdimer Mn(1)-Mn(1) (c) distance as a function of temperature.

6.5 Magnetic phases of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$

Firstly, the maximum observed in χ_{dc} at ~ 100 K was interpreted as a transition from a paramagnetic state to the antiferromagnetically ordered state, Figure 6.3(a). However, this maximum appeared to be too broad for a conventional Neel temperature. In addition, χ_{dc} did not demonstrate the Curie-Weiss behaviour at temperatures above 100 K.

The variable temperature neutron diffraction experiments proved unambiguously that $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ showed a long-range antiferromagnetic order below 75 K. Therefore, the maximum at 90 K on the dc susceptibility curve is not related to the Neel temperature. The magnetic structure is consistent with that commonly found in magnetically ordered manganites ($\text{SrMn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (Cussen *et al.* (1998) and BaMnO_3 (Cussen *et al.* (2000)) with a hexagonal perovskite related structure, in which the moments are normally aligned perpendicular to the hexagonal axis. The moments are parallel with the face which the two-paired octahedra have in common. In addition, antiferromagnetic coupling is present between all nearest neighbour transition metal ions. These characteristics were found in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$, and the magnetic moments were fully compensated within the layers. The moments were aligned within the layers and were parallel with the b axis. Magnetic coupling between the layers is achieved through multiple AF Mn(2)-O-Sr-O-Mn(2) super-exchange pathways with a Mn-Mn separation of ~ 5.7 Å (Vente *et al.* (2001)). The observed magnetic moment of $2.83(2) \mu_B$ is somewhat lower than the theoretical value for Mn^{4+} , $gS = 3 \mu_B$.

The neutron diffraction patterns collected between 60 and 150 K showed an enhanced background level at the relatively large d spacing. This can be attributed to the presence of extensive short-range magnetic correlations with cluster-like behaviour. These magnetic clusters were likely to have a two-dimensional character as the largest nearest-neighbour interdimer Mn-Mn distance was ~ 3.7 Å, and the shortest interlayer Mn-Mn distance was ~ 5.7 Å.

The presence of a small but significant divergence between the FC and ZFC data below the Neel temperature (T_N) indicated that not all the magnetic moments are totally compensated. The small values of the susceptibility, combined with the fact

that the centre of the FC hysteresis loop at 5 K was not centred around the origin, ruled out a minor spin canting, and indicated spin or cluster-glass-like behaviour.

The spin pairing, as has been observed between the spins of two Mn^{4+} ions in the Mn_2O_9 dimers of SrMnO_3 (Battle *et al.* (1988)), is one of the possible short-range coupling mechanisms that occurs in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. Such a spin pairing is unlikely to cause an enhanced background level in the powder neutron diffraction as it is only effective over very short distances (~ 2.5 Å). The neutron diffraction data thus indicate that interdimer coupling was present below ~ 150 K. Above this temperature the contribution to the background from the magnetic fluctuations disappeared (Vente *et al.* (2001)).

The only type of short-range correlations which might be present above 150 K, is spin pairing of the type observed below 350 K in SrMnO_3 (Battle *et al.* (1988)). The *dc* susceptibility of SrMnO_3 above T_N increases with increasing T , in a similar manner to the behaviour of a polycrystalline antiferromagnetically ordered compound. In contrast to this, χ_{dc} of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ decreases with increasing T above 120 K (and thus above T_N), and is analogous to a paramagnet. Therefore, the *dc* magnetic susceptibility data do not indicate any spin pairing in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. However, the structural data show a very similar intradimer Mn-Mn distances for $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and SrMnO_3 (2.53 and 2.50 Å, respectively, at ~ 290 K). This means that such a coupling mechanism is possible.

The MnO_6 octahedra in $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ are irregular, and therefore predicting how the different energy levels of *d* orbitals are arranged is not straightforward. If the octahedra were perfectly regular, the structure would consist exclusively of Mn^{4+} with a half filled t_{2g} triplet and an empty e_g doublet. When the octahedron is elongated, the t_{2g} orbital splits into an e_g doublet and a b_{2g} singlet, which is higher in energy (Goodenough (1963)). Therefore, it is possible that the spin pairing continuously diminishes over a large temperature range, and that it is still present at 300 K, the highest temperature used in present studies. $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ does not behave as a conventional paramagnetic material above T_N .

In the absence of long-range magnetic correlations, the *dc* susceptibility mainly reflects the degree of the short-range order in the magnetic sublattice. In addition to this, the *ac* susceptibility probes the degree of mobility of the moments in response to the oscillating magnetic field. The above mentioned spin pairing is antiferromagnetic in origin. With decreasing temperature, the spin-spin correlations in the dimers

become stronger, and thus the susceptibility does not increase as much as expected on the basis of the Curie-Weiss law. This results in an unreasonably large Weiss temperature (part 6.3). In the absence of a long-range magnetic order in the manganese sublattice, the influence of spin-orbit coupling increases with decreasing temperature, and the paired magnetic moments “freeze” into the lattice. This leads to a decrease of χ_{ac} . The cluster formation starts at ~ 150 K. On further cooling, these clusters grow in number and size, leading to a decreasing slope of the χ_{dc} and eventually to a maximum at ~ 100 K. Around this temperature magnetic susceptibility is mainly due to magnetic clusters. At lower temperatures the number of clusters decreases, while they continue to grow in size. Since the intradimer Mn-Mn interactions remain the dominant magnetic force, χ_{ac} continues to decrease with decreasing temperature in this temperature region. At the Neel temperature (~ 75 K), the clusters have grown large enough to allow for the development of a long range magnetic order, and both magnetic susceptibilities start showing a similar temperature behaviour. The maximum in $d\chi_{ac}/dT$ coincides with the temperature of the onset of long range ordering, and is likely to be related to this effect, Figure 6.4(b). The Mn(1)-Mn(2) intradimer distance increases on cooling through the Neel temperature (Figure 6.10(a)) in spite of the fact that Mn(1) and Mn(2) are coupled antiferromagnetically. Exchange-striction effects would favour a reduction of the Mn(1)-Mn(2) intradimer distance under these conditions. A reduction of the Mn(1)-Mn(2) interdimer distance was observed and shown in Figure 6.10(b). This means that the Mn(1)-Mn(2) intradimer distance is already reduced due to intradimer spin coupling. Below T_N , a compromise has to be achieved between the competing interactions, and as a result the intradimer Mn(1)-Mn(2) distance is somewhat enlarged in favour of the interdimer distances. This effect is so strong that the intradimer Mn-Mn distance actually becomes larger than it originally was at room temperature.

The origin of the upturn below ~ 25 K observed in both dc and ac magnetic susceptibility data is not yet clear. Such an upturn can be produced by the re-entrance of the spin-glass behaviour observed at higher temperatures.

6.6 Measurements of electrical conductivity of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ using a diamond anvil cell

In the high temperature region (above 673 K), Feltz *et al.* (1999) showed that the resistivity of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ demonstrated behaviour typical for materials in which conductivity is due to the hopping of the charge carriers. The resistivity increased with decreasing temperature, and at 530 K was of the order of $10^8 \Omega\cdot\text{cm}$. This means that at room temperature the resistivity can be estimated as $\sim 2.2 \times 10^8 \Omega\cdot\text{cm}$. Estimating the thickness of the sample as $d \sim 30 \times 10^{-4} \text{ cm}$, the width of the sample as $w \sim 50 \times 10^{-4} \text{ cm}$, and the distance between the voltage terminals on the surface as $D \sim 50 \times 10^{-4} \text{ cm}$, one finds that the resistance to measure is $\sim 10^{11} \Omega$. The maximum resistance that is possible to measure in the laboratory is $\sim 10^{10} \Omega$.

Several attempts to measure the temperature dependence of the resistance of the powder sample of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ have been made. It was expected that the magnetic ordering that forms at low temperatures could decrease the resistivity of the material. However, in a temperature range of $16.5 \leq T/\text{K} \leq 300$, the resistance of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ proved to be above $10^{10} \Omega$. It is well known that the application of pressure often results in a lowering of the electrical resistivity of materials, therefore it was decided to measure the resistance of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ under pressure. However, with increased pressure up to the maximum 75 kbar, no resistance could be measured in the entire temperature range. There are several mechanisms responsible for high resistivity of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$:

- $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ only contains Mn^{4+} ions, which means that compared to the materials with mixed valence (that contain both Mn^{4+} and Mn^{3+}) there are no vacancies for charge carriers on Mn sites.
- Materials with layered structure usually demonstrate higher resistivity because the overlap of Mn-O-Mn linkages, which control the conductivity in manganese oxides, is smaller between the layers. For instance, bilayered manganites have higher resistivity in the direction perpendicular to the bilayers than the resistivity within bilayers.

6.7 Concluding notes

The magnetic properties of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ are described as a function of temperature. At temperatures close to room temperature, a high degree of spin pairing within the manganese dimers is present. No sharp transition from a truly paramagnetic to a spin paired state was observed. On cooling, short range correlations become more and more important, and antiferromagnetic clusters start to form at ~ 150 K. Those clusters can be low-dimensional because of the layered nature of this compound. They start to dominate the susceptibility at ~ 100 K. Below this temperature, three-dimensional long-range correlations start to form, resulting in a reduction of the susceptibility. A long-range antiferromagnetic order is finally established at ~ 75 K.

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Chapter 7

Conclusions

The principal aim of this thesis was to study the structural, magnetic and transport properties of the novel layered $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.3, 0.4, 0.5$) and $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ manganites, and to investigate the effect of *external pressure* on transport and magnetic properties of these materials. The substitution of La ions with smaller Pr ones resulted in the following changes in the crystal structure:

- An increase of Mn-O(1) and Mn-O(2) linkages and a decrease of Mn-O(3) bond length;
- A decrease in the interbilayer spacing, i.e. the adjacent bilayers are brought closer to each other with higher Pr-doping level.

The application of such *chemical pressure* and the following changes in crystal structure significantly effect the magnetic and transport properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$). It was shown that in all $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) samples, the majority phase undergoes a transition into a spin-glass state at ~ 50 K. However, no long-range magnetic ordering was found in either of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials in the temperature range of 1.8 K – 300 K. This is in sharp contrast with $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$) materials, which have ferromagnetic ground states. The analysis of the neutron diffraction data makes it possible to attribute the absence of the long-range magnetic order in the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) materials to the elongation of the MnO_6 octahedra along the c -axis. Such elongation results in a greater separation between the magnetic Mn atoms in the lattice, and leads to a lesser degree of the exchange interaction between them. This means that the application of *external pressure* could shorten the MnO_6 octahedra along the c -axis and induce a long-range magnetic ordering in a system.

The application of *chemical pressure* leads to the elongation of MnO_6 octahedra along the c -axis. Such elongation results in variation of the e_g -electron character from $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ state and a resultant reduction of the transfer integral of the e_g electrons. The reduced transfer integral makes the

$\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) materials insulators in a temperature region between 20 and 300 K. The application of *external pressure* may compensate for the effect of *chemical pressure*, i.e. reduce the distortion of MnO_6 octahedra and make the behaviour of the resistivity more metallic-like.

The effect of *external pressure* on *transport* properties of the Pr-base bilayered manganites was investigated. No metal-insulator transition was found at a pressure of up to 10 kbar. A pressure-induced transition from an insulator to a metallic-like behaviour in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ was observed at 13 kbar. A transition develops with increasing pressure and becomes more prominent at 33 kbar. It also disappears beyond 37 kbar leaving only the inflection point on the temperature profile of the resistance. It was observed that the resistivity of $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ below the transition temperature begins to increase at a pressure above 20 kbar. Analysis of the magnetisation data collected under pressures of up to 86 kbar shows that applied pressure weakens the spin-glass state by reducing the temperature hysteresis of the magnetisation. It was also observed that the magnetisation considerably increases with an increase of pressure. This fact, combined with the observed increase in the resistivity at a temperature below ~ 30 K, and at pressure above 20 kbar, indicates that the *external pressure* enhances the antiferromagnetic correlations between the bilayers in a system.

A similar transition from an insulator to a metallic-like behaviour was also observed in $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ in the pressure range between 15 and 28 kbar. However, no such transition was observed for $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ under pressure of up to 60 kbar. The analysis of neutron diffraction data shows that even though the MnO_6 octahedra in this compound are less distorted than in $\text{Pr}_{1.4}\text{Sr}_{1.6}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$, the interbilayer spacing is considerably larger leading to the weakening of the magnetic interaction across the bilayers. The electrical resistivity of $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ decreases with increase of pressure which is characteristic for the activated type of conductivity. Therefore, pressure higher than 60 kbar is needed to induce the transition from an insulator to a metal-like behaviour in this composition.

A relatively simple and reliable technique for measurements of the electrical resistance in a diamond anvil cell in the temperature range between 16 and 300 K has been successfully developed in the course of the project.

All samples contain a small amount of the perovskite impurity phase (2 - 4%) in the form of intergrowths, which is common for the bilayered manganites. Based

on the critical temperatures on the susceptibility curves, the composition of the intergrowth was identified as being close to $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. The symmetry of the intergrowth phase matches the symmetry of the majority phase and exhibits an anisotropic magnetic behaviour. This behaviour has been predicted for the perovskite manganites but has never been experimentally observed due to the twinning of the perovskite crystals.

The magnetic and structural properties of the layered manganite $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ were studied using powder neutron diffraction and magnetic susceptibility techniques between 5 and 300 K. It was found that the structure consists of pairs of face sharing MnO_6 octahedra to form Mn_2O_9 dimers. Three different magnetic phases can be distinguished in the temperature region studied. Below ~ 75 K the Mn^{4+} sublattice is antiferromagnetically ordered with an antiparallel alignment between all nearest-neighbour manganese ions. Between ~ 75 and ~ 150 K, extensive quasi two-dimensional magnetic clusters are present. At temperatures above ~ 150 K, one can observe correlations related to intradimer spin pairing. Truly paramagnetic behaviour is not observed at any temperature below 300 K.

To clarify the effect of pressure on structural properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) manganites neutron diffraction measurements under pressure using the Paris-Edinburgh type pressure cell are needed. However, it was not possible to perform such experiments on a time-scale of this PhD project. It is also desirable to carry out high-resolution transmission electron microscopy experiments of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) manganites to study the structure of $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ intergrowth. However, such equipment was not available during the PhD project.

Chapter 7

Conclusions

The principal aim of this thesis was to study the structural, magnetic and transport properties of the novel layered $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.3, 0.4, 0.5$) and $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ manganites, and to investigate the effect of *external pressure* on transport and magnetic properties of these materials. The substitution of La ions with smaller Pr ones resulted in the following changes in the crystal structure:

- An increase of Mn-O(1) and Mn-O(2) linkages and a decrease of Mn-O(3) bond length;
- A decrease in the interbilayer spacing, i.e. the adjacent bilayers are brought closer to each other with higher Pr-doping level.

The application of such *chemical pressure* and the following changes in crystal structure significantly effect the magnetic and transport properties of $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$). It was shown that in all $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) samples, the majority phase undergoes a transition into a spin-glass state at ~ 50 K. However, no long-range magnetic ordering was found in either of the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.25, 0.3, 0.4$) materials in the temperature range of 1.8 K – 300 K. This is in sharp contrast with $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4$) materials, which have ferromagnetic ground states. The analysis of the neutron diffraction data makes it possible to attribute the absence of the long-range magnetic order in the $\text{Pr}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3, 0.4, 0.5$) materials to the elongation of the MnO_6 octahedra along the c -axis. Such elongation results in a greater separation between the magnetic Mn atoms in the lattice, and leads to a lesser degree of the exchange interaction between them. This means that the application of *external pressure* could shorten the MnO_6 octahedra along the c -axis and induce a long-range magnetic ordering in a system.

The application of *chemical pressure* leads to the elongation of MnO_6 octahedra along the c -axis. Such elongation results in variation of the e_g -electron character from $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ state and a resultant reduction of the transfer integral of the e_g electrons. The reduced transfer integral makes the

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