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ABSTRACT

PROBING THE COMPLEX MAGNETIC, ELECTRONIC AND STRUCTURAL PROPERTIES IN CORRELATED MANGANESE OXIDES

by Peng Gao

Rare-earth Manganese Oxides (*R*MnO₃) exhibit two distinct structural phases: the orthorhombic structure and the hexagonal structure. The doped orthorhombic phase exhibits a metal to insulator transition, charge ordering and a strong response of electron transport properties to magnetic fields (colossal magneto-resistance). At low temperatures, this system may also exhibit a finite polarization which couples to external magnetic fields. The hexagonal phase is known to have a large spontaneous polarization at high temperatures which couples to the low temperature magnetic order. These materials are important from the basic point of view of understanding strong electronic correlations and spin-lattice coupling. From, a practical perspective, they hold promise to produce sensors and storage devices with extremely high sensitivity and high density. However, a detailed understanding of their properties is needed.

In this work, optical, transport and structural measurements, as a function of pressure and temperature, are conducted to explore the physical properties of these materials. Synchrotron based x-ray diffraction and infrared measurements, Raman measurement, laboratory based transport measurements and neutron scattering measurements were conducted on bulk polycrystalline, thin film and single crystal samples. The electronic, structural and magnetic properties are studied in detail. The results will be used to refine theoretical models of these materials.

PROBING THE COMPLEX MAGNETIC, ELECTRONIC AND STRUCTURAL PROPERTIES IN CORRELATED MANGANESE OXIDES

by Peng Gao

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology and Rutgers, the State University of New Jersey - Newark in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Applied Physics

Department of Physics

August 2009

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APPROVAL PAGE

PROBING THE COMPLEX MAGNETIC, ELECTRONIC AND STRUCTURAL PROPERTIES IN CORRELATED MANGANESE OXIDES

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逝去的黄金五年

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LIST OF SYMBOLS

ε	Dielectric Constant			
Å	Angstrom (10 ⁻¹⁰ meters)			
R	Reflectivity			
Ω	Resistance			
ρ	Resistivity			
σ	Conductivity			
λ	Wavelength			
$1 \text{ eV} = 8065.5 \text{ cm}^{-1}$	electron volt			
$k_B = 8.617 \ 343(15) \times 10^{-5} \mathrm{eV} \mathrm{K}$	Boltzmann constant			

CHAPTER 1

INTRODUCTION OF MANGANITE OXIDES

1.1 Goldschmidt Tolerance Factor

The Goldschmidt tolerance factor (*t*) [1]

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$$
(1.1)

is used to judge the degree of ABO_3 perovskites distortion, where r_A , r_B and r_O are the ionic radii for A, B and O. The Jahn–Teller (J-T) distortion strength varies according the ionic radius of the rare earth cation. Two distinct structural phases are found to exist for $RMnO_3$: the orthorhombic structure and the hexagonal structure (see Figure 1.1). The tolerance factor indicates the boundary between the orthorhombic and hexagonal structures. When the ionic radius is larger than the Ho³⁺ ionic radius t > 0.855 and $RMnO_3$ is an orthorhombic perovskite phase. For t < 0.855 and the ion radius $r_R < r_{Ho}$, strong distortions persist and the hexagonal phase $RMnO_3$ becomes stable [2].



Figure 1.1 Phase chart of *R*MnO₃ as a function of ionic radius [2].

The orthorhombic phase can be stabilized in small ion samples at high pressures [3, 4]. Also, deposition of films on substrates which impart strain can stabilize the orthorhombic materials of type I in the hexagonal phase [2, 5, 6]. Structures with different symmetry properties have quite different physical properties. The doped orthorhombic phase show large magnetoresistance while the un-doped rhombohedral phase exhibits large bulk polarization. Understanding the intimate coupling of spin, lattice and charge in these materials as well as their structural stability is the core topic of this thesis work. This will be carried out conducting Infrared (IR), transport and structural measurements as a function of pressure and temperature. Synchrotron based x-ray diffraction and IR measurements, laboratory based transport measurements and Neutron Scattering measurements are being conducted on bulk polystalline materials, thin films and single crystals. The results will be used to refine theoretical models of these materials.

1.2 Magnetoresistance Effect

Magnetoresistance (MR) is the property of a material to change the value of its electrical resistance when an external magnetic field is applied [7, 8]. It is defined by:

$$MR(T) = \frac{\rho(H,T) - \rho(0,T)}{\rho(0,T)} \times 100\%$$
(1.2)

Where $\rho(H, T)$ and $\rho(0,T)$ are the resistivity with and without magnetic field at given temperature (*T*). The first MR effect was discovered on iron and nickel in 1895 by William Thomson [9]. However, it was not possible to be lower the resistance more than 5% and it was named ordinary magnetoresistance (OMR).



Figure 1.2 The magnetoresistance (GMR) of Fe/Cr multilayer at 4.2K [10].

In 1980's, Giant magnetoresistance (GMR) was discovered by two European research groups. MR near 6% in Fe/Cr/Fe tri-layers was observed by a research team led by Peter Grünberg [11] of the Jülich Research Centre (DE), who owns the patent. Simultaneously but independently, this effect was observed in Fe/Cr multilayer by the group of Albert Fert [10] of the University of Paris-Sud (FR). The Fert group first saw the large MR effect (50%) in multilayer (Figure 1.2) that led to its name, and first correctly explained the underlying physics. The discovery of GMR is considered the birth of spintronics and both scientists were awarded the 2007 Nobel Prize in Physics. GMR has been used in the modern hard drive read heads and magnetic sensors. The pioneering work to bring the GMR effect to commercial application was done at IBM by a group lead by Parkin [12].

In the 1950s, the mix-valence perovskite manganites $La_{1-x}Ca(Ba, Sr)_xMnO_3$ were studied by Van Santen and Jonker [13, 14] first. In 1954, Volger [15] showed negative magnetoresistance in $La_{0.8}Sr_{0.2}MnO_3$ with a peak near the Curies temperature. In early 1990s, the MR of the mixed-valence manganite thin films with MR values far beyond GME was found [7, 16] and the name colossal magnetoresistance (CMR) was coined. This extremely high negative MR (even more than 100%) brought new attention to the manganese-based perovskite oxides. CMR materials, especially *3d* transition-metal oxides, possess larger room-temperature magnetoresistivity associated with a metal-insulator transition in a narrow temperature range (see in Figure 1.3). These materials provide opportunities for a higher (than today) density storage devices, magnetic sensors and pushed the concept of spintronics (the use of the electron spin degree of freedom in microelectronic).



Figure 1.3 The colossal magnetoresistance (CMR) behavior for the single crystal La_{0.67}Ca_{0.33}MnO₃ [17].

Many patents have been given for magnetic sensors [18, 19], and a magnetic random access memory (MRAM) device [20, 21], a type of non-volatile semiconductor memory [22]. Understanding the underlying physics in these CMR materials is key to enhancing their sensitivity to small magnetic fields need for device applications.

1.3 The Physics of GMR Materials

Giant magnetoresistance (GMR) [23-25] is a quantum mechanical effect, observed in thin films with alternating ferromagnetic and nonmagnetic layers. GMR systems are typically developed in three configurations: Multilayer GMR, Spin-valve GMR and Granular GMR.

In Multilayer GMR, two or more ferromagnetic layers are separated by a very thin (~1 nm) non-ferromagnetic spacer (e.g. Fe/Cr/Fe) [10]. The two adjacent ferromagnetic layers are anti-parallel RKKY (Ruderman-Kittel-Kasuya-Yosida) coupled [26-29], which is a coupling mechanism through the interaction with conduction electrons by the nuclear magnetic moments or localized inner d or f shell electron spins in a metal. This is, the localized d or f spins interacting via the conduction band electrons. There is an antiferromagnetic high resistance state with magnetic layers having opposite spins. By a small magnetic field, the anti-parallel spin layers can be transformed into the parallel spins with MR change more than 10% (as shown in Figure 1.2). MR ratio is exponentially depending on the nonmagnetic spacer thickness. The characteristic length ξ is typically ~1.5-3 Å at room temperature and even shorter at low temperature [30, 31]. For different nonmagnetic spacer materials like Al, Ag, Au, Si, Pd, Ru, and Ti, in most case, the exchange-bias and the coercive field amplitude decreases exponentially with the spacer thickness and oscillates (changes sign). In some specific cases, a nonmonotonic variation of the exchange-bias field with the spacer thickness is observed [32]. The different seed layer materials for the magnetic tunnel transistor (MTT) were studied by Dijken et al. [33]. For MTT device, the insertion of a Cu or Au seed layer between the metal spin valve and the silicon is found to significantly enhance the device output current and magnetic-field sensitivity and a Pt or Pd seed layer slightly improves the properties of the MTT. In contrast, seed layers of Ta and Ti deteriorate the output current and tunnel barrier breakdown voltage of the MTTs [33].

The spin-valve [34] GMR is also a layered structure (see Figure 1.4), but the two ferromagnetic layers are separated by a thin (~3 nm) non-ferromagnetic spacer.

Magnetizations of two adjacent FM electrodes can be switched independently with different coercive fields. The parallel and anti-parallel alignments correspond to the lower and higher resistance. In the two current model both spin up and spin down electron currents are scattered in the antiparallel configuration while in the antiparallel configuration spin scattering is reduced for on spin channel.



Figure 1.4 Spin-valve GMR [22, 23]. \mathbb{R}^{\uparrow} and \mathbb{R}^{\downarrow} represent electrons resistance for spinup and spin-down respectively. The size of green boxes presents the value of resistance (an anti-parallel spin orientation between FM layers and electrons can result in more electron scattering and higher resistance) [35].

Granular GMR is the effect that occurs in solid precipitates of a magnetic material in a non-magnetic matrix. It can be seen in several magnetic/non-magnetic alloys such as Cu/Co [36, 37] and Co_xAg_{1-x} [38].

1.4 Crystalline Structural Distortion of CMR Materials

CMR oxides have layered (with intervening rock salt layers between the MnO₆ polyhedra) or simple perovskite structures [39]. Here we focus on the simple perovskite structure. The CMR effect has been studied extensively in the cubic perovskites manganite $R_{1-x}A_x$ MnO₃, where *R* is a rear-earth trivalent transition-metal cation (*R* = La, Pr, Nd, Sm, etc.) and *A* is a divalent cation (*A* = Ca, Sr, Ba, etc.). The cubic-like perovskite $R_{1-x}A_x$ MnO₃ can be acquired by chemical doping a perovskite parent

compound $RMnO_3$, which replaces the trivalent rare-earth ion with the divalent alkalineearth ion or by a vacancy (self-dope manganites *e.g.* La_xMnO₃).

The broad range of physical phenomena in CMR materials have attracted intense interest from both experimentalists and theoreticians, such as ferromagnetic (FM) to paramagnetic (PM), metal-insulator (MI) transition, Jahn-Teller (J-T) distortion, charge ordering (CO) and orbital ordering [8, 17, 40, 41]. The low temperature metallic behavior is described by a simple double exchange model [42-44], but Millis [45] *et al.* showed that inclusion of spin lattice coupling into the Hamiltonian is need to describe the behavior at both high and low temperatures.

In this highly correlated system, the detailed studies of the interactions among charges, spins, orbital and atomic coupling are also critical for the understanding of complex oxides such as transition metal oxides, multiferroics materials and high T_C superconductors.



Figure 1.5 The ideal cubic perovskite structure of *R*MnO₃ [46].

An ideal cubic perovskite structure is shown in Figure 1.5. However, because of the ion size difference between R (R and A occupy the same site) and Mn (Mn³⁺ and Mn⁴⁺), the $R_{1-x}A_x$ MnO₃ structure is distorted into orthorhombic, rhombohedra, or even monoclinic unit cells. The structure is governed by the Goldschmidt tolerance factor. The perovskite structure is stable for 0.89 < t < 1.02, and the perfect cubic structure has t

= 1. Relevant ionic radii are list in the Table 1.1. $RMnO_3$ (R = La-Dy) corresponds to the orthorhombic structure where $c/\sqrt{2} < a < b$. Three other types of orthorhombic structures exist: 1) the small t, O-type structure with $a < c/\sqrt{2} < b$, which has the rotation of MnO₆ octahedral about a 110 axis. 2) O⁺₄-type when $a \approx b < c/\sqrt{2}$. 4) O^{*}-type quasicubic structure when $a \approx c/\sqrt{2}$.

Ti ⁴⁺	0.0605	Y ³⁺	0.119	Ca ²⁺	0.134	Na ⁺	0.139
Mn ⁴⁺	0.053	La ³⁺	0.136	Sr^{2+}	0.144	K^+	0.164
Mn^{3+}	0.0645	Pr ³⁺	0.129	Cd^{2+}	0.131	Rb^+	0.172
Mn^{2+}	0.083	Nd ³⁺	0.127	Sn^{2+}	0.130		
Fe ³⁺	0.0645	Sm ³⁺	0.124	Ba ²⁺	0.161		
Co^{3+}	0.061, 0.0545(<i>ls</i>)	Gd^{3+}	0.122	Pb ²⁺	0.149		
Ni ³⁺	0.069	Bi ³⁺	0.096				
Ga ³⁺	0.062						
<u>Al³⁺</u>	0.0535					O^{2-}	0.140

Table 1.1 Ionic Radii for ions in Perovskite Structure Oxide (nm) [47] (*ls* = Low Spin)

Controlled by the tolerance factor and the Jahn-Teller distortion, the MnO₆ octahedron in the typical parent compound LaMnO₃ is tilted and the bond angle of Mn-O-Mn is below 180° (see Figure 1.6). Sophisticated studies of this stoichiometric LaMnO₃ have been conducted [48-52]. The Mn-O-Mn bond angles of LaMnO₃ are ~155°. The MnO₆ octahedron is J-T distorted in such a way that the long and short Mn-O bonds lie in the *ab* plane, giving the pattern of orbital order illustrated (room temperature bond lengths Mn-O1(*m*)= 1.9680(3) Å, Mn-O2(*s*)=1.907(1) Å, Mn-O2(*l*)=2.178(1) Å, average Mn-O=2.0178(4) Å) [51] (note: *s*, *l*, *m*= short, long, medium). At temperature of about 1020 K, the orthorhombic distortion disappears and the compound becomes rhombohedral (quasicubic) with the R-type LaAlO₃ structure. There is also an O-O orthorhombic transition at 940 K. The magnetic moment of LaMnO₃ on the Mn site is

3.7- 3.9 μ_B [48]. LaMnO₃ has been identified either as a charge-transfer insulator or as a Mott-Hubbard insulator [41, 53].



Figure 1.6 Ambient pressure and temperature orthorhombic perovskite structure of LaMnO₃ with space group *Pbnm*, a=5.5367(1) Å, b=5.7473(1) Å, c=7.6929(2) Å [51]. The atomic positions are La at 4*c* (-0.0078, 0.049, 0.25), Mn at 4*b* (0.5, 0, 0), O1 at 4*c* (0.075, 0.4874, 0.25) and O2 at 8*d* (0.7256, 0.3066, 0.0384).

Different chemical doping levels can alter the physical properties of CMR materials. Doping not only changes the ratio of Mn^{3+}/Mn^{4+} for carrier equilibrium but also changes the tolerance factor *t*. It modifies the crystal structure and electronic structure and is called "internal pressure" in analogy with the external pressure. The overlap between Mn 3*d* orbital and O 2*p* orbital can be strongly affected by pressures through by changing the bond lengths and the Mn-O-Mn buckling.

1.5 Electronic Structure

An isolated Mn ion has five degenerated orbital states available to 3*d* electrons. In a crystal, the degeneracy is lifted by crystal field, exchange, and Jahn-Teller distortion combined, as shown in Figure 1.7. The crystal field splits d orbits into two subgroups: three t_{2g} orbits (d_{xy} , d_{zx} , d_{yz}) and two e_g orbits ($d_{x^2-y^2}$, $d_{3z^2-r^2}$). The energy separation between the highest e_g level to the lowest t_{2g} level is $\Delta \sim 1.5$ eV. The exchange splitting is

about 2.5 eV. For the Mn³⁺ and Mn⁴⁺, the intra-atomic correlations ensure that the electron spins aligning parallel (first Hund's rule). Mn⁴⁺ has three t_{2g} electrons with S = 3/2, and Mn³⁺ has one more e_g electron in the state of $t_{2g}^{3\uparrow}e_g^{\uparrow}$ with S = 2 [54].



Figure 1.7 Multiplet splitting of the Mn 3*d* orbital [55] and ligand field splitting of 5fold degenerate atomic 3*d* level into lower t_{2g} (triple degenerate) and higher e_g (double degenerate) levels. Jahn-Teller distortion of MnO₆ octahedron further lifts each degeneracy as shown in the figure [17].

Lower symmetry than cubic field lifts the e_g and t_{2g} degeneracy. The energy of Mn⁴⁺ remains unchanged, but the energy of Mn³⁺ is lower since the eg electron lowers its energy. There is a balance between local distortion lowering energy and elastic strain costing energy. The oxygen octahedron elongates along the distortion axis. Hence the presence of Mn³⁺ is likely to distort its octahedral environment in contrast to Mn⁴⁺. High Mn⁴⁺ concentration will reduce the J-T distortion and destabilize the $e_g (3z^2-r^2)$ orbit.

In the perovskite manganites, several interactions compete with each other (double exchange, superexchange...). The energy magnitude is order of $\sim 1 \text{ eV}$ [55, 56]. The characteristic feature of these systems is an energy surface with many closely lying stated. Changes of temperature, chemical doping, the pressure and the magnetic field can

easily modify interactions and the electronic structure and properties can be easily modified.

1.6 Exchange Interactions

In manganites, the magnetic cations are separated by nonmagnetic (diamagnetic) anion. The exchange interactions between the magnetic ion spins determine the magnetic properties of the manganites. Two important exchange interactions are double exchange (DE) effect and the superexchange (SE) effect.

The double exchange (DE) mechanism was first proposed by Zener [43] and further developed by Anderson and Hasegawa [44]. It occurs only when one ion has an extra electron compared to the other [57]. For $Mn^{3+}-O^{2-}-Mn^{4+}$, the hopping of the e_g conduction electron of Mn^{3+} to the O 2p orbital and from the O 2p orbital to the empty e_g orbital of Mn^{4+} happens simultaneously. DE is a ferromagnetic interaction because the hopping integral has an optimal value only when the spins of neighboring Mn^{3+} and Mn^{4+} are parallel. The probability t_{ij} of the e_g electron transfer between the neighboring Mn sites (*i* and *j*) is expressed in terms of Anderson-Hasegawa relation by:

$$t_{ij} = t_0 \cos(\theta_{ij} / 2)$$
 (1.3)

Where t_0 is the transfer integral determined by the Mn-O bond distances and Mn-O-Mn bond angles which influence the overlap of Mn 3*d* orbital and O 2*p* orbital, θ_{ij} is the angle between the Mn spins (see Figure 1.8). When the core spins are parallel (θ_{ij} =0), it maximizes the hopping rate and minimizes the electronic resistance and vice versa



Figure 1.8 Schematic for double exchange mechanism [17].

Superexchange [44, 58-60] is the interactions between the neighboring magnetic cations (as transition-metal ions) with the same valence (number of electrons) [61], which are well separated by the diamagnetic anions such as O^{2^-} . The orbital configuration of SE interaction follows the rules of Goodenough-Kanamori [54]. SE varies as $\cos(\theta_{ij})$ whereas the double exchange as $\cos(\theta_{ij}/2)$.

When two filled e_g orbitals overlap well with an anion, both Mn-O bonds can be covalent. The Mn-Mn bond distance is smallest and the cations coupling is strongly antiferromagnetic below the magnetic ordering temperature, Neel temperature (Ordinary superexchange between $e_g(\sigma)$). When a filled e_g orbital and an empty one overlap an anion with each site, only one Mn-O bond can be covalent and another can be ionic. The Mn-Mn separation is large and the cation coupling becomes ferromagnetic (direct exchange between e_g orbital and t_{2g} shell). When two e_g orbitals overlap on anion, neither Mn-O bond can be covalent and both of them are ionic. The Mn-Mn bond distance becomes the largest and the coupling is a weaker antiferromagnetism (π -bond superexchange of t_{2g} shell). In general, for manganites, the interaction of Mn⁴⁺-O-Mn⁴⁺ is antiferromagnetic (AF), whereas the interaction for Mn^{3+} -O-M n^{3+} may be ferromagnetic (F) or AF. In LaMnO₃, both F and AF coexist [54].

DE reveals the correlation between ferromagnetism and electronic transportation in doped manganese oxides. The different angular dependence of DE $[\cos(\theta_{ij}/2)]$ and SE $[\cos(\theta_{ij})]$ in conjunction with the competition of DE ferromegnetism and SE antiferromagnetism leads to the complex magnetic phase diagram of manganites versus the doping level *x* (for example La_{1-x}Ca_xMnO₃, see Figure 1.9).



Figure 1.9 The complex magnetic phase diagram of La_{1-x}Ca_xMnO₃ [62].

1.7 Charge and Orbital Ordering

Charge ordering [46, 63-66] is a first order phase transition that occurs when the charge carries with different oxidation states form an ordered superlattice, resulting from the strong long range interatomic Coulomb interactions overcome their kinetic energy (conduction-electron bandwidth W). It accompanies with the abrupt resistance and lattice parameters changes. For some manganites at certain doping level (like *x*=0.5), the

ordering of Mn^{3+}/Mn^{4+} in the crystal lattices, appears as sharp superlattice spots in electron diffraction patterns [67].



Figure 1.10 Charge ordered state of $La_{0.5}Ca_{0.5}MnO_3$ (a) 001 zone-axis electron diffraction pattern obtained at 95 K. The fundamental Bragg peaks labeled *a*, *b*, and *c* can be indexed as (200), (020), and (110), respectively. The presence of superlattice spots with modulation wave vector (1/2, 0, 0) or (0, 1/2, 0) is evident. Kinematically forbidden (100) and (010) spots also appear as a result of multiple scattering. (b) Schematic charge-ordering picture of Mn^{4+} and Mn^{3+} ions. Open and closed circles represent Mn^{4+} and Mn^{3+} ions, respectively. The orientation order of $d_z 2$ orbitals of Mn^{3+} ions which results in the cell doubling along the *a*-axis is also indicated [67].

Charge corresponds to the 3*d* e_g electrons becoming trapped and spatially ordered so the material is an AF insulator (see Figure 1.10). The charge ordered state appears at rational doping levels such as x=1/8, 1/2, or 3/4. A broad bandwidth will suppress the charge ordering but the charge ordering temperature (T_{CO}) will rises when W narrows [68]. The T_{CO} decreases almost linearly when increasing the averaged radius of the *R*-site cations, with a slope: $dT_{CO}/d < r_a > \approx -1332$ K Å⁻¹ [69]. As the tolerance factor or equivalently the averaged ionic radius of the perovskite A-site decreases from (La, Sr) to (Pr, Ca) through (Nd, Sr), orthorhombic distortions of GdFeO₃-type increases, resulting in a decrease in the one-electron bandwidth (W) of the e_g -state carriers and the CO is suppressed shown in Figure 1.11.



Figure 1.11 The magnetic as well as electronic phase diagrams of $La_{1-x}Sr_xMnO_3$ (*a*), $Nd_{1-x}Sr_xMnO_3$ (*b*) and $Pr_{1-x}Ca_xMnO_3$ (*c*). PI, PM and CI denote the paramagnetic insulating, paramagnetic metallic and spin-canted insulating states, respectively. FI, FM and AFM denote the ferromagnetic insulating and ferromagnetic metallic and antiferromagnetic (A-type) metallic states, respectively. At x = 0.5 in $Nd_{1-x}Sr_xMnO_3$, the charge–orbital ordered insulating (CO/I) phase with CE-type spin ordering is present. For 0.3 < x < 0.5 in $Pr_{1-x}Ca_xMnO_3$, the antiferromagnetic insulating (AFI) state exists in the charge–orbital ordered insulating (CO/OOI) phase. The canted antiferromagnetic insulating (CAFI) state also shows up below the AFI state in the CO/OOI phase for 0.3 < x < 0.4 [70].



Figure 1.12 (a) Charge ordering of Mn^{3+} and Mn^{4+} in a mixed crystal with x=1/2. (b) Orbital ordering of the $d_z 2$ orbitals of Mn^{3+} when x=0. (c) Combined charge and orbital ordering when x=1/2 [71].

The charge ordering is closely related to the orbital ordering and spinning ordering (see in Figure 1.12 and Figure 1.13). The A-type antiferromagnetic and C-type orbital structures of LaMnO₃ were observed in experiments [72, 73]. The end compound LaMnO₃ (x = 0) with maximal W as well as other RMnO₃ are strongly affected by both the collective Jahn–Teller effect and the electron correlation effect due to the n = 1 filling

of the e_g band. The collective Jahn–Teller distortion present in LaMnO₃ reflects the orbital ordering such as the alternating $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals on the *ab* plane in Figure 1.13 left panel. (Here, the *x* and *y* axes are taken as along the orthogonal Mn–O bond directions on the *ab* plane.) In this Jahn–Teller distorted and orbital-ordered state, the LaMnO₃ undergoes an AF transition at $T_N = 120$ K, whose suppressed orbital ordering temperature is at $T_{CO} = 780$ K. The detailed orbital ordered and spin order configurations are given by Hotta *et al.* [74, 75].



Figure 1.13 Left panel: Schematic view of the orbital and spin ordering in the *ab* plane of the perovskite manganite LaMnO₃, which shows the Orbital G spin A state. The orbital ordering along the *c* axis is expected to repeat the same pattern [73]. Right panel: Magnetic structures and optimized orbital structure for each magnetic structure [74]. Bottom: CE type AFM structure [75].
1.8 Jahn-Teller Distortion

The Jahn-Teller [76] theorem states that any non-linear ion or molecule which is in an orbitally degenerated state will distort to relieve this degeneracy [77]. Stability and degeneracy cannot exist simultaneously unless the molecular is linear. All orbital degenerate electronic states of non-linear molecules are unstable no matter if the degeneracy is caused by spin or orbital states, except that the two fold spin degeneracy contains an odd number of electrons. In the nonlinear molecules, the degeneracy of electronic states can be removed by the distortion lowering the symmetry. Jahn-Teller distortion is due to electron-lattice coupling due to the displacements of atoms from their ideal crystallographic positions. The distortion of highly symmetric molecule can reduce its symmetry and lower the overall energy of the complex. The Jahn-Teller effect is encountered in octahedral complexes of transition metals, such as Cu, Cr and Mn.

In perovskite manganites, the t_{2g} orbitals have lower energy than e_g orbitals because three e_g orbital points along the bond axis while t_{2g} orbital point to the interstice between bond axes (hence enectorns in the bonds of the latter see less of the charge on the atomic centers). Further, Jahn-Teller distortion destroys the degeneracy of the subgroups and the electronic structure becomes more complex.

In the manganites, the Jahn-Teller distortions lead to three distinct pairs of Mn-O bonds: long (l), medium (m), and short (s) bonds in the MnO_6 octahedral, which includes two normal modes: Q2 mode, in which two of in-plane bonds contract while the other two bonds elongate; Q3 mode, in which the four in-plane Mn-O bonds contract while the two apical Mn-O bonds elongate. And there is also a Q1 mode with the simultaneous contraction or elongation of all six Mn-O bonds.



Figure 1.14 Jahn-Teller distortion of MnO_6 octahedral: (a) The normal mode Q2 mode (Q2>0); and (b) Q3 mode (Q3>0) [50].

Jahn-Teller effect is an electron-lattice coupling, also named dynamical electronphonon coupling. This strong electron-phonon coupling may trap the itinerant electrons into the orbital due to the local structure distortions producing a minimum potential. When this coupling is strong enough, the itinerant e_g electrons can be self-trapped to form a Jahn-Teller polaron in MnO₆ octahedral. As the electrons hop from Mn³⁺ site to Mn⁴⁺ site the distortion is carried along with it.

1.9 Optical Properties of the Orthorhombic Phase

The optical properties of solids reveals detailed information about the crystal symmetry, electronic bands, vibronic bands, density of states, delocalized states and collective excitations. The research on CMR bulk materials and films has been conducted covering these aspects. Advanced optical methods can unravel the intrinsic properties of the material like the dc transport property without the grain boundary effect [78], but the sample should be prepared carefully to avoid the surface region damage for example

during polishing, since induced stress can alter the optical response and alter the properties of the sample [79, 80].

The parent ortho-manganites $RMnO_3$ (space group *Pnma*, Z=4) has 60 phonon mode at the Γ point. Infrared absorption spectra [81] and Raman scattering [3] analysis attributes the atomic motions to the phonon modes for LaMnO₃, YMnO₃ and CaMnO₃.



Figure 1.15 Schematic band diagrams of LaMnO₃. The solid and the open areas represent valence and conduction bands, respectively. e_g and t_{2g} are the Mn e_g and the Mn t_{2g} band [82].

For exampling a wide range of energies (5 meV to 30 eV) in the reflectivity spectrum, the band structure of LaMnO₃ is determined for the transitions of $e_{g\uparrow}^1 \rightarrow e_{g\uparrow}^2$ (~ 1.89 eV), O $2p \rightarrow e_{g\uparrow}^2$ (~4.63 eV), O $2p \rightarrow e_{g\downarrow}$ (~7.71 eV), O $2p \rightarrow 5d$ La (~9.35 eV), $e_{g\uparrow}^1 \rightarrow Mn 4s/4p$ (~11.1 eV) and the upper bound of J-T energy gain (E_0) in forming a local lattice distortion is ~0.5 eV [82] in Figure 1.15.

For the manganites $R_{1-x}A_x$ MnO₃ (0.2 < x < 0.5), the metal-insulator transition temperature (T_{MI}) typically coincides with the Curie temperature (T_C), the FM-PM transition temperature. IR reflective and conductivity spectra were first studied by Okimoto *et al.* [83] on La_{1-x}Sr_xMnO₃ (x = 0.175) crystal samples. A large optical conductivity spectral weight transfer from high frequency to low frequency was observed as the sample enters the metallic phase by cooling the sample or increasing magnetic field in bulk La_{1-x}Sr_xMnO₃ samples [83, 84] and a Nd_{0.7}Sr_{0.3}MnO₃ film[85]. Kaplan *et al.* [85] introduced the combined DE and J-T effects [86] to explain the optical data of a Nd_{0.7}Sr_{0.3}MnO₃ film. Kim *et al.* [87] connect the scaling behavior of the spectral weight with the effect of the spin DE and J-T lattice coupling to holes [88]. Quijada *et al.* [89] quantitatively compared the experimentally deduced e_g kinetic energy with a theory prediction. A strong Drude peak and a middle infrared (Mid-IR) peak is confirmed in the metallic phase by single crystal La_{0.827}Sr_{0.175}MnO₃ [80], La_{0.67}Ca_{0.33}MnO₃ [90] and Nd_{0.7}Sr_{0.3}MnO₃ [79]. Below the T_C , the breathing and stretching modes increase in polycrystal La_{0.7}Ca_{0.3}MnO₃ [91]. The mid-IR peak is assigned to the polaronic absorption and shifts toward the low frequency with the temperature [92, 93].

La_{1-x}Ca_xMnO₃ ($T_{MI} \sim 200$ K at ambient pressure) samples show a tendency to acquire a metallic character at room temperature under pressure [94]. The phonon mode is shielded and the insulating gap is reduced with pressure increase. The main effect of increasing pressure in the low-pressure regime is to reduce the octahedral J-T distortion at a fixed temperature. By contrast, in the high-pressure regime, a pressure-activated localizing mechanism would be the dominant, which is different with the natural delocalizing tendency of pressure [95].

1.10 Multiferrotic Hexagonal Manganites

The series of $RMnO_3$ materials (R: Ho, Er, Tm, Yb, Lu, or Y, Sc, In) have smaller radius R^{3+} ions. The ionic radius of the Y^{3+} cation is similar to those of the smaller rare earth

ions although it is not a rare earth element. Hence it forms a hexagonal phase too. Crystallizing in the hexagonal lattice is normal for those manganites with $r_R < r_{Ho}$ and t < 0.855. These manganites are interesting multiferroics materials (or ferroelectromagnets) [2, 96-99]—they are both ferroelectric ($T_C \sim 900$ K) and strongly frustrated antiferromagnets ($T_N \sim 90$ K) [100].

The definition of a ferroelectric material is "one that it undergoes a phase transition from a high-temperature phase that behaves as an ordinary dielectric (so that an applied electric field induces an electric polarization, which goes to zero when the field is removed) to a low-temperature phase that has a spontaneous polarization whose direction can be switched by an applied field [101] (see Figure 1.16 (a))." The concept is taken from ferromagnetism by replacing the bulk magnetization by the polarization and the external magnetic field by an electric field. In AFE (anti ferroelectric) materials, magnetic dipole moments of the constituent atoms or ions are ordered anti-parallel to each other (see Figure 1.16 (b)).



Figure 1.16 (a) Ferroelectric hysteresis loop [102] and (b) Ordering of the magnetic dipoles in AFE materials [101].

The electronic structure study of YMnO₃ shows that it is semiconducting with insulating ground state and the band gap ~1.5 eV [103] (note: in Prellier's review that it is insulator) and it has a spontaneous polarization close to 5.5 μ C cm⁻² [2]).

1.11 Hexagonal Structure

Starting in the 1950's, some hexagonal rare earth manganese oxides ($RMnO_3$) were studied [104-107]. Recently, the structures have been revisited again for ErMnO₃ [108], YbMnO₃ [109], YMnO₃ [110] and LuMnO₃ [111]). The hexagonal structure is built up with MnO₅ trigonal bipyramids where strong distortions persist at room temperature. In the basal (*ab*) plane, the pyramids are linked at the base corner to construct a triangular lattice. The *R* ion is located between these MnO₅ sheets linking with oxygen atoms. Each consecutive layer of MnO₃ is rotated by 180° along the *c* axis. It was conjectured that there is no significant covalent bonding between the Y 4*d* orbitals and either the oxygen 2*p* or the Mn 3*d* orbitals in Hex-*R*MnO₃ by the tight-binding analysis [101].

At high temperature above these systems have are hexagonal with an inversion center and not net polarization, below the ferroelectric transition temperature T_c , the hex- $RMnO_3$ structure (Y, Ho, and Lu) belongs to space group P6₃mc (#185). In each cell, there are 6 formula units. The atoms positions are: R1 at 2a (0, 0, z) and R2 at 4b (1/3, 2/3, z), Mn at 6c (x, 0, 0) and O1 at 6c (x, 0, z), O2 and O3 at 2a (0, 0, z) and 2a (0, 0, z), and O4 at 4b (1/3, 2/3, z). The Mn³⁺ spins and the associated magnetic exchange are confined to the basal (*ab*) plane, and Mn³⁺ spins are geometrically frustrated due to the quasitriangular lattice [112]. The spontaneous ferroelectric polarization **P**_s is along the six fold c axis [113] due to R-O displacements that occur at T_c .



Figure 1.17 The crystal structure of YMnO₃ in the paraelectric and ferroelectric phases. The trigonal bipyramids depict MnO₅ polyhedra and the spheres represent Y ions. (a) The stacking of two consecutive MnO₅ layers and the sandwiched Y layer, looking down the *c* axis in the paraelectric phase. (b) A view of the ferroelectric phase from a view perpendicular to the *c* axis, showing the layered nature of YMnO₃ [114].

Above T_C , the paraelectric Hex-*R*MnO₃ belongs to space group P6₃/*mmc* (#194). In one cell, there are just 2 formula units. The atoms positions are: R1 at 2*a* (0, 0, 1/2) and 2*a* (0, 0, 0), Mn at 2*d* (2/3, 1/3, 1/4), O1 at 4*f* (2/3, 1/3, *z*), O2 at 4*f* (1/3, 2/3, *z*), O3 and O4 at (0, 0, 3/4).

However, under high pressure (~4 GPa) and high temperature (~1000 K), the hexagonal phase $RMnO_3$ can be converted to an orthorhombic phase [4]. Figure 1.18 illustrates the crystal structure of for hexagonal and perovskite $RMnO_3$ and the 3d orbitals in the MnO_5 and MnO_6 polyhedron. The lattice parameters of some hexagonal and perovskite $RMnO_3$ are listed in Table 1.2.



Figure 1.18 Schematic drawing of the crystal structure and the 3d orbitals in the MnO_n polyhedra for (a) hexagonal and (b) perovskite $RMnO_3$ [4].

	-	110	EI	1 m	YD	Lu
Perovșkite						
$a(\text{\AA})$	5.25975(2)	5.26030(2)	5.24189(3)	5.22797(4)	5.21844(4)	5.19841(2)
$b(\text{\AA})$	5.83535(2)	5.84270(2)	5.82571(3)	5.78618(4)	5.80109(4)	5.78445(3)
c(Å)	7.35568(3)	7.35798(3)	7.33965(4)	7.32732(5)	7.30282(5)	7.29936(3)
m(Å)	1.9437(3)	1.9322(3)	1.9266(5)	1.9420(5)	1.9240(8)	1.9374(5)
/(Å)	2.243(2)	2.214(3)	2.188(4)	2.183(4)	2.292(7)	2.242(4)
s(Å)	1.892(1)	1.927(2)	1.955(2)	1.920(2)	1.868(4)	1.861(3)
<mn-o></mn-o>	2.02613	2.02437	2.0232	2.015	2.028	2.0135
Mn-Oi-Mn	142.2(1)	144.36(1)	144.51(2)	141.22(2)	143.12(3)	140.75(2)
Mn-OII-Mn	143.46(7)	143.25(8)	142.03(1)	143.65(1)	139.2(2)	142.5(1)
<mn-o-mn></mn-o-mn>	143.04	143.62	142.85	142.84	140.51	141.96
Hexagonal						
$a(\mathbf{A})$	6.14666(5)	6.13820(4)	6.11704(4)	6.081(3)	6.06625(4)	6.04011(3)
c(Å)	11.4411(1)	11.4118(1)	11.4556(1)	11.3748(6)	11.3973(1)	11.3648(6)
c/a	1.861	1.859	1.873	1.871	1.879	1.881

Table 1.2 Structural Parameters of the Perovskite and Hexagonal Phase of Group II *R*MnO₃ [4]

1.12 Magnetic of Hexagonal Manganites

The high-spin state manganese ions Mn^{3+} ($3d^4$, S=2) persisting in the Hex-*R*MnO₃ at low temperatures below T_N as a triangular lattice. Typical values of T_N are near ~90 K. The parallel α model of the magnetic structures of the Mn³⁺ lattice has been confirmed by Fiebig [115]. According this model, in a magnetic unit cell, there are six Mn³⁺ [116]. Three Mn_i ions (i= 1, 2, 3) are on the z= 0 plane, and the other three with i= 4, 5, 6 are on the z= c/2 plane. Their sites in the unit cell are shown in Figure 1.19 left panel. The magnetic symmetry is varied by the angle (φ) between the magnetic moment and the x axis. Only three magnetic symmetries are P6₃cm (0°), P6₃cm (90°), and P6₃ (0°~90°) are possible. The temperature dependant magnetic symmetries are shown in Figure 1.19



Figure 1.19 Left panel: Planar triangular magnetic structures of hexagonal *R*MnO₃. A projection of the Mn Spins at z=0 (close arrows) and z=c/2 (open arrows) on the *xy* plane of the magnetic cell show parallel (α model) orientation of neighboring spins on one line. Right Panel: Magnetic symmetry of the hexagonal manganites. Sc, Ho, and Lu show a coexistence of magnetic phases with temperature intervals being sample specific. Intervals are thus given for a single sample. Rare-earth spin ordering below 6 K was not taken into account [115].

The in-plane Mn–O–Mn AF superexchange plays a dominate role on the magnetic order and the magnetic order is also supplemented by a 2-order-of-magnitude weaker interplane Mn–O–O–Mn exchange in the stacked triangular lattice [105]. Below

 $T_{\rm N}$ (73~ 124 K), the strong SE leads to a 120° arrangement of Mn³⁺ spins in the basal plane. In addition to Mn³⁺, the rare-earth ions Ho³⁺ (4 f^{10}), Er³⁺ (4 f^{11}), Tm³⁺ (4 f^{12}), and Yb³⁺ (4 f^{13}) also contribute to the magnetic properties. Below $T_C = 5 - 6$ K, long-range ordering of the two rare-earth sub-lattices [117-121] may be ferromagnetic, ferrimagnetic, or antiferromagnetic [121].

1.13 Thermal Properties of Hexagonal Manganites

Although the T_C (914 K) is quite different from the T_N (80 K), a strong coupling between ferroelectricity and antiferromagnetic [122] was found because of anomalies in the dielectric constant and loss tangent near T_N . By compare the thermal conductivity with the dielectric and the heat capacity, Sharma [123] finds that the thermal conductivity of Hex-YMnO3 exhibits an isotropic suppression in the cooperative paramagnetic state, followed by a sudden increase upon magnetic ordering. They suggest that this behavior, which without an associated static structural distortion, originates from the strong dynamic coupling between acoustic phonons and low energy spin fluctuations in geometrically frustrated magnets. The replacement of magnetic Ho for Y at the ferroelectric active site results in an even larger effect, suggestive of a strong influence of multiferroicity [123]. The dielectric constant exhibits a sharp peak at the Mn spinrotation transition temperature (T_{SR}) for HoMnO₃.

By measuring the low temperature dielectric constant under different magnetic field, reentrant novel phases [124] are observed in the hexagonal ferroelectric HoMnO3. It accompanied by a plateau of the dielectric constant anomaly evolving with field from a narrow dielectric peak at the Mn spin rotation transition at 32.8 K in zero field. That was thought of as the indirect coupling between the ferroelectric and antiferromagnetic orders, arising from a ferroelectric and antiferromagnetic domain wall effect.

Cruz [125] observed thermal expansion anomalies providing evidence of the strong spin-lattice coupling in HoMnO₃. They explained the coupling between magnetic orders and dielectric properties below antiferromagnetic temperature (T_N) with the lattice strain induced by the magnetoelastic effect.

1.14 Optical Properties of Hexagonal Manganites

The optical properties of Hex-*R*MnO₃ were studied with its discovery. In 1969, the AF resonate mode of YMnO₃ was observed only below 40 K (43 cm⁻¹ at 4 K) [126, 127]. The YMnO₃ phonon modes for both ferroelectric and high-temperature paraelectric phases were reported on experiments and shell model lattice-dynamical calculation results by Iliev *et al.* [128, 129]. The coupling between the ferroelectric and magnetic order has been attributed to changes in the phonon spectrum associated with the AF transition [122]. Later, polarized Raman and infrared reflectivity measurements were conducted on the single crystal HoMnO₃ at both ferroelectric and AF phase status. Both Raman and infrared-active Mn-O-Mn phonons are affected by the magnetic ordering [130].

The first observation of two types of second harmonic (SH) spectra in YMnO₃ revealed the noncentro-symmetric ferroelectric charge ordering and the Centro-symmetric antiferromagnetic spin ordering for *d-d* electronic transitions within the Mn³⁺ ions [113]. A series of studies were conducted on Hex-*R*MnO₃ [115, 119, 131-136]. For Hex-*R*MnO₃ (*R*=Y, Er), the photoemission spectroscopy (PES) and x-ray absorption

spectroscopy (XAS) shows that the occupied Mn $(d_{xz}-d_{yz})$ states lie deep below E_F , while the occupied Mn $(d_{xy}-d_x^2)^2$ states overlap very much with the O 2p states. The PES spectral intensity of Mn 3d states is negligible above the occupied O 2p bands and the Mn $d_{3z}^{2} - r^{2}$ state is mostly unoccupied in the ferroelectric phase of YMnO₃ [137]. Souchkov [100] reported the optical conductivity of single-crystal LuMnO₃ (over the energy range of 10–45 000 cm⁻¹ from 4 to 300 K). They found that a symmetry allowed on-site Mn d– d transition near 1.7 eV is blue shifted (~ 0.1 eV) in the antiferromagnetic state due to Mn–Mn superexchange interactions. Similar anomalies are observed in the temperature dependence of the TO phonon frequencies which arise from spin-phonon interaction. They found that the anomaly in the temperature dependence of the quasi-static dielectric constant ε_0 below $T_N \sim 90$ K is overwhelmingly dominated by the phonon contributions [100]. Van Aken *et al.* have studied the influence of antiferromagnetic ordering on the local dielectric moments of the MnO_5 and LuO_7 polyhedra by measuring neutron powder diffraction patterns of LuMnO₃ at temperatures near $T_{\rm N}$. They have demonstrated that the magnetoelectric coupling is weak and can be understood on the basis of the fact that magnetic exchange coupling is predominantly in the ab plane of the MnO₅ trigonal bipyramids and the electric dipole moments originating in the LuO_7 polyhedra are oriented along the hexagonal c axis. Anomalies in the dielectric properties near T_N are caused by the geometric constraints between the MnO_5 and the LuO₇ polyhedra [138].

A strong magnetodielectric effects is revealed on GdMnO₃ sample by the magnetoelectric contribution to the static dielectric permittivity and by the existence of electrically excited magnons (electromagnons). Phonons strongly couple with electromagnons [139]. Inelastic neutron scattering measurements provides evidence for a

strong coupling between magnons and phonons, evidenced by the opening of a gap below $T_{\rm N}$ in the dispersion of the transverse acoustic phonon mode polarized along the ferroelectric axis [140]. The study of HoMnO₃ elucidates the spin-charge coupling and high-energy magnetodielectric effect (dielectric contrast ~8% at 20 T near 1.8 eV). The Mn *d* to *d* excitations are sensitive to the cascade of low-temperature magnetic transitions involving the Mn³⁺ (S=2) moment (spin-charge coupling) and an applied magnetic field modifies the on-site excitations [141].

Recently, the interband optical transition (~1.7 eV) was associated with the transition from the occupied hybridized O 2p state with the d_{xy}/d_{x-y}^{2-2} orbitals to the unoccupied Mn d_{3z-r}^{2-2} state. The interband optical transition (~2.3 eV) is from the occupied hybridized O 2p state with the d_{yz}/d_{zx} orbitals to the unoccupied Mn d_{3z}^{2-2-2} state. The interband optical transition (~2.3 eV) is from the occupied hybridized O 2p state with the d_{yz}/d_{zx} orbitals to the unoccupied Mn d_{3z}^{2-2-2} state. The transition (~5 eV) is the sum of two interband transitions: one from the broad O 2p states at -4 eV to the Mn d_{3z-r}^{2-2} state, and the other from the O 2p states at -2 eV to the Mn 3d states with various orbitals at 3 eV [142].

1.15 Pressure Effect on Hexagonal Manganites

Anomalies in the dielectric constant ε [122] occur at the magnetic ordering temperature $T_{\rm N}$. To get more insight into the coupling between spin and structural parameters and their possible relationship with the magnetic and dielectric properties of ferroic materials, hydrostatic pressure on the magnetic ordering in RMnO₃ at low temperature was applied. The sharp dielectric peak of HoMnO₃ at T_{SR} is shifted by the applied pressure and the peak temperature of $\varepsilon(T)$ decreases linearly with applied pressure at rate at a rate of $dT_{SR}/dp = -2.05$ K/GPa [125]. Powder neutron diffraction experiments of polycrystalline

YMnO₃ show that the spin arrangement of YMnO₃ is not modified but the magnetic moment at saturation is reduced by application of hydrostatic pressure (up to 0.8 GPa). At these low pressures, the applied hydrostatic pressure mainly altered the lattice constant a, whereas c remained almost unchanged [143].

Pressure effects at much higher pressures (6 GPa) were conducted on YMnO₃ and LuMnO₃ in neutron diffraction measurements in the temperature range 10–295 K. Both samples have a significant decrease in the ordered magnetic moment of Mn ions (at T =10 K) from 3.27 (0 GPa) to 1.52 μ_B (5 GPa) for YMnO₃ and from 2.48 (0 GPa) to 1.98 μ_B (6 GPa) for LuMnO₃. This decrease for LuMnO₃ is due to an enhancement of the geometrical frustration effects on the triangular lattice. At the same time, the magnetic symmetry of the triangular AF state (the irreducible representation Γ_2) remains unchanged.

However, spin reorientation of Mn magnetic moments and a change in the symmetry of the AF structure occur in YMnO₃. A spin-liquid state due to magnetic frustration on the triangular lattice forms by Mn ions at normal pressure and $T>T_N = 70$ K, and an ordered triangular AF state with the symmetry of the irreducible representation Γ_1 arises at $T < T_N$. The high-pressure effect leads to a spin reorientation of Mn magnetic moments and a change in the symmetry of the AF structure, which can be described by a combination of the irreducible representations Γ_1 and Γ_2 [144-146]. This high pressure induces a spin-liquid phase in YMnO₃, coexisting with the suppressed long-range AF order. The spin liquid phase exhibits temperature dependence distinctively different from short-range spin correlations seen at ambient pressure. Its formation occurs through an

in-plane Mn-O bond symmetrization and results in reduced magnetoelastic coupling at high pressures [147].

Except for the low temperature magnetic structural change, the pressure could also lead to a phase change from hexagonal-type into an orthorhombic-type at ambient temperature. This transition for $Ho_{0.8}Dy_{0.2}MnO_3$ happens at 9.8 GPa at room temperature, which was detected by a change in vibration modes [148]. Here it should be noted that the end member $DyMnO_3$ is orthorhombic.

1.16 Research Interests for Hex-RMnO₃

Raman and infrared spectroscopy of YMnO₃ at the high-temperature paraelectric and low-temperature ferroelectric phases show only weak bands in the ferroelectric phase because of the noncentrosymmetricity. The structural differences between these two phases of YMnO₃ are very small [101]. By x-ray diffraction measurements [149], it is found that the ferroelectric polarization originates from the tilting of MnO₅ polyhedra and the buckling of *R* layers, which persists up to 1000 K. However, no evidence shows a structural phase transition up to 1000 K for either *R*MnO₃. And it is still questioned by Jeong *et al.* [150] whether the geometric effect is the origin of the electric polarization or whether the off-centering of Mn ions also contributes to the polarization [114, 151, 152]. YMnO₃ forms in both the hexagonal and orthorhombic phases on solution synthesis at ambient pressure [106]. The stability of these structures at high pressures (up to 20 GPa) at ambient temperatures and the change in the electronic structure with pressure will be explored in this thesis.

1.17 Band Structures of Manganites

Due to the hexagonal crystal field, the majority *d*-state of Mn^{3+} ion split in two doublets and one singlet, in the orthorhombic crystal field the splitting of the *d* states are t_{2g} and e_g states [97], which are schemed in Figure 1.20.



Figure 1.20 Schematic orbital splitting for the majority d states of Mn^{3+} ion within orthorhombic and hexagonal crystal fields [97].

Hill [153] calculated band structures for cubic paramagnetic LaMnO₃ along the high symmetry axes of the simple cubic Brillouin zone, which is shown in Figure 1.21. In the band structures plot, the Fermi level is set to zero and the plotted energy range covers from -12 eV to 4 eV. The bands between -7 and -2 eV arises from the oxygen 2p orbitals. The Mn 3*d* bands are above the oxygen 2p bands, and they are separated by an energy gap. The Mn 3*d* bands are splitting into two sub-bands - the lower energy t_{2g} bands, and the higher energy e_g bands - because of the octahedral oxygen anions crystal field. The Fermi level lies near the top of the Mn 3*d* t_{2g} bands and is located in a region of high density of states. La 5*d* electrons occupy a high energy range.



Figure 1.21 Band structures for cubic paramagnetic lanthanum manganite along the high symmetry axes of the Brillouin zone [153].

For hole-doped half metallic materials $La_{1-x}Ca_xMnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ (LSMO), Pickett [154] and Ferrari [155] did the band structure calculations. There is a strongly spin-dependent hybridization between Mn *d* states and O *p* states because the majority Mn *d* bands overlap the O *p* bands while the minority Mn *d* bands are separated by a gap from the O *p* bands; Because of strong local environment effects arising from neighboring cation charge differences (La^{3+} or Ca^{2+}), the localization of the low density of minority carriers lead to effective half-metallic ferromagnetism in the CMR regime [154]. Figure 1.22 [154] shows the minority band structure of FM $La_{1-x}Ca_xMnO_3$. In Figure 1.23 [155], the majority and minority band structure of LSMO are plotted in the same chart. The bands near the Fermi level are constructed mainly from hybridization of the oxygen 2*p* and the manganese 3*d*-orbitals. The conduction bands at the Fermi level correspond to the occupied e_g majority spin states. In the DOS, the peaks at ~1.5 eV below E_F and ~2 eV above E_F correspond to the t_{2g} states for the majority (occupied) and minority (unoccupied) spins.



Figure 1.22 The minority band structure along Γ -X for the series of FM phases La_{1-x}Ca_xMnO₃, x=0, 1/4, 1/3, 1. For the five bands near E_F for x=1/3, the lower band is purely Mn_{La-La}, the upper pair is purely Mn_{La-Ca}, and the middle pair involve all Mn ions. There is a strong decrease in minority gap with increasing Ca content x that arises from the raising of the O p bands as the average neighboring cation charge decreases. Note that for CaMnO₃ (x=1) the actual Fermi level (determined by the majority bands) lies near midgap. The majority band structures (not shown) are strongly metallic in this region [154].



Figure 1.23 Band structures and density of states (centre panel) for hole-doped $La_{2/3}Sr_{1/3}MnO_3$. Minority (majority) spin is shown with solid (dashed) lines [155].

For the hexagonal manganites, by applying the pseudo-self-interaction correction (SIC) on Local-spin-density-functional (LSDA) results, Filippetti [156] calculated the

paraelectric YMnO₃ an insulator. A gap (*Eg*) is 1.40 eV, between the empty $d_{z^2}^{\uparrow}$ band and the fully occupied $pd\sigma$ band (seeing in Figure 1.24).



Figure 1.24 A-type AFM, paraelectric YMnO₃ pseudo-SIC band structure. The gap between empty *d* bands and filled $pd \sigma$ -hybridized bands [156].

1.18 Applications

Now the application of rare earth manganites and crystalline multiferroic – ferroelectric materials is not only limited to the fields of magnetic and optical recording (Figure 1.26), magnetic sensors (Figure 1.25), and magnetic switches, but also extended into the energy saving and producing fields. The manganites are investigated as bolometric infrared detectors [157, 158], as the household active magnetic refrigeration [159], the photo catalyst (LaMnO₃/CdS nanocomposite (10 nm) in Figure 1.27) producing hydrogen from water under visible light irradiation [160] and the possible cathode (Sr-doped LaMnO₃) in solid oxide fuel cell (Figure 1.28) [161]. In future, more and more new applications will be developed.



Figure 1.25 Fluxgate magnetic field sensor [162].



Figure 1.26 Multiferroic magnetic recording read head. (A) Three-dimensional diagram of the read head showing the sensor stack, half gaps, magnetic shields, and a recording track. (B) Crosssection [163].



Figure 1.27 Schematic drawing for H_2 production from water containing sewage sludge solubilized by the HCW method over the LaMnO₃/CdS photo catalyst under visible light irradiation [164].



Figure 1.28 A fuel cell and the reaction it uses to produce electricity [161].

CHAPTER 2

METHODS: SAMPLE PREPARATION AND EXPERIMENTAL METHODS

2.1 Crystal Growth

The manganite research was conducted on polycrystalline, single crystal and thin film samples. Polycrystalline samples can be made by the solid-state reaction method and the citrate method. The solid-state reaction is the most common approach. First stoichiometic component powders were weighted and mixed. The mixed powders were ground, pressed into a pellet and sintered several times until a single phase material was acquired. The final firing is at higher temperature with slow cooling down to make the sample dense and compact.

Single crystal sample can be grown in many ways [165]. The flux method can provide thermal strain free crystals. The crystal growth takes place in a crucible (platinum, quartz) where the components of the desired substance are dissolved into a solvent (flux like tin and lead) and the growth takes place at relatively low temperatures. The constituents of the desired crystal and the flux are kept at a temperature slightly above the saturation temperature long enough to form a complete solution. Then the crucible is cooled slowly in order that the desired crystal precipitates from this saturated solution. Nucleation happens in the cooler part of the crucible. The grown crystals display natural facets so that they can be used for optical experiments without further polishing. A disadvantage is that the crystals are relatively small (size in mm) and sometime the crystals are hard to separate with the condensed flux [166].

Large single crystal sample of many materials can be grown by floating zone technique with polycrystalline rod. The rod is placed inside a quartz tube of an infrared

image furnace (see Figure 2.1). Heat is focused by mirrors onto a region of the feed rod to form a small molten section. The liquid is held in place by surface tension and rotation helps to produces a more uniform heating region of the molten material. The molten (floating) zone is slowly moved downwards along the sample length by translating the sample. While new material is introduced into the molten zone from the feed rod, the crystal is grown on the solidifying end of the float zone, on the seed, which is a material with a similar crystal structure as the feed rod.



Figure 2.1 Floating zone furnace schematic [167].

2.2 Thin Film Deposition

High-quality thin films can be grown on a substrate by physical deposition techniques like sputtering, pulse laser deposition (PLD) and chemical reactive deposition techniques such as molecule beam epoxy (MBE), metal-organic chemical vapor deposition (MOCVD) [168].

PLD [169] method needs a sintered target with the composition of the final material. A focused excimer ultraviolet laser ($\lambda = 248$ nm) beam ablates the ceramic target. The ablation creates a plasma plume which is composed of the components of the target material. The plasma will condense on the substrate and build up a film (see

Figure 2.2). The deposition occurs under an oxygen environment. The laser energy density, the laser pulse rate, the distance between target and the substrate, the substrate temperature, the oxygen pressure, and the annealing process will determine the film properties.



Figure 2.2 Schematic of pulse laser deposition [170].

MOCVD utilizes mixtures of solvent precursors and hence is easy to change the ratio of source components for different compositions or heterostructures. When the liquid or gas metal-organic compounds and metal hydrides are passed through the substrate surface, they will react and deposit on the substrate to form a high quality film.



Figure 2.3 Scheme of the injection-MOCVD set-up [171].

A computer controlled micro-valve injection MOCVD [171] is shown in Figure 2.3. The precursor vapors produced by the flash evaporation of their organic solutions were injected into the reactor [171] and it was used to prepare the film samples used in this thesis [172]. This method has a very high reproducibility with flexibility of composition variation and a broad range of deposition rates can be achieved.

2.3 CMR Films and Substrate

Epitaxial films are the basic material of the CMR application [54, 173, 174]. Lattice mismatch between the film material and a bulk material will introduce the strain. Sometimes, it will deform a film and give the film different physics properties compared with the bulk material. The lattice mismatch along the interface is defined by:

$$\delta = (a_{p \, substrate} - a_{p \, bulk}) / a_{p \, substrate} \tag{2.1}$$

Positive δ corresponds to tensile strains and it elongates the cell in the films' plane and compress the cell along the out-of-plane growth direction (see Figure 2.4), and vice verse for the compressive stress with a negative δ .



Figure 2.4 Schematic diagram of the lattice cell distortion in a strained epitaxial film under (a) tension and (b) compression. The out-of-plane parameter changes corresponding to each stress condition [54].

The common single crystal substrate materials are listed in Table 2.1. The unit cell volume of the film is not conserved and it changed with the substrate and the film thickness. The film is not completely relaxed until it reaches a thickness of the order of 500 nm. In a film thinner than 60 nm, there is no relaxation and it is fully strained [175]. In the film thicker than 60 / 80 nm, the film can be a single crystal phase without dislocation or intermediate layer up to 120 nm [175, 176]. It also can be in two regimes such as in Nd_{0.5}Sr_{0.5}MnO₃ films (thickness 100 nm ~ 200nm) deposited on (001) oriented LaAlO₃: one is strained (close to the substrate) and another is quasi-relaxed component in the upper part of the film, the latter increasing with film thickness [177]. At 103 K, the STO substrate has a 'tetragonal-cubic' transition and the film will follow this structural change [175].

The CMR maganites are sensitive to lattice distortions and structural changes, so the strained CMR films would exhibit different magnetic and electric properties from bulk samples. Checking the morphology of the film, a very smooth single crystal film displays columns under atomic force microscope (AFM). The polycrystalline film will show different size grains inside depending on the film deposition parameters and the grain boundary effect will modify the transport properties [178].

Table 2.1 Common Single Crystal Substrates for CMR Materials

Name	SrTiO ₃	LaAlO ₂	MgO	NdGaO2	$(LaAlO_2)_{a,a}(Sr_aAlT_aO_c)_{a,a}$
Symbol	STO	LAO	-	NGO	LSAT
Lattice structure	Cubic	Rhombohedral (25 °C)	Cubic	Orthorhombic	Cubic (domain I)
Lattice parameter (nm)	a = 0.3905	a = 0.3788 c = 1.311	a = 0.4205	a = 0.5426 b = 0.5502 c = 0.771	<i>a</i> = 0.3868
	Nb:SrTiO ₃ (STON)	Cubic (> 435 °C)			f.c.c. (domain II) a = 0.7737

Source: MTI Corporation Inc. http://www.mtixtl.com/

2.4 Sample Preparation

Polycrystalline $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) was made by solid-state reaction method. The mixed Pr_6O_{11} , CaCO₃ and MnO₂ powders were heated at 1100 °C for 10 hours. A pressed pellet was sintered at 1200 °C for 40 hours with intermediate grindings. The dense pellet was kept at 1300 °C for 10 h for the final firing and cooled slowly by a rate of 1 °C/ min. X-ray diffraction (XRD) is the most common method to determine the crystal structure. Laboratory XRD equipment was used to check the sample structure and crystallization. The XRD pattern (see Figure 2.5) was check by a laboratory x-ray diffractometer (Rigaku RINT-2100).

CMR and multiferroic manganites exhibit magnetic phase transitions which can be examined by measuring dynamic susceptibility, such as ferromagnetic transitions. Typically, χ diverges at the critical temperature of a ferromagnetic phase transition. Critical exponents characterize the nature of the divergence as a function of temperature and dc applied field. Determination of these critical exponents allows one to distinguish between various models of magnetic interactions. Characterizing samples by SQUID (Superconducting Quantum Interference Device) magnetometer, the saturated magnetic moment of bulk PCMO is ~1.65 μ_B /Mn at 5K and 1 T magnetic field measured by SQUID comparable with 1.8 μ_B /Mn [179]. The elements of the PCMO bulk target were determined by Energy Dispersive X-ray analysis (EDX) and the atomic ratio of Pr *vs.* Ca is 3: 7.07 (± 0.61) in 20 sampling points. Transport property was measured by the fourpoint method without an external field.



Figure 2.5 Bulk PCMO X- ray diffraction pattern. Inset (a) Bulk PCMO resistivity (b) Bulk PCMO and PCMO/STO film resistances.



Figure 2.6 PCMO target scanning electron microscope (SEM LEO 1530) surface image.

The PCMO film was deposited on a STO (100) substrate by the PLD method. The KrF Laser ($\lambda = 248$ nm) pulse rate was 1.5 Hz and the energy density on the target is ~1.5 J/ cm². The distance between the target and the substrate is about 6 cm. In the vacuum chamber, O₂ partial pressure is kept at ~120 mTorr and the substrate was hold at 750 C° during the deposition. After 4000 shots, the film is slowly cooling down to room temperature at rate 5 C° / min in an O_2 atmosphere with O_2 partial pressure 500 Torr. The morphology was checked by atomic force microscopy.



Figure 2.7 Left Panel: PCMO/STO film roughness measured by AFM (Atomic Force Microscope). Right Panel: Room temperature θ -2 θ XRD pattern for PCMO on STO.

2.5 Characterization

2.5.1 Neutron Diffraction Basics

Neutrons are scattered by the atomic nuclei and the unpaired electrons (magnetic dipole interaction) [180]. For elastic scattering, neutron scattering follows Bragg's law as x-ray diffractions, but the scattering amplitude of atoms and the relative intensities are not the same. It is advantageous to determine the light elements atom position such as oxygen since their scattering power is comparable to heavy atom in these measurements with neutrons. It can also be use to determine the magnetic ordering (ferromagnetism and type of antiferromagnetic order).



Figure 2.8 Identification of the unit vectors of scattering vector and magnetization vector used in discussion of magnetic scattering, together with the angles α , θ .

The crystallographic quantity of the (*hkl*) reflection from a crystal with lattice parameters a_0 , b_0 , c_0 is defined by [180]:

$$Q = \frac{\lambda^3 N_c^2}{\sin 2\theta} F^2 \tag{2.2}$$

$$F^{2} = F_{nucl}^{2} + q^{2} F_{magn}^{2}$$
(2.3)

$$F_{nucl}^{2} = \left| \sum b \exp(2\pi i (hx/a_{0} + ky/b_{0} + lz/c_{0}) \right|^{2} e^{-2W}$$
(2.4)

$$F_{mang}^{2} = \left| \sum p \exp(2\pi i (hx/a_{0} + ky/b_{0} + lz/c_{0}) \right|^{2} e^{-2W}$$
(2.5)

Where λ is the neutron beam wavelength, N_c is the number of unit cells per unit volume, F is the amplitude factor of per unit cell, θ is the glance angle (Bragg angle), $q^2 = \sin^2 \alpha$ and α is the angle between the scattering vector and magnetization vector, b is the nuclear scattering amplitude, p is the magnetic scattering amplitude and W is Debye.

In an antiferromangnet, alternate atoms along a particular crystallographic direction have magnetic moments pointing oppositely, the crystallographic repeat distance that the magnetic moment of the neutrons see may be doubled or a higher order multiple of the nuclear (or x-ray) unit cell. The magnetic unit cell will be large than the chemical crystallographic cell and in general the magnetic diffraction lines will have different positions form those of nuclear lines. Ferromagnetic peaks occur at the same position as the nuclear Bragg peaks.

2.5.2 Fourier Transform Spectroscopy (FTS) Basics [181]

Many different types of spectrometers and spectroscopic techniques provide spectral measurements over a range of frequencies covering the infrared (IR) to ultraviolet (UV). Two of the more popular instruments are Fourier Transform infrared (FTIR) spectrometers and grating monochromators [181].



Figure 2.9 Scheme of a two beam interferometer with a dispersive sample in arm2 and the production of the path difference (x) in arm1. S =source, D= detector, BS= beam splitter.

Fourier Transform spectroscopy is one of most important spectroscopic method developed with computing technology. It computes the spectrum from the interferogram, which is a function of the path difference between the two arms of the interferometer, of two-beam interferometer by Fourier Transform. The amplitudes of the electric fields for the two different paths represent by $E_1e^{i2\pi vx}$ and $E_2e^{-i\phi(v)}$, where the optical path distance x

in arm 1 (created by moving the mirror) causes the phase change $2\pi vx$ and the sample dispersive properties introduces phase shift $-\Phi(v)$ in the arm 2. The wavenumber (v) is in the unit of cm⁻¹ (8.066 cm⁻¹ correspond to 1 meV energy). Ignoring the influence of the beam splitter, the amplitude of the total EM field on the detector is:

$$E_{total} = E_1(v)e^{i2\pi cv} + E_2(v)e^{-i\phi(v)}$$
(2.6)

The intensity of the fields is:

$$\left|E_{total}\right|^{2} = E_{1}^{2} + E_{2}^{2} + 2E_{1}E_{2}\cos[2\pi vx + \phi(v)]$$
(2.7)

In the whole frequency range, the total power on the detector is:

$$P(x) = \int_{0}^{\infty} \left| E_{total} \right|^{2} dv = \int_{0}^{\infty} \left\{ E_{1}^{2} + E_{2}^{2} + 2E_{1}E_{2}\cos[2\pi vx + \phi(v)] \right\} dv$$
(2.8)

The interferogram function is:

$$I(x) = P(x) - P(\infty) = P(x) - \int_0^\infty (E_1^2 + E_2^2) dv = 2 \int_0^\infty E_1 E_2 \cos[2\pi v x + \phi(v)] dv$$
(2.9)

Extend the interferogram function to negative frequency range then:

$$I(x) = \int_{-\infty}^{+\infty} E_1 E_2 e^{i2\pi v x} e^{i\phi(v)} dv = \int_{-\infty}^{+\infty} (E_1 E_2 \cos\phi + iE_1 E_2 \sin\phi) e^{i2\pi v x} dv$$
(2.10)

Define $p_s(v) = E_1 E_2 \cos \phi$, $p_a(v) = E_1 E_2 \sin \phi$, and the complex spectral power

 $\hat{p}(v) = p_s + ip_a$, so interferogram function is:

$$I(x) = \int_{-\infty}^{+\infty} \hat{p}(v) e^{i2\pi v x} dv$$
(2.11)

The spectral power is:

$$\hat{p}(\mathbf{v}) = \int_{-\infty}^{+\infty} I(x) e^{-i2\pi \mathbf{v} x} dx$$
(2.12)

with back transformation. Since I(x) is a real quantity, $\hat{p}(v)$ must fulfill

$$\hat{p}^{*}(-v) = \hat{p}(v)$$
 (2.13)

$$\hat{p}(v) = \sqrt{p_s^2 + p_a^2} = E_1 E_2$$
(2.14)

and

$$\phi(v) = \arctan(p_a / p_s) \tag{2.15}$$

In a limited range of $-x_{max}$ to x_{max} , the observed interferogram is:

$$I_{obs}(x) = I(x) \cdot S(x) \tag{2.16}$$

Where S(x) is a choosing symmetrical screen function in this range. The observed spectrum is:

$$\hat{p}_{obs}(v) = \int_{-\infty}^{+\infty} I_{obs}(x) e^{-i2\pi v x} dx = \int_{-x_{max}}^{+x_{max}} I(x) \cdot S(x) e^{-i2\pi v x} dx$$
(2.17)

The infrared range in 100 cm⁻¹ \sim 700 cm⁻¹ wavelength is covering the energy range of the crystal phonon vibration (Far infrared: 10 – 667 cm⁻¹ [182]).

Optical Layout of the Infrared Synchrotron U2A Beamline



Figure 2.10 Infrared microscope systems optical layout [183] at the U2A beamline in Brookhaven National Lab.

2.5.3 High Pressure Basics

Applying a large force on a small area will create a huge pressure [184]. The pistoncylinder device, the belt apparatus, and the multiple-anvil devices are powerful tools to create a high pressure environment to study the material phase transition and synthesis at high temperature. A diamond anvil cell (DAC) can be selected for different studies under ultra high pressure (Table 2.2).

 Table 2.2 High Pressure Experiment with Diamonds [185]

Diamond type	Experimental techniques
Type I (Yellow)	Diffraction, Optical
Type I (Raman (ultra) low fluorescence)	Raman, Diffraction, Optical
Type IIA	Infrared, Diffraction, Optical

As the hardest material, diamond, has a wide range of radiation transmission that extends from the near-UV right down to microwave frequencies, except for a region of total infrared absorption that effectively precludes such spectroscopy from about 1850 to 2300 cm⁻¹ [186]. With low Raman fluorescence, it can be used to conduct the high pressure Raman studies. It is also largely transparent to x-rays at the wavelengths used in most structural studies (typically above 10 KeV). A diamond anvil cell is used to create the pressure (hundreds of GPa) existing beneath the crust of earth. The three main components of DAC are: (1) two diamond anvils, each mounted on a high-strength support material through which a radiation path has been drilled. (2) a metal gasket with a central hole, which separates the diamonds; (3) the force generating parts, driving the two anvils together along a common axis. The pressure can be measured by the Ruby Fluorescence method [187] or the Sr-YAG method [188].

Recently, a new Paris-Edinburgh cell is applied to generate a high pressure environment for the sample conducting a neutron diffraction experiment.



Figure 2.11 Diamond anvil cell (DAC) [189] (Left panel) and Paris-Edinburgh (PE) cell [190] (right panel).

2.6 Extracting Optical Coefficients

The IR reflectivity spectrum can be acquired in a limited region. Infrared (IR) phonon spectra are sensitive to local lattice distortions. For extracting the optical coefficients from the reflectivity spectra, there are two methods: (a) Using Kramers-Kronig relationship [191]; (b) Least Squares fitting [192, 193].

Using the Kramers-Kronig (K-K) analysis:

$$\varepsilon_{1} - 1 = \frac{2}{\pi} P \int_{0}^{\infty} \frac{\omega' \varepsilon_{2}(\omega')}{\omega'^{2} - \omega^{2}} d\omega'$$

$$\varepsilon_{2} - 4\pi \frac{\sigma(0)}{\omega} = -\frac{2}{\pi} \omega P \int_{0}^{\infty} \frac{\varepsilon_{1}(\omega') - 1}{\omega'^{2} - \omega^{2}} d\omega'$$
(2.18)

One should make appropriate extrapolations to complete the frequency range. For a low frequency approximation, a possible method is using the Hagen-Rubens relation $R \approx 1 - \sqrt{2\omega\rho_{IR}/\pi}$ (using the dc resistivity as ρ_{IR}) [91] or extrapolate the reflectivity as a constant [93]. For the high frequency region, the reflectivity can be extrapolated by combining the $\omega^{-1.5}$ law or the ω^{-4} dependence [93], or using the reflectivity data from relative materials [90]. More general expressions and useful formulas can be found in Appendix A.

Using classical Drude-Lortez (D-L) model:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \frac{Ne^2}{\varepsilon_0 m_0} \sum_j \frac{f_i}{\omega_j^2 - \omega^2 - i\gamma_j\omega}$$
(2.19)

or factored (TO-LO) [192] model:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_{j} \frac{\Omega_{jLO}^{2} - \omega^{2} + i\gamma_{jLO}\omega}{\Omega_{jTO}^{2} - \omega^{2} + i\gamma_{jTO}\omega}$$
(2.20)

In these models, the complex dielectric constant $\varepsilon(\omega)$ is assumed. By Least-Squares fitting method [192, 194], the reflectivity and transmittance can be simulated to yield physically meaningful optical constants.
CHAPTER 3

INFRARED SPECTRA OF LA_{0.8}MNO₃₋₈/LAO

3.1 Onset of the Increase in Carrier Numbers

 $R_{1-x}A_x$ MnO₃ (R: trivalent rare-earth ions, A: divalent alkaline-earth ions) has been widely studied due to the large magnetoresistance observed [7, 17, 40, 71, 174, 195]. Divalent cation doping induces a change from Mn^{3+} to Mn^{4+} at some manganese sites. The induced holes in the e_g level create a mixed valence system. These materials have also attracted much theoretical and fundamental physics interest since they exhibit intimate coupling of spin, lattice, orbital, and charge degrees of freedom. This coupling results in a ground state energy landscape with multiple minima corresponding to different charge, spin and structural configurations. Small external perturbations (such as temperature, pressure, substrate strain, magnetic fields, and electric fields) can shift the system from one state to another. In addition to chemical doping, a mixed valence on Mn sites can also be induced by defects on the La site in systems such as La-deficient $La_{1-x}MnO_{3-\delta}$ (x > 0, $\delta > 0$). Both ferromagnetic order and metallic conductivity can be obtained [196-198] and the transition temperatures can be adjusted by both the oxygen content and the La deficiency [171, 199]. One of the open questions about these colossal magnetoresistive oxides concerns the transition of the system from the high temperature paramagnetic insulating phase (with Jahn-Teller distortion of the MnO₆ polyhedra which trap the conduction band electrons) to the low temperature conductive ferromagnetic phase [200, 201]. It is thought that just above the metal to insulator transition, regions of metallic phase (Jahn-Teller free) begin to grow within the insulating host and then dominate at low temperatures based on structural and optical mode measurements [202, 203]. The nature of this mixed phase behavior is still under discussion.

Optical experiments are a good way to study the phonon modes and electronphonon coupling in oxides [192]. In addition, information on the free-carrier concentration can be derived. In previous work, it was found that the onset of the increase in the carrier numbers occurs concomitantly with the peak in resistivity and the onset of the ordered magnetic state [79, 83-85, 87, 90, 204-209]. $T_{onset} \sim T_C$ or T_{MI} from the above literature in manganites are summarized in the Table 3.1 below. Here it is shown that this is not always true and a physical model for the difference is suggested. The proposed model possibly works for other manganites, which is that outside of the fluctuation region and below T_C/T_{MI} , regions with local lattice distortions trap the conduction band electrons. As the temperature is lower, these regions release the carriers and hence produce an increase in the number of free carries. The main point is that at temperatures significantly below T_C and the peak resistivity temperature there are insulation regions in the sample.

sample	form	$T_C(\mathbf{K})$	$T_{P/T_{MI}}(\mathbf{K})$	$T_{onset}(N_{eff})$	cut off energy
La _{1-x} Sr _x MnO ₃ x=0.175	S	283 [83]	~283	~283	Adopted at a minimum as a boundy between intra and inter band excitions 1.5 eV
Nu _{0.7} S1 _{0.3} WIIIO ₃	r	-	<i>1 p</i> 180 [85]	100	1.5 CV
$La_{0.7-y}Pr_yCa_{0.3}MnO_3$	S	Series[87]	series	$T/T_{C} = 1$	0.5 eV
La _{0.7} Ca _{0.3} MnO ₃	Р	250	~250	240 [204]	0.5 eV
La _{0.66} Ca _{0.33} MnO ₃	S	307 [90]	-	~307	the total spectral weight of the Drude and mid- IR contributions
$La_{1-x}Sr_xMnO_3$ $0 \le x \le 0.3$	S	369 [84]	~369	~369	The same as above [83]
$La_{1,2}Sr_{1,8}Mn_2O_7$	S	121 [205]	121	~120	0.8 eV
$Nd_{0.7}Sr_{0.3}MnO_3$	S	197.9	~200	~200 [79]	0.8 eV
$Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ x=0,0.05 & 0.2	Р	~100 [206] 0.05	100	~100	0.1,0.05,1.1 eV
La _{0.75} Ca _{0.25} MnO ₃	Р	A 221, B208 [207]	-	~Tc	1.303 eV
$Tl_2Mn_2O_7$	Р	120 [208]	-	~120	<0.2 eV
$La_{1-x}Ca_xMnO_3$ x = 0.1, 0.265.	S	Tc [209]	-	-	0.5 eV

Table 3.1 Summary of $T_{onset}(N_{eff})$ and T_C/T_{MI} for Manganites

Note: P = Polycrystalline, S = Single crystalline, F = Film

3.2 Ambient Pressure Infrared Reflectivity

In this section, a synchrotron infrared spectroscopic study on self-doped $La_xMnO_{3-\delta}$ (*x*~0.8) films is presented. While the metal-insulator transition temperature (T_{MI}) and the magnetic ordering temperature (T_C) approximately coincide (as derived from bulk transport and magnetization measurements), the change in free carrier density onset is at a significantly lower temperature (~45 K below). This indicates the presence of an

insulating phase significantly below the magnetic ordering temperature. La_{0.8}MnO_{3.6} films were epitaxially grown on (001) LaAlO₃ (LAO) substrates by liquid injection metal organic chemical vapor deposition [171]. The x-ray 2θ scan [210] showed no any impurity phase and the *c* axis is perpendicular to the substrate surface because of only (00*l*) diffraction peaks visible. Here the results are for a ~120 nm thick film, which were also found in a ~410 nm film. The *in situ* post-deposition annealing leads to the strain relaxation which are revealed by x-ray diffraction measurements [172]. By the reciprocal space map (RSM) method, it was found that the out-of-plane lattice parameter was relaxed [210] for this ~120 nm thick La_xMnO₃₋₆ (*x*~0.8) film. The lattice parameter is summarized in Table 3.1 and the relaxed *c*-axis parameter is ~1.94 Å on the (0 0 4) reflections. Both the x-ray diffraction (2 θ scan and RSM) and TEM results [198, 211] revealed that the La_{0.8}MnO₃₋₆ film is epitaxial.

Table 3.2 XRD Summary Data of 120 nm La_{0.8}MnO_{3-δ} film [210]

$\overline{2\theta}(^{\circ})$	(hkl)	d	<i>ε</i> (%)
47.067	004	1.9407	0.0258
68.65	044	1.3742	-0.015
68.94	404	1.3692	-0.058

The film resistivity is $4.6 \times 10^{-4} \ \Omega \text{cm}$ (10 K) as acquired by a four-point probe measurement, which is comparable with $2 \times 10^{-4} \ \Omega \text{cm}$ (5 K) for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (x=0.33) films on a LAO substrate [212]. The metal-insulator phase transition temperature ($T_{MI} \sim$ 298 K) and the Curie temperature ($T_C \sim$ 295 K) are quite close (see Figure 3.6) and a high magnetization saturation of 3.66 μ_B/Mn (5 K) is achieved under a 0.2 T magnetic field.





Figure 3.1 XRD diffractions of 120 nm thick film $La_{0.8}MnO_{3-\delta}$ film. a) XRD 2 θ scan of $La_{0.8}MnO_{3-\delta}/LAO$ (Red arrow/Blue arrow); reciprocal space mapping for the film (red) and the substrate peaks (blue) b) (0 0 4) peak shows θ -broadening weighted towards the substrate peaks in 2 θ , θ -broadened c) (0 4 4) and d) (4 0 4) off-axis peaks exhibit more symmetry [210].

Synchrotron reflectivity spectra were measured at the U2A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. This beamline has a Bruker IFS 66v/S vacuum spectrometer equipped with a Bruker IRscope-II microscope, a mercury cadmium telluride (MCT-B) detector, and a KBr beamsplitter for mid-IR; a custom made infrared microscope with long working distant (40 mm) reflecting objective; a 3.5-micron mylar beamsplitter, and a Si bolometer detector for far-IR. The



Figure 3.2 (a) $La_{0.8}MnO_{3-8}/LAO$ reflectivity spectra at 10, 20, 50, 80, 100, 125, 150 (purple dot), 200 (green dash), 225, 245, 255, 265, 275 (dash dot), 282 (dash dot), 304 (dash dot) K on a logarithmic energy scale. The vertical dashed lines indicate phonon positions. The y-scale corresponds to the 304 K spectrum, and the others are shifted up by 0.1 relative to the previous temperatures. (b) LAO substrate reflectivity spectra. The energy is given on a logarithmic scale in (a) and (b). (c) Insert is an expansion of curves in (a) over the range 100 to 550 cm⁻¹ on a linear energy scale.

infrared frequency range covers 100-8000 cm⁻¹ with a spectral resolution of 4 cm⁻¹. A ~ 0.5 -µm-thick gold layer was deposited on the film as a reflective reference mirror. The sample was mounted on the cold finger of a continuous flow cryostat, and the

measurement temperatures were 304 (beginning, lowest curve in Figure 3.2), 282, 275, 265, 255, 245, 225, 200, 150, 125, 100, 80, 50, 20, and 10 K, which included the metal-insulator transition region.

The reflectivity spectra for the film and the bare substrate are given in Figure 3.2 (a) and (b), respectively. The vertical dashed lines correspond to phonon modes seen in other manganites [214, 215]. Note the systematic enhancement of the reflectivity with decreasing temperature. Small spectral variations of the insulating LAO substrate at different temperatures can be seen in Figure 3.2 (b). In Figure 3.2 (a) the spectra (304, 282 and 275 K), show prominent LAO-like resonances in the frequency range 100-550 cm⁻¹ and small differences are found in the region above 550 cm⁻¹.



Figure 3.3 $La_{0.8}MnO_{3.6}/LAO$ reflectivity spectra at 10, 20, 50, 275 and 282 K.

More detailed information can be obtained from the reflectivity spectra on an expanded scale (100-550 cm⁻¹) in Figure 3.2 (c). As the temperature decreases (between 275 K and 200 K), the film resistance drops and the film becomes more reflective. Free carriers screen the substrate, and as a result, the broad peaks at ~200 and ~450 cm⁻¹

become narrow and the reflectivity drops. In the La_{1-x}Ca_xMnO₃ and La_{1-x}Sr_xMnO₃ films substrate systems and bulk samples, this phenomenon is not so obvious [84, 90, 93]. This phenomenon suggests incomplete conversion to the metallic phase over this temperature range. On the other hand, between 150 and 10 K, the reflectivity increases gradually in the whole frequency range except around the peaks at ~200 and ~450 cm⁻¹, as expected. A saturation level is approached below 200 K. The small variations of the reflectivity in the very metallic phase (< 50 K) and the low conductivity region (~280 K) are exhibited in Figure 3.3.

3.3 Drude-Lorentz Fits

As the penetration depth [216] is of the order of the film thickness, the reflection from the substrate cannot be ignored especially at low-frequency range. The reflectivity depends on the film and the substrate dielectric constants and the film thickness, after treating a one-side polished LAO substrate (0.5 mm thick) as a half-infinite plate. The dielectric functions can be described by the Drude-Lorentz (D-L) model [216]:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\Gamma)} + \sum_j \frac{\omega_{p_j}^2}{(\omega_{o_j}^2 - \omega^2) - i\omega\Gamma_j}$$
(3.1)

Using the available LAO dielectric functions [217] as the initial condition, the bare substrate dielectric constant were obtained by least squares fitting [193]. Then fixing the substrate parameters, the reflectivity spectra were fit at each temperature. An example fit at 10 K is shown in Figure 3.6 (a), and fitting parameters at representative temperatures are listed in Table 3.3. The first component corresponds to the Drude contribution and yields results similar to those found previously [87] while the second to

the sixth components correspond to phonons (frequencies less than 700 cm⁻¹ are phonon resonances with values of ~170 cm⁻¹ (for external modes), ~350 cm⁻¹ (for bending modes), ~630 cm⁻¹ (for stretching modes) and ~520 cm⁻¹and ~580 cm⁻¹ (for the oxygen vibrations)) [81, 214, 215]. Frequencies higher than 700 cm⁻¹ model the effect of the polaron and band excitations and have been discussed extensively in the literature [214, 215].



Figure 3.4 N_{eff} vs. *T* at different ε_{∞} .

The value of epsilon infinity (ε_{∞}) 5.2 at 304 K and ε_{∞} =5.6 at 282 K are determined as floating parameters. They are close to the value for the CMR system La₂. _{2x}Sr_{1+2x}Mn₂O₇ (ε_{∞} = 4.9) [218]. At other temperatures ε_{∞} is fixed at 5.5. To understand the stability of the results (temperature dependence of the free N_{eff}) with respect to changes in ε_{∞} , the parameter ε_{∞} is adjusted over the range 3 < ε_{∞} < 8 and fit the data for all temperatures. The result is shown in the figure below (Figure 3.4). Note that the while the amplitudes of the N_{eff} and the Drude weight vary with in ε_{∞} (Figure 3.5), the onset temperature is insensitive.

	304K	282K	275K	265K	150K	125K	10K
€∞	5.2	5.6	5.5	5.5	5.5	5.5	5.5
ω_{o0}	-	0	0	0	0	0	0
ω_{p0}	-	1016	1184	1508	6413	6782	8142
Γ_{θ}	-	17	98	314	531	442	366
ω_{oI}	167	162	167	168	173	175	185
ω_{pI}	1039	925	826	718	760	950	769
Γ_I	34	33	18	18	23	13	21
ω_02	356	350	350	350	378	381	382
ω_{p2}	1500	1515	1455	1319	2489	2941	3271
Γ_2	107	112	100	90	134	128	169
<i>w</i> ₀3	523	524	524	523	535	-	-
ω_{p3}	311	316	383	601	726	-	-
Γ_{3}	60	57	72	123	69	-	-
ω_{o4}	584	585	585	586	585	577	575
ω_{p4}	853	897	885	888	1010	1509	1742
Γ_4	53	54	52	52	52	86	97
ω_{o5}	636	642	641	638	659	656	657
ω_{p5}	615	533	534	448	877	842	893
Γ_5	77	46	48	39	39	30	29
ω_{o6}	908	958	940	984	-	-	974
ω_{p6}	710	826	861	1029	-	-	4226
Γ_{6}	328	400	413	540	-	-	702
ω_{o7}	4881	4177	4304	4129	2123	1732	1 899
ω_{p7}	8541	15085	15952	17064	17908	14955	19233
Г7	2215	3526	3822	4181	3682	3037	1988
ω_08	5564	8988	9178	7795	2654	2318	-
ω_{p8}	19684	17922	17315	6794	13366	15866	-
Γ_{s}	7416	9101	8447	2729	1763	1474	-

Table 3.3 D-L Model Fitting Parameters at 304, 282, 275, 265, 150, 125 and 10 K

Note: ω_{o} , ω_{P} , Γ in unit cm⁻¹.



Figure 3.5 Drude weight *vs. T* with different ε_{∞} .

The optical conductivity $[\sigma(\omega)]$ can be obtained from the dielectric function:

$$\sigma(\omega) = -\frac{i\omega\varepsilon(\omega)}{4\pi} \tag{3.2}$$

Temperature-dependent $\sigma(\omega)$ are plotted for the film [Figure 3.6 (b)] and the substrate [Figure 3.6 (c)]. The spectral weight of the Drude components of the film increases as the temperature decreases and the peak above 1000 cm⁻¹ behaves like a small polaron feature and moves toward the low frequency side with decreasing temperature (as has been discussed in detail in References [93, 219]). The peak maximum shifts from ~5100 cm⁻¹ at 304 K to ~4300 cm⁻¹ at 282 K. The polaron shifts to the low energy side quickly and below 255 K the spectral weight increases dramatically as the carrier mobility increasing with reduced temperature. Below 200 K, the reflectivity spectra and the optical spectra vary slowly with the temperature. Figure 3.6 (c) shows the LAO substrate optical spectra at two different temperatures. The positions do not change significantly with temperature (<4 cm⁻¹) while the amplitudes vary.

are related by:
$$\sigma(0) = \frac{ne^2\tau}{m}$$
, $\omega_p^2 = \frac{4\pi ne^2}{m}$, $\rho = \frac{1}{4\pi\omega_p^2\tau}$. The dc resistivity and calculated

resistivity [from $\sigma(0)$] are plotted in Figure 3.7 (a) with the magnetization. The resistivity data sets have a consistent trend and show a good agreement for temperatures where the sample is more metallic, indicating that the D-L model is appropriate. Figure 3.7 (a) inset shows that the deficient La_{0.8}MnO_{3-δ} is a normal CMR material in terms of the widths of the transition regions (for magnetization and resistivity) compared with a La_{2/3}Ca_{1/3}MnO₃ film [213]. Note the similarity in widths in the magnetization and resistivity transition regions.



Figure 3.6 (a) An example fit of $La_{0.8}MnO_{3-\delta}/LAO$ reflectivity spectra at 10 K. (b) Real part of the optical conductivity spectra of $La_{0.8}MnO_{3-\delta}$ at different temperatures. (c) Real part of the optical conductivity spectra of LAO substrate.



Figure 3.7 (a) Magnetization, calculated and measured dc resistivity of $La_{0.8}MnO_{3-\delta}/LAO$ film. Insert is the comparison for $La_{2/3}Ca_{1/3}MnO_3$ (symbols) and $La_{0.8}MnO_{3-\delta}$ (line). (b) Effective carrier numbers and Drude Weight (free-carrier).

The effective carrier number density $N_{eff}(T, \omega_c)$ is proportional to the integrated optical conductivity spectral weight:

$$N_{eff}(T,\omega_c) = \frac{2mV}{\pi e^2} \int_{0}^{\omega_c} \operatorname{Re}\sigma(\omega')d\omega'$$
(3.3)

A cut-off frequency (ω_c) of 5000 cm⁻¹ was used to calculate the number density (N_{eff}). $N_{eff}(T)$ and Drude weight (DW) (the N_{eff} of free-carrier only) are plotted in Figure 3.6 (b) (see Ref. [204]). By examining the cut-off frequency dependence of the shape of N_{eff} vs. temperature in the broad set of manganite data in Refs. [89, 216], it is found that the onset profile is independent of ω_c for cut-off frequencies ranging from 4800-32,000 cm⁻¹ (see Figure 3.8). Moreover the onset temperature found is insensitive to the choice of ε_{∞} over a physically meaningful range. It can be seen that the onset of the increase in N_{eff} (~253 K) is significantly below T_{MI} and T_C . The free-carrier Drude weight is small compared to N_{eff} , and its onset occurs at ~245 K. The results indicate that the increase in carrier concentration lags the onset of magnetic order by ~45 K.



Figure 3.8 N_{eff} vs. T for a LCMO film at different cutoff energies (Extracted data from Quijada *et al.* [89]. The preprint can be found as <u>arXiv:cond-mat/9803201</u>).

The system under study has a metal-insulator transition occurring and also has a parallel paramagnetic to ferromagnetic transition occurring as the temperature is lowered. Previous works suggested the both transitions coincided. In the high temperature insulating paramagnetic phase the carriers are trapped by local distortion of the MnO₆ polyhedra and a region of coexistence should occur in the first order transition. However, here it is found that significantly below T_C and T_{MI} (Figure 3.7), the onset of increase in carrier numbers occurs. The ratio of T_{onset} to T_C is $T_{onset}/T_C = 5/6 \sim 0.867$. It is possible that by introducing defects into a sample that the region of fluctuations may broaden. In particular, the defects are introduced by the reduced La content in this case. The resistivity and magnetization curves for this film have transition width similar to the classic CMR system LCMO. In the figure above (Figure 3.7 inset), the plots given for

the magnetization and resistivity for the sample $La_{0.8}MnO_3/LAO$ compared with that of the classic $La_{2/3}Ca_{1/3}MO_3$ film [213] as a function of T/T_C . The curves follow each other only with minor broadening.

Those results suggest a more complex mechanism for the transition to the lowtemperature phase in manganites. It is consistent with the existence of regions with significant local distortions below T_{MI} and T_C which trap the e_g conduction electrons. These regions with local distortions constitute an insulating phase which persists for temperatures significantly below T_{MI} and T_C . Low spin scattering will lead to the observed initial large resistivity drop [220] as a result of magnetic ordering of the t_{2g} spins enabling Mn–Mn site hopping [221, 222] when reducing temperature below T_C . Further reductions in resistivity are then due to reductions in the volume of the minority insulating phase which then increases the number of free-carrier. The origin of the flattening of the reflectivity spectra at low temperature is due to the increased number of free-carrier, which limits the penetration depth of the light into the sample.

3.4 Small Polaron

In strongly correlated compounds electron-phonon coupling in the form of polaronic effects has to be considered an important ingredient to understand the complex physical properties. In the manganites, polarons are usually associated with the temperature dependence of high temperature dc resistivity [223] and a mid-IR (MIR) excitation in the optical conductivity [92]. Ziess [224] reported that the high-temperature resistivity of the high quality epitaxial La_{0.7}Ca_{0.3}MnO₃ films (100 nm) on LaAlO₃ and SrTiO₃ has a thermally activated form (see Figure 3.9) and he found that the values of the activation

energies are in favor of a small-polaron hopping model in the adiabatic limit. If the films are polycrystalline like those deposited on Si, they would follow the variable-range hopping (VRH) model [224]. At high temperature, the dynamic Jahn-Teller effect would lead to the strong electron-phonon coupling.



Figure 3.9 Zero-field resistivity of various LCMO films with a thickness of about 100 nm on different substrates [224].

Near T_c , the ordinary Hall effect is hole like with $R_H = 0.06 \pm 0.01 \ \mu\Omega$ cm/T for Ziese's LCMO films, which corresponds to a carrier density of 0.6 holes/unit cell in rough agreement with the doping level in a one-band model. The mobility of the annealed LCMO film is about 0.3 cm²/V s and the optical-phonon frequency $\omega_0 = 2 \ x \ 10^{13} \ Hz = 6.6 \ x \ 10^3 \ cm^{-1}$ for the annealed LCMO film which uses a hopping distance ~7 Å, under the assumption that the carrier density is given by the chemical doping and that all carriers form small polarons [224].

Hartinger *et al.* [92] distinguished small polaron (SP) in LCMO and large polaron (LP) in LSMO, by the distinctive shapes (see in Figure 3.10).



Figure 3.10 Optical conductivity σ for 6K < *T* <295 K. Straight lines represent data in the FM phase, dashed and dotted lines indicate the PM phase [92]. Upper panel: LSMO (400 nm thick). The dotted line is to guide the eyes for the shift of the maximum of the MIR excitation. Lower panel: LCMO (200 nm thick).

In Hartinger *et al.* measurements LCMO (200 nm thick), the strongly temperature-dependent maximum (in the MIR range) losses the spectral weight upon increasing the temperature up to T_C and the temperature dependence is negligible above T_C . The maximum shifts from 1800 to 5300 cm⁻¹. In La_{0.8}MnO₃₋₆, a very similar phenomenon is observed in the optical conductivity spectrum (see Figure 3.6 (b)). The loss in spectral weight is explained in terms of decreasing carrier mobility. In contrast, there is a sharp onset shifting by approximately a factor of 2 in energy in the range 6 K< T < 295 K for LSMO (400 nm thick) until it reaches the insulating phase [92]. Additionally, in the LSMO [213] system, T_C (345 K) is below T_{MI} (401 K) about 55 K. The magnetization and resistivity curves of La_{0.8}MnO₃ and LCMO films follow each



other, but do not follow the curves of LSMO film. Physically, La_{0.8}MnO₃ film is more like LCMO film.

Figure 3.11 Fits of SP model. (a) ρ/T of an as-deposited La_{0.7}Ca_{0.3}MnO₃ film on LaAlO₃ shown as a function of inverse temperature. The solid line is a fit of the polaron model [224]. (b) High temperature dc resistivity of LSMO (upper panel) and LCMO (lower panel). The solid lines are the fit of the adiabatic SP model. For LCMO the curve is linear and corresponds to polaron conduction with an activation energy $E_a = 672 \text{ cm}^{-1}$ [92]. (c) dc resistivity of La_{0.8}MnO_{3-δ} in a limited high temperature range in this work.

At high temperature, the effective activation energy E_a is extracted from a phenomenological expression:

$$\rho = AT \exp(E_a / k_B T) \tag{3.4}$$

In this expression, k_B is Boltzmann constant. In the high limited temperature range, the value of E_a for La_{0.8}MnO_{3- δ} is 592 cm⁻¹, which is close to the values of E_a = 532 cm⁻¹ (66 meV) for annealed LCMO/LAO [224] and E_a = 672 cm⁻¹ for LCMO/NdGaO₃ [92].

Small polaron optical conductivity is given by [225] :

$$\sigma(\omega,T) = \sigma(0,T) \frac{\sinh(4E_b \hbar \omega / \Delta^2)}{4E_b \hbar \omega / \Delta^2} \exp[-(\hbar \omega)^2 / \Delta^2]$$

$$\Delta = 2\sqrt{2E_b E_{vib}}$$
(3.5)

 E_b is the SP binding energy or formation energy, $\sigma(0, T)$ is the dc conductivity, Δ is a broadening factor indicating by how much the localized levels between which the transition occurs, are broadened by the atomic vibration with the characteristic vibrational energy E_{vib} , where E_{vib} is k_BT at a temperature high enough and E_{vib} is $\hbar \omega_{ph}/2$ (the zero vibrational energy) at low temperatures ($k_BT \ll \hbar \omega_{ph}/2$). The strong SP absorption peak is located at ~ $2E_b$, the maximum.

At 300 K, the value of the high temperature E_{vib} is ~208.5 cm⁻¹ (2.585 x 10⁻² eV). Fits to the optical conductivity spectrum with equations (3.5) to extract the binding energy were conducted. Figure 3.12 displays the small polaron optical conductivity fit at 304 K. The dc conductivity is ~28.05 Ω^{-1} cm⁻¹. Treating parameters E_b and E_{vib} as free, the binding energy and vibrational energy are ~5698 cm⁻¹ and ~197.4 cm⁻¹ (284 K), respectively. Using the theoretical value of 208.5 cm⁻¹, E_b is ~6009 cm⁻¹. MIR oscillators are at ~5564 cm⁻¹ (strong one) and 4881cm⁻¹. The fit results are in a reasonable range. These indicate that the oscillator peaks in MIR region connect with the SP binding energy at different temperatures. However, the SP is not symmetric; in the D-L model fitting more than one oscillator has to be used to compensate the small polaron excition. The SP model fits the optical conductivity spectra at 304K well. In the SP model, the E_b at 225 K and 20K are found ~4300 cm⁻¹ and ~2300 cm⁻¹ with both the E_{vib} at ~215 cm⁻¹. The binding energies agree with the oscillators of 225 K (~3700 cm⁻¹ (strong one) and 3400 cm⁻¹), and the oscillator of 20 K (1750cm⁻¹).



Figure 3.12 Small polaron optical conductivity fit. (Red line is the fit with parameters E_b and E_{vib} , Blue line is the fit with one parameter E_b)

The increase of the effective electron-phonon coupling with the temperature will decrease the mobility in the FM phase. In Hall effect measurements, the carrier mobility

will decrease with increasing temperature in the FM region and above T_{MI} the mobility increases slightly [226]. As a consequence, that also will lead to the spectral weight of the polaronic excitation being reduced on increasing temperature.

With increasing temperature, the J-T distortion effect is enhanced, the polaron formation energy increases and more carriers are localized. For La_{0.8}MnO₃- δ , the binding energy 2*E*_b rises from 2210 cm⁻¹ (6 K) to 6040 cm⁻¹ (250 K) like it does happens in LCMO [93]. Above *T*_{MI}, the binding energy remains stable.

The binding energy $2E_b$ increases towards the metal-insulator transition at T_{Ml} , and remains constant above T_{Ml} reflecting the significant role of magnetic interactions in a polaronic system as well as the importance of electron-phonon interactions in the formation of the insulating phase. The observation of SP at low temperature provides further evidences that support the existence of regions with local distortions trapping the e_g conduction electrons, which constitutes an insulating phase and persists for temperatures significantly below T_{Ml} and T_C .

In conclusion, this research has explored the temperature dependent infrared reflectivity spectra of La_xMnO_{3- δ}/LAO (*x*~0.8) system over the range 100-8000 cm⁻¹. While the metal-insulator transition temperature (*T_{Ml}*) and the magnetic ordering temperature (*T_C*) approximately coincide, the free-carrier density onset occurs at a significantly lowered temperature (~45 K below). The conductivity was found to be systematically enhanced at lower temperatures. These results are consistent with the existence of insulating regions at temperatures significantly below the metal-insulator and magnetic ordering temperatures.

CHAPTER 4

NEUTRON DIFFRACTION OF LA_{0.85}MNO₃

4.1 CMR La_{0.85}MnO₃

A polycrystalline sample of La_{0.9}MnO_{3-δ} was synthesized in air by the solid-state reaction method [197]. The saturated magnetization of La_{0.85}MnO_{3-δ} [199] reaches a value of 3.5 μ_B /Mn (theoretical = 3.45 μ_B /Mn) at ambient-pressure at 4 K (0.5 Tesla) and it is a Curie temperature (244.0 ± 1.0 K) near the metal-insulator phase transition temperature (248.0 ± 1.0 K). Chen *et al.* [199] found that at low pressure T_{MI} increases linearly up to a critical pressure, $P \sim 3.4$ GPa, followed by reduction of T_{MI} at higher pressures. Under pressure, the anharmonic inter-atomic potential plays an important role for Mn-O distances, Mn-O-Mn bond angles, and the Jahn-Teller distortion which dominates the reduction of T_{MI} .



Figure 4.1 Ambient temperature and pressure La_{0.85}MnO₃ crystal structure.

Studying the structure of $La_{0.85}MnO_{3-\delta}$ (see Figure 4.1, [199]) by Neutron diffraction methods could acquire more accurate crystal structure information since the oxygen atoms scatter strongly (as compared with x-ray scattering) and more importantly could determine the magnetic structure. It is essential to know if there is a second insulating AF-phase at high pressures. In the following sections, the crystalline and magnetic structures will be discussed under high pressure.

4.2 Neutron Diffraction under High Pressures

Neutron diffraction measurements were conducted at beam line S9 (Pearl), in ISIS Pulsed neutron & Muon Source, in UK. The PEARL High Pressure Station (HiPr) has a medium resolution high-flux diffractometer which has been optimized for data collection from the Paris-Edinburgh (PE) cell (see Figure 4.2). When the standard (though-anvil) scattering geometry of the PE-cell is selected, the main 'transverse' bank covers $83^{\circ} < 2\theta < 97^{\circ}$, *d*-spacing range ~0.5 - 4.1 Å, with $\Delta d/d \sim 0.8\%$, which is constituted by nine detector modules (each module is made of 120 ⁷Li-doped ZnS scintillators type detector elements). The sample temperature can be easily controlled in the range of ~ 90 - 350 K with 2 K variations and the pressure is less than 7 GPa with the normal PE-cell. The pressure medium is the methanol: ethanol (4:1) mixture and the hydrostatic pressure can be deduced from fitting Lead lattice parameters. The detailed experiment conditions are listed in Table 4.1.

 $La_{0.85}MnO_3$ is a monoclinic phase with the space group I 1 2/a 1 (No. 15). Figure 4.3 shows the diffraction patterns at different pressures when the $La_{0.85}MnO_3$ powder is at 298 K. It shows no abrupt structural change in the whole pressure range up to 6.7 GPa.



Figure 4.2 (a) Diffractometer [227], (b) PE cell, (c) and (d) cell parts of PEARL.

Pressure (GPa)	Temperature(K)	Temperature(K)	Pressure (GPa)
6.96 ±0.81	130	130	6.96 ± 0.81
$6.80\pm\!\!0.30$	180	130	6.47 ± 0.56
6.87 ± 0.34	230	130	$4.75\pm\!0.39$
6.69 ± 0.33	298	130	4.27 ± 0.26
0.51 ±0.19	130	298	0 +0.51
0.61 ± 0.19	180	298	0.09 ± 0.49
0.68 ± 0.16	230	298	0.20 ± 0.25
0.85 ± 0.40	298	298	$0.77\pm\!\!0.18$
0.77 ± 0.21	330	298	$0.85\pm\!\!0.40$
0.90 ± 0.20	380	298	$2.55\pm\!0.29$
0.96 ± 0.22	430	298	3.47 ± 0.29
		298	$4.75\pm\!0.32$
		298	5.77 ± 0.29
		298	6.69 ± 0.33
		298	3.62 ± 0.24

 Table 4.1
 Experiment Conditions



Figure 4.3 Neutron diffraction patterns at 298 K.

Temperatures dependent neutron diffraction studies are conducted at low pressure (~0.6 GPa) and high pressure (~6.8 GPa). Figure 4.4 displays the diffraction patterns at temperatures from 130K to 430 K and the fits include no magnetic structure, when the sample is kept at low pressures (~0.6 GPa). When the sample temperature is lower than T_C , temperature dependent fit residuals are easily observed around d= 2.74 Å and d= 3.9 Å (Detailed information is shown in Figure 4.5). La_{0.85}MnO₃ has a ferromagnetic transition at 244K, so magnetic ordering would generate extra peaks.



Figure 4.4 Temperature dependent neutron diffraction patterns at the low pressure range $(0.5 \sim 0.9 \text{ GPa})$, the fits include no magnetic structures.



Figure 4.5 Fit residuals near d = 2.7239 Å surface (002), d = 2.7324 Å (211), d = 2.7560 Å (020), d = 2.7598 Å (2 1 -1) at 130 K and 0.51 GPa conditions.



Figure 4.6 Neutron diffraction patterns at ~6.8 GPa.

Figure 4.6 shows the neutron diffraction patterns at ~6.8 GPa. The temperature dependent residual peaks are kept, but intensities are reduced to compare with the residual peaks at ~0.6 GPa. Plotting the normalized magnetization curve with the residual peak intensity together in Figure 4.7, the residual peak intensity onsite is in coincidence with the magnetic T_C , hence the magnetic order is the ferromagnetic. After checking all the diffraction patterns under different temperatures and pressures, no abrupt structural changes can be founded. Hence La_{0.85}MnO₃ is maintained in the monoclinic phase under high pressures.



Figure 4.7 Normalized magnetization curve and the residual peak intensities.

4.3 Lattice Parameters

At ambient-pressure, the lattice parameters for La_{0.85}MnO₃ [199] are a= 7.8012(13) Å, b= 5.5265(1) Å, c= 5.4818(1) Å and β = 90.828(7) °. The lattice parameters of La_{0.85}MnO₃ under the high-pressure can be extracted by GSAS [228] and EXPGUI [229]. At low pressure (0 - 0.51 GPa), La_{0.85}MnO₃ has a= 7.7931(34) Å, b= 5.5324(17) Å, c= 5.4701(23) Å and β = 90.682(23) °. These values are also close to the corresponding values for La_{0.9}MnO₃ (a= 7.790(1) Å, b= 5.526(1) Å, c= 5.479(1) Å and β = 90.78(1) ° [197]). All lattice parameters of La_{0.85}MnO₃ can be found in Appendix B.

Figure 4.8 displays the pressure dependent trends of the lattice parameters and the cell volumes, when the sample temperature is kept at 298 K. As the figure shows, the unit cell is compressed as the pressure increases. The pressure dependence of volume is fitted by the Murnaghan equation of state, which has the bulk modulus $B_0 = 133.65 \pm 18$ GPa, and its pressure derivative $B_0^{\circ} = 9.0 \pm 7.8$ at zero pressure. These values are

comparable with the high energy x-ray diffraction results [199] ($B_0 = 167.3 \pm 22$ GPa and B_0 ' = 2.0 ± 7.9) obtained over the pressure range ambient to 40 GPa. The large value of B_0 ' indicates the anisotropic compressibility of La_{0.85}MnO₃, where the typical value of B_0 '= 4 ~ 6 corresponds to a crystals with nearly isotropic compression [230]. The lattice parameter *b* and *c* continuously shrink with the pressure increase, but the lattice *a* won't decrease until the pressure is beyond 2 GPa. Angle β increases from 90.68 ° to 91.04 ° degree as the pressure increase from 0.5 GPa to 6.8 GPa and the unit cell volume is reduced by ~ 4%.



Figure 4.8 Pressure dependent lattice parameters and cell volumes at 298 K.

The temperature dependent lattice parameters and cell volumes are illustrated in Figure 4.9 and Figure 4.10. In Figure 4.9, the chart describes the temperature dependent trends of lattice parameters, cell volume and angle β in a temperature range 130 K – 430 K. At low pressure, the temperature can affect the pressure more than it does at high pressure status, so the pressure varies from 0.5 GPa to 0.9 GPa. When the temperature increases, the cell volume and the lattice *a* show different trends from the lattice *b* and *c*.

The cell volume and the lattice *a* increase in a small amount, and the values of lattice *b* and *c*, and angle β are kept constant. Weak temperature dependence in all parameters occurs when one the pressure reaches 6.8 GPa.



Figure 4.9 Temperature dependent lattice parameters and cell volumes at $0.5 \sim 1$ GPa. Inset is the temperature dependence of pressure.



Figure 4.10 Temperature dependent tendencies of lattice parameters and cell volumes at \sim 7 GPa.

At ambient pressure the volume of orthorhombic LaMnO₃ (P*nma*) unit cell is 244.11 Å³ [230]. The cell volumes of La_{0.9}MnO₃, La_{0.85}MnO₃ at ambient pressure (x-ray result) and low pressure (between 0 and 0.51 GPa, neutron result) are 235.836 [197], 236.37 [199] and 235.82 Å³, respectively. The deficiency of La position transforms orthorhombic structure to a small volume monoclinic structure and makes the cell hard to compress in contrast with LaMnO₃ with $B_0 = 108 \pm 2$ GPa [230].



Figure 4.11 Schematic representation of La_{0.85}MnO₃ structure showing the bond angle $\theta_{Mn-O1-Mn}$ (*a* axis) and $\theta_{Mn-O2-Mn}$ (*bc* plane).

For a tight-binding system, the electronic carrier bandwidth W can be calculated by the empirical formula [231]:

$$W = \cos(\omega) / d^{3.5} \tag{4.1}$$

where ω is the average tilting angle between the neighboring octahedral, d is the bond length inside the octahedral. In the monoclinic La_{0.85}MnO₃ cell, the angles $\theta_{Mn-O1-Mn}$ and $\theta_{Mn-O2-Mn}$ correspond to the out-of-plane bandwidth W_1 (along a axis) and in-plane (in bcplane) bandwidth W_2 (two bonds) respectively and the average band width is defined $\langle W \rangle = 1/3(W_1 + 2W_2)$.



Figure 4.12 The pressure dependent average Mn-O bond length, bond angle (<Mn-O2-Mn>), distortion and band width (Left panel this work, right panel work of Chen *et al.* [199]).

In the neutron measurements, a lineal behavior in the average Mn-O bond length (in Figure 4.12) is observed with no cross over behavior. The band width W continuously

In the neutron measurements, a lineal behavior in the average Mn-O bond length (in Figure 4.12) is observed with no cross over behavior. The band width W continuously increases, which is not in agree with the trend of T_{MI} . High resolution neutron diffraction measurements (high q) with high statistics under pressures should be conducted.

4.4 Magnetic Structure Refinement

The external high pressure can induce AF phase into the initial FM manganites such as $La_{0.75}Ca_{0.25}MnO_3$, and $La_{0.67}Ca_{0.33}MnO_3$ [232, 233]. A linear increase of T_C was observed in $La_{0.75}Ca_{0.25}MnO_3$ ($dT_C/dP \sim 12$ K/GPa) [234] and in $La_{0.7}Sr_{0.3}MnO_3$ ($dT_C/dP \sim 5.3$ K/GPa) [232]. The long-range antiferromagnetic order can be suppressed by the high pressure in the Hex-*R*MnO₃ manganites [146, 147] and the ordered magnetic moment values decrease under pressure with rate $dM/dP = -0.35 \mu_B \text{ GPa}^{-1}$ in YMnO₃ and -0.08 $\mu_B/Mn \text{ GPa}^{-1}$ in LuMnO₃.

		130K	180K	230K
	m _a	-0.851 ± 0.798	-0.464 ± 0.647	-0.468 ± 0.354
	m_b	3.020 ± 0.066	2.716 ± 0.068	1.592 ± 0.093
	m _c	0.666 ± 0.345	0.932 ± 0.381	0.191 (fixed)
~0.5 GPa	Μ	3.207 ± 0.174	2.909 ± 0.094	1.670 ± 0.141
	R _p	0.0666	0.0633	0.057
	Chi ²	1.984	1.772	1.833
~6.8 GPa	$m_b(m)$	2.757 ± 0.112	2.456 ± 0.109	1.803 ± 0.126
	R_p	0.0649	0.0712	0.0758
	Chi ²	2.658	2.098	1.921
dM/dP	$\mu_{B} \mathrm{GPa}^{-1}$	-0.07	-0.07	0.02

Table 4.2 The Refined Magnetic Moment in μ_B Units



Figure 4.13 Nuclear and magnetic structure refinements of $La_{0.85}MnO_3$ at 130K. (Upper panel: pressure ~0.5 GPa, low panel: pressure ~6.8 GPa; Phase 1: $La_{0.85}MnO_3$, Phase 2: Pb, Phase 3: WC and Phase 4: Ni).

La_{0.85}MnO₃ has mixed Mn³⁺: Mn⁴⁺ sites with the ratio 0.55/0.45. During the refinements, the form factor of Mn³⁺ is used only. The FM structure refinement fits the diffraction pattern well. Under 0.5 GPa pressure and at 130K, the magnetic moment is ~ $3.2 \pm 0.17 \ \mu_B$ /Mn and the major magnetic component is along the *b* axis. Figure 4.13 illustrates the typical refinement results and the refined magnetic moments are listed in Table 4.2. The crystal structure and the spin direction are shown in Figure 4.14.



Figure 4.14 Structure and spin orientation at 130 K. (Left panel and right panel corresponding to pressure ~0.5 GPa and ~6.8 GPa,respectively).

Due to the low statistics of diffraction data and the rapid suppression of magnetic peak intensity, only a rough estimate of the ordered magnetic moment values and spin orientation can be obtained at 6.8 GPa. Under this pressure, the magnetic moment at 130 K along *b* only and the value is $2.76 \pm 0.11 \ \mu_B/Mn$, where the magnetic moment components along *a* and *c* axis are fixed at 0.
The magnetic order is suppressed in a rate of -0.07 μ_B GPa⁻¹ at 130 K and 180 K. Although the magnetic ordering is suppressed, there does not seem to be pressure dependent of T_C (the magnetic moments are identical at two pressures at 230K which is close to the ambient $T_C \sim 244$ K). The monoclinic crystal structure and the FM state remain stable in the range of pressures up to ~6.8 GPa. The FM peaks persist at high pressures and no AF peaks appear in the temperature range down to 130 K.

4.5 Group Analysis of Magnetic Structure

For FM materials, the magnetic and crystallographic unit cells are of the same size, the magnetic reflections occur at the nodes of the nuclear reciprocal lattice and their intensities therefore add to those of the nuclear reflections. The periodic repetition of a magnetic unit cell can be described by the nuclear unit cell and a 'propagation vector', k, which describes the relation between moment orientations of equivalent magnetic atoms in different nuclear unit cells [235]. In the first Brillouin zone, the moment distribution m_j associated with the atom j of a magnetic structure is:

$$\vec{m}_j = \sum_k \bar{\Psi}_j^k e^{-2\pi i \bar{k}^* \bar{t}}$$
(4.2)

where the vector t is a lattice translation operation and Ψ , the axial vector which is describing the atomic magnetic momentum component along the crystallographic axes.

Element	Rotation matrix	IT notation	Kovalev notation	Jones symbol
g_n	R	$\mathbf{g}_{\mathrm{n}} = \{\mathbf{R} \mid \boldsymbol{\tau} \}$	$g_n = \{hn \mid \tau \}$	· · · · · · · · · · · · · · · · · · ·
g 1	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{E \mid 0 \ 0 \ 0\}$	$\{h_1 \mid 0 \ 0 \ 0\}$	x, y, z
g ₂	$\begin{pmatrix} \overline{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \overline{1} \end{pmatrix}$	$\{C_{2y} \mid 0.5 \ 0 \ 0\}$	$\{h_4 \mid 0.5 0 0\}$	-x +1/2, -y, z
g ₃	$\begin{pmatrix} \overline{1} & 0 & 0 \\ 0 & \overline{1} & 0 \\ 0 & 0 & \overline{1} \end{pmatrix}$	{I 0 0 0}	$\{h_{25} 0 0 0\}$	-x, -y, -z
g4	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \overline{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\{\sigma_y \mid 0.5 \ 0 \ 0\}$	$\{h_{28} 0.500\}$	x+1/2, -y, z

Table 4.3 Symmetry Operators of the Space Group I 1 2/a 1

Note: The notations used are of the International Tables, where the elements are separated into rotation and translation components, and the Jones faithful representations.

For FM La_{0.85}MnO₃ with the space group I 1 2/a 1, the Mn atom occupies the 4*a* site, which has two equivalents positions 1: (0, 0, 0), 2: (0.5, 0, 0), and the propagation vector is $\mathbf{k} = (0, 0, 0)$, which is unchanged under the crystallographic space group. Table 4.3 contains both crystallographic and the magnetic symmetry operators. Using the program Sarah [236], the magnetic representation $\Gamma_{mag} = 1\Gamma_1^{1}+2\Gamma_2^{1}+2\Gamma_3^{1}+1\Gamma_4^{1}$ and the possible basis vectors are deduced and summarized in Table 4.4.

 TD	Pagis Vector	Atom			BV cor	mponen	its	
ш	Basis vector	Atom	m//a	m//b	m//c	im//a	im//b	im//c
Γ_1	Ψ1	1	2	0	0	0	0	0
		2	-2	0	0	0	0	0
	Ψ2	1	0	2	0	0	0	0
		2	0	2	0	0	0	0
	Ψ3	1	0	0	2	0	0	0
		2	0	0	-2	0	0	0
Γ_2	Ψ1	1	2	0	0	0	0	0
		2	2	0	0	0	0	0
	Ψ2	1	0	2	0	0	0	0
		2	0	-2	0	0	0	0
	Ψ3	1	0	0	2	0	0	0
		2	0	0	2	0	0	0
Γ_3	Ψ1	1	0	0	0	0	0	0
		2	0	0	0	0	0	0
	Ψ2	1	0	0	0	0	0	0
		2	0	0	0	0	0	0
	Ψ3	1	0	0	0	0	0	0
		2	0	0	0	0	0	0
Γ_4	Ψ1	1	0	0	0	0	0	· 0
		2	0	0	0	0	0	0
	Ψ2	1	0	0	0	0	0	0
		2	0	0	0	0	0	0
	Ψ3	1	0	0	0	0	0	0
		2	0	0	0	0	0	0

Table 4.4 Basis Vectors for the Space Group I 1 2/a 1 with $k_6 = (0, 0, 0)$

Note: The decomposition of the magnetic representation for the Mn site (0, 0, 0) is $\Gamma_{\text{mag}} = 1\Gamma_1^{-1} + 2\Gamma_2^{-1} + 2\Gamma_3^{-1} + 1\Gamma_4^{-1}$. The atoms of the nonprimitive basis are defined according to 1: (0, 0, 0), 2: (0.5, 0, 0).

In conclusion, this work explored the pressure dependence of the crystal and magnetic structure on La_{0.85}MnO₃ by neutron diffraction method. In the pressure range up to ~6.8 GPa, the monoclinic phase structure remains stable. La_{0.85}MnO₃ has a high bulk modulus value of 133GPa and the anisotropic compressibility. With the pressure increasing, the lattice parameters (*a*, *b*, *c*) and cell volume decrease linearly while the β angle and the electronic carrier bandwidth *W* increase. The FM order of La_{0.85}MnO₃ is suppressed in a rate of -0.07 μ_B GPa⁻¹. In the temperature range down to 130 K, no AF structure was induced by the pressure.

CHAPTER 5

HEX-RMNO3 INFRARED AND RAMAN SPECTRA

5.1 Hex-RMnO₃ Infrared Absorption Spectra

The $RMnO_3$ (R: rare-earth) is an important group of manganese oxides [70, 71, 237, 238]. They exhibit CMR effect in orthorhombic structure (Pnma, Z=4) materials and ferroelectric properties in both the orthorhombic (perovskite structure) and the hexagonal structure ($P6_3mc$, Z=6).

Table 5.1Volume per Formula Unit

	Hex-RMnO ₃	Orth-RMnO ₃
	$(Å^3)$	(Å ³)
YMnO ₃	62.392 ^a , 61.511 ^c	56.441 ^a
HoMnO ₃	62.061 ^a , 62.019 ^c	56.536 ^a
LuMnO ₃	59.846 ^a , 59.823 ^c	54.873 ^a
LaMnO ₃	-	61.028 ^b

a [4], b [230], c this experiment

The small *R* ion radius hexagonal *R*MnO₃ is the stable ferroelectric phase at ambient conditions, but the hexagonal structure can be converted to the dense orthorhombic phase (see Table 5.1) by the simultaneous high pressure and high temperature treatments (for example 4 GPa and 1000 °C) [4, 239-241]. High temperature and high pressure synthesis is the most common method (see Table 5.2) to acquire the small ion radius orthorhombic *R*MnO₃ (R = Y, Ho, Er, Tm, Yb, Lu). If only the high temperature condition exists (above *Tc*), the hexagonasl structure can be transform to a paraelectric (high symmetry hexagonal) phase (P6₃/mmc, *Z*= 2). By a solution based

Sample	Temperature (°C)	Pressure (kbar)	Reference
	650	34	Waintal [239]
YMnO ₃	900	45	Waintal [239]
	1000	35	Wood [243]
	<2100	15	Aken [239]
II. March	950	45	Waintal [239]
HomnO ₃	1000	35	Wood [243]
LuMnO ₃	750	42	Waintal [239]
	800 (30min)	50	Okamoto [244]
ErMnO ₃	675	42	Waintal [239]
TmMnO ₃	780	42	Waintal [239]
XI-M.O	700	42	Waintal [239]
Y DIMINU ₃	1000	40	Wood [243]
RMnO ₃ (Y,			
Ho, Er, Tm,	1000	40	Zhou[4]
Yb, Lu)			
Y(Ho)MnO ₃	1020 (5h)	35	Lorenz [240]
RMnO ₃ (Sc, Y, Dy-Lu)	800 (30min)	50	Uusi-Esko [241]

Table 5.2 Example of High Pressure Orthorhombic Phase Transition Conditions

Beside the bulk materials, the $RMnO_3$ films also show the structure diversity. An appropriate perovskite substrate will force the small ion hexagonal $RMnO_3$ to grow as an orthorhombic film [245] instead of the hexagonal phase, and the ZrO_2 (Y₂O₃) (YSZ) substrates can epitaxially stabilize hexagonal DyMnO₃ and TbMnO₃ films, which are normally of orthorhombic structure [6]. When the normal hexagonal $RMnO_3$ films are deposited on a YSZ substrate, thickness dependence is observed in the *c*-axis oriented hexagonal films [6]. Under high pressure conditions, the important parent compound, orthorhombic LaMnO₃ undergoes complex changes on both structure and electronic properties. Below 15 GPa, LaMnO₃ is the orthorhombic Pnma structure with the large Mn-O bond distortions [246]. The Jahn-Teller (J-T) distortion will be reduced with the pressure increase. At ~15 GPa, a phase transition happens [246] with the new phase is still an insulating phase; however, the precise atomic structure of this new phase is not clear. Above 18 GPa, the J-T distortion is completely suppressed and the e_g electron is delocalized. LaMnO₃ shows an insulator-metal (IM) transition for pressures beyond 30 GPa [230].

By contrasts, the J-T distortion does not exist in hexagonal $RMnO_3$ materials because of the different local symmetry. The lattice energy of the hexagonal structure is lower than the corresponding orthorhombic phase and the hexagonal $RMnO_3$ does not show an IM transition. Previous works have studied the Hex- $RMnO_3$ structure and antiferromagnetic ordering under pressures up to ~6.7 GPa [143, 147]. Under hydrostatic pressure conditions, Hex- $RMnO_3$ has both lattice parameters and internal atomic structural change; the ordered Mn magnetic moment is suppressed by pressure. A Raman scattering experiment [148] reveals a new possibility of the phase transition from a hexagonal structure to an orthorhombic structure (Ho_{0.8}Dy_{0.2}MnO₃) at high pressure ~10 GPa at room temperature.

5.2 High Pressure Hex-RMnO₃ X-ray Diffraction

In this work, a series experiments are conducted to discover the hydrostatic pressure effects on the structural, vibrational and optical properties of $RMnO_3$ (R= Y, Ho, Lu). They were done in a pressure range up to 20 GPa at room temperature (298 K) by synchrotron x-ray powder diffraction and infrared (IR) spectroscopy methods.

Finely ground RMnO₃ (R = Y, Ho, Lu) polycrystalline powders (< 500 mesh), which are made by solid-state reaction method and were sealed into a diamond anvil cell (DAC). Monochromatic x-ray ($\lambda = 0.4066$ Å) powder diffractions under high pressures were completed at X17C beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. A charge-coupled device (Mar 165, 2048 × 2048 pixels with 79µm resolution pixels) at a distance of ~250 mm from the sample was used to record the 2-D diffraction rings, which were integrated to yield intensity vs. 2 θ diagrams by the program Fit2D. Methanol/Ethanol/Water (16:3:1) mixture was used as the pressure medium in x-ray diffraction experiments. The pressures generated by DAC were calibrated by the Ruby Fluorescence method. Multiple ruby chips were placed in the cell in order the check the pressure homogeneity and the variation in pressure is reported as pressure error bars.

Diffraction patterns of $RMnO_3$ are shown in Figure 5.1 (a) in the pressure range up to ~20 GPa. Three diffraction patterns of the $RMnO_3$ are similar at ambient pressure. The diffraction peak positions will shift toward high 2θ value and the peak intensities are varied with the pressure increasing. In the whole pressure range, no abrupt shape change or new diffraction peaks are observed. It implies that the P6₃*cm* structure persists in the experimental pressure range. The ambient pressure lattice parameters (*a* and *c*) extracted



Figure 5.1 (a) X-ray powder diffraction patterns of $RMnO_3$ at various pressures (T = 298 K). From left panel to right panel are diffraction patterns of YMnO₃, HoMnO₃ and LuMnO₃. Pressure dependent (b) normalized lattice parameters *a*, *c*, and (c) cell volumes.

by Rietveld methods are a = 6.11505 Å, c = 11.3781 Å (YMnO₃), a = 6.13450 Å, c = 11.41790 Å (HoMnO₃) and a = 6.03965 Å, c = 11.36235 Å (LuMnO₃). These lattice parameter values are close to the values in publications [4] (YMnO₃ a = 6.14666 Å, c = 11.4411 Å, HoMnO₃ a = 6.13820 Å, c = 11.4118 Å and LuMnO₃ a = 6.04011 Å, c = 11.3648 Å). Figure 5.1 (b) illustrates normalized lattice parameters and it exhibits nonlineal decreasing tendency with the pressure increasing. At the same pressure, the compressibility of a is much larger than that of c. The RMnO₃ unit cell volume changes are displayed in the Figure 5.1 (c). The pressure dependence volumes are fitted by the Murnaghan equation of state:

$$V(P) = V_0 (1 + B_0' \frac{P}{B_0})^{-1/B_0'}$$
(5.1)

where a solid has a certain equilibrium volume V_0 , the zero pressure bulk modulus B_0 and the bulk modulus pressure derivative B_0 '. Both B_0 and B_0 ' values are bigger than the corresponding values of orthorhombic LaMnO₃ ($B_0 = 108 \pm 2$ GPa, B_0 ' = 8.5 \pm 0.4) [230].

5.3 Hex-RMnO₃ Infrared Absorption Spectra

The elementary unit cell of the hexagonal ferroelectric $P6_{3}cm$ structure contains six formula units. According symmetry arguments there are 60 vibrational modes in the first Brillouin zone ($\Gamma_{tot} = 10A1 + 5A2 + 10B1 + 5B2 + 15E1 + 15E2$), which are listed in Table 5.3 [128]. Among them, 23 modes are IR active phonon modes (9A1+ 14E1) [128]. The corresponding phonon frequencies and atomic displacements directions of IR modes can be found in Table 5.4. The pressure dependent synchrotron infrared (IR) absorption spectra were measured at the U2A beam line, at NSLS. The vacuum infrared microscope provided a spectral resolution of 4 cm⁻¹ in far IR (100 - 650 cm⁻¹) range. It was equipped with a 3.5-micron Mylar beam splitter, a 40 mm working distant reflecting objective and a Si bolometer detector. CsI and Vaseline grease were used to dilute the *R*MnO₃ powder and acted as the pressure medium in this experiment.

Atom	Wyckoff notation	Site symmetry	Irreducible representations
R(Lu)	2(a)	$C^{ u}_{3 u}$	A1+B1+E1+E2
R(Lu)	4(b)	C_3	A1+A2+B1+B2+2E1+2E2
Mn	6(c)	C_s^{v}	2A1+A2+2B1+B2+3E1+3E2
0	6(c)	C_s^{v}	2A1+A2+2B1+B2+3E1+3E2
0	6(c)	C_s^{v}	2A1+A2+2B1+B2+3E1+3E2
О	2(a)	$C^{\nu}_{3 u}$	A1+B1+E1+E2
Ο	4(b)	C_3	A1+A2+B1+B2+2E1+2E2

Table 5.3 Atomic Position, Site Symmetry and Vibrational Modes of RMnO₃ [128]



Figure 5.2 Absorption spectra of different pressure media under pressures.

	YMnO ₃	[128]		H	oMnO ₃ [1:		LuMnO ₃ [247]		
Mode symmetry	Calc. TO/LO	Expt IR	Expt. Raman	Theory (TO/LO)	Expt. IR (TO/LO)	Expet. Raman (TO/LO)	Direction and sign of the largest atomic displacements	Expt. IR (TO/LO ε_{∞} =4.92)
Al	147/147		148	125/127			+z(<i>R</i> /Y1) -z(<i>R</i> /Y2)	$\omega_{\mathrm{TO},1} (E / / c)$	118.65
A1	204/216		190	195/234			rot.xy(MnO5)	$\omega_{\mathrm{TO},2} \left(E / / c \right)$	223.08
Al	222/269	265	257	245/270		262/262	+z(<i>R</i> /Y1, <i>R</i> /Y2) - z(Mn)	$\omega_{\mathrm{TO},3} (E / c)$	263.41
Al	299/301		297	291/295		295/295	x(Mn), z(O3)	$\omega_{\mathrm{TO},4} \left(E / / c \right)$	298.27
Al	388/398	398		404/428		411/-	+z(O3) -z(O4) +x, y(O2) -x, y(O1)		
Al	423/467	428	433	430/460		427/427	+z(O4,O3)-z(Mn)		
Al	492/496		459	468/474		463/463	+x, y(O1,O2) -x, y(Mn)	$\omega_{TO,5} (E \parallel c)$	476.48
Al	588/601	612		598/614			+z(O1,O2) -z(Mn)	$\omega_{\mathrm{TO},6} (E / / c)$	567.82
Al	662/662		681	673/673		685/685	+z(O1) -z(O2)		
El	117/118			107/110			+x,y(Mn,O3,O4) - x, y(<i>R</i> /Y1, <i>R</i> /Y2)		
El	147/149			143/143	136/146		+x, $y(R/Y1)$ -x, y(R/Y2)		
El	158/158			149/149	160/164		+x, $y(R/Y2)$ -x, y(R/Y1)		
El	212/231	211		231/231			+x, y(O1,O2) -x, y(<i>R</i> /Y1, <i>R</i> /Y2)		

Table 5.4 Summary of Infrared Modes and Raman Frequencies (in cm⁻¹) in Hexagonal P6₃*mc R*MnO₃ and Description of the Atomic Displacements

Note: x, y, and z mean the directions of the displacements of the atoms.

	YMnO ₃ [128] HoMnO ₃ [130]							LuMnO ₃ [247]
Mode symmetry	Calc. TO/LO	Expt IR	Expt. Raman	Theory (TO/LO)	Expt. IR (TO/LO)	Expet. Raman (TO/LO)	Direction and sign of the largest atomic displacements	Expt. IR (TO/L) ε_{∞} =4.9	0) 2
E1	233/245	238		247/253	230/278		x,y(Mn,O3), $z(O1,O2)$ $\omega_{TO,1}/\omega_{LO,1} (E \perp c)$		266.16/280.76
EI	250/337	281		262/336	289/301		+x, y(O1,O2) -x, y(O3)	$\omega_{ ext{TO,2}} / \omega_{ ext{LO,2}} \left(E \perp c ight)$	297.01/345.57
El	353/367	308		337/358	303/326		+x, y(O1,O2,O3) -x, y(O4,Mn)	, y(01,02,03) -x, y(04,Mn) $\omega_{T0,3}/\omega_{L0,3} (E \perp c)$	
E1	390/403		376	359/397	355/357	354	+x, y(O1) -x, y(O2)		
El	410/415		408	398/410	369/410	369	+x, y(O1) -x, y(O2)	$ω$ _{TO,4} / $ω$ _{LO,4} ($E \perp c$)	412.41/410.73
El	459/477	457		471/491	418/476	419	+x, y(O4,O3) -x, y(O2,O1,Mn)	$\omega_{ ext{to}, ext{5}}/\omega_{ ext{lo}, ext{5}}\left(E\perp c ight)$	425.36/422.48
E1	492/527	491		497/537	479/551	480	+x,y(O4,O3,O1,O2) -x, y(Mn)		
<i>E1</i>	559/559			568/571			x, y(O4)		
<i>E1</i>	586/589	596		585/586	593/601		x, y(O3)	$\omega_{ ext{to},6} / \omega_{ ext{lo},6} (E \perp c)$	598.85/607.40
E1	635/635		632	648/648		636	x, y(O3) -x, y(O4)		

Table 5.4 Summary of Infrared Modes and Raman Frequencies (in cm⁻¹) in Hexagonal $P6_3mc RMnO_3$ and Description of the Atomic Displacements (Continued)

Note: x, y, and z mean the directions of the displacements of the atoms.

At ambient pressure, the pressure medium CsI only has an absorption peak near 100 cm^{-1} (see in Figure 5.2). When the pressure increases, this peak will shift to high energy frequency, but the medium does not create strong feature peaks. The pressure dependent IR optical density of diluted *R*MnO₃ is displayed in Figure 5.3 and Figure 5.4. The ambient *R*MnO₃ optical density spectra in this experiment agree with the published YMnO₃ spectrum [128]. For LuMnO₃ sample, except phonons at ~211, 238, 265, 281, 306, 398, 428, 457, 491, 596, and 612 cm⁻¹, three new phonon peaks at 154 cm⁻¹, 333 cm⁻¹ and 416 cm⁻¹ are observed.

All phonons of $RMnO_3$ shift to high energy with the pressure increase as expected. The phonons of LuMnO₃ and HoMnO₃ are more sensitive with the pressure than phonons of YMnO₃. For three samples, the phonon at ~306 cm⁻¹ (E1) has the largest rate of change, which is attributed to the displacements of atoms O1, O2, O3 along a positive direction and atom O4, Mn along a negative direction in the *ab* plane[128]. The phonon (~401 cm⁻¹) of the LuMnO₃ sample splits when the pressure reaches ~12 GPa. The peak at ~333 cm⁻¹ shifts quickly with the pressure increasing and merges with the phonon near ~401 cm⁻¹. Phonon peak shift and merger also happen in HoMnO₃ sample, but it is not observed in YMnO₃ sample. From the density function calculations, it was found that the most pressure sensitive mode belongs to the oxygen atoms only. The oxygen atoms have significant oscillation amplitudes with O ions moving in *ab* plane under high pressure.

The phonon position changes and the intensity redistributions indicate that the crystal structure is modified by the hydrostatic pressure. However, no common features were found between the Hex-RMnO₃ IR optical density spectra and the Orth-DyMnO₃

absorption spectrum, which can be seen in Figure 5.5, even for pressure reaching ~ 20 GPa. Hence the optical density results show no phase change to the orthorhombic phase and prove that the P6₃*cm* structure is stable under high pressure at ambient temperature as shown by x-ray diffraction.



Figure 5.3 Pressure dependent IR optical density spectra of Hex-*R*MnO₃ at room temperature. (a) YMnO₃ IR absorption spectra (Pressure: 0.00, 0.58, 1.17, 2.01, 3.02, 3.96, 4.98, 7.11, 7.97, 8.74, 9.35, 10.04, 10.99, 11.94, 12.98, 14.03, 15.08, 16.04, 17.11, 18.07, 19.40 GPa). (b) HoMnO₃ IR absorption spectra (Pressure: 0.00, 0.58, 1.08, 2.01, 3.19, 4.13, 5.23, 5.91, 7.03, 8.14, 9.00, 10.29, 11.07, 12.56, 13.33, 14.03, 15.61, 16.40, 17.10, 18.25, 19.22, 20.46, 22.06 GPa). (c) LuMnO₃ IR absorption spectra (Pressure: 0.00, 1.74, 2.95, 4.16, 5.30, 6.64, 7.99, 9.26, 10.88, 12.37, 14.04, 15.24, 17.31, 18.69, 20.56 GPa). The lines are shifted up by 0.2 relative to the previous pressures.



Figure 5.4 Examples of IR absorption spectra of $LuMnO_3$ at some neighboring pressures without shifts.



Figure 5.5 The room temperature hexagonal and orthorhombic $RMnO_3$ optical density spectra (YMnO₃ at 19.40 GPa, HoMnO₃ at 22.06 GPa, LuMnO₃ at 20.56 GPa, DyMnO₃ at ambient pressure). Note that DyMnO₃ is orthorhombic phase.



Figure 5.6 Phonon frequencies at different pressures.



Figure 5.7 High pressure and high temperature IR absorption spectra of LuMnO₃.

Can the hexagonal to orthorhombic phase transition temperature be reduced significantly by increasing the pressure? To compare with the conditions used by Waintal [3], the optical density spectrum of LuMnO₃ powder is measured *in situ* when it is heated up to 400 C° under ~10 GPa pressure. The spectrum, Figure 5.7, shows that the absorption spectra return back to the initial spectra after thermal treatment and no phase change happens. This implies the temperature plays a more important role on the phase transition than the pressure. Thermal treatment will provide the atoms energy to overcome the barrier to break the bonds and transform between different positions to construct a new symmetry.

Figure 5.8 illustrates the absorption spectra of an orthorhombic structure $HoMnO_3$ in the pressure range of 0 to 20 GPa. In the whole pressure range, the phonons of $HoMnO_3$ shift to high energy, but no phase transition occurs. Again, this shows that temperature plays a critical role.



Figure 5.8 Pressure dependent IR optical density spectra of Orth-HoMnO₃ at 298 K (Pressure: 0.00, 0.59, 1.59, 2.57, 4.06, 4.87, 6.30, 8.78, 10.21, 12.67, 14.38, 17.22, 19.56 GPa).

5.4 Single Crystalline LuMnO₃ Raman Spectra

Raman spectroscopy is a good way to study vibrational, rotational, and other lowfrequency modes in a system. This technique is used here to investigate the modes of single crystalline LuMnO₃, which is polished along the *ab* plane. The excitation laser energy on the sample was ~10 mw at 514.5 nm wavelength and the beam size was ~10 µm in diameter. At ambient pressure and 300 K, Raman shift lines are found at 145, 252, 308, 464 and 680 (641 + 680) cm⁻¹ shown in Figure 5.9. The peaks at 1117, 1277 and 1552 cm⁻¹ are the second order scattering as shown by Litvinchuk [130]. This free space configuration makes the $z(xx)\overline{z}$ and $z(xy)\overline{z}$ configuration and correspond the A1(LO) + E2 modes [130] with detailed information about those frequency given in Table 5.5.



Figure 5.9 Ambient pressure Raman spectrum of LuMnO₃ single crystal (P6₃*cm*) *ab* plane polished. (Inset: the two Lorentz peaks fit to the main peak and shoulder at \sim 680 cm⁻¹).

To study the Raman shift under high pressures, an *ab* plane oriented thin LuMnO₃ single crystal piece (20 μ m thick) was loaded into the type I diamond cell with the methanol: ethanol (4: 1) mixture medium. The low fluorescent diamond has a high intensity feature at ~770 cm⁻¹ and a broad low intensity feature at ~370 cm⁻¹. Two known phonons of methanol: ethanol (4: 1) mixture [248] below 1000 cm⁻¹ are at 432 cm⁻¹ and 882 cm⁻¹. The Raman spectra of LuMnO₃ for pressures range up to ~17 GPa are plotted in Figure 5.11 and it shows that the phonon frequencies continually increase with the pressure increase. The pressure dependent phonon peak positions can be found in the Figure 5.11.

Frequency (cm ⁻¹)	145	252	308	464	641	680
Mode	E2	E2	A1(LO) or E2	A1(LO)	E2	A1(LO)
displacement	+x,y(Lu) -x,y(Lu)	z(Mn, Lu)	x(Mn), z(O3) or +z(O2) -z(O1), x,y(O4)	+x,y(O1,O2) -x, y(Mn)	x,y(O3, O4)	+z(O1) -z(O2)

Table 5.5 Raman Shift, the Corresponding Modes and Atomic Displacements



Figure 5.10 *ab* plane high pressure Raman spectra of LuMnO₃ (upper panel: 7.96, 9.18, 9.97, 10.99, 11.78, 12.45, 13.13, 14.07, 15.13, 16.05, 17.24 GPa; lower panel: diamond, 1.12, 2.20, 2.98, 3.97 GPa). The diamond spectrum is shown as the curve at the bottom.

The peak near 252 cm⁻¹ is assigned as the E2 mode which originates from the counter motion of Mn, Lu along *c* axis; small peak centered near 308 cm⁻¹ is identified as E2 /A1 (LO) modes here which correspond to the displacement of O and Mn atoms; the peak at 464 cm⁻¹ assigned to the A1 mode is due to the counter motion of Mn and apical O (O1 and O2) in *ab* plane; the peak at 680 cm⁻¹ is identified as the A1 mode which

originates from the apical O ion vibration along the *c* axis. The phonon at ~308 cm⁻¹ becomes broad and overlaps with the low intensity feature peak of the diamond, thus it is hard to tell the exact peak position at each pressure. The new peaks of Ho_{0.8}Dy_{0.2}MnO₃ [14] appeared at ~10 GPa, which were assigned to B_{2g} (near 670 cm⁻¹) and A_g (near 235 cm⁻¹) modes of an orthorhombic phase. Here, they can be observed on a single crystalline LuMnO₃ sample and they persist with pressure increase. No new evidence is found to prove the hexagonal-orthorhombic phase transition for LuMnO₃.



Figure 5.11 Pressure dependent phonon peak positions.

In conclusion, these studies have explored the hexagonal $RMnO_3$ structure under hydrostatic pressures. The hexagonal $RMnO_3$ is a very stable phase under high pressures up to ~20 GPa. Without thermal treatment, no phase change occurs in the Hex- $RMnO_3$. Although the orthorhombic phase has a smaller volume per formula unit, thermal treatment is necessary to break the chemical bonds and covert the hexagonal phase. While the structure of the hexagonal $RMnO_3$ remains stable under hydrostatic pressure, the atomic displacements show anisotropy.

CHAPTER 6

SUMMARY AND FUTURE WORK

6.1 Summary

On the self doped La_xMnO_{3- δ} system, the temperature dependent infrared reflectivity spectra of La_xMnO_{3- δ}/LAO (*x*~0.8) were studied over the range 100-8000 cm⁻¹. While the metal-insulator transition temperature (*T_{Ml}*) and the magnetic ordering temperature (*T_C*) approximately coincide, the free-carrier density onset occurs at a significantly lower temperature (~45 K below). The conductivity was found to be systematically enhanced at lower temperatures. These results are consistent with the existence of insulating regions at temperatures significantly below the metal-insulator and magnetic ordering temperatures.

On bulk La_{0.85}MnO₃, in the pressure range up to ~6.8 GPa, the monoclinic (I 1 2/a 1) phase structure remains stable. La_{0.85}MnO₃ has a high bulk modulus value of 133 GPa and the anisotropic compressibility. With the pressure increasing, the lattice parameters (a, b, c) and cell volume decrease linearly while the β angle and the electronic carrier bandwidth *W* increase. The FM order of La_{0.85}MnO₃ is suppressed in a rate of -0.07 μ_B GPa⁻¹. In the temperature range down to 130 K, no AF structure was induced by the pressure.

The hexagonal $RMnO_3$ is a stable phase under high pressures up to ~20 GPa. Although the orthorhombic phase has a smaller volume per formula unit, thermal treatment is necessary to break the chemical bonds and covert the hexagonal phase. Without thermal treatment, it is hard to create a phase change in the Hex- $RMnO_3$. The structure of hexagonal $RMnO_3$ remains stable under hydrostatic pressure, but the atomic displacements show anisotropy.

6.2 Future Work

Optical, transport and structural measurements, as a function of pressure and temperature, provide valuable information needed for understanding strong electronic correlations and spin-lattice coupling. However, there are still open questions to be addressed in future.

The Hall effect is a good way to determine the carrier density and mobility in CMR materials. The Hall effect measurements are suggested to extract the exact carrier density and mobility of both self doped $La_xMnO_{3-\delta}$ film and bulk samples. The $La_{0.8}MnO_{3-\delta}$ (~120 nm) /LAO, the thickness dependence of N_{eff} will be expanded to understand the thickness/strain dependence of the change with temperatures. $La_{0.8}MnO_{3-\delta}$ /LAO films (413 and 36 nm) will be studied. For all three films (thinned substrates measured in a DAC) the resistance under pressure will be studied for comparison. In addition, the cell parameters of the films under pressure will be determined by x-ray diffraction.

In the pressure range up to \sim 7 GPa, temperature range down to 130 K, the AF phase was not observed in the La_{0.85}MnO₃. At a lower temperature, will the AF phase appear under the high pressure condition? It is essential to know if there is a second insulating AF phase at high pressures in the full temperature range, especially at low temperature. Higher resolution, lower temperature neutron diffraction measurements must be conducted.

Thermal treatment is necessary to break the chemical bonds and covert the hexagonal phase into orthorhombic phase. What is the relationship between the synthesis pressure and temperature? High pressure laser heating experiments will be conducted to explore the structural phase space (hexagonal vs. orthorhombic phases). The structural differences between these two hexagonal phases of YMnO₃ are very small [101]. By x-ray diffraction measurements [149], it is found that the ferroelectric polarization originates from the tilting of MnO₅ polyhedra and the buckling of *R* layers, which persists up to 1000 K. However, no evidence shows a structural phase transition up to 1000 K for *R*MnO₃. It is still questioned by Jeong *et al.* [150] whether the geometric effect is the origin of the electric polarization or whether the off-centering of MnO₅ polyhedra are tilting or if Mn ions are shifting. Although the second-order scattering [130] was reported on the HoMnO₃ single crystal, this effect on the single crystal LuMnO₃ points to the need for measurements at different laser wavelengths.

APPENDIX A

PHONON MODEL

A.1 Dipole Lorentz Oscillator Model

The general reference of the phonon model is the book "Optical Properties of Solids" published by Oxford University Press [249]. The displacement x of an oscillating electron in an electric field of light wave of frequency ω_0 is described by a equation of motion:

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} + m_0 \omega_0^2 x = -eE$$
 (A.1)

 γ is the damping rate, *e* is the electric charge of electron and *E* is the electric filed of the light wave. The motion of the nucleus is ignored with the assumption of mass of nucleus much larger than mass of electron ($m_N \gg m_0$). The three items on the right hand side are acceleration, the damping and the restoring force of an atomic dipole oscillator. The damping is the effect of the friction force which is proportional to the velocity and impedes of the motion. The time dependence of electric field is

$$E = E_0 e^{-i\omega t - \Phi} = \widetilde{E}_0 e^{-i\omega t}$$
(A.2)

The solution of the displacement *x* has the same form:

$$x(t) = X_0 e^{-i\omega t - \Phi'} = \widetilde{X}_0 e^{-i\omega t}$$
(A.3)

Putting this form into the equation, then one can get

$$\widetilde{X}_{0} = \frac{-e\widetilde{E}_{0}/m_{0}}{\omega_{0}^{2} - \omega^{2} - i\gamma\omega}$$
(A.4)

The displacement of an electron will create a dipole moment. That is the classical macroscopic polarization. The resonant polarization in a unit volume that contains N atoms is given by:

$$P_{\text{resonant}} = Np = -Nex = \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} E$$
$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$
(A.5)

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}_{background} + \vec{P}_{resonant} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi \vec{E} + \vec{P}_{resonant}$$

In an isotropic medium, $\vec{D} = \varepsilon_0 \varepsilon \vec{E}$, So

$$\varepsilon(\omega) = 1 + \chi + \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}$$

Re $\varepsilon(\omega) = 1 + \chi + \frac{Ne^2}{\varepsilon_0 m_0} \frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 - (\gamma\omega)^2}$ (A.6)

$$\operatorname{Im} \varepsilon(\omega) = \frac{Ne^2}{\varepsilon_0 m_0} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 - (\gamma \omega)^2}$$

When the frequency is zero or infinite,

$$\varepsilon(0) = \varepsilon_{st} = 1 + \chi + \frac{Ne^2}{\varepsilon_0 m_0 \omega_0^2}$$

$$\varepsilon(\infty) = \varepsilon_{\infty} = 1 + \chi$$

$$\varepsilon_{st} - \varepsilon_{\infty} = \frac{Ne^2}{\varepsilon_0 m_0 \omega_0^2}$$
(A.7)
(A.7)

Substitute (A.7) into (A.6), one can get

$$\varepsilon(\omega) = \varepsilon_{\omega} + (\varepsilon_{st} - \varepsilon_{\omega}) \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}$$
(A.9)

If the working frequencies is close to the resonant frequency, where $\omega \approx \omega_0 \gg \gamma$, Δ , then

$$\operatorname{Re} \varepsilon (\Delta \omega) = \varepsilon_{\infty} - (\varepsilon_{st} - \varepsilon_{\infty}) \frac{2\omega_0 \Delta \omega}{4(\Delta \omega)^2 + \gamma^2}$$

$$\operatorname{Im} \varepsilon (\Delta \omega) = (\varepsilon_{st} - \varepsilon_{\infty}) \frac{\gamma \omega_0}{4(\Delta \omega)^2 + \gamma^2}$$
(A.10)

A real material has many characteristic resonant frequencies and each oscillator contributes to the polarization. The total polarization P and the complex dielectric constant ε will be:

$$\vec{\mathbf{P}} = \left(\frac{Ne^2}{\varepsilon_0 m_0} \sum_j \frac{1}{\omega_j^2 - \omega^2 - i\gamma_j \omega}\right) \vec{E}$$

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m_0} \sum_j \frac{1}{\omega_j^2 - \omega^2 - i\gamma_j \omega}$$
(A.11)

where ω_j and γ_j are the frequency and the damping term of a resonance line. In this classical model, each dipole oscillator has the same term and it will lead the oscillator strength to be the same.

In the experiment, the absorption strengths are different for different absorption lines. It can be only explained and shown by the quantum mechanical transition possibility. Assigning the oscillator strength f_i to each transition, the ε can be written by:

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m_0} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j \omega}$$
(A.12)

where $\sum_{j} f_{j} = 1$. This means that a particular electron is involved in several transitions at the same time, the absorption strength is dividend into these transitions.

A.2 Free Electron Drude Model and D-L Model

Metal and doped semiconductors contain significant numbers of free electrons. A free electron is not bounded to any atoms and the restoring force is zero, therefore the nature resonant frequency $\omega_0 = 0$.

In an ac field, the motion of a free electron satisfies:

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} = -eE = -e\widetilde{E}_0 e^{-i\omega t}$$
(A.13)

The free electron displacement is

$$x(t) = \widetilde{X}_0 e^{-i\omega t}, \widetilde{X}_0 = \frac{e\widetilde{E}_0}{m_0(\omega^2 + i\gamma\omega)}$$
(A.14)

Then dielectric constant

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{(-\omega^2 - i\gamma\omega)}$$
(A.15)

satisfies the electric displacement

$$\vec{\mathbf{D}} = \varepsilon \varepsilon_0 \vec{E} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \frac{Ne^2}{m_0} \frac{1}{(-\omega^2 - i\gamma\omega)} \vec{E}$$
(A.16)

where N is the number of free electrons in a unit volume, $\omega_p = (\frac{Ne^2}{\varepsilon_0 m_0})^{\frac{1}{2}}$ the plasma

frequency.

Combine the Drude model and Lorentz model together, the D-L model is

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \frac{Ne^2}{\varepsilon_0 m_0} \sum_j \frac{f_i}{\omega_j^2 - \omega^2 - i\gamma_j\omega} = 1 + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\gamma_j\omega}$$
(A.17)

A.3 Phonons

The Lorentz model can be used to describe the lattice vibration- the phonon. The motion equations of a pair of ions with effective charge $\pm q$ are:

$$m_{+} \frac{d^{2} x_{+}}{dt^{2}} = -K(x_{+} - x_{-}) + qE(t), m_{-} \frac{d^{2} x_{-}}{dt^{2}} = -K(x_{-} - x_{+}) - qE(t), \Longrightarrow$$
(A.18)

Using the reduce mass $\frac{1}{\mu} = \frac{1}{m_+} + \frac{1}{m_-}$, it turns into

$$\frac{d^2}{dt^2}(x_+ - x_-) = -\frac{K}{\mu}(x_+ - x_-) + \frac{q}{\mu}E(t)$$
(A.19)

Let the relative displacement be $x = x_{+} - x_{-}$. Putting the TO mode nature irrational

frequency
$$\Omega_{TO}^2 = \frac{K}{\mu}$$
, which is at $\bar{q} = 0$, into (A.19) yields

$$\frac{d^2}{dt^2}x + \Omega_{TO}^2 x = \frac{q}{\mu}E(t)$$
 (A.20)

and add the phenomenological damping rate γ ,

$$\frac{d^2}{dt^2}x + \gamma \frac{d}{dt}x + \Omega_{TO}^2 x = \frac{q}{\mu}E(t)$$
(A.21)

It is the same equation as the dipole motion equation (A.1), thence,

$$\varepsilon(\omega) = 1 + \chi + \frac{Nq^2}{\varepsilon_0 \mu} \frac{1}{(\Omega_{TO}^2 - \omega^2 - i\gamma\omega)} = \varepsilon_{\infty} + (\varepsilon_{st} - \varepsilon_{\infty}) \frac{\Omega_{TO}^2}{(\Omega_{TO}^2 - \omega^2 - i\gamma\omega)}$$
(A.22)

N is the number of cell per unit volume. Setting $\gamma = 0$ for a undamped system, let

$$\varepsilon(\omega) = 0 = \varepsilon_{\omega} + (\varepsilon_{st} - \varepsilon_{\omega}) \frac{\Omega_{TO}^2}{(\Omega_{TO}^2 - \omega^2)}, \qquad (A.23)$$

then, a solution is acquired

$$\omega = \left(\frac{\varepsilon_{st}}{\varepsilon_{\infty}}\right)^{\frac{1}{2}} \Omega_{TO} \tag{A.24}$$

This is the LO phonon frequency Ω_{LO} . TO phonon modes will generate a transverse electric field wave, and the LO phonon modes will generated the longitudinal electric wave (the electric field generated by LO modes is along the propagation direction). The light (EM wave) only couples to a TO phonon mode.

A.4 Polarons

The free carriers (electron) will be attracted by the positive ion and repelled by the negative one in a polar solid. This will produce a local displacement of the lattice. This lattice distortion will travel with the free electrons through the crystal. This electron with the local lattice distortion is called a polaron [249]. The strength of electron –phonon interaction can be described by a dimensionless constant:

$$\alpha_{ep} = \frac{1}{137} \left(\frac{m^* c^2}{2h v \upsilon_{LO}} \right)^{\frac{1}{2}} \left[\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{ST}} \right]$$
(A.25)

where m^* is the effective mass derived form the band structure. $m^* = \hbar^2 (\frac{d^2 E}{dk^2})^{-1}$, which

assumes a rigid lattice theoretically. In fact, we can only measure the polaron mass m^{**} .

If
$$\alpha_{ep}$$
 is small, it will be $\frac{m^{**}}{m^*} = \frac{1}{1 - \alpha_{ep}/6}$. The polaron can modify the band gap by

$$\Delta E_g = -\alpha_{ep} \hbar \Omega_{LO} \tag{A.26}$$

If
$$\alpha_{ep}$$
 is small, the polaron radius (r_p) is $r_p = (\frac{\hbar}{2m^*\Omega_{LO}})^{\frac{1}{2}}$. When α_{ep} is small, but

the polaron radius is much bigger than the unit cell size, it is called large polaron. If α_{ep} is not small and the polaron radius is about the cell size, it is called small polaron. For a small polaron, the charge will be completely trapped and it can moves only by hopping to a new site.

A.5 Double Damping Drude Model

The factorized (TO-LO) model [192] is:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_{j} \frac{\Omega_{jLO}^{2} - \omega^{2} + i\gamma_{jLO}\omega}{\Omega_{jTO}^{2} - \omega^{2} + i\gamma_{jTO}\omega}$$
(A.27)

Let $\Omega_{LO} = \Omega_p$, $\gamma_{LO} = \gamma_p$, $\Omega_{TO} = 0$, $\gamma_{TO} = \gamma_0$, one can get the Double-damp Drude model

$$\varepsilon(\omega) = \varepsilon_{\omega} \left(1 - \frac{\Omega_{P}^{2} + i(\gamma_{P} - \gamma_{0})\omega}{\omega(\omega - i\gamma_{0})}\right)$$
(A.28)

 γ_p is the line width of plasma response at $\omega = \Omega_P$, γ_0 is the line width of the absorption center at $\omega = 0$. The completed format is

$$\varepsilon(\omega) = \varepsilon_{\infty} \left[\prod_{j} \frac{\Omega_{jLO}^{2} - \omega^{2} + i\gamma_{jLO}\omega}{\Omega_{jTO}^{2} - \omega^{2} + i\gamma_{jTO}\omega} - \frac{\Omega_{p}^{2} + i(\gamma_{p} - \gamma_{0})\omega}{\omega(\omega - i\gamma_{0})}\right]$$
(A.29)

The first term on right side describes the excitations with the restoring force. The second term can describe one without the restoring forcing.

A.6 Optical Conductivity and Sum Rules

For electrons in an ac field, the velocity of the electron is

$$\nu(t) = \dot{x}(t) = \frac{d(\widetilde{X}_0 e^{-i\omega t})}{dt}$$
With $\widetilde{X}_0 = \frac{e\widetilde{E}_0}{m_0(\omega^2 + i\gamma\omega)}$
(A.30)
$$\nu(t) = -\frac{e\tau}{m_0} \frac{\widetilde{E}_0 e^{-i\omega t}}{(1 - i\tau\omega)},$$

 τ is the scattering time $\tau = \frac{1}{\gamma}$. By the current density $j = -Ne\nu = \sigma E$, the conductivity is

derived as $\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}$ with $\varepsilon(\omega) = 1 + \frac{i\sigma}{\varepsilon_0\omega}$. By Maxwell's equation, the conductivity

 σ is $\varepsilon_{\infty} + \frac{i\sigma}{\varepsilon_0 \omega} = \varepsilon(\omega)$. Comparing these two formats, give the optical conductivity as

$$\sigma(\omega) = -\frac{i\omega}{4\pi}\varepsilon(\omega) \tag{A.31}$$

The sum rules reflect rigorous limitation of the optical properties ($\varepsilon = \varepsilon_1 + i\varepsilon_2$). The inertial sum rule for $n(\omega)$:

$$\int_{0}^{\infty} [n(\omega) - 1] d\omega = 0$$
 (A.32)

The dc-conductivity sum rule:

$$\int_{0}^{\infty} [\varepsilon(\omega) - 1] d\omega = -2\pi^{2} \sigma(0)$$

$$\int_{0}^{\infty} \operatorname{Re} \sigma(\omega) d\omega = \frac{\pi}{2} \frac{N_{all} e^{2}}{m}$$

$$N_{eff}(\omega) = \frac{m}{2\pi^{2} e^{2}} \int_{0}^{\omega} \omega' \varepsilon_{2}(\omega') d\omega'$$
(A.33)

In the limit $\omega \to \infty$, the value of N_{eff} is the number of electrons in the system N_{all} .

Kramers- Kronig relations:

$$\varepsilon_{2} - 4\pi \frac{\sigma(0)}{\omega} = -\frac{2}{\pi} \omega P \int_{0}^{\infty} \frac{\varepsilon_{1}(\omega') - 1}{\omega'^{2} - \omega^{2}} d\omega'$$

$$\varepsilon_{1} - 1 = \frac{2}{\pi} P \int_{0}^{\infty} \frac{\omega' \varepsilon_{2}(\omega')}{\omega'^{2} - \omega^{2}} d\omega'$$
(A.30)

P means the principal value of the integral and $\sigma(0)$ is the dc conductivity.

APPENDIX B

NEUTRON DIFFRACTION REFINEMENT PARAMETER SUMMARY

In this section, the neutron diffraction refinement results are summarized in the tables: Table B.1 Lattice parameters and cell volumes, Table B.2 MnO_6 polyhedral volumes, bond lengths and bond angles at fixed temperatures and Table B.3 MnO_6 polyhedral volumes, bond lengths and bond angles at fixed pressures.

Note: P = Pressure, T = Temperature, T= ton, $^{\circ}C =$ Celsius and B= release pressure in the tables.

P & T	P (GPa)	<i>T</i> (K)	a (Å)	error	b (Å)	error	c (Å)	error	β (rad)	error	volume (Å ³)	error
7°C 7T	0.0	280	7.7931	0.0034	5.5324	0.0017	5.4701	0.0023	-0.0119	0.0004	235.82	0.041
7°C 15T	0.09	280	7.7856	0.0039	5.5215	0.0025	5.4829	0.0037	-0.01435	0.0007	235.64	0.039
7°C 20T	0.20	280	7.7967	0.0017	5.5203	0.0020	5.4698	0.0018	-0.01383	0.0005	235.4	0.027
7°C 27T	0.77	280	7.7949	0.0012	5.5198	0.0015	5.4522	0.0014	-0.01313	0.0004	234.57	0.021
25°C 27T	0.85	298	7.7923	0.0023	5.5153	0.0027	5.4554	0.0027	-0.0137	0.0007	234.45	0.046
25°C 42T	2.55	298	7.7974	0.0014	5.4890	0.0013	5.4315	0.0015	-0.0179	0.0003	232.43	0.037
25°C 49T	3.47	298	7.7904	0.0016	5.4886	0.0018	5.4066	0.0018	-0.01597	0.0005	231.14	0.039
25°C 56T	4.75	298	7.7746	0.0017	5.4631	0.0017	5.4024	0.0019	-0.01905	0.0004	229.42	0.044
25°C 63T	5.77	298	7.7625	0.0018	5.4517	0.0019	5.3848	0.0021	-0.01848	0.0005	227.84	0.046
25°C 70T	6.69	298	7.7479	0.0019	5.4390	0.0021	5.3787	0.0023	-0.0203	0.0006	226.62	0.049
7°C B14T	3.62	280	7.7806	0.0014	5.47637	0.00153	5.4150	0.0016	-0.01733	0.0004	230.69	0.035
-143°C 70T	6.96	130	7.737	0.0018	5.43598	0.00186	5.3698	0.0020	-0.02024	0.0005	225.8	0.045
-143°C B50T	6.47	130	7.7396	0.0024	5.44154	0.00264	5.3751	0.0027	-0.01998	0.0007	226.33	0.061
-143°C B17T	4.75	130	7.7587	0.0292	5.4596	0.00284	5.3985	0.0030	-0.01913	0.0009	228.64	0.069
-143°C B14T	4.27	130	7.7651	0.0016	5.46514	0.00162	5.4026	0.0017	-0.0187	0.0005	229.23	0.038

 Table B. 1
 Lattice Parameters and Cell Volumes

P & T	P (GPa)	<i>T</i> (K)	a (Å)	error	b (Å)	error	c (Å)	error	β (rad)	error	volume(Å ³)	error
27T -143°C	0.51	130	7.7853	0.0012	5.5123	0.0013	5.4482	0.0012	-0.014	0.0003	233.785	0.021
27T -93°C	0.61	180	7.7856	0.0012	5.5142	0.0013	5.4491	0.0012	-0.0135	0.0003	233.923	0.02
27T -43°C	0.68	230	7.7912	0.001	5.5154	0.0001	5.454	0.0009	-0.0139	0.0003	234.326	0.018
7°C 27T	0.77	280	7.793	0.0022	5.5149	0.0025	5.4558	0.0025	-0.0138	0.0007	234.448	0.046
57°C 27T	0.77	330	7.7986	0.0008	5.5143	0.0011	5.4596	0.001	-0.0142	0.0003	234.758	0.017
107 ° C 27T	0.90	380	7.7978	0.0011	5.5136	0.0009	5.4637	0.0011	-0.0144	0.0002	234.879	0.022
157°C 27T	0.96	430	7.7998	0.001	5.5155	0.0009	5.4658	0.001	-0.0137	0.0002	235.118	0.02
							•					
-143°C 70T	6.96	130	7.737	0.0018	5.436	0.0019	5.3698	0.002	-0.0202	0.0005	225.804	0.045
-93°C 70T	6.80	180	7.7392	0.0018	5.4366	0.0019	5.3725	0.002	-0.0199	0.0005	226.003	0.045
-43°C 70T	6.87	230	7.7413	0.0019	5.4401	0.0021	5.3729	0.0022	-0.0195	0.0006	226.226	0.048
25°C 70T	6.69	298	7.7479	0.0019	5.439	0.0021	5.3787	0.0023	-0.0203	0.0006	226.634	0.052

 Table B. 1
 Lattice Parameters and Cell Volumes (Continued)
P & T	P (GPa)	Mn1-O1- Mn1 band angle (°)	Mn1-O2- Mn1 band angle (°)	Polyhedral volume (Å ³)	Mn-Ol (Å)	error	Mn-O2 (1) (Å)	error	Mn-O2 (2) (Å)	error	Mn-O Average	error
7°C 7T	0.0	166.2 (23)	162.3 (12)	10.13	1.962	0.005	1.98	0.029	1.957	0.031	1.9663	0.0217
7°C 15T	0.09	165.6 (18)	161.9 (9)	10.131	1.962	0.004	1.92	0.023	2.02	0.021	1.9673	0.016
7°C 20T	0.20	161.1 (20)	164.6 (11)	10.15	1.976	0.006	1.94	0.04	1.98	0.04	1.9653	0.0287
7°C 27T	0.77	165.8 (9)	162.5 (5)	10.077	1.9638	0.002	1.938	0.016	1.987	0.016	1.9629	0.0113
25°C 27T	0.85	163.4 (21)	163.8 (13)	10.048	1.969	0.005	2.031	0.026	1.886	0.027	1.962	0.0193
25°C 42T	2.55	165.9 (12)	162.7 (6)	9.976	1.9641	0.0025	1.923	0.014	1.983	0.014	1.9567	0.0102
25°C 49T	3.47	166.9 (11)	162.3 (5)	9.923	1.9604	0.0004	1.928	0.016	1.97	0.016	1.9528	0.0108
25°C 56T	4.75	166.5 (13)	162.9 (7)	9.838	1.9572	0.0027	1.917	0.016	1.968	0.017	1.9474	0.0119
25°C 63T	5.77	169.1 (10)	161.8 (5)	9.775	1.9494	0.0017	1.933	0.016	1.947	0.016	1.9431	0.0112
25°C 70T	6.69	169.7 (10)	161.6 (4)	9.721	1.9448	0.0016	1.94	0.016	1.934	0.017	1.9396	0.0115
7°C B14T	3.62	169.1 (9)	161.8 (4)	9.894	1.9539	0.0015	1.933	0.015	1.966	0.015	1.951	0.0105

 Table B. 2
 MnO₆ Polyhedral Volumes, Bond Lengths and Bond Angles at Fixed Temperatures

P & T	P (GPa)	Mn1-O1- Mn1 band angle (°)	Mn1-O2- Mn1 band angle (°)	Polyhedral volume (Å ³)	Mn-O1 (Å)	error	Mn-O2 (1) (Å)	error	Mn-O2 (2) (Å)	error	Mn-O Average	error
-143°C 70T	6.96	0.004	0.003	9.69	1.9405	0.0004	1.9452	0.0005	1.9281	0.0005	1.9379	0.0005
-143°C B50T	6.47	0.11	0.5	9.704	1.9403	0.0016	1.944	0.019	1.932	0.02	1.9388	0.0135
-143°C B17T	4.75	0.14	0.7	9.807	1.9445	0.0018	1.958	0.025	1.936	0.026	1.9462	0.0176
-143°C B14T	4.27	0.8	0.4	9.836	1.9491	0.0004	1.969	0.014	1.925	0.015	1.9477	0.0098

 Table B. 2
 MnO₆ Polyhedral Volumes, Bond Lengths and Bond Angles at Fixed Temperatures (Continued)

P&T	P (GPa)	T (K)	Mn1-O1- Mn1 band angle (°)	Mn1-O2- Mn1 band angle (°)	Polyhedr al volume (Å ³)	Mn-O1 (Å)	error	Mn-O2 (1) (Å)	error	Mn-O2 (2) (Å)	error	Mn-O Average (Å)	error
27T -143°C	0.51	130	158.5 (6)	166.63 (32)	10.022	1.9811	0.0019	1.962	0.0019	1.94	0.002	1.961	0.0019
27T -93°C	0.61	180	158.4 (5)	166.70 (30)	10.026	1.9817	0.018	1.943	0.018	1.96	0.018	1.9616	0.018
27T -43°C	0.68	230	159.8 (7)	165.8 (4)	10.051	1.9786	0.002	1.957	0.017	1.951	0.017	1.9622	0.012
7°C 27T	0.85	280	165.277 (12)	162.8 (6)	10.077	1.965	0.0027	1.988	0.017	1.935	0.017	1.9627	0.0122
57°C 27T	0.77	330	162.9 (13)	164.4 (7)	10.068	1.9716	0.0033	1.975	0.017	1.941	0.019	1.9625	0.0131
107°C 27T	0.90	380	166.4 (10)	162.5 (5)	10.084	1.9633	0.002	1.935	0.013	1.992	0.013	1.9634	0.0093
157°C 27T	0.96	430	162.3 (13)	164.8 (7)	10.081	1.9734	0.0035	1.941	0.022	1.976	0.023	1.9635	0.0161
-143°C 70T	6.96	130	170.814 (4)	161.060 (3)	9.69	1.9405	0.0004	1.9452	0.0005	1.9281	5x10 ⁻⁴	1.9379	0.0005
-93°С 70Т	6.80	180	170.5 (9)	161.6 (4)	9.686	1.9415	0.0014	1.955	0.016	1.916	0.017	1.9375	0.0115
-43°C 70T	6.87	230	170.3 (10)	161.7 (5)	9.699	1.9423	0.0016	1.939	0.017	1.934	0.018	1.9384	0.0122
25°C 70T	6.69	298	169.7 (10)	161.6 (4)	9.721	1.9448	0.0016	1.94	0.016	1.934	0.017	1.9396	0.0115

 Table B. 3
 MnO₆ Polyhedral Volume, Bond Lengths and Bond Angles at Fixed Pressures

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