Structure- Property Relationships of Some Mixed Transition Metal Perovskites

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by

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Abstract

This thesis describes the preparation, characterisation and physical properties of a series of binary transition metal containing perovskite materials of the type Ln$_2$CoMnO$_6$ and Ln$_2$NiMnO$_6$ (Ln=La, Pr, Nd, ‘Pm’, Sm, Eu and Gd). We show the temperature dependence of x-ray diffraction (XRD), infrared spectroscopy, magnetic, x-ray absorption spectroscopy (XAS), electrical resistivity and neutron diffraction.

These techniques have been used to determine the physical characteristics of the materials and structure property relationships have been derived. These are explained using orbital overlap and bond covalency arguments within the metal oxygen sublattice.

Changes in electrical resistivity, electrical band gap, magnetic Curie temperature, infrared absorption and unit cell volume are observed upon changing size of lanthanide ion. These properties have been explained by considering orbital overlap arguments.

The local and electronic structure have been investigated using X-ray Absorption Spectroscopy (both K-edge EXAFS and L-edge XANES), allowing the determination of oxidation states of the transition metal ions within the sub-lattice which are shown to be non-integral. Magnetism has also been used to tentatively assign oxidation states of the transition metal ions which is in agreement with the XAS.

La$_2$CoMnO$_6$ and La$_2$NiMnO$_6$ have been reported previously as having an orthorhombic or pseudo-cubic structure. Neutron diffraction has shown for the first time that this is not true. Due to B-site ordering of the transition metal ions, the true structure is monoclinic. Furthermore, we have observed a structural phase transition where the symmetry changes from monoclinic to rhombohedral upon heating.
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Chapter 1

Introduction and Literature Review

1.1 Introduction

This chapter introduces the aims of the thesis. It then gives a brief survey of the properties of perovskites and related materials described in the open literature. The literature review is divided into six sections discussing perovskites in general, structure of perovskites, the electrical / electronic properties, magnetism, charge ordering and optical properties. A major theme of this thesis concerns the relationships between the structure and physical properties, which are developed throughout this chapter. In the final part of this chapter a brief summary is given which gives details of the issues that will be addressed in later chapters.

1.2 Aim

Transition metal perovskites have been extensively studied for their structural, magnetic and electronic properties. For example, lanthanum cobaltate (LaCoO₃) has been widely investigated due to its novel electronic properties. Below 77 K, the Co³⁺ ions exist in a diamagnetic low spin state. In the temperature range 77-200 K there is a spin-state transition. Between 200 and 400 K, the high and low spin Co³⁺ pairs disproportionate to Co²⁺ and Co⁴⁺ and finally at 700 K, LaCoO₃ becomes metallic [1],
these changes being observed by magnetic and electrical measurements and by Mössbauer spectroscopy.

LaMnO$_3$ is also a widely studied perovskite material, which is semiconducting at room temperature. A Jahn-Teller distortion driven by the lifting of $e_g$ orbital degeneracy (in octahedral symmetry) gives rise to an irregular octahedral geometry [2]. The Jahn-Teller distortion decreases in magnitude with increasing temperature and LaMnO$_3$ becomes metallic at 800 K [3]. In contrast LaNiO$_3$ is metallic at all temperatures and is paramagnetic [4].

The primary aim of this study is to determine the consequences on the structural and electronic properties, of forming the single-phase binary transition metal containing materials La$_2$CoMnO$_6$ and La$_2$NiMnO$_6$. It is interesting to determine whether the properties of the parent materials, spin-state transitions in the cobalt ion, Jahn-Teller distortion in the manganese ion and the metallic nature of LaNiO$_3$ still are present in the single phase materials. It may also be possible to switch the properties thermally or to use the electronic transition in one ion to switch another electronic transition in the other transition metal.

Changing the rare earth ion in the parent material is known to affect their electronic and structural properties [5]. To this end, the effects of changing the lanthanide ion on the physical properties such as the magnetism, resistivity, crystal structure and the optical properties have been studied. The development of structure property relationships is therefore a subsidiary aim of our work.
An additional motivation for the work is that these materials have potential applications in fast thermally driven infrared optical switches, which at ambient temperature are transparent in the infrared region but when heated absorb infrared light. They will then be used as thermally switched filters.

1.3 Literature Review

1.3.1 Perovskites: General Features

Perovskites (named after the prototype mineral perovskite CaTiO₃ discovered by Gustav Rose in 1830 and named after Count Lev Aleksevick von Perovski) are a group of materials, which have similar crystal structures and are based upon a simple cubic structure [6]. They have the general formula ABX₃, where A is a large cation (e.g. Ca, La, Au); B is a smaller metal and X is a halogen or oxygen. Some examples of perovskites include CaTiO₃, LaAlO₃, NaNbO₃ and LaNiO₃.

It is also possible to have mixed cation sites on both the A and B sites e.g.

La₀.₆₇Ca₀.₃₃MnO₃ and GdFe₀.₂Cr₀.₈O₃

Owing to the structural and chemical flexibility of perovskites, there is a very diverse chemistry among this interesting group of materials.

Perovskites in general, have received much interest in the past 45 years – primarily a result of their wide-ranging physical and structural properties. Their properties are determined largely by the structure, electronic nature of the ions, the ions size and the
stoichiometry of the material [7]. Non stoichiometry can also affect their properties as observed for LaMnO₃ which is an insulator and possesses an orthorhombic structure [8]. However, upon oxidation to LaMnO₃.15 the resistance decreases and the structure becomes rhombohedral (more symmetrical) [9].

The electrical, magnetic and structural properties of perovskites have many industrial and commercial uses including applications as catalysts [10], for high temperature fuel cells [11,12], in the petrochemical industry [13], as electric conductors, permanent resistance materials and magnetic media. In this thesis we focus on the electronic properties and their role in influencing the infrared absorption spectra.

1.3.2 The Structure of Perovskites

The ideal perovskite structure is cubic, but this structure is not very common (at room temperature and pressure); even the prototype mineral perovskite (CaTiO₃) is slightly distorted and is orthorhombic [14]. The perovskite structure is based upon the rhenium trioxide structure (figure 1.1) which has a simple cubic structure based on corner sharing of BO₆ octahedra. The A metal ion then occupies the twelve fold oxygen co-ordination position within the centre of the cube [15] (figure 1.2).

![Figure 1.1 Pictorial representation of ReO₃ (The ReO₆ octahedra are corner shared)](image)
A distortion away from the cubic structure reduces the symmetry, which in turn can influence the electronic properties of the compounds. The distortion can be classified by three mechanisms, displacement of the B site cation, displacement of the A site cation and by tilting or rotation of the BX₆ octahedra [16]. The degree of distortion is determined by the size of the interstitial cation ions and that of the transition metal(s) present. These effects lead to a change (figure 1.2) away from the (ideal) cubic structure to either rhombohedral, tetragonal, orthorhombic or monoclinic (with decreasing symmetry). The degree of distortion can also be increased by the presence of impurities or defects, which can be introduced by doping or non-stoichiometry. For example, LaMnO₃ with the orthorhombic structure becomes monoclinic when doped with Ca on the A site [17].

Figure 1.2 Pictorial representation showing possible structures of a perovskite material (cubic CaTiO₃ and the same material distorted to a monoclinic structure).
The mechanisms responsible for the distortion from the ideal perovskite structure result in some interesting properties. The distortion of the BX$_6$ octahedra can be a result of a Jahn-Teller distortion, displacement of the A and B cations normally results in ferroelectric or relaxor materials. While tilting of the octahedra occurs when the A cation is too small for the dodecahedral site and shortens the A-X bonds as to maintain orbital overlap [18].

Glazer developed a method of classifying and characterising perovskites with tilted octahedra [19]. He based his work on the earlier structural work of Megaw [20], used the concepts of soft [21] and normal mode analysis [22]. Glazer lowered the symmetry from the ideal cubic by tilting layers of octahedra around the four-fold axes of the cubic structure, which is achieved in two ways: either the octahedra all rotate in the same direction or they alternately rotate in different directions between layers. The notation used he used is as follows. Each tilt system is represented by the symbol $a^b c^k$, where $abc$ represent the magnitude of the rotation around the pseudo-cubic axis and the superscripts represent the sense of the tilt along the axis, + indicating the same direction, -, indicating the opposite direction. The superscript 0 represents no tilt around the pseudo-cubic direction. For example, the system $a^+a^+a^+$ represents three equal, in-phase tilts around the pseudo-cubic directions. The ideal perovskite structure is represented by $a^0a^0a^0$. The most common tilt system is $a^+b^-b^-$ [19], a single in-phase tilt and two anti phase tilts of equal magnitude and represents for example the system BaCeO$_3$ between 4.2 and 563 K. In total Glazer found 23 independent tilt system, and showed the relationships between the psuedo-cubic structure and the new crystallographic unit cells. However, recently Woodward has re-evaluated this work and found that the number of tilt systems is actually less than 23 [23] it is this work
which is used later in this thesis to help determine the structure of the materials synthesised.

The powder diffraction pattern also shows two fundamental characteristics when octahedral tilting is present and the symmetry is reduced. Firstly there is a splitting of the fundamental reflections (those which can be indexed to that of the pseudo-cubic structure) and secondly superlattice reflections occur between the fundamental reflections [17]. It should be also noted that often the occurrence and magnitude of octahedral tilt is a function of temperature and pressure.

It has been suggested by Goldschmidt [24] that the degree of distortion depends on the “tolerance factor” (t), which is defined in terms of ionic radii,

\[ t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}} \]  

**Eqn 1**

where \( r_A \), \( r_B \) and \( r_X \) are the ionic radii of atoms A, B and X respectively. For an ionic, hard sphere model the cubic structure is only stable with \( t=1 \); however the cubic structure can be observed if \( 0.89 < t < 1 \). Distorted perovskite structures occur if \( 0.8 < t < 0.89 \). Below values of 0.8 other structures are adopted. Perovskites exhibit a wide range of bonding from strongly ionic \( \text{LaAlO}_3 \) [25] to covalent \( \text{LaCoO}_3 \) (Co-O being covalent only) to materials on a continuum between the extremes. As the tolerance factor is dependant on the ionic radii and assumes a hard sphere nature of the ions, it only gives an indication as to the effects that the ion size may have on the structure. Other factors such as partial covalency, Jahn Teller distortions and non-stoichiometry also need to be considered [26]. For example, the tolerance factor of
LaCoO$_3$ is 0.88 and 0.842 for LaMnO$_3$, and so a distortion from the ideal cubic structure would be expected which is born out in practice.

The range of distorted perovskite structures is broad with the distortion decreasing as the size of the transition metal ion increases. In the system (LaTMO$_3$) where TM is chromium or manganese the structure is orthorhombic [27], while LaCoO$_3$ is rhombohedral [28,29]. The changes in the structure occur as a result of octahedral tilting and transition metal displacement from the idealised position. The lanthanum cobaltate structure has been studied over a wide temperature range (4-1248 K) by elastic neutron diffraction and shows a linear increase in Co-O bond length with increasing temperature and a decrease in the distortion of the CoO$_6$ octahedra.

LaMnO$_3$ possesses an orthorhombic structure [28] but LaMnO$_{3.15}$ is rhombohedral. The MnO$_6$ octahedra in LaMnO$_3$ possess a Jahn Teller distortion [1] with long-range frozen ordering. The Jahn Teller effect displaces the basal oxygen and the Mn-O bond lengths become in-equivalent 1.918 Å, 2.145 Å (basal) and 1.973 Å (apical) at room temperature (figure 1.3) [30]. The Jahn Teller distortion has been shown by neutron diffraction to decrease at higher temperatures [29]. Increasing the oxygen content introduces Mn holes and a mixture of Mn$^{3+}$ and Mn$^{4+}$ ions are thought to be present in order to charge balance the charges, which removes the long range ordering of the Jahn Teller distorted ions [30].

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1 La$^{3+}$, Co$^{3+}$, Mn$^{3+}$ and O$^{2-}$ radii being 103.2, 54.5, 64.5 and 140 pm respectively
Figure 1.3 The removal of orbital degeneracy in Mn$^{3+}$ and its consequence on the MnO$_6$ octahedra

Interesting structural phase transitions have also been observed in perovskites and related materials as a function of temperature and/or pressure. For example, neutron diffraction has shown LaGaO$_3$ transforms from an orthorhombic to rhombohedral structure at 420 K [31], (this study being motivated by the need for a substrate for epitaxial high temperature superconducting films). Similar changes are also seen in related materials e.g. La$_2$MgGaO$_6$ [32].

The effect of changing the lanthanide (A) ion has been studied by various workers, including White [33] and Marezio et al [34,35]. Marezio [34] studied the orthorhombic orthoferrite materials (LnFeO$_3$ where Ln is a lanthanide). The unit cell volume, the a and c axial cell lengths and Fe-O-Fe bond angles all decrease upon reducing the radius of the lanthanide ions; however, the b axis increases. The effect of changing the radius of the lanthanide ion has also been studied for the cobaltate system (LnCoO$_3$), where the Co-O-Co bond angle decreases from 164° to 150° upon changing the lanthanide (Ln) from La to Gd. A linear dependence of the Co-O-Co bond angle and lanthanide ionic radius is observed for this system and many other related systems [36]. The effect of the ionic radius of the A atom has also been studied with mixed Ln ions as seen for the series of materials Nd$_{1-x}$Sm$_x$NiO$_3$ with
values of $x=0$ to $1$ [37]. The overall cell volume and the axial cell lengths $a$ and $c$ increase. However, the $b$ axis decreases as the effective (average) rare earth ionic radius increases. The average ionic radius determines the Ni-O-Ni bond angle and hence the amount of orbital overlap. These effects are in turn reflected in the electrical properties of the bulk material, which with increasing averaged A ion radius show a reduction in the resistivity (increasing Ni-O-Ni bond angle) [38].

The structure of YNiO$_3$ as well as the other nickelates is of interest due to the changes in structure, which occur upon changing the lanthanide ion. The degree of distortion increases with decreasing lanthanide size from orthorhombic LaNiO$_3$ to monoclinic YNiO$_3$. Alonso et al [39] describe the structure of the nickelates containing the smaller lanthanide ions as monoclinic, which allows two individual sites for the different nickel ions corresponding to Ni $^{3+}$($\delta$) where $\delta<0.3$. It has been suggested after structural determination by neutron diffraction that the Ni-O bonds can possess two different lengths indicating two different oxidation states. Shannon [40] first suggested that the transition metal – oxygen (TM-O) bond distance is related to the oxidation state of the transition metal ion, thus making it possible to determine indirectly the unknown oxidation state of a transition metal (TM) ion; by comparing the TM-O distance to that of a standard oxide material of known oxidation state. This approximation is only valid, however, if the type of bonding in the two systems is similar in nature. In his work Shannon collated many TM-O bond distances (from XRD) with varying oxidation states. The TM-O bond distance was found to increase as the transition metal oxidation state decreases as expected.
Only a small amount of work has been published on the structures of the binary transition metal related perovskites \( \text{La}_2\text{Co}_{1-x}\text{Mn}_x\text{O}_6 \) and \( \text{La}_2\text{Ni}_{1-x}\text{Mn}_x\text{O}_6 \), including that of Zhongqin [41] and Narasimhan [42] who described the structure where \( x=0.5 \) as pseudo-cubic (a structure which was assumed to be close to that of a cubic system). Materials with \( x>0.5 \) are reported to be orthorhombic and for \( x<0.5 \) the structures are shown to be rhombohedral. Asai et al [43] indexed the X-ray diffraction pattern of \( \text{La}_2\text{CoMnO}_6 \) and \( \text{La}_2\text{NiMnO}_6 \) as orthorhombic (Pbnm). They performed Rietveld analysis assuming a monoclinic space group \( (P\ 2_1/c) \), which is a sub group of Pbnm in order to allow the two transition metal ions to accommodate specific sites. However, using this lower symmetry space group they were only able to obtain the position of the rare earth ions. The inability to determine accurate oxygen atom positions may be due, in part, to the fact that the experiment was carried out using X-ray powder diffraction, using which not only is it not possible to differentiate the different transition metal ions owing to their similar scattering length but also the much more weakly scattering ions are difficult to detect in the presence of the heavier lanthanide. The structure of \( \text{Gd}_2\text{NiMnO}_6 \) has been described by Marsh et al [44] as an orthorhombic perovskite that is isomorphic with \( \text{GdFeO}_3 \). They propose that the manganese and cobalt ions have the +3 valence state as suggested by the magnetic data.

Ganguly et al [38] studied the structure of \( \text{La}_2\text{Ni}_{1-x}\text{Mn}_x\text{O}_6 \) which they determined as rhombohedral for \( x<0.5 \) and orthorhombic for \( x>0.5 \). Arnott et al [46] investigated \( \text{La}_2\text{CoMnO}_6 \) (\( x=0.5 \)) and reported the co-existence of two phases at room temperature: one with a rhombohedral structure and the second as an orthorhombic structure, which has not been reported by any other workers. Shaobin et al [47] suggested a
pseudo-cubic structure for values of $x=0.5-0.8$. Thus, it can be seen that for mixed transition metal containing perovskites there is still considerable debate as to their crystal structure and its variation with composition.

In some materials ordering of octahedral tilts, charge and/or defects occur, resulting in superlattice reflections, are observed by diffraction experiments as satellite peaks. Structures which have shown superlattice reflections include LaSr$_2$Mn$_2$O$_7$ where a $\frac{1}{4}$, $-\frac{1}{4}$, 0 supercell (the numbers determine the degree that the cell is expanded in each direction) is observed based upon the orthorhombic Pnma structure [48]. In NaV$_2$O$_5$ a 2$a,2b,4c$ superstructure is observed due to charge ordering [49]. Interestingly in the material Ba$_{3.75}$Pr$_{9.5}$Ti$_{18}$O$_{54}$ only the c-axis is doubled [50]. Another system exhibiting superstructure is Ce$_{1/3}$NbO$_3$ where the a and c axes are found to contain the parameters $\sqrt{2}a$, b, $\sqrt{c}$ based upon a orthorhombic cell which is reduced in symmetry by a monoclinic distortion, the superstructure being caused by octahedral tilting [51].

1.3.3 Electronic Properties of Perovskites

Although the structures of the perovskites are quite similar, their electronic properties are diverse, ranging from metallic for LaNiO$_3$ [4] to the insulating LaCrO$_3$ [30], with the majority of perovskites being semiconducting, for example, LaMnO$_3$ [2]. In the series of materials LaTMO$_3$ (where TM is a transition metal) as the transition metal changes sequentially across the periodic table from Sc to Cu a change is observed at Cr/Mn from insulating to semiconducting behaviour while at Ni and Cu the materials are found to be metallic. Many undergo temperature or composition driven electronic phase transitions, which change electrical properties from that of insulators to metals.
LaNiO$_3$ is metallic over a wide temperature range [4]. However, by changing the lanthanide, a temperature driven insulator to metal transition is introduced, the temperature of which is lanthanide dependent. LaCoO$_3$ is semiconducting ($\rho=60 \ \Omega \text{cm}$) at room temperature becoming metallic in nature at 600K when charge disproportionation occurs of Co$^{3+}$ to Co$^{2+}$ and Co$^{4+}$ [52]. LaMnO$_3$ possesses high resistivity at room temperature ($\rho=10^4 \ \Omega \text{ cm}$) due to a Jahn Teller distortion where there is a removal of the e$_g$ orbital degeneracy within the octahedral crystal field. It has been suggested by electronic structure calculations that without the Jahn Teller distortion, LaMnO$_3$ would be metallic with the Fermi level lying in the e$_g$ band [33]. However, experimentally at 800 K LaMnO$_3$ becomes metallic due to a decrease in the dynamic Jahn Teller distortion with consequence changes in the Fermi level [53]. Changes in the electrical properties are often accompanied by changes in the unit cell volume with discontinuities in the lattice parameters observed upon heating to a temperature; examples are NdNiO$_3$ and SmNiO$_3$ where electrical transition occurs at 200 and 210 K respectively and changes in lattice parameters are observed [54].

The effect of the lanthanide ionic radius on the electrical properties of the bulk materials has been extensively studied. The lanthanide ionic size has been shown to affect the temperature at which the metal to insulator transitions occur; for example, in the nickelate system [54] metal to insulator transition occurs at 200 K for NdNiO$_3$ [55] and at 210 K for SmNiO$_3$. Frand et al [56] studied the effect of the Sm:Nd ratio on the metal to insulator transition temperature (proportional to the average lanthanide ionic radii) in Sm$_{1-x}$Nd$_x$NiO$_3$ and found a linear relationship of 2.3 K/x%. The lanthanide ionic radius can also affect the resistivity at room temperature and hence band gap and width. The lanthanide ion provides competition with the transition metal
orbitals for σ bonding with the O orbitals affecting the bandwidth. Decreasing the size of the lanthanide ion decreases the TM-O-TM bond angle reducing orbital overlap through which conduction occurs and hence changes the resistance by altering the bandgap and width [37].

The physical properties of the systems Ln$_2$Co$_x$Mn$_{1-x}$O$_6$ and Ln$_2$Ni$_x$Mn$_{1-x}$O$_6$ have received little attention. Their resistivities have been investigated as a function of temperature [42,56,51] and transition metal ion ratio; but the effect of the lanthanide ion has not been studied. Both the LaCo$_x$Mn$_{1-x}$O$_3$ and LaNi$_x$Mn$_{1-x}$O$_3$ materials are semiconducting except for the end member LaNiO$_3$ which is metallic [5]. Ganguly et al [38] reported that upon increasing the manganese content the resistivities increase linearly at room temperature although Jonker [57] reported that for x=0.5 the resistivity reaches a maxima. DFT (density functional theory) calculations have been carried out by Zhongqin et al [41] on LaMn$_{1-x}$Co$_x$O$_3$ for x=0.25 and 0.75, which were predicted to be metallic with an orthorhombic structure. For x=0.5, a half metallic nature was found and they showed the material could exist in both orthorhombic and rhombohedral forms. However, upon structure optimisation it was found the orthorhombic form is the most stable. These theoretical calculations are born out in practice as described previously.

1.3.4 Charge Ordering in Perovskites

Charge ordering refers to the ordering of the oxidation state of transition metal ions in specific lattice sites of a mixed valence material [58]. Such ordering localises electrons in a material rendering it insulating or semiconducting, because the charges
are localised and electrons cannot readily hop from one cation site to another [59]. The earliest example of charge ordering was found in Fe$_3$O$_4$ [60] (magnetite), which undergoes an order to disorder transition at 120 K. The loss of ordering in Fe$_3$O$_4$ is known as the Verwey transition and is observed in the magnetic properties as a large discontinuity in the magnetic susceptibility as the temperature increases [59].

The temperature at which charge ordering is lost appears to be controlled significantly by the ionic radius of the lanthanide or equivalent ion [60]. For example, in Ln$_{0.5}$Ca$_{0.5}$MnO$_3$ upon changing the rare earth ion from Nd to Y the charge ordering temperature changes from 220 K to 250 K respectively, with a linear increase observed with increasing ionic radius of the lanthanide [60]. Electrical transitions are often seen upon the loss of ordering, for example, for Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ [61] where a change in the band gap change is observed. The presence of ordering affects the electrical properties in that it can create an additional potential that impedes the flow of carriers. Changes are also observed in the lattice parameters: for example, for Nd$_{0.45}$Sr$_{0.55}$MnO$_3$ there are discontinuities observed in the lattice parameters when charge ordering is lost on raising the temperature [62]. The loss of charge ordering can lead to a change of space group as seen in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ where a change from monoclinic to orthorhombic is observed from X-ray diffraction [63]. The charge ordered state usually lowers symmetry of a crystal structure from that expected e.g. Pnma to P 21/m [64], since the different ions in different oxidation states are distinct species localised on specific atom positions. The infrared spectra can also show prominent band splitting at temperatures lower than the ordering temperature, which indicates an octahedral distortion [65]. A comprehensive review of charge ordering effects can be found in the work of Rao et al [61]
1.3.5 Magnetic Properties of Perovskites

The magnetic properties of perovskite related materials are varied and depend on the transition metal, lanthanide and composition (ratio of ions and oxygen content). LaCoO$_3$ is particularly interesting: at temperatures less that 77 K, the Co$^{3+}$ ions are in a diamagnetic low spin state. As the temperature rises above 77 K the population of the high spin Co$^{3+}$ paramagnetic state gradually increases. The initial population change between the low spin to high spin states is achieved as they are separated by approximately 10 meV which can easily be accessed thermally [65]. In the region 200 K to 400 K, the low and high spin pairs disproportionate to Co$^{2+}$ and Co$^{4+}$ (figure 1.4) [1,66]. That is, above 400 K the energy gap between the valence and conduction bands tend to zero and there is transfer of an $e_g$ electron from the high spin to low spin cobalt ion (charge disproportionation) [67]. The transitions are observed magnetically as an increase in the overall moment with increasing temperature.

![Figure 1.4 Low - High spin state transition of Co$^{3+}$ ion in LaCoO$_3$ and subsequent charge disproportionation](image)

LaMnO$_3$ is antiferromagnetic [68]. However, upon doping with Ca, the material becomes ferromagnetic due to changes in the oxidation states of the manganese ions from all Mn$^{3+}$ to a mixture of Mn$^{3+}$ and Mn$^{4+}$ for which exchange coupling can occur [69]. LaNiO$_3$ is paramagnetic at all temperatures. On doping LaNiO$_3$ with manganese
the material exhibits Curie Weiss behaviour instead of Pauli paramagnetic behaviour even at very low dopant concentrations [70]. Ferrimagnetic perovskites and similar magnetic structures also occur, in for example Li_{1-x}Ni_{1+x}O_2 [71], Gd_{1-x}La_xMn_2Ge_2 [72] and Fe_3O_4 [73] where the transition metal ions of different spin states or different numbers of unpaired electrons are found on different sublattices.

The onset of long-range magnetic behaviour in a solid solution of the type Ln_2MM'_{06} along with the suppression of metallicity indicates the role of magnetic interactions in the localisation of charge carriers [74]. The interplay between magnetic properties and metal to insulator transitions in oxide perovskites is an issue of much interest. For example, LaNiO_3 [71] is metallic down to 1.5 K with Pauli temperature independent magnetic behaviour, whereas LaCrO_3, LaMnO_3, LaFeO_3 and LaCoO_3 are insulators or semiconductors with localised moments. The effect of transition metal has also been investigated [75-78] on the electrical and magnetic property relationships.

Extensive studies on the magnetism of Ln_2CoMnO_6 and Ln_2NiMnO_6 by NMR (based on interpretation of coupling constants and chemical shift values) and magnometry have been reported [43,79,80]. Interpretation of the data gives contrasting results, some suggesting the Co/Mn and Ni/Mn pairs are found in the +2/+4 oxidation state respectively [81] and others the +3/+3 oxidation state respectively [44]. The difference in behaviour may result from the fact that it was not possible to saturate fully the material with a magnetic field and hence order the magnetic moments. The studies agree that the materials are ferromagnetic in nature with a Curie temperature of 233 K for La_2CoMnO_6 and 275 K for La_2NiMnO_6. The choice of lanthanide affects
the Curie temperature: as the ionic radius of the lanthanide ion decreases, so does the exchange angle and hence the Curie temperature [83].

The work of Goodenough has allowed the formation of empirical rules [84], which allow us to predict the nature of the magnetic superexchange which occurs (in a nearly linear bond) between the cations via the anion intermediate. The nature of the interactions depends on the electronic configuration and number of d-electrons. For two cations possessing half filled $e_g$ orbitals, weak antiferromagnetic interactions will dominate, while if there is a mixture of partially filled and unfilled $e_g$ orbitals, ferromagnetic interactions dominate.

1.3.6 The Optical Properties of Perovskites

Optical measurements such as IR and Raman were shown to be useful in studying the relationships between lattice vibrations and superconductivity [85]. For example, in La$_{2-x}$Sr$_x$CuO$_4$ a vibrational mode becomes soft when a material in the system exhibits superconductive properties. This approach can be extended to other electrical properties such as free carrier concentrations and insulator to metal transitions [86].

The vibrational spectra of LaCoO$_3$ have been extensively studied as a function of temperature and pressure [87]. Dramatic changes are observed in the infrared spectra where changes in spin state occur with increased phonon screening resulting from an increase in free carrier absorption / reflection [88]. Rao has suggested that there is relationship between the infrared spectra and the electrical properties of a material
where the reflection of infrared radiation increases with increasing conductivity (the infrared radiation being either absorbed or reflected by the electrons) [88].

Blasse et al [89] have studied the infrared spectra of various $A_2BB'O_6$ based perovskites. They observed that when there is a $BB'$ ion size mismatch, there is a removal of the three fold degeneracy of the $T_{1u}$ vibration mode predicted for cubic symmetry. For example, $Ba_2CaMoO_6$ possesses two shoulders on the TM-O stretch, whereas $Ba_2MgWO_6$ is closer to the spectrum expected for cubic symmetry with a simplification in the spectroscopic profile, indicative of a smaller mismatch in size between MgW than for CaMo.

Yue et al [90] have studied the vibrational spectra of the $LaMn_{1-x}Co_xO_3$ system. They suggested that the spectrum observed is related to the crystal phase in the system. They predicted from group theory three infrared active bands (given by $3F_u$) and one inactive band ($F_{2u}$). These are attributed to the B-O stretching vibration of the BO$_6$ octahedra ($\nu_1$), the bending vibration of the B-O bond ($\nu_2$) and the lattice vibration ($\nu_3$) where $\nu_1 > \nu_2 > \nu_3$. The observed frequency shifts are reported to be related to both the geometry and electronic factors. The authors propose that the B ion is an electron acceptor and the B-O bond becomes more covalent as the frequency of the B-O stretch increases.

Interestingly, the infrared spectrum of $LaMnO_3$ possesses anharmonic modes in the infrared absorption spectra at 1000 cm$^{-1}$ [91]. These are attributed to the Jahn Teller distortion present in the MnO$_6$ octahedra where there are two different lying Mn-O
bonds having different lengths. These anharmonic modes decrease in intensity as the
temperature is increased and eventually disappear, as the distortion is lost.

1.4 Summary

The above brief review of perovskites has shown that their physical and structural
properties are wide ranging. It is also evident that it is possible to rationalise the
physical properties in terms of their structure and vice-versa.

In the systems which are the subject of this thesis (Ln$_2$CoMnO$_6$ and Ln$_2$NiMnO$_6$)
there are unanswered questions or conflicting results. In this work we will provide by
use of X-ray and neutron diffraction a structure, which allow us to rationalise the
properties previously observed. We will also gain information on the oxidation states
of the transition metal ions by the use of XAS (X-ray absorption spectroscopy) a
method not previously used in studying this system. In addition we will study other
physical properties such as infrared absorption, magnetism and electrical conductivity
which will allow us to understand the effect the lanthanide ions has on its structure.

1.5 References

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Chapter 2

Theory & Experimental Techniques

2.1 Introduction

In this chapter the techniques used to synthesise and investigate the perovskite materials are introduced. We describe the synthetic procedures employed and we outline the role of X-ray and neutron diffraction techniques, X-ray absorption spectroscopy, infrared spectroscopy and measurement of magnetic and electrical properties. For each technique, an overview is given followed by an introduction to the relevant theory and experimental and analysis procedures. We also give an introduction to the generation of synchrotron radiation and neutron beam.

2.2 Synthesis

Monophasic, polycrystalline perovskite materials of the type Ln$_2$CoMnO$_6$ and Ln$_2$NiMnO$_6$ (Ln = La, Pr, Nd, (Pm)$^1$, Sm, Eu and Gd) with known oxygen content were prepared using the following modified nitrate decomposition method [1]. Stoichiometric quantities of Ln(NO$_3$)$_3$.6H$_2$O (>99% Aldrich), (Co(NO$_3$)$_3$.6H$_2$O (99.999% Aldrich) Mn(NO$_3$)$_3$.6H$_2$O (99.999% Aldrich) and Ni(NO$_3$)$_3$.6H$_2$O (99.999% Aldrich), as appropriate, were dissolved in a minimum quantity of distilled
water in a crucible. The solution was heated to remove the water (at 600 K) and the solid remaining decomposed at 900 K for 30 minutes, resulting in a brown pungent gas being evolved. The resulting grey/ black powder was ground and pressed into a pellet and heated for a further 16 hours at 1400 K (with a ramp rate of 1 K min⁻¹). The material then was processed through several heating/ grinding cycles, after each cycle the sample was cooled at 1 K per minute to room temperature. This process was repeated until monophasic crystalline materials were prepared the crystallinity of which could not be improved by further treatments, as measured by line width in the X-ray diffraction pattern.

To confirm that the material was monophasic, XRD data was collected using a Siemens D5000 X-ray diffractometer, with Cu Kα₁ wavelength 1.5402 Å (obtained by use of a graphite monochromator) over the two theta range 10 to 60 degrees, with a scan speed of 0.05 2-theta s⁻¹. The data (figure 3.1) confirms the sample to be single phase in the powdered form (within the noise level of the diffraction pattern) by comparison of the pattern with similar materials. No peaks additional to those expected for the desired materials were observed.

The oxygen content was inferred from mass changes during the synthesis. The initial weight of the empty crucible was noted after heating when empty at 900 K for half an hour and cooling in a sealed desiccator. A theoretical calculation was made as to the ideal weight of the sample after processing using equation 1 below

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1 Due to the radioactive nature of Pm it cannot be used within a synthesis safely however in this work a mix of Sm and Nd ratio 1:1 which gives an average ionic radii the same as that of Pm
Me(NO₃)₃ + Mn(NO₃)₃ + 2Ln(NO₃)₃ → Ln₂MeMnO₆ + 12NO₂ + 3O₂  \( 1 \)

where Me = Co or Ni. The theoretical and experimental weights were then compared to ascertain the oxygen content.

It is possible to determine the crystallinity from the FWHM (full width at half maximum height) of the diffraction peaks within the X-ray diffraction patterns. Initially the peaks in the diffraction patterns were quite broad which was gradually improved by repeated grinding, palletising and sintering. It was found that at least three sinterings were required to produce the materials used for this study.

2.3 Crystal Structure of Materials

2.3.1 Introduction

X-ray powder diffraction is a widely used technique for phase and structure identification. However, it is sometimes not possible to determine fully the structure of materials (containing lighter elements or elements of similar atomic number) using X-rays and hence neutron diffraction has to be used (although a strong scientific case has to be given because of its expense). It is also possible to use diffraction techniques to observe structural changes, which can occur upon changing physical conditions such as temperature or pressure.

\[ \text{By use of JCPDS database on the diffractometerers software} \]
Laboratory based X-ray diffraction is most commonly used to identify materials by comparison with databases of materials which have been previously determined, and to confirm a single phase and crystallinity. The use of synchrotron radiation means that diffraction patterns with better defined narrower peak shapes, and a lower signal to noise ratios can be collected [2], due to high flux making it possible to refine structures using the Rietveld method [3], although refinement of laboratory X-ray data can also be achieved for less complex structures. Structure solution from both X-ray and neutron diffraction will be discussed later.

2.3.1.1 Synchrotron Radiation

Synchrotron radiation is produced when an electron beam travelling close to the speed of light is accelerated in a magnetic field, causing the beam to bend. The bending beam of accelerated electrons emits a broad spectrum of electromagnetic radiation (the synchrotron radiation). As illustrated in figure 2.1, the magnets in a synchrotron source steer the beam of electrons and form a polygonal path. The light is emitted at a tangent to the bending beam. The wavelength of the light depends on the energy of the electron beam and the magnetic fields. A shorter wavelength is produced with a higher beam energy. By increasing the magnetic field strength, the beam bends more, causing a higher acceleration, and hence a shorter wavelength. A radio frequency klystron replaces the energy loss caused by emitting synchrotron.

There are two other magnet arrays placed in the beam of electrons to produce two differing types of synchrotron radiation. The first is an undulator, which oscillations of the electron beam leading to an interference effect, hence producing an intense narrow
beam of light by constructive interference. The other type of magnets placed between
the dipole magnets are ‘wigglers’, which cause the beam to make a hairpin turn and
hence produce very short wavelength (harder) light. The wiggler magnets are
superconducting, being held at liquid helium temperatures to produce a field of up to
6 T.

Figure 2.1 Production of synchrotron radiation by bending a beam of electrons in a
magnetic field (below). Also pictured is an artist’s impression of the SRS at
Daresbury (above).

2.3.1.2 Production of Neutrons
Neutrons can be produced by the ‘spallation’ process, as implemented at the ISIS facility based at the Rutherford Appleton Laboratory (RAL), or by thermal methods from a nuclear reactor. At ISIS (used in this study) a beam of protons hits a heavy metal target, and the resulting nuclear spallation give rise to a stream of “white” neutrons.

In a spallation source protons are accelerated using a linear accelerator (linac), which accelerates the protons to \(~70\) MeV and the beam is pulsed. The beam is then further accelerated and stored in a synchrotron. Further acceleration is achieved by ‘surfing’ on a sinusoidal magnetic beam. The protons are ‘kicked’ into the extracted proton beam and travel at \(~200\) ns intervals to the heavy metal target (e.g. tantalum). Within the target, the protons excite the nuclei and the energy is dissipated by emitting neutrons (see Figure 2.2), a proportion of which leaves the target, the remainder of the neutrons triggering other reactions. The neutrons leaving the target need to be moderated so their wavelength (speed) is useful for the study of condensed matter, which is achieved by hydrogenous moderators (normally liquid methane) around the target, the temperature of which determining the energy distribution.
The wavelength of the neutrons is determined by their energy and given by

$$\lambda = \left( \frac{h^2}{2mE} \right)^{\frac{1}{2}} \quad (2)$$

where $h$ is Planck's constant, $m$ is mass of the neutron and $E$ the energy of the neutron.
2.3.2 X-ray Diffraction

X-rays for diffraction experiments in the laboratory are produced by bombarding a metal target (typically copper, cobalt or molybdenum) with a beam of electrons emitted from a heating filament. The beam of electrons ionises electrons from the K-shell (1s) of the metal target and X-rays are emitted as the resultant vacancies are filled by electrons from higher filled electron shells L (2p) or M (3p). The result is two intense lines in the emission spectrum. The beam of X-rays can be monochromated to provide a single wavelength using a filter or by reflecting a X-ray beam from a crystal monochromator (typically graphite). The later is most common and the wavelength is selected according to the Bragg equation (eqn 3), (a derivation of which can be found in section 2.3.2.1)

$$\lambda = 2d \sin \theta \quad (3)$$

The use of laboratory based equipment allows for convenient identification of the phases. Indexing programs such as TREOR [4] provide a useful tool in obtaining unit cell parameters and crystal symmetry.
2.3.2.1 X-ray Scattering

X-rays are scattered by their interaction with electrons of the atoms and interference occurs between X-rays scattered from different parts of the atom, causing the scattering factor $f_x$ of an atom to decrease with increasing scattering angle, $\theta$. The scattering factor is defined as

$$\text{atomic scattering factor } f_x = \frac{\text{amplitude scattered by electrons from an atom}}{\text{amplitude scattered by single electron}}$$

which is proportional to the atomic number and hence the scattering factor is very small for light atoms such as hydrogen and boron, hence the difficulty in using X-ray diffraction for determining the position of light atoms in crystals when in the presence of atoms with a large atomic number. The problem is, as noted, solved by neutron diffraction whose scattering is effected by the nucleus. However, neutron experiment can readily distinguish elements of small and similar atomic number.

The scattering amplitude from the unit cell contents is determined by summing the scattering amplitude, $f$, from all the atoms in the unit cell, taking into account the path or phase difference between all the scattered waves which is expressed as the structure factor $F_{hkl}$; it is a ratio of the amplitude scattered by all the atoms in the unit cell to the amplitude scattered by a single electron. It also describes the phase angle of the
scattered wave. It is therefore not a simple number but is a vector or a mathematical complex number.

2.3.2.2 Lattice Parameters

In the classical Bragg theory of diffraction the scattering from a crystal is described in terms of reflections from a lattice plane or a set of lattice planes. For specific angles of incidence the lattice planes are regarded as a mirror, and hence it is possible to model a crystal as a stack of reflecting planes of separation $d$. This makes it possible to derive relationship between $\theta$ and $d$ and hence calculate the angle the X-ray must make, with the plane in order for constructive interference of the scattered X-ray to occur. A reflection is therefore an intense spot arising from constructive interference (the addition of two waves which are perfectly in phase upon scattering) of the scattered X-rays.

Consider the reflected wave at point P, the path difference is $\delta = AB - BC$. As, $AB = BD$ and $\delta = CD$ and $CD = AD \sin \theta$, therefore $\delta = 2d \sin \theta$ (Figure 2.3). The condition for reflection with constructive interference is that the difference in path length between the scattered waves must be an integral number of wavelengths $n\lambda$, giving the celebrated Bragg equation
Hence there are different orders of reflection specified by \( n \) from the \( n \)th plane.

### 2.3.2.3 Atomic Positions

The intensity of the diffracted beam gives information on all the atomic positions within the unit cell, the relative intensities being equal to the relative intensities of the square of the \( F_{hkl} \) values.

Consider a system with two atoms, one with an atomic position at the origin with atomic scattering factor \( f_0 \) and another with scattering factor \( f_1 \) at a distance from origin defined by vector \( r_1 \) which can be expressed in terms of components or fractional co-ordinates along the unit cell vectors \( a, b, c \) where

\[
r_1 = u_1 a + v_1 b + w_1 c \quad \text{(6)}
\]
where $u_1v_1w_1$ are fractions of unit cell lengths (and hence atomic co-ordinates). The path difference (PD) is expressed as

$$PD = \lambda(hu_1+kv_1+lw_1) \quad (7)$$

where $h$, $k$ and $l$ are Miller indices. As the structure factor is a summation of the atomic scattering factors it can be considered as the resultant of the two vectors (the length of which are proportional to the size of scattering factor) and the angle between them, $\phi_1$, and is equal to $2\pi/\lambda(PD)$ and therefore

$$\phi_1 = 2\pi(hu_1+kv_1+lw_1) \quad (8)$$

Therefore $F_{hkI}$ can be obtained from adding the vectors representing the atomic scattering factors of all atoms present in the unit cell (the angles being measured with respect to the origin and not the angle between the vectors). More conveniently, $F_{hkI}$ can be represented as a complex number for example

$$F_{hkI} = \sum_{n=0}^{N} f_n \exp(2\pi i(hu_n + kv_n + lw_n)) \quad (9)$$

Where $f_n$ is the atomic scattering factor for atom $n$ and $2\pi(hu_n+kv_n+lw_n)$ is the phase angle $\phi_n$ of the $n$th atom in the unit cell, with fractional co-ordinates $u_n$, $v_n$, $w_n$. The

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3 Other physical and geometric factors need to be considered including temperature, Lorentz polarisation factor, multiplicity factor, absorption factor, etc.
amplitude $F_{hkl}$ and hence intensity $I_{hkl}$, of the diffracted X-ray beam from a set of $hkl$
planes can be calculated from the ‘structure factor’ as long as we know the positions
of the atoms within the unit cell and the atomic scattering factors of the atoms. (In
refining a diffraction pattern to obtain the crystal structure a guess is usually given as
to the atomic positions)

2.3.3 Neutron Diffraction:

Materials can also diffract neutrons, the wavelength of the neutrons being related to
the mass and velocity of the particle, using the de Broglie relationship:

$$\lambda = \frac{h}{p}$$

The scattering of neutrons is caused by two effects.

a) Nuclear scattering due to interactions of the neutrons with the atomic nuclei.

b) Magnetic scattering due to interactions of the magnetic moments of the neutrons
with permanent magnetic moments of atoms or ions.

If there is no applied magnetic field, the magnetic moments of the atoms in a
paramagnetic material are randomly arranged. As a result, the magnetic only
contributes a diffuse background to the sharp maxima occurring when the Bragg
condition is satisfied. In ferromagnetic materials below their Curie temperature, the
magnetic moments are regularly arranged, so the resultant spins of adjacent atoms are
parallel in the absence of an external field; diffraction effects giving rise to magnetic
structure peaks.
Neutron diffraction allows the atomic positions of the lighter elements to be determined exactly (including H by isotope substitution) as the scattering occurs by the interactions with the neutrons and not the electrons of the atoms.

2.3.3.1 Measuring the diffraction Patterns in a Neutron Experiment

Using a neutron spallation source, the method for determining the d-spacing (d_{hkl}) is to measure the time of flight (TOF) of the neutron from the source to sample and then over the scattering path to the detector, which allows the determination of the neutron velocity (v), which can be substituted into the equation 10 below.

$$\lambda = \frac{0.3955}{v} = \frac{0.0039557}{L} \quad (10)$$

where T is the time of flight and L is the length of flight.

Substituting into the Bragg equation: $$\lambda_{hkl} = 2d_{hkl} \sin \theta \quad (11)$$

we have

$$T_{hkl} = 505.55685Ld_{hkl} \sin \theta \quad (12)$$

Hence, in the energy dispersive technique different d spacing can be measured at a fixed scattering angle. An array of detectors is set around the sample to measure at three fixed angles: backscattering, 90° and at low angle. The resolution of the diffractometer is then defined by the timing uncertainty, angular uncertainty and flight path uncertainties.
2.3.4 Structure Refinement – Rietveld Profile analysis

The technique developed by Rietveld [5,6], known as profile analysis, circumnavigates the fact that accurate intensity and hence structure factors (for individual \( d_{hkkl} \)) cannot be obtained because of overlap of peak intensities in powder diffraction techniques. The essential idea is to fit to the whole profile assuming that it is possible to describe the peak shape by a parameterised analytical function. The procedure is as follows.

For a given point \( I \) in the diffraction pattern there is a measured intensity \( Y_I \). A function (eqn 13) composed of the observed and calculated intensity is minimised using a least squares procedure for each point on the diffraction pattern.

\[
S = \sum W_i \left| Y_i - Y_{ic} \right|^2
\]  

(13)

where

\( W_i = \) weighted function where \( w = 1/Y_I \)

\( Y_I = \) observed intensity at \( I^{th} \) step

\( Y_{ic} = \) calculated intensity at \( I^{th} \) step

and the sum is over all data points.

Usually many reflections contribute to the observed intensity \( Y_I \). The calculated intensity \( Y_{ic} \) depends on the structure factor \( |F_k|^2 \) values obtained from the structural model. Other contributions to the intensity are parameters defining the background, a function which describes the shape of the Bragg peak and the zero point, which
corrects for any shift in the peak position by detector errors. The full expression for peak intensity is given by:

\[ y_{IC} = s \sum_k m_k L_k |F_k|^2 G(\Delta \theta_{ik}) + y_{ib} \]  

(14)

Where \( s \) is the scale factor (places experimental on same scale as calculated), \( L_k \) is the Lorentz-polarisation factor for the reflection \( k \), \( F_k \) is the structure factor, \( m_k \) is the multiplicity factor, \( \Delta \theta_{ik} = 2\theta_i - 2\theta_k \) where \( 2\theta_k \) is the calculated position of the Bragg peak corrected for the zero-point shift of the detector, \( G(\Delta \theta_{ik}) \) is the reflection profile function and \( y_{ib} \) is the background intensity. The sum is over all reflections contributing to the intensity at that point.

The reflection profile is a function of both the sample and instrument, and varies as a function of 2\( \theta \). The most common function is a combination of Lorenztian and Gaussian components, known as the pseudo-Voigt function.

It is necessary to assess the quality of the model for which several R-factors are defined as follows:

1. The profile

\[ R_p = \frac{\sum |Y_i - Y_{ic}|}{\sum Y_i} \]  

(15)
(2) The weighted profile

\[ R_{wp} = \left[ \frac{\sum w_i (Y_i - Y_{ic})^2}{\sum w_i Y_i^2} \right]^{1/2} \]  

(16)

where \( w_i \) is the weighting factor.

(3) The expected

\[ R_e = \left[ \frac{\left( N - P \right)}{\left( \sum w_i Y_i^2 \right)} \right]^{1/2} \]  

(17)

where \( N \) and \( P \) are the number of profile points and refined parameters respectively.

(4) The goodness of fit

\[ \chi^2 = \left( \frac{R_{wp}}{R_e} \right)^2 \]  

(18)

which should approach the ideal value of unity.

A difference plot is also used to discern the quality of the refinement, which displays the difference between the observed and calculated profiles. Bond lengths and angles also provide a good indication as to the validity of a model.
In a refinement, first the lattice parameters, the zero point and the background are refined, after which the peak shape is refined. After convergence is reached the atom co-ordinates can be refined. In this work, the GSAS suite of programs[8] was used in the refinement of the high-resolution X-ray and neutron powder data collected.

A reasonably good starting model is required as no effort is made to allocate observed intensity to any particular Bragg reflection. As a result one can use an isostructural material with a known structure or computer modelling techniques to provide a starting model.

2.3.5 Experimental

2.3.5.1 Laboratory Based X-ray Diffraction

Powder XRD was initially carried out to confirm the single-phase composition of the synthesised materials and obtain the lattice parameters. The materials were finely ground to ensure random orientation of the crystallites, which is necessary for the Bragg diffraction conditions to be met in powdered samples. The samples were laid in an amorphous ceramic plate and pressed into place to ensure that all Bragg conditions are met. The XRD patterns were measured using a Siemens D500 Diffractometer (Figure 2.4) which uses Cu K-α₁ radiation (λ= 1.540562 Å) and a graphite monochromator. In a typical experiment a two-theta range of 10-60° with a step size of 0.05° and a counting time of 5 seconds per step was used.
High temperature measurements were made on a converted Philips diffractometer. A heating element is placed below a platinum sample holder, the temperature being controlled by an Oxford Instruments ITC4. The patterns were measured at 25 K intervals from ambient to 975 K. The two-theta range was 12-40° with a step size of 0.05° and a counting time of 20 s. The diffractometer had a Cu K-α source, a nickel filter and soller slits. The sample is placed on the Pt foil by being mixed in acetone and the slurry placed on the foil and the solvent evaporates off. These measurements only allowed the lattice parameters to be obtained and give an indication as to phase changes.

2.3.5.2 High Resolution X-ray Diffraction

High resolution X-ray diffraction data were collected at the Synchrotron Radiation Source (SRS) Daresbury on station 9.1, using an image plate system (Figure 2.5). The samples were loaded into a capillary tube and mounted on a goinometer, which was rotated throughout the experiment on its axis, ensuring that all conditions for
diffraction were met. The sample was aligned in the beam using a spotting scope. The image plate was calibrated using a Si standard and the scanner calibrated using a grid. A collection time of 30 minutes was used and the exposed image plate scanned using a Molecular Dynamics scanner and associated software. Peak intensities and position were obtained using software. A wavelength of 0.4868Å was used and selected by a Si 111 monochromator.

Figure 2.5 Setup for the Image Plate measurement of X-ray diffraction pattern at station 9.1 at the SRS, Daresbury.

2.3.5.3 Neutron Diffraction

Neutron diffraction experiments were carried out on the High-Resolution Powder Diffraction station (HRPD) on beam line S8 at the ISIS Pulsed Neutron Facility at Rutherford Appleton Laboratory, Didcot, which has a 70 MeV linear proton accelerator, an 800 MeV Proton synchrotron and a target station made of tantalum. The ejected neutron pulses are moderated using liquid methane at 90K. The beam line is 100m long which reduces the flight path uncertainty.
On HRPD the backscattering detector (Figure 2.6) with Zn-S scintillators with a range of $160^\circ \leq \theta \leq 176^\circ$ was used and a time of flight range of 30-130 msec measured. The samples were placed in a cylindrical vanadium (12 mm diameter) can and mounted in a furnace, which was controlled using an Eurotherm controller. A counting time of 12 hours per temperature was used for most experiments. The data were collected using a Digital Alphestation 500/266 using in house software and converted for use in GSAS by in-house software. The resolution of the backscattering detector can be as great as

$$\frac{\Delta d}{d} \approx 4 \times 10^{-4}$$

making it the highest resolution neutron powder diffractometer currently available.

![Figure 2.6 Schematic of HRPD at ISIS (RAL) showing detector positions in relation to sample position in experiments the 1m position was used (the beam enters from the left).](image)

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2.4 X-ray Absorption spectroscopy (XAS)

2.4.1 Introduction:

X-ray absorption spectroscopy can provide information on the local structure of specific atom types. It is of particular value in the study of disordered systems as it allows accurate bond distances to be obtained for the specific atoms and not the average bond distances given by diffraction.

In an X-ray absorption experiment we scan below and above the X-ray absorption edge. The X-ray absorption edge is manifested by a large jump in the absorption coefficient (the energy at which it occurs is a characteristic of each element). Each edge is asymmetric with a long tail to high photon energy EXAFS (Extended X-ray absorption fine Structure) and some structure close to the absorption edge [12-14]. The pre-edge structure is a result of electron transfer from an occupied K-shell to
unoccupied orbitals and known as XANES (X-ray absorption near edge structure).

Figure 2.7 Typical EXAFS spectrum showing associated features.

The edge is the onset of excitation to the continuum creating photo electrons. For single atoms or monatomic gases a smooth tail is observed beyond the edge. However, in molecules and solids, fine structure (i.e. EXAFS) is observed in the smoothly declining intensity of the tail of the absorption edge (Figure 2.7). This fine structure is due to the emitted photoelectron, which travels outward from the emitting atom, being scattered by neighbouring atoms and the pattern therefore depends on the interatomic distances, number and type of atoms and the wavelength of the photoelectron.

2.4.2 EXAFS and Synchrotron Radiation
In EXAFS experiments a synchrotron source is used, primarily because of the need for a white X-ray source but also because of the greater intensity compared to conventional X-ray sources.

2.4.3 EXAFS Theory

Let us consider in more detail, the process of X-ray absorption and photo electron creation. At low energies there is no absorption of X-rays which pass through the material with slight attenuation by core electrons. As the energy increases the X-rays are absorbed and electrons are ejected from the core shell of the atom resulting in the absorption edge. This edge occurs at an energy value ($E_b$) specific to the element the corresponding energy is known as the binding energy. Additional X-ray energy increases the final state energy ($E_f$) of the photoelectron in the form of kinetic energy.

![Figure 2.8](image)

*Figure 2.8 Photoelectron wave emitting from central atom and how it is attenuated with upon hitting other atoms.*
The output of the EXAFS experiments is a plot of absorption of the radiation through an energy range of 500-1000 eV above the edge, analysis of which yields local structural information which is atom specific.

2.4.3.1 Plane Wave Equation

The theory of EXAFS is well developed [15], and the following equation describes the scattering of a plane wave emitted from a central atom by atom j which is derived from electron scattering theory [15]

\[
\chi(k) = -\sum_j S_j(k) \frac{N_j f_j(k, \pi)}{k R_j^2} e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda} \sin[2k R_j + 2\delta_j(k) + \theta_{j(k)}] \tag{19}
\]

The equation contains four major parts where \( N_j \) is the number of scattering atoms (the greater the numbers of atoms in each co-ordination shell the greater the back scattering and so it is possible to determine the number of atoms in each co-ordination shell). The first part is due to the amplitude of back scattering and takes account of the co-ordination number \( N_j \) and the distance \( R_j \) from the central atom; as the frequency modulation depends on the distance between emitting and surrounding scattering atoms it is possible to obtain the distance between the emitting and surrounding atoms in successive co-ordination shells. \( f_j \) describes the backscattering amplitude of neighbouring atoms of \( j^{th} \) type; the amplitude of scattering will depend on the number of electrons present in each scattering atom and so it is possible to determine the type of atom in each co-ordination shell. The second term is the Debye-Waller factor \( \sigma_j \)
that takes account of the thermal motion of the atoms, which accounts for the smearing out of EXAFS as a result of the atoms having a static disorder and thermal motion. The distribution is assumed to be Gaussian. This thermal parameter is temperature sensitive and decreases with decreasing temperature. The next term accounts for the loss of the potential energy due to inelastic scattering. The final term contained in the sine function describes the interference effects where $\delta$ is the central atoms phase shift and $\theta$ is the phase shift caused by the neighbouring atom. The factor of two is in place to account for the outgoing and reflected phase shift.

2.4.4 XANES

The absorption edge can show fine structure associated with the various transitions to empty (or partially filled) electronic states. The position of the spectroscopic features preceeding the edge can depend on the details of the oxidation state, site symmetry, surrounding ligands and the nature of the bonding. In this study, the XANES of the synthesised material are compared with those of standards where the oxidation states are known, which allows us to see if there is any contribution to the XANES from non-integral formal oxidation states shown by a mixture of two different oxidation states.
2.4.5 Analysis of EXAFS Data

Analysis of EXAFS data was carried out using the suite of programmes available at the Daresbury labs. The process has three stages. Calibration and summation of the data is carried out with EXCALIB, the background subtraction by EXBROOK and the EXAFS simulation and curve fitting by EXCURV98 [16].

2.4.5.1 Calibration of Data

EXCALIB allows the addition of two or more spectra which increases the signal to noise ratio. It converts the millidegree scale provided by the data acquisition program at the station to an eV scale, and allows glitch removal (although only from electronic spikes).

2.4.5.2 Background subtraction

EXBROOK is used to remove the background contribution and has several stages. The pre-edge is subtracted first; being fitted with a polynomial that is extrapolated beyond the edge. The pre-edge fit is then subtracted from the experimental data. Next the EXAFS $\chi(E)$ is obtained from the experimental data and obtained using:-

$$\chi(E) = \frac{\Delta\mu(E)}{\mu_0(E)}$$

(20)
where $\Delta \mu(E) = \mu(E) - \mu_0(E)$; $\mu(E)$ is the measured absorption and $\mu_0(E)$ is the absorption
coefficient of the isolated atom. $\mu_0(E)$ is assumed to be a smooth background which
passes through the centre of the oscillations of the spectrum. The background is
therefore removed and $\chi(E)$ obtained by a cubic spline through the experimental data
and by subtracting this from the experimental $\mu(E)$ curve. The last stage of
background removal is to convert the photon energy ($E$) to the photoelectron wave
vector $k$ which is achieved using equation 21

$$k = \sqrt{\frac{2m}{\hbar^2}} (E - E_0) \quad (21)$$

where $\hbar^2 = h/2\pi$ ($h=$Plancks constant) and $E_0$ is the threshold energy for a particular
absorption edge.

At high $k$ values there is a large attenuation of the EXAFS amplitude and as a result
$\chi(k)$ is often multiplied by some power of $k$ to give $k^n\chi(k)$. A weight of 3 is normally
chosen, which prevents the larger amplitude oscillations from dominating the
spectrum in the determination of interatomic distances.

2.4.5.3 Derivation of Local structure

EXCURV98 [17] is a curve-fitting program which fits the $k^n\chi(k)$ spectra to a model
of the local structure. The co-ordination number, N, the interatomic distance R, and
the Debye Waller factor, ($\sigma$) are refined using a least squares method (eqn 22)
\[ R = \sum_i \left( \chi_{\text{obs}}^i - \chi_{\text{calc}}^i \right) k_0^n \]  

(22)

where \( \chi_{\text{obs}} \) is the observed spectrum and \( \chi_{\text{calc}} \) is the spectrum for the model, calculated using the EXFAS equation shown previously and \( k^n \) is the weighting factor. The calculations were carried out using both the single scattering curved wave approximation [18] and the full multiple scattering calculations using Rehr-Alber small atom theory [19].

2.4.5.4 Multiple Scattering

Only single scattering of a photoelectron by its neighbours has been considered so far. If, however the absorbing atom, the nearest neighbour and the next nearest neighbour are arranged in a linear or nearly co-linear array (between 150 and 180°) multiple scattering becomes important. The outgoing photoelectron is strongly forward scattered by the intermediate atom resulting in a significant enhancement of the EXAFS amplitude. Large phase shifts are also observed when multiple scattering is present. In perovskites based on a distorted cube, the TM-O-TM bond angle are in the range 150 to 180° (especially for the larger lanthanides). Therefore it is important to include multiple scattering components in the refinement. Initially atomoic positions are provided into the fitting routine which also defines symmetry of the site is used. The bond angle is then refined along with the co-ordination number, the bond length and the Debye-Waller factor.
2.4.6 Experimental

EXAFS experiments were carried out using the SRS at Daresbury. The measurements were carried out in transmission mode at station 7.1 (Si (111) monochromator) and 8.1 (using a Si (220) monochromator). A picture of the experimental arrangement is shown in Figure 2.9. The X-ray beam passes through to the monochromator which consists of two silicon crystals. Both crystals may be rotated to change the Bragg angle and allow a single wavelength to pass into the experimental hutch. The radiation first passes through the first ionisation chamber \(I_0\), then through the sample and finally through the second ionisation chamber \(I\). A plot of \(I/I_0\) is obtained against X-ray energy.

The samples were ground in a pestle and mortar and then placed onto sticky tape and layers were built up until a large enough absorption was observed by the detectors. The sample was aligned using a laser pre-aligned to the beam which can be placed in and out of the beam as required. The wavelength of the X-rays entering the hutch is selected by the elements that are to be probed. The absorption edges of some ions and associated XANES may fall into the measured region of the atom of interest therefore only certain combinations of cobalt, manganese, nickel and the lanthanides could be probed.

Combined EXAFS/XRD experiments were also carried out using station 9.3 at the SRS facility Daresbury. The EXAFS experiments used the fluorescence mode (with a 13 element solid state Ge detector) as not a large enough edge jump could be seen in
transmission due to the flux of X-rays entering the hutch. The sample was prepared as a solid disc by being ground with silica and pressed to 10 tonnes in a die. The diffracted X-rays were measured using a 120° INEL position sensitive detector. The silicon (220) monochromator was used. The sample was placed in a furnace which was controlled by a Eurotherm controller and the sample heated at a controlled rate and the EXAFS scans run in Qu-EXAFS mode allowing only one scan to take 10 minutes which is considerably quicker than standard transmission EXAFS.

Figure 2.9 Typical experimental setup for an EXAFS experiment at the SRS Daresbury
2.5 Magnetism

2.5.1 Introduction

The magnetic properties of solids are predominantly associated with electrons. Many atomic nuclei have intrinsic magnetic dipole moments but their magnitudes are $1/1830^{th}$ of that associated with electrons. The measured magnetic information of a material has a wealth of information relating to oxidation states, bonding, orbital interactions and structure. This section briefly introduces some of these factors relating to magnetic solids.

2.5.2 Magnetism of Individual Atoms Within Solids

When a solid is placed in a magnetic field $H$, it develops a magnetization (magnetic moment per unit volume) $M$, given by $M = \chi H$, where $\chi$, is the magnetic susceptibility.

The magnetic induction, $B$, is defined as:-

$$B = H + 4\pi M = \mu M$$  \hspace{1cm} (23)$$

where $\mu$ is the permeability. Substances with a weak negative magnetic susceptibility are called diamagnetic (diamagnetic substances tend to move towards the weakest region of a magnetic field) while those with a positive susceptibility are called paramagnetic (paramagnetic substances tend to move towards the strongest part of a magnetic field).
The magnetic properties of solids are determined by orbital and spin motions of electrons in atoms and their interaction with each other. The relationship between the magnetic moment, \( \mu \), and angular momentum, \( J \), of an electron of charge, \( e \), and mass, \( m \), can be expressed as:

\[
\mu = -\frac{e}{2m}J \tag{24}
\]

The angular momentum, \( J \), is quantized and the lowest value of, \( \mu \), is the Bohr magneton, \( \mu_B \). The orbital motion of an electron in an atom gives rise to a magnetic moment, which is related to the orbital angular momentum, \( L \), by

\[
\mu_L = \frac{eL}{2mc} = \beta[L(L+1)]^{1/2} \tag{25}
\]

The spin magnetic moment is then given by

\[
\mu_S = \frac{eS}{mc} = \beta[S(S+1)]^{1/2} \tag{26}
\]

where \( S \) is the spin angular momentum.

The observed magnetic moment can therefore be used to determine the number of unpaired electrons in each atom. The magnetic susceptibility \( \chi_M \) of a paramagnetic ion has a temperature dependence as described by the Curie-Weiss law where

\[
\chi_M = \frac{C}{T-\theta} \tag{27}
\]

where \( C \) is the Curie constant and \( \theta \) is the Weiss constant.
2.5.3.1 Magnetism in Bulk Materials

The magnetism in solids is more complicated than that of the isolated atoms because of the possibility of interaction (coupling) between atomic moments. The origin of the coupling comes from the Pauli exclusion principle namely that electrons of parallel spin are correlated as to avoid the same region of space. Thus, a pair of electrons of like spin will be higher in energy than a pair with opposite spin by an amount known as the interatomic exchange energy, and known as exchange coupling. Direct exchange, occurs between moments on atoms which are close enough to have significant overlap. This exchange is strong but decreases with increasing distance. Indirect exchange, couples moments over a larger distance. Exchange can also occur through intermediary nonmagnetic ions which is known as superexchange, which occurs predominantly in insulators or through itinerant electrons (Ruderman, Kittel, Kasuya and Yosida [20] - often referred to as RKKY) in metals.

The exchange energy, $H_{\text{ex}}$, of two atoms, $i$ and $j$, separated by a distance $r_{ij}$, with spins $S_i$ and $S_j$ respectively is given by:

$$H_{\text{ex}} = -\sum_y J(r_y) S_i \cdot S_j$$  \hspace{1cm} (28)

where $J$ is the exchange parameter. For electrons belonging to the same atom, $J$ is positive. For direct interatomic exchange, $J$ can be positive (parallel alignment of spins) or negative (antiparallel alignment of spins and lower energy). For indirect exchange, $J$ can be positive or negative in the case of superexchange or oscillatory for RKKY [21].
Superexchange describes interactions between localised moments of ions in insulators that are too far apart to interact by direct exchange and operates through an intermediary nonmagnetic ion. The strength of the exchange is determined by the extent of orbital overlap [22]. Localised electron states are stabilised by a mixture of exited states involving electron transfer between the cation and anion.

2.5.3.2 Types of Magnetism in Bulk Materials

There are five basic types of magnetism found in solids, which can be co-operative (mutual interaction between moments) and non co-operative (individual moments behave independently of each other) these include:

a) Diamagnetism (non co-operative):
A diamagnetic material has closed electron shells, and displays weak temperature independent magnetic susceptibility.

b) Ideal Paramagnetism (non co-operative)
Ideal paramagnetic materials atoms have identical atomic moments and located in isotropic surroundings that are sufficiently separated from one another. The temperature dependence of the susceptibility follows the Curie-Weiss law at temperatures above which any ordered magnetic states exist.

c) Ferromagnetism (co-operative)
Ferromagnetic materials have a long-range colinear order in which magnetic moments align in a parallel fashion to give a net permanent magnetic moment within a domain. Illustrated in figure 2.10. Applying an external field then enlarges the domains of an orientation parallel to the field at the expense of others. The spontaneous magnetisation decreases with increasing temperature (as the thermal energy increases and becomes comparable to and eventually exceeding the exchange energy) and then disappears at the Curie temperature where a ferromagnet becomes paramagnetic obeying the Curie-Weiss law.

d) Antiferromagnetism (co-operative)
Antiferromagnetic materials have a long range ordering but the exchange parameter $J$ is negative and the moments of neighbouring atoms are exactly opposed so there is no overall spontaneous magnetization (figure 2.10b). Below the ordering temperature (called the Neel Temperature) an antiferromagnet consists of two identical interpenetrating sublattices in which the spins of one lattice are opposed to the spin of the other. Most antiferromagnetic material are non-metallic solids e.g. MnO, NiO etc [22] but some metals e.g. Cr, PtFe$_3$ also exhibit antiferromagnetic properties.

e) Ferrimagnetism (co-operative)
Ferrimagnetic materials occur when two or more different magnetic species are present. They occupy different kinds of lattice sites producing two sublattices (as in spinels [20]) Figure 2.10c. The moments within each sublattice are ferromagnetic and but the coupling between the sublattices is antiferrimagnetic. As the overall moments of the two sublattices are different, there is an overall magnetization, the temperature
dependence of which is similar to that of ferromagnetic materials but decreases more rapidly with increasing temperature.

![Magnetic moment alignment of individual atoms (top ferromagnetism, middle antiferromagnetism and bottom ferrimagnetism)](image)

There are other types of magnetism, which are predominantly subdivisions of the five main types described above. For example, metamagnetism, in which there is a field induced magnetic transition from a state of low magnetization to one of relatively high magnetization [21]. The temperature dependence is similar to that of ferromagnetic materials although at lower temperatures the moment initially increases and the reaches a maximum (over a low temperature range).

2.5.4 Measurement of Magnetic Properties

For low temperature magnetic susceptibility measurements (5-350 K) a superconducting quantum interference device (SQUID) was used. A SQUID measures changes in the magnetic flux of a solenoid coil as the sample is introduced with the presence of an applied magnetic field.

When the sample is placed in the coil, the inductance is given by
\[ L = L_0(1 + 4\pi\zeta\kappa) \]  

(20)

where \( L \) is the observed inductance, \( L_0 \) is the inductance of the coil in a vacuum, \( \zeta \) is a filling factor, and \( \kappa \) is the magnetic susceptibility. The inductance \( L \) can be measured with an inductance bridge.

Mutual inductances are measured with a bridge circuit, consisting of a primary coil and two secondary coils wound in opposition and connected in series. If the two secondary coils are perfectly balanced, the induced voltage would exactly cancel out. Introducing a sample in one of the secondary coils unbalances the bridge, and the imbalance is a measure of the magnetic susceptibility. The technique can be made very sensitive by utilising the Meissner effect of superconductors relates to the quantized expulsion of magnetic fields from a superconducting substance when the substance is cooled below its superconducting temperature. The only possible values of magnetic flux which may be trapped within a superconducting ring are multiples of \( \hbar c/2e = 2 \times 10^{-7} \) Oe cm\(^2\). It is possible to produce a region of zero magnetic field by placing a superconducting coil in a magnetic field that produces a flux of less than \( \hbar c/2e \). A current is then introduced to cancel the flux resulting in the lowest quantized state (a zero magnetic field). The applied current is thus a measure of the flux that existed initially – this device is the SQUID.

This method is not practical at high temperatures and therefore, other less sensitive methods are used such as the Gouy balance, which consists of a cylinder which is suspended from the beam of an analytical balance. The end of the cylinder containing the sample is then placed between the plane parallel pole pieces of a magnet.
2.5.5 Experimental

Magnetic measurements have been carried out on two instruments. Low temperature high field measurements have been carried out using a MPMS SQUID and the high temperature measurements being carried out using an inductance bridge.

2.5.5.1 Sub ambient Temperature Magnetic Measurements

For the SQUID measurements, a field of 1000 G was applied and the sample cooled to 5 K. The sample was then heated and magnetic measurements were taken every 5 K until 350 K was reached. The samples of known weight were placed in gelatine capsules. The capsule was loaded into the sample holder packed with other empty capsules to prevent the sample moving and to provide an averaged environment for the sample. Tape with very little magnetism was used to hold the capsules in place. The SQUID provides accurate measurements of magnetic susceptibility and magnetic moment as a function of temperature. High magnetic fields can be applied which can reduce the randomness of the domains within ferromagnetic materials. It is however, not possible to measure above 350 K and for this reason another method was used for measurements above this temperature.

2.5.5.2 Post Ambient Magnetic Measurements

An inductance bridge was used to measure the magnetic susceptibility of the sample above ambient temperature. Large fields cannot be applied and therefore the
measurements are only an indication of relative changes, which occur as a function of temperature. The powdered samples were placed in a glass tube and a thermocouple placed inside in contact with the sample. The temperature was controlled by a heating coil around the sample holder. A computer collated the data obtained from the bridge and controls the temperature controller. In order to confirm the relative changes observed in the SQUID measurements at low temperature, these experiments were also repeated using the cryostat attachment for the bridge. A temperature range of 77-675 K was therefore attainable.

2.6 Electronic Properties of Solids

2.6.1 Introduction:

There is no unified model for interpreting the electronic properties of transition metal oxides and related materials. Detailed here are two complimentary methods to describe the electronic structure and hence properties of the oxide based materials, namely crystal field theory (describing localised electrons) and band theory (describing extended states). These are described briefly in order to understand observations made later in the thesis and both models are required to understand the properties of the materials studied.

2.6.2 Crystal Field Theory

Crystal field (CF) theory describes how the d electrons of configurations \( d^n \) are perturbed by their chemical environment.
For a transition metal ion with an octahedral configuration in a crystal field, the d orbitals are divided into two sets denoted $e_g$ and $t_{2g}$ (according to their symmetry behaviour) where the lobes of two orbitals (maximum probability) are pointing towards the nearest neighbour oxygens and they have three nodal planes in each of these directions respectively. The octahedral environment gives rise to a crystal-field splitting between the two sets of orbitals with an energy difference, $\Delta$, which in crystal field are the result of electrostatic perturbations of the d orbitals, but in the more general, ligand field theory takes into account orbital overlap and covalent interactions.

$$
\begin{array}{cccc}
\text{T}_{2g} & \text{E}_g & \text{E}_g & \text{T}_{2g} \\
\text{E}_g & \text{T}_{2g} & \text{E}_g & \\
\end{array}
$$

Figure 2.11 Crystal field splitting of orbitals in octahedral and trigonal configurations

The electronic configurations for ions in octahedral sites are obtained by arranging the electrons in the $t_{2g}$ and $e_g$ orbitals according to the Pauli exclusion principle. The ground states satisfy Hund’s first rule which states that the repulsion between the electrons is minimised by placing them as far apart as possible with parallel spins in different orbitals [23]. Different possibilities of electronic configuration can then occur according to the magnitude of the splitting, $\Delta$, and the exchange energy. If the splitting is large, then the orbitals are filled bottom up first. If the exchange energy is more favourable, the lowest energy configuration is found by the single filling of the orbitals so that the spins can be parallel. This results in low and high spin configurations respectively. Examples are shown in Table 2.1
<table>
<thead>
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<th>N</th>
<th>Configuration</th>
<th>High Spin</th>
<th></th>
<th></th>
<th>Low Spin</th>
</tr>
</thead>
<tbody>
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<td>t_{2g}^1</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>t_{2g}^2</td>
<td>-</td>
<td></td>
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</tr>
<tr>
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<td>-</td>
<td></td>
<td></td>
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<tr>
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<td>T_{2g}^4</td>
<td></td>
<td></td>
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<td>T_{2g}^5</td>
<td></td>
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</tr>
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<td></td>
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<tr>
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<td>t_{2g}^6 e_g^3</td>
<td>-</td>
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<tr>
<td>10</td>
<td>t_{2g}^6 e_g^4</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 2.1 Possible electronic configurations of 3d transition metal ions in octahedral symmetry*

Certain electronic configurations have a tendency to occupy distorted environments, specifically d^4 and d^7 [24] ions generally show a tetragonal distortion of an octahedral site with two lengthened M-O bonds. This distortion is regarded as a consequence of the Jahn-Teller theorem which states a non-linear molecule in an electronic state with orbital degeneracy will distort so as to lower its symmetry and remove this degeneracy. Degeneracy occurs, when the t_{2g} and e_g orbitals are empty, half filled or completely full. Distortion may also be caused by other effects, for example, ion-packing and chemical-bonding effects. Jahn-Teller distortions are also confined to systems with localised electrons [25].
2.6.3.1 Band Theory

The band model describes how electrons move in a periodic lattice [26,27]. The electrons are considered to be delocalised, but perturbed by a periodic potential of a crystal lattice. However, d states cannot be represented satisfactorily by a free electron basis. In this case, the approach used is the linear combination of atomic orbitals (LCAO), which is known as the tight binding method. The bands are formed as a result of orbital overlap, with the low lying orbitals remaining unperturbed whilst the orbitals at a higher energy contribute to the orbitals of the valence and conduction band. It is possible to describe insulators, semiconductors and metals using this approach.

Consider a one dimensional model of a linear chain of alternating transition metal and oxygen atoms. Orbitals are formed for electrons in the chain by the linear combination of the atomic orbitals. The crystal orbitals must be in the form

\[
\Psi_k = \sum_n \exp(ika) \Phi_n
\]  

(30)

where \( \phi_n \) is an atomic orbital located in unit cell number \( n \), in the lattice and, \( a \), is the spacing between the unit cells and \( k \) is the wave vector for the crystal orbitals (wavevector). The corresponding wavelength is given by

\[
\lambda = 2\pi / k
\]  

(31)
the range of $k$ values is chosen, so that all possible linear combinations are generated just once. The form for $\Psi$ above is appropriate for just one basis atomic orbital in fact there are many basis functions the most important being the metal $d$ and the oxygen $2p$ orbitals. When orbital overlap is permitted the $d$ and $2p$ orbitals mix together giving bonding and antibonding contributions whose mixing is governed by symmetry constraints. The band-structure diagram as a function of $k$ – i.e. the mixing between $p$ and $d$ orbitals smoothly between $k=0$ and $k=\pi/a$. The band energies are forced apart as $k$ changes resulting in bonding and antibonding orbitals. The Fermi level ($E_F$) is defined as the top filled level in the ground state. The density of states is defined as the number of allowed electron states per unit volume (or unit cell).
2.6.3.2 Band Structure of Metals

In metals, the highest occupied (valence) band is only partially filled (Figure 2.12c). Some levels just below $E_F$ are vacant, and some above $E_F$ are occupied. Electrons in singly occupied states close to $E_F$ are able to move and are responsible for the high conductivity of metals. In some metals, the energy bands overlap which is responsible for the metallic properties, for example, when the 2s and 2p orbitals overlap, both of which may be partially full. Upon heating, the thermal vibration hinders the flow of electrons in a metal causing a decrease in conduction with increasing temperature.

2.6.3.3 Band structure of Insulators

In insulators, the valence band is full and separated by a large gap (forbidden gap) from the next energy band which is empty (Figure 2.12b).

2.6.3.4 Band Structure of Semiconductors

Semiconductors have a similar band structure to insulators. However, the band gap is smaller (Figure 2.12b). Some of the electrons have sufficient thermal energy to be promoted into the empty band allowing conduction to occur. As the thermal energy of the electrons is increased, more electrons are able to move into the conduction band and the conductivity increases with increasing temperature.
2.6.3.5 Transition Metal Compounds

In transition metal compounds, the presence of partially filled metal d orbitals becomes important. These can overlap to give a metallic d band, giving the material a high conductivity for example TiO and VO [28] where the d_{xy}, d_{xz} and d_{yz} orbitals overlap strongly to form a t_{g} band which is only partially filled with electrons and hence metallic conduction occurs. However, this overlap can also be limited so the orbitals become localised on individual atoms as seen for example in NiO which is non-metallic in which the green colour is a green material due to d-d transitions within individual Ni^{2+} ions [29].
2.6.4 Experimental Methods Used to Determine Electrical Properties

Electrical measurements have been carried out using the 4-wire method both at ambient, sub-ambient and high temperature.

Rectangular pellets were cut from pressed discs prepared by annealing pressed pellets of the powdered samples. Contacts for the ambient and sub-ambient measurements were made using silver paint – the wire being attached to the samples with silver paint used to make rings around the sample and to hold the wires in place. The sample wires were then attached to a Fluke 8840A Multimeter and used in the 4-wire mode. The 4-wire technique eliminates any contribution to the resistivity due to non-ohmic contacts. The sample temperature was controlled using the cryostat detailed above with special connections being available for connection to the Fluke meter.
2.7 Infrared Spectroscopy

2.7.1 Introduction

Atoms in solids vibrate at frequencies of $10^{12}$ to $10^{13}$ Hz [30]. These vibrations can be excited to higher energy states by the absorption of infrared radiation. In this work, infrared spectroscopy was used to determine the effect of temperature driven electronic transitions on the infrared absorption properties of the materials. It was been found that electronic transitions can be observed by changes in the infrared spectrum; they hence give a good indication as to the optical switching properties of the material as the temperature is increased.

2.7.2 Theory

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region i.e. 14,000 to 20 cm$^{-1}$. However, the most informative region for this study is the mid-IR region, 4000 to 50 cm$^{-1}$. Infrared vibrational spectroscopy involves the examination of the twisting, bending, rotating and vibrational motions of bonds within the crystalline lattice (Figure 2.13).

![Figure 2.13 Stretching, deformation and rotational modes](image)
The energy of a quantum harmonic oscillation is given by

\[ E = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \]

(32)

Where \( h \) is Planck’s constant, \( k \) is the bond strength, \( \mu \) is the reduced mass of the molecule and \( v \) is the vibrational quantum number. At room temperature, most molecules are in the ground state (\( v=0 \)) and promotion to the first excited state (\( v=1 \)) requires the absorption of infrared energy.

The number and nature of absorption bands observed in the vibrational spectrum depends upon the number of atoms present in one unit of the material and its symmetry [31]. Group theory allows us to undertake a detailed analysis of allowed vibrational modes of the atoms within the unit cell (detailed descriptions can be found in many text books). However, in this work the infrared spectra were only used as a tool to investigate the manifestations of the electronic phenomenon and to determine how they can influence the infrared spectrum.

2.7.3 Experimental

Infrared vibrational measurements were carried out using a Nicolet Instruments 760 Magna FT-IR Spectrometer at a resolution of 4cm\(^{-1}\) and 32 scans were collected. A
DTGS KBr detector and a XT-KBr beam splitter was used for the Mid-IR measurements.

Samples of known mass (~1mg) were ground in a pestle and mortar; FTIR grade KBr (~200mg) was added and the materials ground together. They were then pressed in a Die (13mm in diameter) producing a disc at a pressure of 10 tonnes. This disc was then weighed, allowing the spectra to be normalised by weight to permit direct comparisons of peak intensities. To ensure a constant environment within the sample chamber and the spectrometer, a dry source of air flows through the spectrometer; CO$_2$ was also removed from the air. The sample was placed in the spectrometer and the spectrum obtained over the range 350 to 4000 cm$^{-1}$. For far infrared measurements, FTIR grade polyethylene was substituted for the KBr matrix. A spectrum was obtained over the range 50 to 700 cm$^{-1}$. It is not possible to perform the far IR measurement quantitatively due to the nature of the polyethylene. A solid substrate beam splitter and DTGS polyethylene detector was used for the far infrared measurements.

Infrared spectra as a function of temperature were obtained using a modified Oxford Instruments cryostat with a temperature range of 12-800 K. The cryostat was sealed and evacuated to a pressure of ~$10^{-5}$ mbar using an Edwards Pico Dry Turbo pump. The temperature was controlled by an Oxford Instruments ITC4. The cryostat contains a cold head, which is cooled by a displex pump, a sample head, which contains a heating cartridge. The temperature controller balances the degree of heating and cooling of the sample to give a steady sample temperature. A bellows unit allows the same cryostat to be used for sub and post ambient temperatures. At sub-ambient
temperatures the bellows are filled with helium gas and drive the cold head onto the sample head. At higher temperatures the bellows are removed by vacuum. The cryostat was suspended above the infrared spectrometer and the background taken without the sample in the sample head after evacuation. The background was saved and used for each temperature measurement. The sample was then loaded into the cryostat evacuated and the sample head cooled to 12 K. Spectra were recorded at approximately 25 K intervals starting at 12 K up to a temperature of 800K.

In the next four chapters we now go onto to describe the structural and physical properties of the perovskites under study using the techniques detailed in this chapter.

2.8 References


Chapter 3

Structural Studies of the $\text{Ln}_2\text{CoMnO}_6$ System

3.1 Introduction & Summary

This Chapter presents and discusses the structural data collected for the $\text{Ln}_2\text{CoMnO}_6$ series of materials, where Ln = La, Pr, Nd, 'Pm', Sm, Eu and Gd. The structural information has been obtained by the use of powder X-ray diffraction, coherent neutron scattering and extended X-ray absorption fine structure (EXAFS).

In the first part of this Chapter, the effects of the lanthanide ionic radius upon the unit cell parameters and the crystal symmetry are probed by X-ray powder diffraction techniques. The temperature dependence of the structural properties of this series has been investigated and we have deployed a concerted multi technique effort on $\text{La}_2\text{CoMnO}_6$, because of its rather unusual superstructure. As we shall see, the X-ray data indicate that $\text{La}_2\text{CoMnO}_6$ is unique (in this system) in that it changes symmetry (reversibly) upon heating. A synchrotron X-ray diffraction study was carried out (due to its increased signal to noise ratio and well defined Bragg peak profile [1]) and provided more information than the standard powder diffraction techniques (in that it allowed us to determine atomic positions in an orthorhombic setting). More detailed
structural information was obtained using coherent neutron scattering, as it was possible to distinguish between cobalt and manganese ions allowing us to determine the mechanism responsible for the superstructure observed in the X-ray diffraction experiments. Using neutron diffraction, we show that, in La$_2$CoMnO$_6$, there is evidence for charge ordering and a monoclinic distortion. A phase transition is also observed where the monoclinic structure transforms to a rhombohedral structure (a first order transition at 625 K). In the final part of this Chapter, the local structure is investigated using EXAFS. These data provide evidence for charge disproportionation and allow us to infer indirectly the oxidation states of the transition metal ions in the TM-O sublattice.

In later Chapters, it will be shown how the structural information can aid the development of structure - electronic property relationships, which are argued by Rao as one of the primary aims of solid state chemistry [2].

3.2 Results

3.2.1 Room Temperature X-ray Diffraction Study

The materials Ln$_2$CoMnO$_6$ (Ln≠La) all have diffraction patterns, which show systematic absences consistent with the Pnma space group. The laboratory X-ray diffraction pattern of the orthorhombic material Pr$_2$CoMnO$_6$ is shown in Figure 3.1; experimental details can be found in Chapter 2.3.5. However, La$_2$CoMnO$_6$ is unique

* Pm is radioactive and therefore dangerous to use – to this end a mixture of Nd and Sm is used for which the average ionic radii is that of Pm – a more detailed description is given in the synthesis section of Chapter 2
in the series in that it possesses extra reflections, which can be indexed assuming a
doubling of the c-axis. The dependence of the unit cell axial lengths and unit cell
volume for the series of materials as a function of the lanthanide ionic radius are
reported in Table 3.1 and shown graphically in Figure 3.2. The overall unit cell
volume, as expected decreases linearly with the reduction in lanthanide radius.
However, examination of the lattice parameters shows that although the b and c axes
decrease linearly with decreasing size of lanthanide ion as expected, interestingly, the
a axial length increases linearly.

Figure 3.1 Powder X-ray Diffraction Pattern of Pr$_2$CoMnO$_6$ (typical of all materials
in the series)
<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>A/Å</th>
<th>B/Å</th>
<th>C/Å</th>
<th>Unit cell Volume/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>5.426</td>
<td>7.778</td>
<td>5.518</td>
<td>232.86</td>
</tr>
<tr>
<td>Pr</td>
<td>5.490</td>
<td>7.695</td>
<td>5.442</td>
<td>229.91</td>
</tr>
<tr>
<td>Nd</td>
<td>5.514</td>
<td>7.662</td>
<td>5.418</td>
<td>228.77</td>
</tr>
<tr>
<td>Nd/Sm (Pm)</td>
<td>5.534</td>
<td>7.633</td>
<td>5.395</td>
<td>227.91</td>
</tr>
<tr>
<td>Sm</td>
<td>5.560</td>
<td>7.597</td>
<td>5.371</td>
<td>226.86</td>
</tr>
<tr>
<td>Eu</td>
<td>5.573</td>
<td>7.578</td>
<td>5.359</td>
<td>226.29</td>
</tr>
<tr>
<td>Gd</td>
<td>5.588</td>
<td>7.556</td>
<td>5.343</td>
<td>225.59</td>
</tr>
</tbody>
</table>

Table 3.1 Unit Cell Parameters of the series Ln₂CoMnO₆

![Figure 3.2a Change in lattice parameters as a function of lanthanide ionic radius](image)

Figure 3.2a Change in lattice parameters as a function of lanthanide ionic radius
Figure 3.2b Change in unit cell volume as a function of lanthanide ionic radius

Rietveld refinement of Nd$_2$CoMnO$_6$ and La$_2$CoMnO$_6$ (in Pnma) has been possible using high-resolution X-ray diffraction data, which were obtained using the same instrument in order to investigate and compare the superstructure of La$_2$CoMnO$_6$ and Nd$_2$CoMnO$_6$. The experimental, refined and difference plots from the Rietveld analyses are shown in Figure 3.3. The atom positions, cell parameters and selected bond distances are detailed in Table 3.2. For orthorhombic LnTMO$_3$ structures in the Pnma space group the only atomic sites than can be occupied by the transition metals are the 2c, and hence, only an averaged TM-O bond length can be determined for the cobalt and manganese ions of 1.94Å. Reducing the symmetry of the space group (for example to monoclinic) allows for the possibility of the transition metal ions to occupy separate atomic sites, hence yielding TM-O bond lengths for each transition metal ion. When the patterns are refined using the monoclinic space group P 2$_1$/c which is a sub-group of Pnma [3,4], it is only possible to obtain positions of the rare earth ions to any degree of accuracy with the errors being too high for oxygen atoms.
This is reflected in the R factors and the esds. The transition metals site on special position and hence are fixed and not refinable.

Figure 3.3 Rietveld refinement of the powder diffraction pattern of \( \text{Nd}_2\text{CoMnO}_6 \) (Pnma)
Parameter | $La_2CoMnO_6$ | $Nd_2CoMnO_6$
---|---|---
a/Å | 5.42645(13) | 5.525313(12)
b/Å | 7.77823(14) | 7.68912(16)
c/Å | 5.51845(10) | 5.423769(20)
La x | -0.0491(9) | -0.0485(4)
Y | 0.25 | 0.25
Z | 0.005912(7) | 0.00621(12)
UISO | 0.006891(12) | 0.00737(10)
Co/Mn x | 0 | 0
Y | 0 | 0
Z | 0.5 | 0.5
UISO | 0.00370(64) | 0.00390(46)
O x | 0.5081(6) | 0.50781(6)
Y | 0.25 | 0.25
Z | -0.0901(13) | -0.08903(14)
UISO | 0.00860(13) | 0.00943(6)
O x | 0.74583(12) | 0.78986(16)
y | -0.4913(7) | -0.45843(12)
z | -0.75981(12) | -0.78916(13)
UISO | 0.00865(17) | 0.00943(19)
$\chi^2$ | 4.134 | 5.646
wR_p | 6.78% | 7.58%
R_p | 5.98% | 6.03%

Table 3.2 Results of Rietveld refinement of $La_2CoMnO_6$ and $Nd_2CoMnO_6$ (space group = Pnma)

3.2.2 Variable Temperature X-ray Diffraction

The thermal properties of the material (as observed by DSC (differential scanning calorimetry)) show that $La_2CoMnO_6$ is unique in that it undergoes a large exothermic transition at 600 K which is not observed in any of the other materials in the series. For this reason the temperature dependence of the X-ray diffraction pattern was followed.

The temperature dependent behaviour of the unit cell axial lengths a, b, c for $La_2CoMnO_6$ are shown in Figure 3.4. The cell volume (Figure 3.4a) shows three distinct regions; 350-420 K, 420-600 K and 600-1000 K. When the a, b and c axial
lengths are examined separately, it is clear that they do not all exhibit the same
temperature dependencies in that there is not a 1:1:1 relationship (Figure 3.4 b, c and
d). Whereas a & c show a single discontinuity at 400 K, b shows discontinuities at
500 K and 600 K. The same peculiarity is not observed for the temperature
dependence of the unit cell axial lengths of the other materials in the series, where
there is a linear increase in the b and c lattice parameters and a slight decrease for the
a axial length (Figure 3.5 a,b,c). The overall cell volume, however increases linearly
(Figure 3.5d) with increasing temperature.

Figure 3.4 Temperature dependence of unit cell and volume of La$_2$CoMnO$_6$
Figure 3.5 Changes in lattice parameters and unit cell volume of Gd$_2$CoMnO$_6$ as a function of temperature (typical of the series except La$_2$CoMnO$_6$)

The room temperature X-ray diffraction pattern of La$_2$CoMnO$_6$ exhibits extra diffraction peaks that cannot be attributed to the orthorhombic diffraction pattern. These reflections disappear at 600 K (Figure 3.6), the same temperature at which changes occur in the lattice parameters. Below 600 K, it is possible to index the pattern to the orthorhombic space group Pnma by incorporating a doubling of the c axis. Above 600 K, the superlattice peaks giving rise to the doubled c-axis, are not present in the diffraction pattern and the material appears to be orthorhombic. These reflections are evident in both the laboratory based XRD patterns and those obtained at higher resolution at both the synchrotron and at ISIS.
Figure 3.6 Change in X-ray diffraction pattern upon increasing temperature of La$_2$CoMnO$_6$ (note loss of superlattice reflections at low two theta at 600 K)

It is possible to follow indirectly the temperature dependence of the thermal motion [5] of the atoms by measuring the intensities of the diffraction peaks. In this study, the temperature dependence of the intense 121-diffraction peak has been investigated. The peak height decreases in the temperature range 290 - 600 K (as expected), above which it begins to increase in magnitude (Figure 3.7). By measuring the integrated peak area of the most intense Bragg diffraction peak (121), it is possible to follow indirectly changes of the thermal motion and disorder of the atoms (Figure 3.7). On raising the temperature discontinuities are observed at 400 and 600 K. For other materials in the series the peak intensity decreases linearly without discontinuities and
a linear decrease with temperature in the peak height is observed.

![Graph showing integrated intensity of the 121 reflection as a function of temperature]

**Figure 3.7** Changes in integrated peak intensity of the 121 reflection as a function of temperature

3.2.3 Neutron Diffraction Study of La$_2$CoMnO$_6$

As discussed, X-ray diffraction was unable to provide a detailed structure, and was quite unable to provide a model for the superstructure. Hence, we turn to neutron diffraction. Owing to time constraints, the measurements were only carried out on the most interesting material, La$_2$CoMnO$_6$. To understand fully the nature of the crystal structure and how it changes, accurate parameters are needed for the lanthanide, transition metal and oxygen atoms. Neutron diffraction will also allow us to determine the structural bases for the extra reflections in the X-ray diffraction patterns: either the cobalt and manganese ions are ordered (as shown by the fractional occupancies of the atomic sites) or octahedral tilting is present.
The room temperature (ca 298 K) neutron diffraction pattern of La$_2$CoMnO$_6$ is shown in Figure 3.8. Clearly, there is a splitting of the 111-diffraction peak, which is not consistent with the orthorhombic space group; this feature was not seen by the X-ray diffraction methods used previously. The pattern was indexed by the systematic absences to the monoclinic space group of P 2$_1$/n (14) [3]. Thus analysis of the neutron diffraction data indicates a lower symmetry than suggested by the X-ray diffraction pattern. In order to obtain accurate atom positions for La$_2$CoMnO$_6$, the theoretical work of Woodward [6] was used as a starting model for the Rietveld analysis of the structure; the work provides initial rare earth, transition metal and oxygen positions for materials with a known space group. The experimental, refined and difference profiles for the Rietveld refinement are also shown in Figure 3.8; the lattice parameters, atom positions, thermal parameters are detailed in Table 3.3. The weighted R-values are also given. By refining the fractional occupancies of each of the transition metal sites, it is clear that each transition metal prefers a separate specific atomic site, where the 2c and 2d sites are found to be 88% ordered. Exchanging the transition metal on the alternative atomic sites results in a poorer quality refinement, reflected by the increase in the weighted R-values [7]. If the refinement is allowed to converge while refining the fractional occupancies the initial ordered state is obtained. Selected bond distances are given in Table 3.4
Figure 3.8 Neutron diffraction pattern and associated Rietveld analysis of $\text{La}_2\text{CoMnO}_6$ at room temperature (the red line is the theoretical model, the black line the observed diffraction pattern and the green line the residual after analysis)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>295 K</th>
<th>400 K</th>
<th>425 K</th>
<th>625 K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space Group</strong></td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>R3</td>
</tr>
<tr>
<td>A</td>
<td>5.525192 (18)</td>
<td>5.531033 (9)</td>
<td>5.534741 (12)</td>
<td>5.487977 (16)</td>
</tr>
<tr>
<td>B</td>
<td>5.487598 (13)</td>
<td>5.491251 (6)</td>
<td>5.494840 (11)</td>
<td>5.487977 (16)</td>
</tr>
<tr>
<td>C</td>
<td>7.778682 (25)</td>
<td>7.781928 (13)</td>
<td>7.787753 (17)</td>
<td>5.487977 (16)</td>
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<tr>
<td>α</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>60.7239 (10)</td>
</tr>
<tr>
<td>β</td>
<td>89.9995 (12)</td>
<td>89.9370 (6)</td>
<td>89.9408 (9)</td>
<td>60.7239 (10)</td>
</tr>
<tr>
<td>γ</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>60.7239 (10)</td>
</tr>
<tr>
<td>La x</td>
<td>0.00721 (7)</td>
<td>0.00486(11)</td>
<td>0.00494(11)</td>
<td>0.25019 (4)</td>
</tr>
<tr>
<td>Y</td>
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<td>0.02185(12)</td>
<td>0.25019 (4)</td>
</tr>
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<td>Z</td>
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<td>0.24421(9)</td>
<td>0.25019 (4)</td>
</tr>
<tr>
<td>UISO</td>
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<td>0.00286(9)</td>
<td>0.00343(12)</td>
<td>0.01155(13)</td>
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<tr>
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<td>0</td>
</tr>
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<td>0.5</td>
<td>0.5</td>
<td>0</td>
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<tr>
<td>Z</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>UISO</td>
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<td>0.0858(13)</td>
<td>0.07057(23)</td>
<td>0.01626(13)</td>
</tr>
<tr>
<td>Mn x</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Y</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Z</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>UISO</td>
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<td>0.07057(12)</td>
<td>0.01626(18)</td>
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<tr>
<td>O x</td>
<td>0.28938 (16)</td>
<td>0.2858 (9)</td>
<td>0.28367 (14)</td>
<td>0.80011 (8)</td>
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<tr>
<td>Y</td>
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<td>0.26403 (10)</td>
<td>0.26608 (16)</td>
<td>0.68728 (8)</td>
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<td>Z</td>
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<td>0.03604 (12)</td>
<td>0.03683 (19)</td>
<td>0.25640 (12)</td>
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<td>UISO</td>
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<td>0.00204(11)</td>
<td>0.00581(17)</td>
<td>0.02077(21)</td>
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<td>O x</td>
<td>0.26456 (16)</td>
<td>0.26457 (14)</td>
<td>0.26347 (15)</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
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<td>0.27665 (12)</td>
<td>0.27601 (12)</td>
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</tr>
<tr>
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<td>0.01938(16)</td>
<td>-</td>
</tr>
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<td>O x</td>
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<td>0.56722 (13)</td>
<td>0.56645 (14)</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>-0.00192 (9)</td>
<td>-0.00176 (9)</td>
<td>-0.00448 (18)</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>0.24366 (23)</td>
<td>0.24237 (11)</td>
<td>0.24084 (12)</td>
<td>-</td>
</tr>
<tr>
<td>UISO</td>
<td>0.00739(12)</td>
<td>0.00641(8)</td>
<td>0.00509(13)</td>
<td>-</td>
</tr>
<tr>
<td>Co:Mn Ordering</td>
<td>90%</td>
<td>90%</td>
<td>80%</td>
<td>80%</td>
</tr>
<tr>
<td>Rp</td>
<td>8.76%</td>
<td>8.08%</td>
<td>10.26%</td>
<td>10.78%</td>
</tr>
<tr>
<td>wRp</td>
<td>10.24%</td>
<td>9.67%</td>
<td>12.02%</td>
<td>12.1%</td>
</tr>
<tr>
<td>χ²</td>
<td>18.11</td>
<td>17.84</td>
<td>3.729</td>
<td>10.03</td>
</tr>
</tbody>
</table>

Table 3.3. Results of Rietveld Refinement of neutron diffraction data for La₂CoMnO₆

A dramatic change in the (111) diffraction peak (Figure 3.9) is observed at 625 K, which is a clear indication of a structural change. The diffraction pattern was indexed...
to rhombohedral symmetry with the space group of R-3 (in the rhombohedral setting). The results of the Rietveld refinement are shown in Figure 3.9: the lattice parameters, atom positions, thermal parameters and selected distances are detailed in Table 3.3. The transition metal site preference is 80% which is 8% different from the room temperature data. There are also no superlattice reflections present. The weighted R-values are lower than those obtained at room temperature. Selected bond distances are given in Table 3.4

![Neutron diffraction pattern and associated Rietveld analysis of La$_2$CoMnO$_6$ at 625 K (the black line is the observed diffraction pattern, red the theoretical fit and green the residual after Rietveld analysis)](image)
Table 3.4 Selected bond distances for La$_2$CoMnO$_6$ at 300 and 625 K

The diffraction patterns obtained at 375 and 450 K represent either side of the previously observed phase transition at 400 K suggested by X-ray diffraction. The superlattice reflections show a change in their profile and intensity of the peaks above 400 K. In Table 3.3 the lattice parameters, atom positions thermal parameters. The site preference for the transition metal ions at 450 K are significantly different from those derived at 290 and 400 K, which is reflected in the percentage occupation of the site by the transition metal ion of 88% and 80% respectively.

At 575 K, the diffraction pattern shows the presence of both the monoclinic and rhombohedral phases (Figure 3.10). The split 111-diffraction peak of the P 2$_1$/n structure is superimposed on the 111 and -1-1-1 diffraction peak for the R-3 structure (inset). Due to the interesting multi phase nature of the material at 575 K, it was decided to sacrifice collection time and follow the transition upon cooling. The diffraction pattern was therefore collected at 20 K intervals upon cooling. The diffraction patterns around the 111-diffraction peak are shown sequentially as a function of decreasing temperature in Figure 3.11. The transition is reversible, which
is shown pictorially in Figure 3.11 where it can be seen that the intensity grows and the shape of the superlattice reflections changes upon cooling. We also note that there is a slow transformation of the mixed phase monoclinic and rhombohedral symmetries to a single-phase monoclinic structure, which is reflected in the diffraction peak intensities of the two phases as the material is cooled (Figure 3.11). The data collected are of a poorer quality than those measured upon heating, hence it is not possible to refine the data easily; the decrease in quality due to a decrease in collection time leads to a lower signal to noise ratio.

![Figure 3.10 The bi-phasic nature of La$_2$CoMnO$_6$ at 575 K (the inset shows the region around the 111 reflection)](image)

*Figure 3.10 The bi-phasic nature of La$_2$CoMnO$_6$ at 575 K (the inset shows the region around the 111 reflection)*
Figure 3.11 The diffuse nature of the transition upon cooling shown sequentially are the diffraction patterns around the 111 reflection).
Figure 3.12 shows the percentage of the material that possesses the rhombohedral structure in the bi-phasic temperature range upon cooling. This information is obtained by refining the diffraction pattern using Rietveld analysis and incorporating two phases. The amounts of the phases within the pattern are also refined as a function of temperature. It can be seen that the \( -1-1-1 \) reflection of the rhombohedral diffraction pattern decreases in intensity and broadens upon cooling.

3.2.4 Local Structure (EXAFS)

Powder X-ray diffraction and neutron diffraction averages data over the whole crystal and may not able to give accurate TM-O bond lengths for the local structure especially when disorder is present. Therefore, a method of accurately determining the bond distances from specific transition metal ions is required; hence we now turn to Extended X-ray Absorption Fine Structure (EXAFS) (Chapter 2.4).
An example of the experimental EXAFS and associated Fourier transform for the Co K-edge of \( \text{La}_2\text{CoMnO}_6 \) and the corresponding theoretical fits are shown in Figure 3.13. The results of the refined model are given in Table 3.5, which details the number, type and distance of atoms in each co-ordination shell around the cobalt and manganese ions, which are determined using Mn K and Co K edge XAS are shown in Table 3.5. The Debye-Waller factors are also shown for each atom (containing both thermal and disorder components). The results show that the transition metal ion is surrounded by six oxygens with equal bond lengths. The second shell containing the next transition metal ion has been assumed to be different to the excited atom. The two transition metal ions are very similar electronically and therefore the EXAFS is unable to differentiate between the two different ions in the second shell. The quality of each fit is also shown by the R value. The TM-O distances are considerably different for cobalt and manganese (1.99 Å and 1.86 Å respectively), which is also reflected in the second shell of the EXAFS where the O-TM distance is different from that of the first shell. Changing the lanthanide shows that only the TM-O-TM bond angle decreases from 180 to 173° for La and Nd respectively, but the TM-O bond distances remain unchanged. It is only possible to determine properly both the TM-O bond distance for the second shell and the TM-O-TM bond angle by using a multiple scattering model since the bonded atoms are in a collinear array [8] with a TM-O-TM angle tending to 180°, which as discussed in Chapter 2.4.5.4 tries to maximise multiple scattering effects.
Figure 3.13 EXAFS and associated fourier transform of the Co-K edge of La$_2$CoMnO$_6$

In order to infer the oxidation states of the transition metal ions present in the materials, EXAFS data have also been obtained for LaCoO$_3$, La$_2$CoO$_4$, LaMnO$_3$, CaMnO$_3$ and MnO$_2$ where the transition metal ions are in known oxidation states, which allows the TM-O distance of the mixed TM materials to be referenced to a material with a known oxidation state [9]. The TM-O bond distances and oxidation states are listed in Table 3.6. All atoms are in a six-fold co-ordinated position.
Table 3.6 Selected bond distances of standards

<table>
<thead>
<tr>
<th>Material Studied</th>
<th>TM Oxidation State</th>
<th>TM-O distance/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO₃</td>
<td>+3</td>
<td>1.94</td>
</tr>
<tr>
<td>La₂CoO₄</td>
<td>+2</td>
<td>1.99</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>+3</td>
<td>1.95</td>
</tr>
<tr>
<td>CaMnO₃</td>
<td>+4</td>
<td>1.88</td>
</tr>
<tr>
<td>MnO₂</td>
<td>+4</td>
<td>1.87</td>
</tr>
</tbody>
</table>

The effect of temperature on the EXAFS of La₂CoMnO₆ has also been investigated. The results of the EXAFS for La₂CoMnO₆ system are given in Table 3.7. They show an increase in the Debye – Waller factor, but the Mn-O and Co-O bond lengths increase only slightly. As a result of the quality of the data collected, which is poor especially at higher temperatures where thermal vibration becomes a problem in the EXAFS it is only possible to determine the first shell information.

Table 3.7 Bond distances obtained from EXAFS as a function of temperature

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>Co-O/Å</th>
<th>Mn-O/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>1.99</td>
<td>1.85</td>
</tr>
<tr>
<td>390</td>
<td>1.99</td>
<td>1.86</td>
</tr>
<tr>
<td>490</td>
<td>2.00</td>
<td>1.87</td>
</tr>
<tr>
<td>590</td>
<td>2.01</td>
<td>1.88</td>
</tr>
</tbody>
</table>
3.3 Discussion

3.3.1 X-ray Diffraction

Linear dependent changes in the lattice parameters of Ln$_2$CoMnO$_6$ are, as expected, seen as the ionic radii of the lanthanide decreases. As observed in other materials for example, the orthoferrites [11] as the lanthanide decreases in size, the TM-O-TM bond angle decreases to maintain orbital overlap between the lanthanide ion and the TM-O sublattice [10]. The changes in bond angle are also shown by EXAFS where the TM-O-TM bond angle decreases from 180° (1) to 173° (2) for La and Nd respectively. The a axial length increases, but b and c decrease which is due to elongation of the intra atomic oxygen distances from layers of the TM-O sublattice.
Throughout the series, it is assumed the TM-O bond length remains constant as the electronic configuration of the transition metal controls this. EXAFS data have also shown that the TM-O bond distance does not vary with lanthanide ion [9,12]. Similar changes have been observed in the cell volume in the orthoferrites [11] and the Sm$_{1-x}$Nd$_x$NiO$_3$ system [13]. The bond angle is controlled by a steric effect but electronic effects control the bond distance in that the oxidation state of the transition metal controls the TM-O distance.

In addition, there is also a change in the ratio of the lattice parameters a, b, and c with lanthanide radius. For the La$_2$CoMnO$_6$ material, the axial lengths have the ratio $c > b > \sqrt{a}$ and for the rest of the series the ration is $a > b > \sqrt{c}$, which has also been observed for other systems including the Ni/Mn system and the orthoferrites [11,14] which also shows this anomaly but with no reason suggested. This anomaly is also seen in other physical properties of the series, for example, resistivity where lanthanum fails to fit...
in with the trends exhibited by the other lanthanides (Chapter 4.2.2). This anomalous behaviour in the lanthanum based material may be a result of the fact that lanthanum is the only lanthanide in the +3 oxidation state with no occupied f orbitals.

The orthorhombic Pnma space group (a'\(a'\)a'\(a'\) in Glazer notation) has only one site for the transition metal atoms and so only gives an averaged bond length for both cobalt and manganese of 1.94 Å. Unfortunately using XRD it is has proved difficult to obtain a fit of the data using the monoclinic P 2\(\text{i}\)/c space group and to obtain two different TM-O bond distances as suggested by the local structure. There are a number of explanations for this difficulty, which could be due to the low scattering power of oxygen relative to the lanthanide [15] or the fact that it is not possible to distinguish between cobalt and manganese and hence determine which ion should occupy which atomic position. Asai et al [16] suggested that there could be a site preference for cobalt and manganese if the material was charge ordered. The quality of the refinement did not improve upon swapping the cobalt transition metal ion from the 2c to 2d atomic positions and vice versa for manganese, which is probably due to the similar X-ray scattering factors of cobalt and manganese which possess similar numbers of electrons [17]; hence it is not possible to determine whether charge ordering is present by X-ray diffraction techniques. It has, however, been possible to infer that charge ordering is present from the EXAFS data where the second shells TM-O distance is different from that of the first shell indicating a different transition metal occupies the second shell from that of the excited transition metal. It is also possible to infer charge ordering from the neutron diffraction data.
The superlattice reflection noted for the lanthanum based material may be due to either charge ordering [18] or octahedral tilting [19]; XRD is unable to differentiate between the two mechanisms. Charge ordering can be determined by transition metal site preference. However, as XRD is unable to differentiate between the two transition metal ions, as they have very similar electronic configurations, only an averaged transition metal site is determined. X-ray resonance scattering has by previous workers used to distinguish between the two transition metal atoms [20]. Unfortunately, however the resonant edges for cobalt and manganese are very close in energy and hence it would not be possible just to excite individually the transition metals being probed. It is for this reason that we turn to neutron diffraction where the scattering cross sections of the transition metal ions are not linearly dependent on the atomic number. Indeed, and as the scattering power is negative for manganese and positive for cobalt. A and B atom site ordering will therefore have a major effect on the diffraction pattern.

Generally, we expect the cell volume and unit cell parameters to increase linearly with temperature. As discussed previously, discontinuities in the lattice parameters usually indicate an electronic or structural phase transition. There are two discontinuities observed for La$_2$CoMnO$_6$; the former is associated with an electrical transition and the latter is associated with the loss of superlattice reflections but no electrical transition, which indicates that either charge ordering or octahedral tilting is lost. The a and c axial lengths increase with temperature but show two discontinuities at 400 and 600 K. However, the b axial length decreases in value at 600 K temperature this effect has also been previously observed for doped manganese materials upon loss of charge ordering [21].
For materials not showing these anomalous changes in cell volume, lattice parameters and peak intensity i.e. Nd$_2$CoMnO$_6$ the a lattice parameter is relatively insensitive to increasing temperature showing only a slight decrease with increasing temperature, which is analogous to the changes seen with reduction in the lanthanide ionic radius. It may indicate that the bond angles are increasing in size as the temperature increases as shown by the local structure data.

The X-ray diffraction peak intensity is related to the Debye–Waller factor, $G$, by

$$I = I_0 \exp \left(-\frac{G}{T} \right)$$

where $I$ is the measured peak intensity at temperature $T$ and $I_0$ the peak intensity at room temperature. The Debye Waller factor should increase linearly as the thermal motion increases and hence the integrated peak intensity should therefore decrease linearly. In La$_2$CoMnO$_6$, the plot of peak intensity vs temperature shows obvious discontinuities at 400 and 600 K, the same temperatures at which there are changes in the lattice parameters and cell volume. The peak height can also be an indication of the degree of disorder. The peaks may decrease in height as the temperature is increased as the atoms are displaced from their atomic sites given by the structural data due to an increase in thermal motion [5].

### 3.3.2 Neutron Diffraction

Neutron diffraction has enabled the determination of accurate oxygen positions in a monoclinic space group P2$_1$/n (a$^+$a$^-a^-$ in Glazer notation), and allowed us to decide whether cation ordering or octahedral tilting causes the supercell reflections observed in the diffraction patterns. The crucial factor is the increased resolution and the ability
to distinguish between the cobalt and manganese ions. The splitting of the 111-diffraction peak has not been observed by powder XRD due to the resolution of the equipment used. A slight shoulder, however, is observed in the XRD pattern but is not as distinct as seen in the neutron data; moreover, this shoulder is only observed in the X-ray diffraction pattern by counting for a long period of time and with very small increments of 2θ which are not viable using laboratory based equipment. Even using station 9.1 on the SRS it was not possible to detect the splitting despite the increase in resolution.

The low temperature neutron structure (300 K) shows the cobalt and manganese ions have preferential site ordering, resulting in the superlattice reflections which are caused by the doubling of the c-axis as observed for Ce1/3NbO3 [22]. Above 400 K the site preference decreases slightly and changes in the superlattice reflections are observed as the ordering is lost which has been observed in other systems such as NaV2O5 [23]. The superlattice reflections change shape and their intensity alters. Studies on LaSr2Mn2O7 have shown the loss, or partial loss of charge ordering, increases electron mobility [24]. At the temperature where changes are seen in the superlattice reflections, a change in the electrical band gap is observed indicating a change in electron mobility. The reduction of charge ordering is also reflected in changes in the X-ray peak intensity. B-site ordering in the material has lowered the symmetry to P 21/n from Pnma which has also been observed in other systems [25]. The Co-O and Mn-O bond lengths determined by neutron diffraction are 1.99 and 1.87 Å respectively (similar to that shown by EXAFS). These bond lengths indicate that the formal oxidation states of the transition metal ions are different. The TM-O-TM bond angle is also similar as observed by EXAFS ~180° which shows the
material is monoclinic with a high degree of orthorhombic character, which is also shown by the beta angle of the lattice which is very close to 90°. It is important to note that the apparent loss of B-site ordering with increasing temperature is not due to a randomisation between the two cation sites, but due to an increase in thermal motion. This space group has also been reported for YNiO₃ in which the Ni ions are found in two slightly different oxidation states (inferred from bond lengths) each of which are found on specific sites [26].

The reduction of symmetry to the monoclinic space group could not be determined using X-ray diffraction techniques, which may be due to the relative broadness of the diffraction peaks, which is in part due to the low crystallinity of the material despite extensive efforts to improve it by changing the heating cycles upon synthesis. A compromise has to be reached: in order to retain the chemistry of the system it is not possible to heat to very high temperatures; doing so would sinter the material and dramatically improve the crystallinity but oxygen would be lost. The fluorescence of the manganese ion under the X-ray light may be artificially broadening the line width and peaks may be lost in the background [27]. Unfortunately a limited range of wavelengths were available for the laboratory based X-ray sources and the difference in the wavelengths is small.

At 625 K the structure was indexed to a higher symmetry – the space group R-3 in the rhombohedral setting (a' a' a' in Glazer notation). Superlattice reflections were not observed for this space group, which could indicate that the transition metal ions are not fixed upon the B position (in the structure A₂B₂X₆) and are moving due to thermal vibration or possibly randomised (but this is not likely). Upon refinement we have
shown that the B-site ordering is kept. Upon refinement, the TM-O bond distances at 625 K are shown to be 1.99 and 1.85 Å for Co-O and Mn-O respectively which is comparable to the local structure determined by EXAFS as a function of temperature. The difference in bond lengths inferred from the two techniques is a result of the slightly mixed nature of the 2c and 2d atomic position. The site ordering preference is reduced within this structure as shown by the fractional occupancy of the sites. The temperature of the transitions are too low for atoms to randomly diffuse from one site to another. The loss of ordering is due to changes in thermal motion and not movement of ions from one site to another of the transition. Changes of crystal symmetry upon complete loss of ordering have been seen in other materials e.g. Nd_{0.5}Sr_{0.5}MnO$_3$ [28] which changes from Imma to Pnmm.

The biphasic behaviour observed is not normal for first order phase transitions. At 575 K, the two structures R-3 and P 2/n co-exist as has been observed for other materials (for example Ba$_5$RTi$_3$Nb$_7$O$_{23}$ (where R is Dy/Sm)) where two phases are seen in the X-ray diffraction pattern as a function of temperature. The same anomaly is also observed in ferroelectric materials where the ferroelectric transition occurs over a broader temperature than expected [29]. These diffuse phase transitions have been reported for ferroelectrics such as BaTiO$_3$. In such transitions the physical properties change over a broad temperature range and often occur in materials with multi-ion occupancy of the A or B atom sites (as in La$_2$CoMnO$_6$). These transitions have only been established by neutron observation and are thought to be caused by internal stress or small particle size [30]. The particle size of the powdered La$_2$CoMnO$_6$ studied has been determined to range from 0.2 to 1.5 μm by SEM which would indicate that strain is possibly present in the materials. Particle size effects for
ferroelectric materials have also been observed for Pb$_{4.95}$A$_{0.05}$Ge$_{2.5}$Ti$_{0.5}$O$_6$ which shows a broad range of particle size. However, the temperature over which the phase transformation occurs broadens as the particle size decreases [31]. In PLZT (lead zirconium titanate), the tetragonal to cubic phase transitions shows diffuse behaviour with both phases co-existing over a temperature range of 500 – 625 K [32].

Cooling leads to a reversion to the monoclinic structure with the super structure returning. The monoclinic and rhombohedral phases co-exist, however, until the temperature falls below 500 K, hence showing that the diffuse phase transition occurs over a temperature range from 500 to 625 K. It should be noted that there is a long lead in the tail of the exothermic transition observed by DSC at the same temperature for this structural transition, which could also indicate a diffuse phase transition.

We have also shown that the transition from the rhombohedral phase to the monoclinic phase (upon cooling) does not occur at a constant rate. The percentage change with decreasing temperature is less at lower temperatures. There is also significant broadening of the peaks upon cooling. This broadening suggests the presence of strain in the system and may explain the aforementioned monoclinic structure at low temperature.

### 3.3.3 Local Structure

The EXAFS local structure indicates that the Mn and Co to oxygen bond lengths (1.85 and 1.99 Å respectively) are significantly different from those suggested by powder X-ray diffraction (1.94 Å). Shannon [9] suggested that by comparing the inter-atomic
transition metal (TM) to oxygen distances of materials where the oxidation state is unknown with standards containing the same transition metals in a known oxidation state, it would be possible to infer the unknown oxidation state of the transition metal ion. This approximation is valid as long as similar bonding is found in the unknown and reference systems. For La$_2$CoMnO$_6$ it was found that the TM-O bond distances for cobalt and manganese are comparable to materials with TM-O octahedra containing Co$^{2+}$ and Mn$^{4+}$ ions (in La$_2$CoO$_4$ and CaMnO$_3$ respectively). Therefore it can be inferred that in La$_2$CoMnO$_6$ the cobalt and manganese ions are in the +2 and +4 oxidation state respectively, which is also confirmed by the bond distances provided by analysis of the neutron diffraction data. The latter values are slightly different, which is possibly because there is probably some site disorder in the neutron data and hence a slight averaging may be observed of cobalt and manganese ions.

As the lanthanide varies, it is possible to see that the TM-O bond distances for Co-O and Mn-O remain constant at 1.99 and 1.85 Å. However, using EXAFS, the calculated TM-O-TM bond angle decreases with decreasing size of the lanthanide (X for La and Y for Gd), indicating that the TM-O bond distance is electronically controlled and geometrically constrained [33] as seen in the cobaltate system [34]. As the temperature increases, there are no dramatic changes in the local structure. The small changes in TM-O bond distances can be accounted for by thermal expansion. This information is again confirmed by the neutron diffraction experiments, even when the transition from P21/n to R-3 is observed where no dramatic changes in bond lengths are measured. We can therefore infer that for all the materials in the series being studied that the cobalt and manganese cations are in the +2 and +4 oxidation state respectively which does not change at higher temperatures.
3.4 Summary

The results presented in this chapter have shown clearly that the supposedly orthorhombic or pseudo cubic structure of La$_2$CoMnO$_6$ is not correct: by the use of neutron diffraction we have found that the material posses a monoclinic structure exhibiting orthorhombic character. The transition metal ions also show a strong site preference that will help to explain some of the physical properties observed later in this thesis.

EXAFS has also allowed us to determine the oxidation states for the transition metal ions in sub-lattice. By use of XRD and EXAFS it has also been shown how the lattice parameters change upon changing the lanthanide, which we suggest is a result of the need to maintain orbital overlap between the oxygen atom and lanthanide (observed by changing TM-O-TM bond angle in the local structure).

For the first time a large structural transition has been observed in La$_2$CoMnO$_6$ where upon increasing temperature a diffuse phase transition is observed from monoclinic to rhombohedral symmetry.

3.5 References


Chapter 4

Physical Properties of the $\text{Ln}_2\text{CoMnO}_6$ Series of Materials

4.1 Introduction & Summary

This Chapter presents and discusses the physical property data collected for the $\text{Ln}_2\text{CoMnO}_6$ series of materials, where Ln = La, Pr, Nd, ‘Pm’, Sm, Eu and Gd. The temperature dependence of the physical properties measured includes magnetic susceptibility, electrical resistivity and infrared absorption. The electronic structure of the transition metal ions has also been probed by use of L-edge XANES spectroscopy.

In the first part of the Chapter, the effect of the lanthanide ionic radius upon the ferromagnetic Curie temperature is probed using a SQUID magnometer (superconducting quantum interference device). As we shall see, it is possible to infer the oxidation state of the transition metal ions present in the sublattice of the materials from their magnetic moment. The electrical resistivities of the materials as a function of lanthanide ionic radius and temperature are then described, where we observe relationships between both the resistivities and band gaps and the radius. The infrared spectra are described as a function of lanthanide and temperature and again further relationships are developed. Finally we attempt to assign oxidation states to the transition metal ions by the use of L-edge spectroscopy.

The dependence of the physical properties on the lanthanide ion size are then rationalised using the structural data described in Chapter 3, allowing structure – property relationships to be derived. Arguments to rationalise the structure property
relationships in terms of changing covalency, bond angle and orbital overlap are then described.

4.2 Results

4.2.1 Magnetic Properties

Figure 4.1 shows a plot of the magnetic moment versus temperature for La$_2$CoMnO$_6$, illustrating a decrease in magnetic moment with increasing temperature, which is typical of a ferromagnetic material (Chapter 2.5.3). The majority of the materials in the series were found to be ferromagnetic and behave in a similar manner. However, Gd$_2$CoMnO$_6$ is the exception in that the magnetic moment initially increases with temperature. However, above 25 K the material starts to behave ferromagnetically and the moment decreases in value which is interpreted later. The associated Curie temperature (the temperature at which the magnetic moment is zero), for each material is tabulated in Table 4.1 and shown graphically in Figure 4.2. As expected, the Curie temperature is proportionally dependant on the radius of the lanthanide.

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Curie Temp/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>233</td>
</tr>
<tr>
<td>Pr</td>
<td>190</td>
</tr>
<tr>
<td>Sm</td>
<td>175</td>
</tr>
<tr>
<td>Pm</td>
<td>160</td>
</tr>
<tr>
<td>Nd</td>
<td>140</td>
</tr>
<tr>
<td>Gd</td>
<td>125</td>
</tr>
</tbody>
</table>

*Table 4.1 Magnetic Curie temperature as a function of lanthanide*
Figure 4.1 Temperature dependence of magnetic moment of La$_2$CoMnO$_6$ (typical of most materials in the series)

Figure 4.2 Magnetic Curie temperature as a function of lanthanide ionic radius

Figure 4.3 shows the high temperature magnetic susceptibility of La$_2$CoMnO$_6$. The Figure is representative of all materials in the series (in the region 290 – 990 K),
where no deviations from paramagnetic behaviour are observed temperature above the Curie temperature.

![Figure 4.3 High temperature magnetic susceptibility behaviour of La$_2$CoMnO$_6$ typical of all materials in the series](image)

**4.2.2 Room Temperature Electrical Measurements**

The electrical properties of the materials in annealed pressed pellet form were measured using a 4-wire probe method (Chapter 2.6.4). The room temperature results are shown in Table 4.2.
<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Resistivity / $\Omega \text{cm}$</th>
<th>Ionic Radii/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>350</td>
<td>1.061</td>
</tr>
<tr>
<td>Pr</td>
<td>1320</td>
<td>1.013</td>
</tr>
<tr>
<td>Nd</td>
<td>3300</td>
<td>.995</td>
</tr>
<tr>
<td>Pm</td>
<td>40000</td>
<td>.979</td>
</tr>
<tr>
<td>Sm</td>
<td>533000</td>
<td>.964</td>
</tr>
<tr>
<td>Eu</td>
<td>$&gt;10^6$ *</td>
<td>.95</td>
</tr>
<tr>
<td>Gd</td>
<td>$&gt;10^6$ *</td>
<td>.938</td>
</tr>
</tbody>
</table>

Table 4.2 Resistivities of the series of materials Ln$_2$CoMnO$_6$ as a function of lanthanide

A plot of resistivity versus ionic radius of the lanthanide ion (Figure 4.4) reveals an almost linear relationship between ionic radius and resistivity. However, the resistivity of the lanthanum based material appears anomalous as has been observed in other properties of the series, for example, the magnetic Curie temperature as is discussed further later in this Chapter. The materials resistivities remain constant with changing current or on reversing the polarity of the electrodes (2.6.4).

* The Actual value of the resistance of the material was out of range of the equipment used
4.2.3 Temperature Dependence of Resistivity:

The temperature dependence of the resistivity for La₂CoMnO₆ is shown in Figure 4.5; an Arrhenius plot of resistivity is also shown, allowing a band gap to be obtained. Below 400 K, there is a slight negative slope that dramatically increases in gradient at ca. 400 K. This effect is only observed for the lanthanum-based material and is reversible, reproducible and repeatable even when changing the batch of material. A typical plot for the other materials studied in the series Ln₂CoMnO₆ is shown in Figure 4.6. Again, the resistivity is current independent and no effect is seen upon changing electrode direction, indicating that the materials are ohmic. The decrease in the resistivity with increasing temperature indicates that the materials are semiconducting. The limited temperature range of the measurements is due to the nature of the conducting glue used to attach the electrodes to the sample, which is known to fail
at 500 K by melting. Therefore measurements were not performed close to this temperature to prevent contamination of the cryostat.

Figure 4.5 Temperature dependence of resistivity of La$_2$CoMnO$_6$

The band gaps obtained are tabulated in Table 4.3 and plotted in Figure 4.8 as a function of lanthanide ionic radius; the data can be fitted by a polynomial relationship.
Figure 4.6 Temperature dependence of the resistivity of $\text{Pr}_2\text{CoMnO}_6$ which is typical of all materials in the series except $\text{La}_2\text{CoMnO}_6$. 
### Table 4.3 Band gap as a function of lanthanide

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Band gap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.75</td>
</tr>
<tr>
<td>Pr</td>
<td>0.97</td>
</tr>
<tr>
<td>Sm</td>
<td>1.15</td>
</tr>
<tr>
<td>Pm</td>
<td>1.37</td>
</tr>
<tr>
<td>Nd</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*Figure 4.7 Band gap as a function of lanthanide ionic radius*
4.2.4 Room Temperature Infrared Spectra

The room temperature infrared spectrum in the spectral range 50 – 4000 cm\(^{-1}\) for La\(_2\)CoMnO\(_6\) (Figure 4.8) contains four main peaks. The inset shows in greater detail the profile of the four main modes of vibration. These have been assigned as:-

*Figure 4.8 Infrared absorption spectrum for La\(_2\)CoMnO\(_6\) (typical of all materials in the series)*
\[ v_{\text{M-O}} \] 606cm\(^{-1}\), \[ \delta_{\text{O-M-O}} \] 416cm\(^{-1}\), \[ \delta_{\text{O-M-O}} \] 290cm\(^{-1}\), \[ v_{\text{Ln}} \] 182cm\(^{-1}\)

Where \( v \) is a stretching mode and \( \delta \) is a deformation mode. However, this assignment is tentative due to the possibility of mixing occurring between the stretching and deformation modes.

The complexity of the spectroscopic profile for each of the modes increases with decreasing lanthanide ion size, as shown in Figures 4.9. The wavenumbers of these modes and their integrated intensities are tabulated in Table 4.4. All of the materials with the general formula Ln\(_2\)CoMnO\(_6\) (Ln = La, Pr, Nd, (Pm), Sm, Eu and Gd) have these four bands present in their infrared spectrum. We also note a linear relationship between the normalised integrated band intensity for the TM-O stretch and the ionic radius of the lanthanide ion as shown in Figure 4.12, which decreases in intensity upon decreasing size. Figure 4.13 shows the relationship between the wavenumber of the deformation mode, which decreases in value, with decreasing size of the lanthanide ion.
Figure 4.9 Changes in spectroscopic profile with changing lanthanide (the smaller the lanthanide the more distorted the vibrational modes.

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>$\nu/cm^1$</th>
<th>$\delta/cm^1$</th>
<th>$\delta/cm^1$</th>
<th>$\nu/cm^1$</th>
<th>Integrated Band intensity of stretch mode</th>
<th>Integrated Band intensity of deformation mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>606</td>
<td>419</td>
<td>290</td>
<td>182</td>
<td>58.71</td>
<td>21.764</td>
</tr>
<tr>
<td>Pr</td>
<td>598</td>
<td>446</td>
<td>274</td>
<td>178</td>
<td>57.542</td>
<td>25.111</td>
</tr>
<tr>
<td>Nd</td>
<td>596</td>
<td>451</td>
<td>271</td>
<td>178</td>
<td>56.794</td>
<td>27.908</td>
</tr>
<tr>
<td>(Pm)</td>
<td>593</td>
<td>455</td>
<td>276</td>
<td>180</td>
<td>53.155</td>
<td>27.317</td>
</tr>
<tr>
<td>Sm</td>
<td>593</td>
<td>458</td>
<td>277</td>
<td>181</td>
<td>51.27</td>
<td>21.996</td>
</tr>
<tr>
<td>Eu</td>
<td>591</td>
<td>460</td>
<td>274</td>
<td>171</td>
<td>50.942</td>
<td>25.841</td>
</tr>
<tr>
<td>Gd</td>
<td>590</td>
<td>464</td>
<td>276</td>
<td>182</td>
<td>50.341</td>
<td>25.996</td>
</tr>
</tbody>
</table>

Table 4.4 Changes in the infrared spectra as a function of lanthanide
4.2.5 Temperature Dependence of Infrared Spectra

The infrared spectra obtained between 15 and 780 K revealed some interesting changes in the transition metal oxygen (TM-O) stretching frequencies, band intensities and baseline ordinate positions.

The relative integrated band intensities of the transition metal oxygen bond stretch shows no major discontinuities with increasing temperature (Figure 4.11), except for a small discontinuity in the gradient of the graph. The change occurs at the same temperature as larger changes are observed in other features of the spectra. The wavenumber of the TM-O stretch initially decreases with increasing temperature as expected but then becomes constant.
Figure 4.11 Changes in Infrared spectrum as a function of temperature
The profile of the TM-O bond deformation mode also changes with increasing temperature. At low temperatures, the profile appears to be complex due to distortion of the octahedra around the transition metal. However, as the temperature increases the splitting decreases and the spectroscopic profile decreases in complexity (Figure 4.12.

![Figure 4.12 Changes in infrared spectral profile upon increasing temperature](image)

Significant changes are observed when the relative absorption of the baseline ordinate is measured at arbitrary points in the region from 1000 cm\(^{-1}\) to 4000 cm\(^{-1}\). At low temperatures, the baseline remains constant at 1000 cm\(^{-1}\) and 3000 cm\(^{-1}\). However, above a specific temperature, the baseline ordinate increases linearly with temperature. The region of the infrared spectra that is sensitive to changes in temperature was found to change with the size of lanthanide ion. For example, the lanthanum based material is very temperature sensitive at ~1000 cm\(^{-1}\) and is
insensitive 3000 cm\(^{-1}\); whereas, for the neodymium material, the 3000 cm\(^{-1}\) region is very temperature sensitive whilst only small changes are observed at 1000 cm\(^{-1}\) (Figure 4.13).

**Figure 4.13 Temperature dependence of infrared spectrum of \(\text{Nd}_2\text{CoMnO}_6\)**

### 4.2.6 Electrical and Infrared Relationships

A relationship between the infrared vibrational spectrum and the electrical properties of materials has been proposed elsewhere [1,2]. Figure 4.14 shows the relationship between resistivity and the normalised infrared integrated intensity of the transition metal – oxygen-stretching mode. Data are not shown for the europium and gadolinium based materials, as their resistivities were too high to be measured using the available equipment; although it would be possible to predict the value of their
resistivity by extrapolation of the curve. It can be seen that the relationship is almost linear and again only the lanthanum-based material shows anomalous behaviour. The degree of ramping (gradient) in the baseline ordinate (in the spectral region $1000 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$) also decreases with ionic radius.

Figure 4.14 Correlation between integrated band intensity of TM-O stretch as a function of resistivity

Upon heating $\text{La}_2\text{CoMnO}_6$, a dramatic change in the band gap (see section 4.2.3) is observed which is also reflected in the measurements made at specific points on the base line ordinate of the infrared spectrum. As the band gap changes, the infrared absorption starts to increase dramatically at the same temperature as shown in Figure 4.15. Changes in the integrated band intensity of the TM-O stretch are also observed at the same temperature where changes are observed in the resistivity at 400K.
2.4 H

Absorption Resistivity

Figure 4.15 Change in IR absorption and electrical resistivity as a function of temperature

4.2.7 L-edge Spectroscopy

The L-edge XANES (X-ray absorption near edge structure) for the cobalt and manganese ions of La$_2$CoMnO$_6$ are shown in Figure 4.16 and 4.17 respectively.

Also shown in Figure 4.16 and 4.17 are the edges of materials in which the oxidation state of the transition ion is known. It is clear that the spectroscopic profile and peak position is sensitive to the oxidation state of the transition metal ion being probed. By looking at materials with known oxidation states and comparing the spectroscopic profile and peak position to materials with unknown oxidation states it is possible to determine the oxidation states of the unknown transition metal ions, assuming that the bonding is similar in nature (e.g. degree of covalency / ionicity). The cobalt ion in La$_2$CoMnO$_6$ shows similar features in its L-edge absorption structure to the cobalt ion in CoO suggesting that the Co is in the +2 oxidation state in La$_2$CoMnO$_6$. The manganese ion in La$_2$CoMnO$_6$ shows spectral profile similar to that of the manganese
ion in MnO$_2$ and CaMnO$_3$ suggesting that the Mn ion in La$_2$CoMnO$_6$ is in the +4 oxidation state.

Figure 4.16 Co L-edge XANES

Figure 4.17 Mn L-edge XANES
4.3 Discussion

4.3.1 Introduction

In order to understand the changes in the physical properties across the series of the lanthanide materials, it is important to understand the effects of the ionic radius on the structure. It is observed that there are changes in the TM-O-TM bond angle, and consequently the orbital overlap between the TM-O-TM sublattice and the lanthanide ion.

In the previous Chapter, the relationship between the lanthanide ionic radius and the unit cell parameters was discussed. The overall unit cell volume decreases with decreasing lanthanide ionic radius but the TM-O distance remains unchanged leading to a decrease in the TM-O-TM bond angle in order to accommodate the TM-O sublattice. The bond angle must change in order to maintain the orbital overlap between the oxygen atoms of the TM-O sublattice and the lanthanide ion. Consequently, the bond angle affects the degree of orbital overlap within the TM-O-TM sublattice where there is competition between the lanthanide and the transition metals for σ bonding with the oxygen p orbitals [3] resulting in changes of the properties of the material, such as resistivity. This structural argument can now be used to understand the changes seen in the physical properties of the materials with the lanthanide ion.

4.3.2 Magnetism
The oxidation state of the transition metals in the materials can be determined from
the ordered magnetic moment. La$_2$CoMnO$_6$ is the only material in the series La,
Pr...Gd in which the lanthanide ion does not possess a magnetic moment, as its
electronic configuration in the +3 oxidation state is that of the noble gas configuration
[Xe]. Therefore, this material most readily provides information regarding the
oxidation states and magnetic structures of the TM-O sublattice.

The Ln$_2$CoMnO$_6$ materials in this study are ferromagnetic. Consequently the
transition metal and rare earth (not La) ions moments disorder with increasing
temperature. Therefore, it is not possible to determine whether the cobalt ion
undergoes a spin state transition as observed in one of the parent materials LaCoO$_3$
[4].

The magnetic moment of La$_2$CoMnO$_6$ is 3.6 J T$^{-1}$ mol$^{-1}$ at 4 K, suggesting the
presence of three unpaired electrons. Using Hund's rule which states that the ground
state of an electronic configuration is that possessing the greatest multiplicity [5], we
can infer that for the cobalt ion to possess three unpaired electrons the electronic
configuration must be d$^7$ (high spin). A configuration of high spin d$^7$ in an octahedral
field indicates that at low temperatures the cobalt ion possesses a formal oxidation
state of +2. Thus in the temperature range studied the +3 low spin state required for a
spin state population exchange to occur is not present [6].

\[ \mu = 2\sqrt{s(s+1)} \]

This has been obtained using the spin only equation $\mu = 2\sqrt{s(s+1)}$. Co$^{3+} \mu_{\text{eff}} = 4.89$ and Co$^{2+} \mu_{\text{eff}} = 3.87$
La$_2$CoO$_4$ also shows high spin state Co$^{2+}$ with a moment of 3.78 $\mu_B$ [7]. The electronic configuration is $t_{2g}^5 e_g^2$ where there are three unpaired electrons. Therefore, it is possible to infer the electronic configuration of the cobalt at 4 K to be the same in La$_2$CoMnO$_6$. It can also be inferred also that the manganese ion possesses the formal oxidation state $+4$ in order to maintain charge balance. The moment of Mn$^{4+}$ in the high spin state would also be 3.78 $\mu_B$ ($t_{2g}^3 e_g^0$). CaMnO$_3$ has Mn in the $+4$ high spin oxidation state with three unpaired electrons with the configuration $t_{2g}^3$ with a moment also of 3.78 $\mu_B$ [8].

Assuming a combination of Co$^{2+}$ and Mn$^{4+}$, the overall ordered magnetic moment of La$_2$CoMnO$_6$ is lower than predicted for the spin only contribution (a predicted value of 3.78 $\mu_B$). The difference between measured and predicted magnetic moment may be due to clustering of similar ions together [9], or of domain wall formation within the superlattice [10]. The possibility of clustering may be inferred from the degree of ordering of the transition metal ion at room temperature, which was calculated to be 88% by Rietveld analysis of the neutron diffraction patterns, indicating the presence of ca. 12% Mn-O-Mn or Co-O-Co.

The ferromagnetic nature of the materials can also be confirmed by use of the rules described by Goodenough [11] as described in Chapter 1 (section 1.3.5). Goodenough states that ferromagnetic behaviour dominates when one transition metal ion has partially filled $e_g$ orbitals and the other has empty $e_g$ orbitals. In La$_2$CoMnO$_6$, cobalt has partially filled $e_g$ orbitals whilst the manganese ion has empty $e_g$ orbitals. Furthermore, the magnetic interactions and associated ordering reduce the metallicity of the system as described by Goodenough [12].
A direct correlation between the ionic radius of the lanthanide ion and the Curie temperature is observed resulting from changes in the superexchange angle (which was also reported for the orthoferrites LnFeO$_3$ (Ln = lanthanide) [13]) where the orbital overlap through which the exchange occurs decreases with lanthanide radius. The degree of hopping of the electrons is proportional to the bandwidth [14] and hence the stabilisation by superexchange. This hopping occurs through the two transition metal oxides indirectly through an intervening oxygen atom occurring in a linear fashion. The coupling occurs from the occupied $e_g$ orbital of the cobalt through the oxygen to the unoccupied $e_g$ orbital of the manganese ions – as seen in LaMnO$_3$ [14]. Some spin up density will therefore be transferred into an empty $e_g$ orbital of the neighbouring manganese atom. It is possible to consider this system in the same manner as LaMnO$_3$ as there are also alternating long and short TM-O bonds along the cubic cell axis. Therefore, as the angle of exchange decreases from 180° to a minimum the extent of exchange also decreases. The superexchange angle or orbital overlap is determined by the TM-O-TM bond angle that reduces as the size of the lanthanide decreases.

At higher temperatures no changes were observed in the temperature dependence of the magnetic susceptibility at the temperature driven phase transitions, manifested by structural and electrical changes, indicating that there are no changes in the crystal field occurs as a result of the transitions.

The gadolinium-based material is particularly interesting. The initial moment at low temperatures increases with temperature, which is not normal ferromagnetic
behaviour. However, it quickly follows ferromagnetic behaviour, which is suggested to be due to the gadolinium sublattice contribution to the f-d exchange interaction [15] which modifies the magnetic 3d sublattice and gives negative f-d superexchange energies and a large anisotropy. This effect is due to the magnetic moment of the gadolinium sublattice opposing the 3d lattice due to a negative molecular field from the Co$^{2+}$ and Mn$^{4+}$, which is known as metamagnetism.

### 4.3.3 Electrical Resistivity

The electrical resistivity of perovskites [16] is primarily governed by the TM-O sublattice though which the conduction and valence bands are formed via orbital overlap along the distorted cube edge. The magnitude of the orbital overlap is determined by geometrical factors i.e. the bond angle of the TM-O-TM bond. The resistivity is also determined by the nature of these ions and by defects within the system. For example, LaMnO$_3$ has a high resistivity ($\rho \sim 10^4$ $\Omega$ cm at 290 K) whilst LaMnO$_{3.15}$ has a resistivity of 800 $\Omega$ cm at 290 K [17]. Therefore, with decreasing orbital overlap there is an increase in resistivity as the conduction and valence band become further separated in energy.

It has also been suggested, that as the acidity (tendency to withdraw electrons [18]) of the lanthanide decreases, the TM-O bond covalency increases [19,20]. As the covalency decreases, the electrons become more localised (and can be described by the localized-electron model) [21] and they have a lesser tendency to hop [22]. The localisation of electrons means that the bandwidth is lower, and the band gap and the resistivity increases as has been shown in this system. Decreases in covalency result
in a decrease of the degree of orbital overlap resulting in narrower bands and hence lower electron mobility. There is consequently leading to a decrease in conductivity and possibly a larger band gap (vide infra). The Lewis acidity of the lanthanide increases as the charge density on the lanthanide increases (the same charge is concentrated on a smaller area with increasing acidity).

With increasing covalency (larger orbital mixing) the carriers become itinerant and the electrical conduction increases becoming metal like. These covalency effects have also been used to describe changes seen in the TlLnX₂ series where, as the Ln-X bond decreases in length, the lanthanide decreases in ionic radius and hence the covalency of the Tl-X bond increases whilst for the Ln-X bond the covalency decreases (X= O or halide) [23].

The electrical resistivity measurements have only been performed using pressed powders (at 10 tonne), and the values of the resistivities obtained therefore can only be taken as an indication of the true resistivity of the material (a single crystal is required for definitive electrical measurements). Pressing of the powders may introduce voids, which will affect the resistivity and there may also be inherent grain boundary effects that will alter the real value of the resistivity. The resistivity values may also be altered by the addition of other temperature dependent carrier production effects [24].

The temperature dependence of the electrical properties indicates that the materials are all semiconducting (the resistivity decreasing with increasing temperature). There is a correlation between the ionic radius and the measured band gap, which has the same reason as was discussed for changes in the room temperature resistance.
measurements. The band gap increases due to decreasing orbital overlap [25], which increases the separation between the valence and conduction bands.

We found that with the apparent transition in the resistivity of La$_2$CoMnO$_6$ there is an associated structural transition (Chapter 3). The temperature dependent XRD experiments where the unit cell volume increases with temperature, show a discontinuity as the electrical transition is passed. Changes in lattice parameters at the same temperature at which electrical transitions occur have also been seen in other materials, for example in the nickelates NdNiO$_3$ and SmNiO$_3$ [26]. Neutron diffraction data provided further insight into the nature of this transition. Below the temperature where the resistivity changes occur, the charges appear to be ordered and have a site preference of ca. 90%. As the temperature increases above 400 K, this site preference decreases to ca. 80% and the resistivity drops. Charge ordering can create an additional potential that impedes the flow of carriers [27]. Indeed, such ordering generally localises electrons in a material rendering it insulating or semi-conducting because when charges are localised, electrons cannot readily hop from one cation site to another [28]. Thus, effectively two band gaps exist, one for the charge ordered state and the second for the region with decreasing charge ordering, which has been seen in other charge ordered materials e.g. Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ [29].

### 4.3.4 Infrared Spectroscopy

The number and nature of bands observed in the vibrational spectrum of a molecule depends upon the number of atoms present and the symmetry of the unit cell [30].
Thus it is possible to infer, qualitative local structural data from the spectroscopic profile of the bands in the spectra [31] (as described in Chapter 1.3.6).

The materials spectroscopic profile becomes increasingly complex as the radius of the lanthanide decreases, since the unit cell of the materials become increasingly distorted from an idealised cubic structure [32] leading to the loss of the three fold degeneracy around the transition metal. There is also a correlation between the wavenumber of the deformation mode and the lanthanide ionic radius. The strength of the TM-O-TM bond must therefore be changing as the relationship between the strength of bonds and the frequency is defined by:

\[ \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

where the frequency is determined by the effective mass (\(\mu\)) and bond strength (\(k\)).

The bond strength decreases as the lanthanide radius decreases due to changes in bond covalency as discussed earlier when describing the changes in resistivity. The charge density increases as the lanthanide decreases in size, which means that there is greater orbital overlap with the oxygen (\(\sigma O-\sigma Ln\)), whereas the TM-O (\(\sigma TM-\sigma O\)) orbital overlap decreases owing to a redistribution of electrons. This change in electron density results in a decrease of the strength of the TM-O bond and changes the force constant and hence the wavenumber of the stretching mode decreases. The increase in the lanthanide and oxygen overlap means more energy is required to deform the bridge and hence the wavenumber increases for this mode [33].

As the temperature increases, the lattice will expand and hence the interatomic distances also increase. Reducing the overlap of the bonding orbitals weakens the
bonding and hence the force constants decrease. As the vibrational modes frequency is proportional to the force constant of a bond, the frequency decreases with increasing temperature. There is an apparent reduction of the change in frequency of the mode as the temperature increases in the same temperature region as the crystal structure changes from monoclinic to rhombohedral.

The band intensity is proportional to the sum of the squares of the electric dipole moment in each direction.

Thus, as the temperature increases, the bond length increases and hence the dipole moment increases, hence the intensity decreases [34]. However, this equation is too simplistic a model for solids and there appear to be no rules governing the band intensities of materials as a function of temperature [35].

We find that the frequency of the metal-oxygen bond stretch decreases as the temperature increases as expected and shows no discontinuities and hence no apparent phase transitions. The integrated band intensities also show a generally trend of decrease and again follow the above simple rules. Indeed, only the lanthanum based material shows a small discontinuity and hence a possible indication as to a phase transition.

Interestingly, when the base line ordinate is investigated as a function of temperature it appears to be insensitive at low temperatures. At a specific temperature, the absorption increases. The background absorption is either due to the reflection or absorption of the infrared radiation by the free carriers within the system [36] and
becomes a good indication as to changes in the free carrier mobility as observed in the electrical measurements. Tests have also been undertaken using KBr as a function of temperature, and no significant changes were observed. Hence the changes seen are due to our materials.

The spectroscopic profile of the deformation mode decreases in complexity as the temperature is increased, indicating that the local structure is increasing in symmetry, the thermal vibration of the molecule is increasing, there is an increase in disorder or a combination of the above explanations.

The integrated intensity of the TM-O stretch and the resistivity relationship is due to changes in covalency and hence dipole moment as described previously. The bonds become stronger or more covalent upon decreasing the radius of the lanthanides and hence changing the resistivity due to the structure property relationships. Many of these properties are tied together and many correlations can be seen.

The degree of background ramping is also an indicator to the electrical resistivity of the material [37]. The background above 1000 cm\(^{-1}\) to 4000 cm\(^{-1}\) is due to the concentration of free carriers that are present in the material at a specific temperature. As the size of the lanthanide ion decreases the degree of ramping in the background decreases and indicates the materials resistivities are decreasing as are the concentration of free carriers. The change in resistivity with lanthanide ion is borne out in practice by measuring the resistivities at room temperature. Changes in resistivity suggest that the number, mass or mobility of free carriers are decreasing with decreasing size of lanthanide ion and confirmed by the resistivity. Upon
investigating the infrared background as a function of temperature (in the spectral region 1000-3000 cm\(^{-1}\)) the resistivity decreases at the same temperature as the baseline absorption increases for La\(_2\)CoMnO\(_6\). The baseline absorption therefore indicates a change in the number of carriers, mobility or mass and hence when a change in band gap is observed changes in the background absorption in the infrared spectrum is seen. An increase in the infrared reflectivity or absorption occurs as a result of increased number of free electrons, which can reflect or absorb the infrared radiation.

4.3.5 L-edge XANES

It has been shown previously by various workers \[38,39\] that the L-edge spectrum profile is sensitive to the oxidation state of the ions and the geometry surrounding that ion. The transition in of the L-edge is from the p orbitals to the empty d orbitals. The oxidation state of the transition metal ions is controlled by the d orbitals and the electrons excited will jump into the lowest energy d orbitals not occupied. The occupation of the orbitals is also geometry determined. In this work it is clear from the spectra obtained for the material La\(_2\)CoMnO\(_6\) that they posses similar spectra to materials containing the transition metal ions in the oxidation states Co\(^{\text{3+}}\) and Mn\(^{\text{4+}}\), which has also been confirmed by the magnetic moment, neutron diffraction data and the local structure. This technique becomes more useful in assigning an oxidation state for the other system presented later in this thesis. We are therefore able to confirm that the oxidation states of the transition metal ions in the materials La\(_2\)CoMnO\(_6\) are Co\(^{\text{3+}}\) and Mn\(^{\text{4+}}\). This result is also true of the other materials in the
series upon changing lanthanide ion, the spectroscopic profile remains the same despite changing the lanthanide.

4.4 Summary

In this Chapter we have shown how the physical properties of the series of materials can be understood in terms of the structural data measured previously (Chapter 3). Changes observed in physical properties upon changing lanthanide have also been interpreted using arguments based upon changing orbital overlap and bond covalency.

4.5 References:


Chapter 5

Structural Studies of the Ln$_2$NiMnO$_6$ System

5.1 Introduction & Summary

This Chapter presents and discusses the structural data collected for the Ln$_2$NiMnO$_6$ series of materials, where Ln=La, Pr, Nd, ‘Pm’*, Sm, Eu and Gd. The structural information has been obtained by the use of powder X-ray diffraction, coherent neutron diffraction scattering and extended X-ray absorption fine structure spectroscopy (EXAFS).

In the first part of this Chapter, the effects of lanthanide ionic radius on the unit cell parameters and crystal symmetry are reported from data collected using standard X-ray powder diffraction techniques. A determination of the temperature dependence of the structural properties has also been undertaken with a concerted effort on La$_2$NiMnO$_6$. A multi technique study was carried out on La$_2$NiMnO$_6$ because of discontinuities observed in the lattice parameters with increasing temperature and a large exothermic transition, which is observed in the thermal analysis which was not observed in other materials in this series. A synchrotron X-ray study was also carried out as discussed in chapter 2 this provides higher quality data [1] than that obtained by standard laboratory X-ray powder techniques allowing the accurate determination of atomic positions in an orthorhombic setting. More detailed structural information
was obtained using neutron diffraction which showed there is a significant site ordering and the true structure is monoclinic. A first order phase transition is observed on heating, where the monoclinic structure transforms to a rhombohedral structure. In the last part of this Chapter, the local structure is investigated using EXAFS. The local structural data provides evidence for possible charge disproportionation and allows us to infer a possible oxidation state for the transition metal ions in the TM-O sublattice (as seen in chapter 3).

In Chapter 6, it will be shown how this structural information can aid in the development of structure – property relationships [2] as discussed in previous Chapters. The final Chapter draws conclusions from both sets of materials studied in this thesis.

5.2 Results

5.2.1 Room Temperature X-ray Diffraction Study

The materials Ln$_2$NiMnO$_6$ all have diffraction patterns which show systematic absences consistent with the Pnma space group. The X-ray diffraction pattern of the La$_2$NiMnO$_6$ obtained from a laboratory based X-ray diffractometer is shown in Figure 5.1 can be indexed to an orthorhombic structure. The dependence of the unit cell axial lengths and unit cell volume for the series of materials as a function of lanthanide ionic radius are reported in Table 5.1 and are shown graphically in Figure 5.2. The overall cell volume decreases linearly with the reduction in lanthanide ionic radius.

* Pm is radioactive and therefore dangerous to use — to this end a mixture of Nd and Sm are used for
However, upon examination of the lattice parameters it was found that the b and c axial lengths decrease linearly whilst the a axial length increases linearly with decreasing lanthanide radius.

![Graph](image)

**Figure 5.1** Diffraction pattern of Nd$_2$NiMnO$_6$ typical of all materials in the series

![Graph](image)

**Figure 5.2** Changes in lattice parameters as a function of lanthanide ionic radius

which the average ionic radius is that of Pm
Rietveld refinement of La$_2$NiMnO$_6$ (in Pnma) was possible using high resolution synchrotron X-ray diffraction (only La$_2$NiMnO$_6$ was measured due to time constraints). The experimental, refined and difference plots from the Rietveld analysis are shown in Figure 5.4. The atom positions, cell parameters and selected distances are shown in Table 5.2. For orthorhombic LnTMO$_3$ (in Pnma) the only atomic positions that can be occupied by the transition metals are the 2c (mirror positions). It
is only possible therefore, to determine an averaged TM-O bond length for the nickel and manganese ions of 1.95 Å. Reducing the symmetry (as previously discussed Chapter 3.2.1) to monoclinic allows for the transition metal ions to occupy separate sites. It would then in principle be possible to determine unique Ni-O and Mn-O bond lengths. When the diffraction patterns were refined using the monoclinic space group P21/n, which is a sub-group of Pnma [3], it was only possible to obtain positions for the rare earth ions to any degree of accuracy and not the oxygen atoms. It was also not possible to determine if distinct sites for the transition metal ions existed. As changing the transition metal to the alternative site had no effect on the quality of the refinement.

![Figure 5.4 Results of Rietveld analysis of La$_2$NiMnO$_6$ of a high resolution powder diffraction pattern](image)

*Figure 5.4 Results of Rietveld analysis of La$_2$NiMnO$_6$ of a high resolution powder diffraction pattern*
Table 5.2 Results of Rietveld refinement of $La_2NiMnO_6$ and $Nd_2NiMnO_6$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$La_2NiMnO_6$</th>
<th>$Nd_2NiMnO_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/Å</td>
<td>5.42645(13)</td>
<td>5.525313(12)</td>
</tr>
<tr>
<td>b/Å</td>
<td>7.77823(14)</td>
<td>7.68912(16)</td>
</tr>
<tr>
<td>c/Å</td>
<td>5.51845(10)</td>
<td>5.423769(20)</td>
</tr>
<tr>
<td>La x</td>
<td>-0.04867(7)</td>
<td>-0.04833(6)</td>
</tr>
<tr>
<td>Y</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Z</td>
<td>0.005846(12)</td>
<td>0.00644(16)</td>
</tr>
<tr>
<td>UISO</td>
<td>0.006862(16)</td>
<td>0.00725(21)</td>
</tr>
<tr>
<td>Ni/Mn x</td>
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<td>0</td>
</tr>
<tr>
<td>y</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>UISO</td>
<td>0.00230(16)</td>
<td>0.0045(12)</td>
</tr>
<tr>
<td>O x</td>
<td>0.5068(8)</td>
<td>0.50871(11)</td>
</tr>
<tr>
<td>Y</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Z</td>
<td>-0.0901(8)</td>
<td>-0.08903(12)</td>
</tr>
<tr>
<td>UISO</td>
<td>0.00860(15)</td>
<td>0.00943(23)</td>
</tr>
<tr>
<td>O x</td>
<td>0.74583(18)</td>
<td>0.78986(21)</td>
</tr>
<tr>
<td>y</td>
<td>-0.4913(8)</td>
<td>-0.45843(14)</td>
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<tr>
<td>z</td>
<td>-0.75981(11)</td>
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<tr>
<td>UISO</td>
<td>0.00865(17)</td>
<td>0.00943(12)</td>
</tr>
<tr>
<td>$\chi^2$</td>
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<td>5.476</td>
</tr>
<tr>
<td>wR_p</td>
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<td>7.98%</td>
</tr>
<tr>
<td>R_p</td>
<td>6.48%</td>
<td>6.53%</td>
</tr>
</tbody>
</table>

Table 5.2 Results of Rietveld refinement of $La_2NiMnO_6$ and $Nd_2NiMnO_6$

5.2.2 Variable Temperature X-ray Diffraction

$La_2NiMnO_6$ was found to be unique (in this series) in that it undergoes a large exothermic transition at 675 K as observed by differential scanning calorimetry (DSC). The other materials in the series did not show any thermal transitions in the DSC within the temperature range studied. For this reason the temperature dependence of the X-ray diffraction pattern was measured a converted X-ray diffractometer.

The temperature dependent behaviour of the unit cell axial lengths $a$, $b$ and $c$ for $La_2NiMnO_6$ are shown in Figure 5.5. The cell volume (Figure 5.5) shows three
distinct regions; 270-400 K, 400-670 K and 670-1000 K. However, when the axial lengths are examined separately, it is clear they do not all exhibit the same temperature dependencies in that there is not a 1:1:1 relationship. Whereas a & b show a single discontinuity at 670 K, c shows discontinuities at 470 and 670 K. Interestingly, the c-axial length also decreases at 670 K. The same features are not observed for the temperature dependence of the unit cell axial lengths of the other materials in the series: Figure 5.4 shows a linear increase in the b and c lattice parameters and a slight decrease for the a axial length (Figure 5.5b). The overall cell volume of the materials Ln2NiMnO6 (Ln≠La) increases linearly with increasing temperature but show no discontinuities as exhibited by the lanthanum containing material.

![Figure 5.4 Changes in lattice parameters and unit cell volume of La2NiMnO6 as a function of temperature](image)

*Figure 5.5 Changes in lattice parameters and unit cell volume of La2NiMnO6 as a function of temperature*
Figure 5.6 shows the temperature dependence of the X-ray diffraction patterns of La$_2$NiMnO$_6$. Temperature dependent changes are observed in the peak intensities of the intense 121 diffraction peak for La$_2$NiMnO$_6$ but not seen for other materials in this series. The integrated peak intensity of the 121 diffraction peak is shown in Figure 5.7, and discontinuities are observed for the lanthanum based material allowing us to follow indirectly the thermal motion and disorder of the atoms.
Figure 5.7 Changes in integrated peak intensity of the 121 diffraction peak as a function of temperature of $\text{La}_2\text{NiMnO}_6$.

5.2.3 Neutron Diffraction Study of $\text{La}_2\text{NiMnO}_6$

X-ray diffraction was unable to provide a detailed structure in terms of atomic positions or charge ordering, or to explain the processes occurring when discontinuities were observed in the lattice parameters, hence, a neutron diffraction study was undertaken. Due to time constraints measurements were only carried out on the most interesting material $\text{La}_2\text{NiMnO}_6$. To understand fully the nature of the crystal structure and how it changes with temperature, accurate lanthanide, transition metal and especially oxygen atomic positions are required. Neutron diffraction also allows us to determine the degree of B-site ordering (if any) present in the material as the scattering lengths of nickel and manganese are dramatically different.
The room temperature (ca. 298 K) neutron diffraction pattern of La$_2$NiMnO$_6$ is shown in Figure 5.8, and clearly shows a splitting of the diffraction peak at 114 ms, which is inconsistent with Pnma. This splitting was not observed by the X-ray diffraction methods used previously. The pattern was indexed by use of the systematic absences to the monoclinic space group P2$_1$/n (14) [4], and therefore possesses a lower symmetry than suggested by X-ray diffraction. In order to obtain accurate atomic positions for La$_2$NiMnO$_6$, the theoretical work of Woodward [5] has been used to provide a starting model for the atom positions input to the Rietveld Profile Analysis of the diffraction pattern; we recall that this work provides theoretical initial rare earth, transition metal and oxygen positions for perovskite materials with an indexed diffraction pattern. The experimental, refined and difference profiles for the Rietveld refinement are shown in Figure 5.8. In Table 5.3 the lattice parameters, atom positions, thermal parameters and weighted R-values, selected distances are listed in Table 5.4. By refining the fractional occupancies of each of the transition metal sites, it was clear that each transition metal prefers the separate atomic sites 2c (Mn) and 2d (Ni) which are found to be 85% ordered. Exchanging the transition metal positions (Mn to 2d and Ni to 2c) resulted in a poorer quality refinement. Furthermore, when the occupancies were refined, it was found that they reverted to the ordered structure (2c (Mn) and 2d (Ni)) which strongly suggests the presence of B-site ordering.
Figure 5.8 Neutron diffraction pattern of \( \text{La}_2\text{NiMnO}_6 \) at room temperature and associated Rietveld analysis (the black line is the observed diffraction pattern, red the theoretical fit and the green line the residual of the Rietveld analysis).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>295 K</th>
<th>675 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>P2₁/n</td>
<td>R-3</td>
</tr>
<tr>
<td>A</td>
<td>5.467038 (34)</td>
<td>5.47456 (16)</td>
</tr>
<tr>
<td>B</td>
<td>5.510480 (31)</td>
<td>5.47456 (16)</td>
</tr>
<tr>
<td>C</td>
<td>7.751242 (36)</td>
<td>5.47456 (16)</td>
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<td>α</td>
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<td>90</td>
<td>60.6712(12)</td>
</tr>
<tr>
<td>La x</td>
<td>-0.2142 (11)</td>
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</tr>
<tr>
<td>y</td>
<td>-0.00522 (13)</td>
<td>0.24964 (21)</td>
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<tr>
<td>z</td>
<td>0.26290 (7)</td>
<td>0.24964 (21)</td>
</tr>
<tr>
<td>UISO</td>
<td>0.00451 (12)</td>
<td>0.01198 (17)</td>
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<tr>
<td>Ni x</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>y</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>z</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>0.01859 (13)</td>
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<tr>
<td>Mn x</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>y</td>
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<td>0.5</td>
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<tr>
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<td>0.5</td>
</tr>
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<td>y</td>
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<td>0.69173 (5)</td>
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<td>z</td>
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<td>0.02025</td>
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<tr>
<td>y</td>
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<td>z</td>
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<tr>
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<td>-</td>
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<td>y</td>
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<td>-</td>
</tr>
<tr>
<td>z</td>
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</tr>
<tr>
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<td>-</td>
</tr>
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<td>85%</td>
</tr>
<tr>
<td>Rp</td>
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<td>4.92%</td>
</tr>
<tr>
<td>wRp</td>
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<td>6.28%</td>
</tr>
<tr>
<td>χ²</td>
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<td>17.31</td>
</tr>
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</table>

*Table 5.3 Results of Rietveld Refinement of neutron diffraction data for La₂NiMnO₆*
### Table 5.4 Selected bond distances for La$_2$NiMnO$_6$ at 300 & 675 K

<table>
<thead>
<tr>
<th>Temp / K</th>
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<th>TM-O/Å</th>
<th>O-TM-O/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>Ni</td>
<td>2.011</td>
<td>179.97</td>
</tr>
<tr>
<td>295</td>
<td>Ni</td>
<td>1.976</td>
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</tr>
<tr>
<td>295</td>
<td>Ni</td>
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<td>295</td>
<td>Mn</td>
<td>1.908</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>TM</th>
<th>TM-O/Å</th>
<th>O-TM-O/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>Ni</td>
<td>2.0074</td>
<td>180</td>
</tr>
<tr>
<td>675</td>
<td>Mn</td>
<td>1.928</td>
<td>180</td>
</tr>
</tbody>
</table>

There is a dramatic change in the 111 and -1-1-1 diffraction peaks (Figure 5.9) at 675 K, which clearly indicates a structural change. The diffraction pattern is consistent with a material possessing rhombohedral symmetry with the space group R-3 (in the rhombohedral setting). The results of the Rietveld profile analysis at 675 K are shown in Figure 5.10. The lattice parameters, atomic positions, thermal parameters and selected distances are detailed in Table 5.5. The transition metal site preference was again determined to be 85%. 

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Figure 5.9 Neutron diffraction pattern and associated Rietveld refinement of $\text{La}_2\text{NiMnO}_6$ at 675 K (the observed diffraction line black, the red line is the theoretical model and green the residual from the Rietveld analysis).

The diffraction pattern was also collected at 625 K to determine if there was any diffuse nature to the transition (as observed in $\text{La}_2\text{CoMnO}_6$). However, the material was found still to be a monophasic, monoclinic material at 625 K. The pattern was only collected for one hour. The splitting of the 111 peak, however, is sufficient to show the monoclinic nature of the material.
5.2.4 EXAFS

In order to determine indirectly the oxidation states of the transition metal ions a method of accurately determining local structure surrounding specific transition metal ions is required. For this reason, Extended X-ray Absorption Fine Structure (EXAFS) measurements were undertaken.

An example of the experimental EXAFS and associated Fourier transform of the Ni K-edge of La$_2$NiMnO$_6$ and corresponding theoretical fits are shown in Figure 5.10. The results given in Table 5.5 detail the number, type and distance of atoms in each co-ordination shell around the nickel and manganese ions determined using the Ni K and Mn K edge XAS. The Debye Waller factors are also shown in Table 5.5 (containing both thermal and disorder components). The results show that each transition metal ion is surrounded by six oxygens with 1.91, 2.01 Å bond length. The second shell containing the next transition metal ion has been assumed to be the alternative to that of the examined edge. This assumption can be justified from the results of the neutron diffraction experiments and the fact that the two transition metal ions are very similar electronically and thus EXAFS is unable to differentiate between them. The quality of the fit is also given by the R-value in Table 5.5. The TM-O distances derived from analysis of the first shell are considerably different for nickel and manganese (2.01 & 1.91 Å respectively). The difference in TM-O bond distance between the two transition metal ions is reflected in the second shell of the EXAFS where the O-TM distance is different from that of the first shell justifying the choice of the alternative transition metal ion. It is only possible to accurately determine the
TM-O distance for the second shell and the TM-O-TM bond angle by using a multiple scattering model as a result of the bonded atoms are in a collinear array [6] with a TM-O-TM angle close to 180° (see Chapter 2.4.5.4).

![Figure 5.9 Example of EXAFS (Ni-K edge) and associated fourier transform.](image)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Ni – k</td>
<td>2.01</td>
<td>3.94</td>
<td>178</td>
<td>28</td>
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<tr>
<td>Mn - k</td>
<td>1.92</td>
<td>3.93</td>
<td>178</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 5.5 Selected bond distances obtained from EXAFS analysis

In order to infer the oxidation states of the transition metal ions present in the materials, EXAFS data have also been obtained for LaNiO₃, La₂NiO₄, LaMnO₃, CaMnO₃ and MnO₂ where the transition metal ions are in a known oxidation state. The standards allow the TM-O distance of the mixed transition metal materials to be referenced to a material with known oxidation state [7]. The TM-O bond distances and known oxidation states are listed in Table 5.6 (all in six fold co-ordinated sites).
The effect of temperature on the local structure of La$_2$NiMnO$_6$ has been investigated. The results of the analyses are shown in Table 5.7 for the Ni-K and Mn-K edges. The bond distances show an increase in the thermal parameters as expected, with the bond lengths only increasing very slightly and possibly within experimental error. It was only possible to obtain first shell information from the data, due to its low quality especially at higher temperatures where thermal vibrations cause the Debye-Waller factor to increase and the oscillations at high k to decrease [8].

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>Ni-O/ Å</th>
<th>Mn-O/ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>2.01</td>
<td>1.91</td>
</tr>
<tr>
<td>390</td>
<td>2.01</td>
<td>1.92</td>
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<tr>
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<td>2.01</td>
<td>1.92</td>
</tr>
<tr>
<td>590</td>
<td>2.02</td>
<td>1.93</td>
</tr>
</tbody>
</table>

Table 5.7 Changes in bond distances obtained from EXAFS upon increasing temperatures
5.3 Discussion

5.3.1 X-ray Diffraction

The linear changes in lattice parameters observed on changing the lanthanide ion are the result of accommodating the decreasing size of the lanthanide and maintaining orbital overlap between the lanthanide and the TM-O sublattice as previously observed in the Ln$_2$CoMnO$_6$ (Chapter 3.2.1) and the orthoferrites [9]. With decreasing size of lanthanide, the TM-O-TM bond angle decreases. As shown by EXAFS, where the TM-O-TM bond angle decreases from 180 to 173° for La$_2$CoMnO$_6$ and Nd$_2$CoMnO$_6$ respectively where the TM-O-TM bond angle is 178 for La$_2$NiMnO$_6$ (as determined by EXAFS). Unfortunately, owing to edge overlap, it is not possible to determine the EXAFS of any other of the materials in this system [10] and it is found that the energy of the transition metal K edge and the lanthanide L edges overlap. In this system (and as noted in others) the a axial length increases, but b and c decrease with the lanthanide ion size, which is due to an elongation of the intra atomic oxygen distances from layers of the TM-O sublattice [11]. Throughout this system, it has been assumed that the TM-O bond length does not change significantly as it is determined by electronic effects, whereas the bond angle is controlled steric effects [12].

Changes were observed in the ratio of the lattice parameters a, b and c with changing lanthanide. For La$_2$NiMnO$_6$, the axial lengths have the ratio c > b/$\sqrt{2}$ > a while for the rest of the series the ratio is a > b/$\sqrt{2}$ > c. This observation has also been made for other materials, for example, the orthoferrites and the Ln$_2$CoMnO$_6$ series of materials.
when the effect of lanthanide ion has been investigated. The anomalous behaviour of the lanthanum based material has not been explained previously, however, it may be a result of the lack occupied of f orbitals in lanthanum when in the +3 oxidation state. It has already been observed that similar anomalies are also observed in other physical properties, for example the magnetic Curie temperature where lanthanum fails to fit linearly in the trend exhibited by the other lanthanides in the series (Chapter 6.2.1).

The orthorhombic space group Pnma (a⁺a⁻a⁻ in Glazer notation) allows for only a single mixed site for the transition metal atoms and hence gives an averaged bond length for the nickel and manganese to oxygen bonds of 1.95 Å. Using the XRD data (as for the Ln₂CoMnO₆ series of materials), it was not possible to obtain a satisfactory fit of the data using a lower symmetry space group and hence obtain two different TM-O bond distances as suggested by the local structure information from XAS. Powder X-ray diffraction again was not able to determine whether charge ordering is present in the system, the X-ray scattering factors of nickel and manganese are still not great enough in difference. However, X-ray diffraction is useful in that it allows phase identification, determination of crystal symmetry and the lattice parameters [13] – which have been used in this study to good effect. Neutron diffraction is required to fully understand the structural nature of these materials. X-ray resonance scattering would be of little use as the edges of the ions are very similar in energy although it has been used in the past to show the presence of charge ordering [14]. However, as the neutron scattering lengths are very different it is very easy to distinguish between the two atoms (give reference and values) [15].
Unit cell volumes and axial lengths were expected to increase linearly with temperature [16] with discontinuities in the lattice parameters being indicative of electronic or structural phase transitions (Chapter 1.3.3) [17]. La$_2$NiMnO$_6$ shows two discontinuities at 470 and 670 K in the unit cell volume. The a and c axial lengths increase with temperature but show two discontinuities at 470 K and 670 K, however, the b axial length decreases in value at 675 K. This effect was also seen previously for La$_2$CoMnO$_6$ when the monoclinic to rhombohedral transition was observed. A similar change was observed in calcium doped LaMnO$_3$ which was attributed to a loss of ordering of the transition metal ions [18].

The other materials in the series did not show this anomaly, suggesting that, over the temperature range studied no detectable phase transitions occur. However, the a axial length decreases slightly suggesting that the bond angles are increasing with increasing temperature which is analogous to changes in the a-axis axial length upon increasing size of lanthanide.

5.3.2 Neutron Diffraction

Neutron diffraction allowed us to determine accurate oxygen positions in a monoclinic space group P2$_1$/n (a' a' a in Glazer notation). It also allowed us to show that there is charge ordering within the material, which does not decrease upon increasing the temperature even in the R-3 state. If the material was not charge ordered, the expected space group would be Pnma (as suggested by Woodward [19]). However, the bond distances determined for the transition metal – oxygen octahedra are interesting. Manganese has different bond lengths for the apical and basal bonds.
as observed for the Jahn Teller distorted Mn$^{3+}$ ion in LaMnO$_3$ [20], which suggests that manganese is in the +3 oxidation state with a Jahn Teller distortion which would also suggest a particular electronic configuration of $t_{2g}^3 e_g^1$ [21] and is further discussed in Chapter 6. The derived TM-O-TM bond angle is very similar to that obtained by EXAFS of ca. 180°. La$_2$NiMnO$_6$ is more monoclinic in nature than La$_2$CoMnO$_6$, which is reflected in the distorted cube angle, which is 91° (in La$_2$CoMnO$_6$ the angle is 90° and hence the material shows strong orthorhombic character). The magnitude of the a and b axes are reversed in comparison to La$_2$CoMnO$_6$ which is also reflected in the intensities of the 111 -1-1-1 reflections.

It was not possible to determine the reduction of symmetry to monoclinic from orthorhombic using X-ray diffraction. This work shows, for the first time, that the true structure of these materials is monoclinic. Previous work has indexed the material as orthorhombic [22] or pseudo-cubic [23] whilst some have tried unsuccessfully to refine the structure using the monoclinic P2$_1$/c structure (a sub-group of Pnma [24]). The inability to determine the monoclinic symmetry from the X-ray diffraction pattern may be due to the relative broadness of the diffraction peaks. The width of the diffraction peaks was found to improve with heating to higher temperatures followed by slow cooling. However, in order to maintain the chemical composition of the system it was not possible to heat above 1475 K: doing so would sinter the material but oxygen would be lost. Manganese is fluorescent under the copper source X-ray radiation which would artificially broaden the line width and add to the diffuse background [25]. Unfortunately, a limited range of wavelengths are available for laboratory based X-ray sources and the difference in wavelengths are small.
At 675 K the structure was indexed to a higher symmetry – the space group R-3 (a'a'a' in Glazer notation) in the rhombohedral setting. Upon refinement, the transition metals still showed a site preference (85%), which is the same as for the P2_1/n refinement at room temperature. The transformation from monoclinic to rhombohedral symmetry is a first order phase transition and was also observed in La_2CoMnO_6. A similar transition has been observed in Nd_{0.5}Sr_{0.5}MnO_3 [26] where a change from Imma to Pnmm is seen.

Unlike La_2CoMnO_6, there is no diffuse nature observed in the transition over the temperature range measured using neutron diffraction. The difference in behaviour may be due to the nature of the sample for which particles of 1.9μm and 2.9μm were obtained. The lack of this diffuse phase transition may also be a result of the material being less strained or the particles being larger in nature than those synthesised for La_2CoMnO_6 and PLZT [27] where diffuse phase transitions are observed.

5.3.3 Local Structure

The local structure obtained from EXAFS measurements indicates that the manganese and nickel to oxygen bond lengths (1.91 and 2.01 Å respectively) are significantly different from that derived by powder X-ray diffraction (1.95 Å) in the orthorhombic setting. Shannon suggested, that, by comparing the inter-atomic transition metal (TM) to oxygen distances of materials where the oxidation state is unknown with standards containing the same transition metals in a known oxidation state, it would be possible to infer the unknown oxidation state of the transition metal ion. The Shannon approximation is valid only if similar bonding is found in the unknown and reference
systems. For La$_2$NiMnO$_6$ it was found that the TM-O distances for nickel and manganese are comparable to standards containing Ni$^{2+}$ and Mn$^{4+}$ ions in La$_2$NiO$_4$ and CaMnO$_3$. However, this result contradicts the results obtained from neutron diffraction for which the manganese to oxygen distance are significantly different. In this case the MnO$_6$ octahedra has three distinct Mn-O values similar to those expected for manganese in the +3 oxidation state, and which shows long range ordering. The EXAFS data were also refined using this model and the difference between the R factors was too small to allow us to distinguish between these models. Further investigations were necessary to determine the true oxidation state of the transition metal ions which are covered in Chapter 6 which discusses the information obtained from magnetism and L-edge XAS (X-ray absorption spectroscopy). However, it was possible to infer that there is B-site ordering of the transition metal ions (as indicated by the difference in bond lengths between the first and second shells of both edges studied) from the L-edge EXAFS studies.

Upon increasing the temperature, no dramatic changes are observed in the TM-O bond distance. Only the first shell was analysed. The small changes that occur can be attributed to increases in thermal motion of the atoms, which is indicated by the Debye-Waller factor.

5.4 Summary

It has been shown that La$_2$NiMnO$_6$ is monoclinic (previously thought of as orthorhombic) and at 675 K transforms to rhombohedral. It has also been observed for the first time that the manganese ion appears to posses a Jahn Teller distortion and
hence is in the +3 oxidation state and the nickel ion is also in the +3 oxidation state; these ions being B-site ordered. The distortion present is not as strong as found in other Jahn Teller distorted systems containing Mn and there is therefore the possibility that the ions may possess some +2 and +4 character. This issue is addressed further in the following chapter.

The effect of lanthanide ionic radius has also been investigated and the variation in lattice parameter discussed. The other materials also studied (within the temperature range studied) do not show the monoclinic to rhombohedral transition.

It is possible to see differences and similarities in the structure of the system presented in this chapter and the Ln₂CoMnO₆ series described in chapter 3. Both materials are monoclinic with B-site ordering. However, the octahedra in the nickel / manganese materials are more distorted and there is the possibility that the manganese are in a different oxidation state and this may mean that the manganese ion possesses a Jahn Teller distortion. Both of the lanthanum materials in both series undergo a temperature driven phase transition from a monoclinic structure to rhombohedral one.

5.5 References


[10] www.srs.dl.ac.uk


Chapter 6

Physical Properties of the Ln$_2$NiMnO$_6$ Series of Materials

6.1 Introduction & Summary

In this chapter the physical property data collected for the Ln$_2$NiMnO$_6$ series of materials (where Ln= La, Pr, Nd, ‘Pm’, Sm, Eu and Gd) are presented and discussed. The temperature dependence of the physical properties measured include magnetic susceptibility, electrical resistivity and infrared absorption. The electronic structure has also been investigated by the use of L-edge spectroscopy.

In the first part of this chapter, the effect of the lanthanide ionic radius upon the Curie temperature is probed using a SQUID magnometer (a super conducting quantum interference device). The magnetic data does not allow us to determine the oxidation states of the transition metal ions; it is only when other techniques are used that it is possible to suggest an oxidation state. The electrical resistivities and band gaps are then described, where we find a relationship between the physical values and the lanthanide ionic radius. The infrared spectra are also measured as a function of lanthanide ion radius and temperature. Finally the electronic structure of the materials has been probed using L-edge XANES spectroscopy, by comparison to materials of known oxidation state it is shown that the materials under investigation do not posses ions with integral oxidation states.
The derived relationships between the physical properties and the lanthanide ions are discussed in terms of structure-property relationships. Arguments to rationalise the structure-property relationships are then outlined.

6.2 Results

6.2.1 Magnetic Properties

Figure 6.1 gives a plot of magnetic moment versus temperature for La$_2$NiMnO$_6$ showing a decrease in the magnetic moment with increasing temperature. All of the materials in the series behave in a similar manner. However, at low temperatures many show an initial increase in the magnetic moment with temperature (figure 6.3). The associated Curie temperature; which is tabulated in Table 6.1 and shown graphically in Figure 6.3 is seen to be linearly dependent on the ionic radii of the lanthanide as expected. However, La$_2$NiMnO$_6$ does seem to be anomalous in that it slightly deviates from the linear variation.

![Figure 6.1 Magnetic moment as a function of temperature of La$_2$NiMnO$_6$](image)

*Figure 6.1 Magnetic moment as a function of temperature of La$_2$NiMnO$_6$*
<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Curie Temperature / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>287</td>
</tr>
<tr>
<td>Pr</td>
<td>255</td>
</tr>
<tr>
<td>Sm</td>
<td>221</td>
</tr>
<tr>
<td>Pm</td>
<td>203</td>
</tr>
<tr>
<td>Nd</td>
<td>187</td>
</tr>
<tr>
<td>Eu</td>
<td>159</td>
</tr>
<tr>
<td>Gd</td>
<td>140</td>
</tr>
</tbody>
</table>

*Table 6.1 Magnetic Curie temperature as a function of lanthanide ionic radii*

*Figure 6.2 Variation of Curie temperature with lanthanide ionic radii*

Figure 6.4 shows the high temperature magnetic susceptibility of La$_2$NiMnO$_6$ (290 – 990 K) where no deviations from paramagnetic behaviour are observed upon
increasing temperature; this is typical of all materials studied. This data is representative of all materials in the series.
Figure 6.3 Magnetic moment of Pr$_2$NiMnO$_6$ as a function of temperature showing metamagnetic transition at low temperature.

Figure 6.4 High temperature magnetic susceptibility as a function of temperature for La$_2$NiMnO$_6$ (typical of all materials in the series).
6.2.2 Room Temperature Electrical Measurements

The room temperature electrical resistivities were measured using the 4-wire probe method, the materials resistivities do not change upon changing current or by the reversing polarity of the electrodes. The measured values are tabulated in Table 6.2 and shown as a graphically as a function of lanthanide ionic radius in Figure 6.5. Again there is a good linear relationship between ionic radii and resistivity. However, lanthanum again appears to be anomalous.

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Resistivity/Ωcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>541</td>
</tr>
<tr>
<td>Pr</td>
<td>619</td>
</tr>
<tr>
<td>Sm</td>
<td>659</td>
</tr>
<tr>
<td>Pm</td>
<td>711</td>
</tr>
<tr>
<td>Nd</td>
<td>950</td>
</tr>
<tr>
<td>Eu</td>
<td>1283</td>
</tr>
<tr>
<td>Gd</td>
<td>1806</td>
</tr>
</tbody>
</table>

*Table 6.2 Electrical resistivities as a function of lanthanide.*
Figure 6.5 Dependence of resistivity on lanthanide ionic radius.

6.2.3 Temperature Dependence of Resistivity

Figure 6.6 shows the temperature dependence of the resistivity for La$_2$NiMnO$_6$. The resistivities throughout the temperature range are current and electrode polarity independent. The limited temperature range of the experiments is due to the nature of the glue used to attach the wires to the sample, which is known to fail at 500 K by melting. Measurements were not therefore performed close to this temperature as doing so may contaminate the cryostat. All materials appear to be semi-conducting. The material is clearly semiconducting with the resistivity decreasing with increasing temperature; similar behaviour is seen for all the other materials studied.
Figure 6.6 Temperature dependence of the resistivity of the $\text{La}_2\text{NiMnO}_6$.

The band gaps are calculated from the slope of Arrhenius plot of resistivity; and are given in table 6.3 and shown graphically as a function of lanthanide ionic radius in figure 6.7. The band gap is a measure of the activation energy required to excite one electron from the valence band to the conduction band (Chapter 2.6). We are assuming intrinsic semiconducting behaviour, which may not be correct (in order to check this different transport properties would have to be measured).
Table 6.3 Variation of band gap with lanthanide ionic radius

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Band Gap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>.9</td>
</tr>
<tr>
<td>Pr</td>
<td>1</td>
</tr>
<tr>
<td>Sm</td>
<td>1.07</td>
</tr>
<tr>
<td>Pm</td>
<td>1.15</td>
</tr>
<tr>
<td>Nd</td>
<td>1.23</td>
</tr>
<tr>
<td>Eu</td>
<td>1.32</td>
</tr>
<tr>
<td>Gd</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 6.7 Variation of Band Gap with lanthanide ionic radius

6.2.4 Room Temperature Infrared Spectra

The room temperature infrared spectrum of La$_2$NiMnO$_6$ (Figure 6.8) contains four main peaks; the inset shows in greater detail the profile of the four main modes of
vibration, which have been assigned as: $v_{M-O} \approx 615 \text{ cm}^{-1}$, $\delta_{O-M-O} \approx 426 \text{ cm}^{-1}$, $\delta_{O-M-O} \approx 298 \text{ cm}^{-1}$, $v_{L_a} \approx 190 \text{ cm}^{-1}$ where $v$ is a stretching mode and $\delta$ a deformation mode.

These assignments are based upon previous workers working on similar materials. However it is possible that mixing could be occurring between the stretching and deformation modes, making this assignment tentative. All of the materials in the series show similar infrared absorption spectra.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{LaNiMnO4_Infrared_Spectra}
\caption{Typical infrared absorption spectra of $La_2NiMnO_6$. (The inset shows the vibrational modes enlarged)}
\end{figure}

The relative wavenumber of the modes and relative intensities are tabulated in Table 6.4. As the size of the lanthanide ion decreases, the complexity of the spectroscopic profile for each of the modes increase. There is also a linear relationship between the normalised integrated band intensity for the TM-O stretch and the ionic radius of the
lanthanide ion as shown in Figure 6.9. Figure 6.11 depicts the dependence of the wavenumber of the deformation mode on the lanthanide ionic radius.

![Graph of integrated band intensity vs. ionic radius](image)

*Figure 6.9 Dependence of integrated band intensity of the TM-O stretching mode lanthanide ionic radii*

![Graph of wavenumber vs. ionic radius](image)

*Figure 6.10 Change in wavenumber of deformation mode as a function of ionic radii.*
6.2.5 Temperature Dependence of Infrared Spectrum

The transition metal oxygen (TM-O) stretching frequency, band intensity and baseline ordinate positions have been measured as a function of temperature, revealing a number of interesting features.

The relative integrated band intensities of the transition metal oxygen stretch show no major features (Figure 6.11) and all materials in the series exhibit similar behaviour. The profile for the TM-O bond deformation mode changes as the temperature increases. At low temperatures, the profile appears to be complex (due to octahedral distortion) but upon heating the complexity decreases.

Figure 6.11 Changes in infrared absorption properties of Sm$_2$NiMnO$_6$ (which are typical of all materials in the series)
Significant changes are observed in the relative absorption of the baseline ordinate in the region from 1000 to 4000 cm\(^{-1}\). At low temperatures there is no change, however upon increasing temperature the absorption increases. It is also found that changing the lanthanide ionic radius alters the region of the infrared spectrum that is sensitive to changes with temperature. For La\(_2\)NiMnO\(_6\) the 1000cm\(^{-1}\) region is sensitive; however, for Nd\(_2\)NiMnO\(_6\) the 3000cm\(^{-1}\) region is more temperature sensitive.

6.2.6 Electrical and Infrared Relationships

Figure 6.12 shows the relationship between the electrical resistivity and the normalised infrared integrated intensity of the TM-O stretching mode. We note that the relationship is nearly linear and that the lanthanum based material does not fit in exactly with the trend exhibited by the other materials. The degree of ramping (gradient) of the baseline ordinate (in the spectral region 1000 to 4000 cm\(^{-1}\)) also decreases with ionic radius (Figure 6.15) as does the electrical resistivity.
Figure 6.12 Relationship between integrated band intensity of the TM-O stretching mode as a function of resistivity.

Having studied various electronic and spectroscopic properties we now return to the question of oxidation state of the transition metal ions – information which could not be properly determined from the magnetic and structural data. We have used the techniques of L-edge XANES spectroscopy to determine the oxidation state of the transition metal ions by comparison which standards.

6.2.7 XANES

The Ni and Mn L-edge XANES for the La$_2$NiMnO$_6$ are shown in Figures 6.13 and 6.14 respectively, which also shows the transition metal L-edges for materials in known oxidation states.
We see that for the materials with known oxidation states, that the centre of the Ni-L edge depends on the oxidation state. The higher the oxidation state the higher the energy of the level and no changes are observed in spectroscopic profile. The Ni L-edge of La$_2$NiMnO$_6$ is close to the standard containing +3 oxidation state but also shows some character of a transition metal ion with a mixed oxidation state.

The Mn L-edges shows that only the spectroscopic profile changes with oxidation state. It is evident that the profile for the Mn in La$_2$NiMnO$_6$ is similar to that of the standard of Mn$^{+3}$. We also observe that upon changing the lanthanide ion the spectroscopic profile or position does not change for each L-edge spectra.

![Ni L edge XANES](image)

*Figure 6.13 Ni Ledge XANES of La$_2$NiMnO$_6$ and materials with known oxidation states*
Figure 6.14 Mn L edge XANES of La$_2$NiMnO$_6$ and materials with known oxidation states

6.3 Discussion

6.3.1 Introduction

In order to explain the changes in physical properties as the lanthanide ionic radius contracts, it is important to consider the effect of lanthanide on the structure, especially Ni-O-Mn bond angle and consequently the orbital overlap within the TM-O sublattice. The effect of varying the charge density of the lanthanide on the covalency of the TM-O bonds is also important.
In Chapter 5 the relationship between the lanthanide ionic radius and the unit cell parameters was discussed. The overall unit cell volume decreases with decreasing lanthanide ionic radii. The TM-O distance does not change upon decreasing lanthanide ion size and hence in order to accommodate the TM-O sublattice and maintain orbital overlap with the lanthanide the Ni-O-Mn bond angle decreases. The bond angle influences the degree of orbital overlap of the Ni-O-Mn sublattice. There is competition between the lanthanide and the transition metal for σ bonding with the oxygen p orbitals [1] affecting the covalency / ionicity of the bonds. This argument can be used to explain the observations in the physical properties of the materials as the lanthanide is changed.

It is also important to understand how changes in the charge density of the lanthanide ion can affect the electrons in the TM-O bond. The formal charge on the lanthanide remains constant as the size of the ion decreases which means that the charge density increase, which in turn results in the electron density being pulled from the TM-O sublattice still further. This can result in the electrons becoming more localised on the transition metal ions and changes the covalency of the bonds.

6.3.2 Magnetism

The oxidation state of the transition metal ions may in some cases be inferred from the ordered magnetic moment. La$_2$NiMnO$_6$ is the only material in the series in which the lanthanide ion does not possess a magnetic moment. Its electronic configuration in the +3 oxidation state is that of the noble gas configuration [Xe]. Therefore, this
material provides the simplest indirect information regarding the oxidation states or magnetic structure of the TM-O sublattice.

The magnetic moment of \( \text{La}_2\text{NiMnO}_6 \) is \( 1.6 \, \text{J T}^{-1} \, \text{mol}^{-1} \) at 4 K, suggesting the presence of one unpaired electron. As seen in Chapter 5 the manganese ion possesses a Jahn Teller distortion, which indicates that it is in the +3 oxidation state (manganese can only be Jahn Teller distorted if in the +3 oxidation state). This means the electronic configuration is therefore \( t_{2g}^3 \, e_g^1 \) (four unpaired electrons for a high spin state) the Jahn Teller distortion arising from the lifting of the orbital degeneracy of the \( e_g \) orbitals. In order to charge balance the nickel ion has to be in the +3 oxidation state as well. This means that the nickel ion's electronic configuration is \( t_{2g}^5 \, e_g^2 \) (three unpaired electron).

If the material is assumed to be ferromagnetic the overall contribution the order magnetic moment would be an average of the two ions, and hence would be a contribution from 3.5 unpaired electrons – which is clearly not the case. If the material is assumed to be ferrimagnetic the overall moment would be the difference between the individual moments [2]. The magnetic moments in a ferrimagnet align themselves opposite to each other, giving a net magnetic moment of one; hence the ideal magnetic moment would be \( 1.78 \mu_B \).

The ordered magnetic moment of \( \text{La}_2\text{NiMnO}_6 \) for the ferrimagnet is slightly lower than predicted for the spin only contribution (a predicted value of \( 1.78 \mu_B \)). This discrepancy may be due to clustering of similar ions together [3], or domain wall formation within the superlattice [4]. The possibility of clustering may also be
inferred from the degree of ordering of the transition metal ions at room temperature, which was calculated to be 90% by Rietveld analysis of the neutron diffraction patterns, indications the presence of ca. 10% Mn-O-Mn or Ni-O-Ni. The possibility of a canted ferromagnet cannot also be ruled out where the magnetic moments adopt a helical arrangement of orientations, with neighbouring spins being canted by a small angle.

There is a correlation between the ionic radius of the lanthanide ion and the Curie temperature, which results from changes in the superexchange angle [5]. The orbital overlap through which the super exchange mechanism occur decreases with decreasing lanthanide ionic radius. The coupling occurs from the occupied $e_g$ orbital of the Ni ion through the oxygen atom to the unoccupied $e_g$ orbitals of the manganese ions. Therefore, as the bond angle Ni-O-Mn decreases from 180 to a minimum the degree of exchange also decreases [6].

At higher temperature >290 K, no changes were observed in the magnetic susceptibility through the phase transitions (described in chapter 5). Suggesting that there are no changes in the crystal field occurring as a result of these transitions.

The initial increase in the magnetic moment in the materials at low temperature is also interesting, as it is not normal ferromagnetic / ferrimagnetic behaviour. The moment does however, follow normal behaviour above 20 K. The behaviour is probably due to lanthanide sublattice to TM-O sublattice f-d exchange interaction. The f-d interaction modifies the magnetic 3d sublattice and gives negative f-d interaction. The magnetic moment of the lanthanide opposes the 3d lattice - known as metamagnetism [7]. This
argument is supported at the material containing lanthanum does not show this behaviour. Lanthanum has no unpaired electrons for the exchange mechanism to occur.

6.3.3 Electrical Resistivity

The measurement of electrical resistivity has only been performed on samples which were pressed powders (at 10 tonne), and as a result the values of resistivities obtained can only be taken as an indication of the true resistivity of the material (a single crystal is required for definitive electrical measurements). By pressing the powders we may introduce voids, which will affect the resistivity; there may also be inherent grain boundary effects that will alter the real value of resistivity. However, it is hoped to minimise these effects by sintering the discs after pressing. The resistivity values may also be altered by the addition of other temperature dependent carrier production effects [12].

The temperature dependence of the electrical resistivity suggests that the materials are semiconducting (the resistivity decreases with increasing temperature). The resistance of the materials is also higher than expected based upon the parent materials, due to charge ordering. Neutron diffraction has shown that La$_2$NiMnO$_6$ is charge ordered and there is no evidence to suggest otherwise for the other materials in the series (they all show ferromagnetic behaviour). Charge ordering creates an additional potential that impedes the flow of carriers [13].
The TM-O sublattice from which the orbitals of the conduction and valence bands are formed (via orbital overlap along the distorted cube edge) primarily governs the electrical properties of perovskite materials [8]. As noted, the degree of the orbital overlap depends on geometrical factors especially the bond angle of the TM-O-TM bond. The resistivity is also determined by the nature of these ions and defects within the material. Hence, with decreasing orbital overlap there is an increase in electrical resistivity as the conduction and valence band become increasingly further apart in energy. Thus, as observed in this system, as the lanthanide ion decreases, the resistivity increases.

As the Lewis acidity (electron withdrawing tendency [9]) of the lanthanide increases upon the decreasing ionic radius, the TM-O bond covalency decreases. As the covalency of the TM-O bond decreases, the electrons become more localised (and can be described by the Localised-electron model [10]). The localisation results in a lower bandwidth and a wider band gap and resistivity increases.

With increasing covalency (increased orbital overlap) the charge carriers become more itinerant and the electrical mobility increases. These covalency effects have also been used to describe changes seen in TILnX₂ series where, as the Ln-X bond decreases in length, the lanthanide decreases in ionic radius and hence the covalency of the Tl-X bond increases whilst for the Ln-X bond the covalency decreases (X=O or a halide) [11].
6.3.4 Infrared Spectroscopy

The vibrational bands observed in the infrared spectrum of a molecule depend upon the number of atoms present and the symmetry of the unit cell [14]. It is therefore possible to infer qualitative local structural data from the spectroscopic profile and position of the bands in the spectra [15].

The materials spectroscopic profile shows an increasing complexity as the ionic radius of the lanthanide decreases in ionic radius. This increase in complexity is a result of the octahedra TMO$_6$ of the materials become increasingly distorted away from the aristotype cubic structure [16] leading to the loss of the three fold degeneracy around the transition metal. There is also a relationship between the wavenumber of the deformation mode and the lanthanide ionic radius, which suggests that the strength of the TM-O-TM bond must be changing as the relationship between the strength of bonds and the wavenumber is defined by:-

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where the wavenumber is determined by the effective mass ($\mu$) and bond strength ($k$).

The bond strength decreases as the lanthanides ionic radius decreases due to changes in bond covalency as discussed above, when describing the changes in resistivity. The charge density increases as the lanthanide ionic radius decreases meaning there is increased orbital overlap with the oxygen and the lanthanide ($\sigma$O-$\sigma$Ln), whereas the TM-O ($\sigma$TM-$\sigma$O) orbital overlap decreases as a result of a redistribution of electrons between the bonds. This change in electron density results in a decrease in the strength of the TM-O bond and force constant of the bond changes and the
wavenumber of the stretching mode decreases. The increase in the lanthanide and oxygen overlap means more energy is required to deform the bridge of the TM-O-TM bond and hence the wavenumber increases for this vibrational mode [17].

On raising the temperature the unit cell will increase in size (as shown by XRD) and hence the interatomic distances must also increase (as shown by EXAFS) This results in a reduction in the overlap of the bonding orbitals and a weakening of the bonding and hence the force constants decrease. As the vibrational modes’ frequency is proportional to the force constant of a bond, the frequency decreases with increasing temperature.

The band intensity is proportional to the sum of the squares of the electric dipole moment in each direction. A simple treatment would suggest that as the electric dipole is proportional to the bond length, as the bond increases so does the dipole and the intensity decreases [18]. However, this equation is too simplistic a model for solids and there appear to be no strict rules governing the band intensities of materials as a function of temperature [19].

It is seen that the frequency of the metal-oxygen bond stretch decreases as the temperature increases (as expected) and shows no discontinuities and hence no apparent phase transitions. The integrated band intensities also show a general trend of decreasing and again follow the above simple rules

When the base line ordinate is plotted as a function of temperature there appears to be no changes at low temperatures. However, at a specific temperature the absorption
dramatically increases. This background absorption is either due to the reflection or absorption of the infrared radiation by the free carriers within the system [20] and it is possible to infer the free carrier mobility as has been done in that it is seen that the a change in infrared absorption is een upon change in band gap (chapter 4).

There is a decrease in complexity in the spectroscopic profile of the deformation mode as the temperature is increased, which means that the local structure is increasing in symmetry suggesting that the TMO₆ octahedra are becoming closer in symmetry to that in the aristotype perovskite.

The relationship between the integrated intensity of the TM-O stretch and the resistivity results from changes in covalency and hence electrical dipole moment as described previously. The bonds become stronger or more covalent as the ionic radius of the lanthanides decrease hence changing the resistivity. The gradient of the infrared background is also an indicator as to the electrical resistivity of the material [21]. The background above 1000 cm⁻¹ to 4000 cm⁻¹ is as a result of the number of free carriers that are present in the material. As the size of the lanthanide ionic radius decreases the gradient of the background decreases and indicates that the materials’ conductivity is decreasing as is the number of free carriers. Changes in resistivity suggest that the number, mass or mobility of free carriers are decreasing with decreasing size of lanthanide ionic radius. The infrared spectrums gradient as a function of temperature (in the spectral region 1000-3000 cm⁻¹) allows us to measure electrical resistivity changes indirectly. As the baseline absorption changes there is therefore a change in the concentration of carriers, their mobility or mass, and hence, when a change in band gap is observed, changes in the gradient of the infrared spectrum are observed.
An increase in the infrared reflectivity or absorption occurs as a result of increased number of free electrons that can reflect or absorb the infrared radiation.

6.3.5 L-Edge XANES Spectroscopy

It is clear that the position and spectroscopic profile of the L edge XANES spectrum depends on the oxidation state of the transition metal ions being probed. The transition occurs from a sharp dipole allowed transition from the 2p to 3d orbitals and the energy and spectral profile is dependent upon the oxidation state, spin state and symmetry surrounding the ion under investigation. A few systems have been investigated previously by this technique including NiX2P2 (where X=Cl, Br and P=PEt2 or PPh3) [21] and various geological samples containing Fe [23]. From the data obtained for the nickel edge it clear that the oxidation state is close to that of Ni3+. It is also clear that the manganese ion is close in spectroscopic profile to the +3 oxidation state. However, it is also clear that there is a degree of +2 character in the spectrum of the nickel L edge. It is also clear that the spectrum of the Mn L edge is not quite the same as the +3 manganese standards. We therefore infer from these and the data neutron diffraction, magnetic and K-edge EXAFS data that the oxidation states of the transition metal ions are non-integral. The nickel transition metal ion is present in both the +3 and +2 state and the manganese ion exists in the +3 and +4 oxidation state. It is possible to say that there is a greater percentage of the +3 oxidation states of both ions as they posses characteristics of this oxidation state (for example a structural distortion possibly arising form a Jahn Teller distortion).

6.4 Summary
In this chapter we have shown how the physical properties of the series of materials can be understood in terms of the structural data measured previously (Chapter 5). Changes observed in physical properties upon changing lanthanide have also been interpreted using arguments based upon changing orbital overlap and bond covalency. The use of L-edge spectroscopy has also allowed us to provide an indication of the oxidation state of the transition metal ions.

6.5 References

[14]


Chapter 7

Conclusions

7.1 Introduction

In this final chapter we present a brief summary of the main results described and discussed in the previous four chapters for the systems $\text{Ln}_2\text{NiMnO}_6$ and $\text{Ln}_2\text{CoMnO}_6$. Conclusions are then drawn and comparisons made between the two systems. We also draw together structure property relationships. Finally we make suggestions for further work.

7.2 Summary of Results

7.2.1 Structural studies

Both the effects of temperature and lanthanide radius on the perovskite structure of $\text{La}_2\text{CoMnO}_6$ and $\text{La}_2\text{NiMnO}_6$ have been investigated using X-ray diffraction, neutron diffraction and EXAFS. The unit cell volume varies with lanthanide radius for both systems, as expected, decreasing with decreasing ionic radius. When the temperature dependence of the unit cell volume was investigated, anomalies were observed for $\text{La}_2\text{CoMnO}_6$ and $\text{La}_2\text{NiMnO}_6$. However, for the other materials in both series the
expected uniform increase in unit cell volume was observed over the temperature range studied.

Neutron diffraction has shown that La$_2$NiMnO$_6$ and La$_2$CoMnO$_6$ are monoclinic with a strong site preference for the transition metal ions. Neutron diffraction also showed that the anomalies observed in the temperature dependent X-ray diffraction studies were due to structural transformations from monoclinic to rhombohedral with a slight reduction in site ordering. The derived TM-O bond distances for La$_2$CoMnO$_6$ show the TMO$_6$ octahedra to be regular. However, in La$_2$NiMnO$_6$ strongly distorted MnO$_6$ octahedra are observed.

The EXAFS studies of both series of materials showed that the two transition metal ions in the material have significantly different TM-O bond distances. Analysis of the second co-ordination sphere suggests the presence of site ordering. No significant changes were observed with increasing temperature. The small changes seen were due to either experimental error or to the expected increases in bond distance with temperature as a result of thermal motion.

7.2.2 Physical Properties

The temperature dependence of the magnetic properties in both systems suggests that superexchange processes occur within the TM-O sublattices. In materials with Ln≠La, antiferromagnetic interactions occur between the TM-O sublattice and the lanthanide ions – the phenomenon known as metamagnetism; Ln$_2$CoMnO$_6$ has ferromagnetic interactions. However, no conclusive assignment could be made as to the exact nature
of the magnetism (ferromagnetism or ferrimagnetism) for the Ln$_2$NiMnO$_6$ system. The ordered magnetic moment of La$_2$CoMnO$_6$ suggests the presence of Mn$^{4+}$ and Co$^{2+}$. However, in La$_2$NiMnO$_6$, the value of the ordered magnetic moment cannot readily provide an indication of the oxidation states for the transition metal ions. No changes in magnetic properties are observed when the materials transform from monoclinic to rhombohedral.

In both series of materials, the resistivity was found to depend on the size of lanthanide ion. All materials were found to be semiconducting within the temperature range studied. The conductivity decreases with decreasing lanthanide ionic radius within a series of materials. The measured band gap was also found to be dependent on lanthanide ionic radius, with the band gap inversely proportional to the size of the lanthanide ion. The band gap in La$_2$CoMnO$_6$ is also observed to vary with temperature. In addition, the infrared absorption properties of the materials depend on lanthanide ion size with a decrease seen in the gradient of background ramping. The energy of the vibrational modes was found to be related to the ionic radius of the lanthanide ion within each system. The temperature dependence of the materials infrared absorption has also been investigated with changes observed in the background ramping upon heating. We have also shown that the electrical properties map onto the infrared properties with a dramatic change in infrared absorption observed when the band gap of La$_2$CoMnO$_6$ changes.

An investigation into the L-edge XANES of the transition metal ions in the materials has also allowed us to confirm the oxidation states of the transition metal ions in Ln$_2$CoMnO$_6$ and to suggest oxidation states for the transition metal ion in
Ln$_2$NiMnO$_6$, which has been possible by comparison of the spectroscopic line shape and peak position with those of standard materials with known oxidation states.

### 7.3 Structure Property Relationships

Both series of materials have been reported in the literature as possessing either orthorhombic or pseudo-cubic structures [1]. The present study shows that this is not the case. In order to rationalise the electrical, electronic and magnetic properties of the materials there has to be a high degree of distortion in the materials which is confirmed by the presence of a monoclinic structure which is only observed using high resolution neutron diffraction.

Previous workers [2] have reported that when the resistivity is measured as a function of transition metal ion ratio in the material LaCo$_x$Mn$_{1-x}$O$_3$ that a maximum is observed for $x=0.5$; whereas it is thought that the relationship should be linear between the extremes. This anomaly can now be explained in terms of the site ordering which is thought to render a material insulating or semiconducting [3], due to pinning of electrons on specific sites. Site ordering has been shown to be present by EXAFS (by alternating long and short bonds), magnetic measurement and neutron diffraction.

The assignment of the oxidation states from the magnetic moment also means that the TM-O distances for the two different transition metal ions cannot be the same as suggested by an orthorhombic structure. For $+2/+4$ systems, the TM-O distances must be significantly different, which cannot be accommodated in an orthorhombic
material. For the magnetic moment to be as close to the theoretical value, a low
degree of transition metal ion clustering of the same type must be present as observed
in this study. By studying the EXAFS it is clear that the structure must accommodate
the two different TM-O distances measured; which is clearly required if there is site
ordering.

In this thesis it has been shown how changes in structure and physical properties with
lanthanide ionic radius can be understood. The changes can be rationalised by
considering changes in orbital overlap and the TM-O bond covalency as a function of
lanthanide ionic radius. The TM-O bond distances are thought to remain constant
upon changing lanthanide ionic radii. However, the unit cells volume decreases with
the size of lanthanide ion, meaning that the TM-O-TM bond angle must decrease in
order to maintain the Ln-O orbital overlap, which in turn decreases the TM-O orbital
overlap. The change in orbital overlap is found to affect the magnetic Curie
temperature, resistivity and band gap. The charge on the lanthanide ion does not
change with atomic number. However, the size of the ion does change, resulting in an
increase in charge density with decreasing ionic radius of the lanthanide ion. Thus, the
lanthanide ion has the ability to change the bonding slightly in the TM-O sublattice in
that the bonds become more ionic in nature for the smaller lanthanide ion. The
increase in resistivity and changes in the strength of the bonds (as apparent from the
infrared absorption energies) are a consequence of the decreasing size of lanthanide
ionic radius and increasing TM-O ionicity.

The oxidation states for the transition metal ions present has been a matter of debate
for some time in these materials [4]. For the Ln$_2$CoMnO$_6$ series of materials, all
methods used suggest the presence of Co^{2+} and Mn^{4+}, whereas, for the Ln₂NiMnO₆ system the evidence is not as conclusive. The EXAFS and magnetism tentatively suggests the presence of Ni^{2+} and Mn^{4+} ions. However, neutron diffraction suggests the presence of Ni^{3+} and Mn^{3+}, which is Jahn Teller, distorted. The L-edge XANES measurements strongly suggest the presence of Mn^{3+} and Ni^{3+} with also some Ni^{2+} and Mn^{4+} also present. Therefore, we suggest that oxidation states of the transition metal ions in Ln₂NiMnO₆ are non-integral and that the transition metal ions are present in two different oxidation states with a larger percentage of the +3 oxidation state.

In this thesis it has been shown that is possible to rationalise the physical properties of the materials by understanding their structure and vice versa. This work has shown strong structure-property relationships in both systems. We have also shown for the first time, that the materials in the series Ln₂NiMnO₆ and Ln₂CoMnO₆ are monoclinic and undergo a thermally driven monoclinic to rhombohedral transition. Oxidation states have also been assigned to the transition metal ions present. The observed structural properties also explain the anomalies observed previously in the physical properties of the materials.

7.4 Suggestions for Further Work

A) The measurement of the electrical properties at higher temperature will allow us to observe if any changes in band gap occur when the materials transform from monoclinic to rhombohedral.
B) A neutron diffraction study of other materials in the series will allow the
determination of the degree of site ordering and monoclinicity. It will also allow
us to observe if any other thermally driven transitions occur such as the
transformation from monoclinic to rhombohedral symmetry.

C) The growth of single crystals will allow the electrical properties to be measured
precisely.

D) It is also possible that a combination of vanadium and manganese may switch
oxidation states upon heating. Therefore it may be interesting to investigate the
$\text{Ln}_2\text{VMnO}_6$ series of materials.

### 7.5 References


   (1998)