

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES



**First Principle Determination of Electronic
Structure and Magnetic Properties of
 CaMnO_3**

By: Abeje Aychiluhem Menkir

A thesis submitted in partial fulfillment of the
requirements for the Masters degree.

Addis Ababa university

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university

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Date

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Acronym

AF	Antiferromagnetic
ASW	Augmented Spherical Waves
BZ	Brillouin Zone
CPMD	Car-Parrinello Molecular Dynamics
DFPT	Density Functional Perturbation Theory
DFT	Density Functional Theory
DOS	Density of State
FM	Ferromagnetic'
FPMD	First Principle Molecular Dynamics
G-AF	G type Antiferromagnetic
GGA	Generalized Gradient Approximation
GGA +U	Generalized Gradient Approximation plus Hubbard U correction
GUT	Graphical User Interface
LDA	Local Density Approximation
LSDA	Local Spin Density Functional Theory
Mn	Manganese
O	Oxygen
PM	Paramagnetic
PW	Plane Wave
PWSCF	Plane Wave Self Consistent Field
USPA	Ultra Soft Pseudopotential Approximation
LAPW	Linearized Augmented Plane wave

Abstract

During last decade predicting the stable structure of Manganite and estimating ground state properties of such system using first principles density functional theory has tremendous attention. For this thesis the electronic structure, magnetic and phonon vibrational properties of the perovskite Calcium Manganites have been investigated using first principle calculation. The calculation is done based on the density functional theory using generalized gradient approximation, generalized gradient approximation with Hubbard U correction and ultrasoft pseudopotential approximations on Plane wave basis set. The aim of this work is to investigate the structural, electronic, magnetic and phonon vibrational properties of the Calcium Manganite for cubic structure. In addition electronic properties of its orthorhombic structure will be investigated. A detailed analysis of structural properties, band structure, density of states and the effect of distortions of a crystal structure is done for different magnetic configuration with Hubbard U correction and with out U. The total energy, Fermi energy, the equilibrium lattice parameter and magnetic moment are also calculated and they are in good agreement with the experimental and other theoretical calculations.

CHAPTER 1

General introduction

1.1 Thesis outline

In this thesis there are five chapters and they are organized in the following way. The first chapter includes the general, specific objectives and introductory parts. In chapter 2 we will see the periodicity of arrays of atoms in a crystal, plane wave bases set and k point sampling on the BZ. In chapter 3 the methods of electronic structures or tools will be presented as well as some approximation for this calculation. In chapter 4 computational techniques is presented. In chapter 5 analyses of the calculated results is presented in detail. And finally the conclusion part of the computational result will be discussed.

1.2 Objectives

1.2.1 General objective

The general objective of this thesis is studying the structural, electronic, magnetic and phonon vibrational properties of the cubic structure of the Calcium Manganite. Besides we will investigate the ground state electronic properties of a compound in its orthorhombic crystal structure by using Quantum Espresso Package. And finally we will compare the previous theoretical calculated and the experimental results with the present theoretical result.

1.2.2 Specific objective

We will calculate the equilibrium lattice parameter, k point's mesh, charge density and kinetic energy cutoff from the convergence of the total energy of CaMnO_3 for PM and FM configurations. We will simulate total energy versus lattice parameters, total energy versus charge density cutoff, total energy versus kinetic

energy cutoff and total energy versus k points mesh for the cubic structure. Based on the equilibrium lattice parameter and other parameters, simulation of band structure, density of state and phonon dispersion relation for cubic structure will be done. Whereas in the case of orthorhombic structure we will only simulate both the band structure and density of state. For cubic and orthorhombic structure, we will simulate the band structure and density of state for undistorted and distorted structure with and without Hubbard U correction. And finally based on calculated results and simulation we will analyze in details the properties of the material.

1.3 Computational Methodology

In order to investigate the structural, magnetic, electronic and phonon vibrational properties of the Calcium Manganite, the methodology includes the following important tools and input files. The five broad crucial tools for this calculation are the methods of electronic structure using DFT, the Quantum Espresso Package (version 4.1) software, Fedora (version 9.0) operating system including Xmgrace and Xcrysden softwares, input files and a single computer.

The first category includes the methods of electronic structure called DFT. All theoretical results are computed with the implementation of DFT. Within this DFT we used the two vital approximations are called GGA and USPA. We also used Hubbard U correction on GGA. The second broad category is the software called Quantum Espresso Packag. It is a collection of other utility packages like PWSCF, FPMD, CPMD and GUI. But in our work all results are calculated from the PWSCF package only. The third one is the operating system that is installed in a single personal computer is called Fedora 9.0 version. It is on this environment in which all computations are done. Besides we do have another softwares called Xmgrace and Xcrysden package to simulate the nature of a material and to see the structure of a compound respectively.

The fourth category to get the desired computational results and different

simulations is input files. Those files comprises of vital information about the system that we study. We used different input files for different magnetic configurations through out the calculation. Some of the input parameters that are incorporated through the calculation in the input files are 4 x 4 x 4 k point mesh in the BZ, 30 Ry for Kinetic energy cutoff, 300 Ry for charge density cutoff and 71 and 60 points in the irreducible BZ for the cubic and orthorhombic structure respectively.

1.4 Introduction

A Perovskite is any material with the same type of crystal structure as Calcium Titanate (CaTiO_3) known as the Perovskite structure. Perovskites take their name from this compound, which was first discovered in the Ural mountains of Russia by Gustav Rose in 1839 [1]. The general chemical formula for Perovskite compounds is ABO_3 , where 'A' and 'B' are two of very different sizes, A is a rare earth or alkaline earth and B is a transition metal. The crystal structure is cubic or nearly cubic and O is an anion that bonds to both. The 'A' atoms are larger than the 'B' atoms. The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold coordination. The relative ion size requirements for stability of the cubic structure are quite stringent, so slight distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of A cation, B cation or both are reduced.

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Colossal magneto resistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo power and the interplay of structural, magnetic and transport properties are commonly observed features in this family [2]. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications.

Calcium manganite is one of the Perovskite compounds. Its chemical formula is CaMnO_3 . Where Ca is a non transition metal for which coulomb ionic bonding favor the maximum number of O neighbor, whereas Mn is a transition metal where the d states favor bonding with the O states. The formal ionic configuration of CaMnO_3 is $\text{Ca}^{+2}\text{Mn}^{+4}\text{O}^{-2}$. In the octahedral crystal field, the 3d orbital of the Mn^{+4} ion split into lower three-fold degenerated t_{2g} levels and higher two-fold degenerated e_g levels; the occupation being t_{2g}^3 and e_g^0 [3].

At ground state CaMnO_3 has a crystal structure called orthorhombic with 20 atoms in the primitive cell and this structure can be regarded as a distorted perovskite [4]. The magnetic structure is G-type has the lowest energy and so is energetically the most favorable. The magnetic interactions between the Mn ions are due to super exchange interactions. The observed Neel temperature is about 130 K. But at high temperature it has cubic structure.

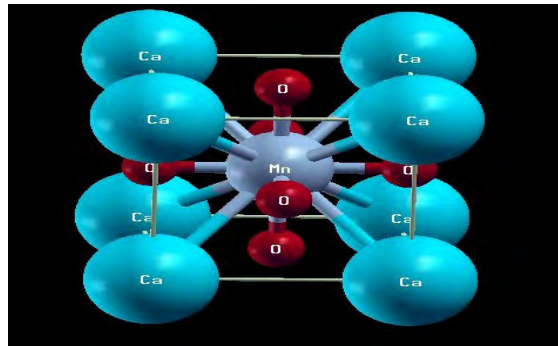


Fig 1.1 The ideal cubic structure of CaMnO_3

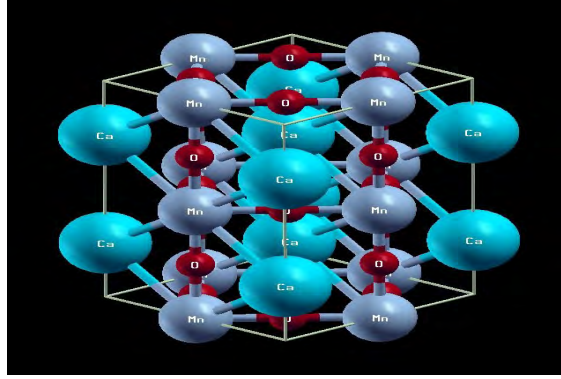


Fig 1.2 The G type AF and orthorhombic structure of CaMnO_3

Nowadays different kinds of novel materials are invented like perovskite compounds. Since they are very crucial for different applications, we have to investigate those unique properties.

In general there are two methods of studying the different properties of a material. They are experimental and theoretical methods. The theoretical method is one of systematic and scientific methods of studying those properties of a material. On this research the different properties of the Calcium Manganite (CaMnO_3) are investigated based on the theoretical methods because of investigating their physical, optical, mechanical, structural and other properties in the experimental laboratory is quite difficult and needs huge effort and a lot of money.

Using theoretical method important properties of CaMnO_3 was investigated previously by different researchers. They used different methodology. However for this work the properties of this strongly correlated perovskite compound will be investigated by a new software called Quantum Espresso Package [5]. This new package works on the principle of PWSCF calculation using quantum mechanical aspect of the materials.

The Quantum-Espresso is a full abinitio package implementing electronic structure and energy calculations, linear response methods (to calculate phonon dispersion curves, dielectric constants, and Born effective charges) and third-order an harmonic perturbation theory. It is a collection of electronic structure codes for

plane wave pseudopotential calculations. Its main components are: PWSCF, FPMD and CPMD as well as a GUI for creating input files and a code to create pseudopotentials. PWSCF is a set of programs for electronic structure calculations within DFT and DFPT using a plane wave basis set and Pseudopotentials. It is particularly well suited for the calculation of ground state calculations for solids.

CHAPTER 2

Regular solids and plane wave bases set

2. Periodicity of atoms in a crystal, sampling on BZ and plane wave bases set

2.1 Introduction

Crystal is the term used for some solid material structure. It generally consists of single atoms or ions, but it may also contain molecules. In crystals atoms are placed at certain relative coordinates. They don't move under normal conditions. Every atom or molecule forming the crystal interacts with all other atoms or molecules. Every unit structure attracts with each other with some physical forces. There are no bonds between any unit structures forming the crystal.

A crystal is an ordered state of matter in which the positions of the nuclei (and consequently all properties) are repeated in space. When a crystal grows in a constant environment, the form develops as if identical building blocks were added identically. The building blocks are atoms or groups of atoms, so that the crystal is a three dimensional periodic array of atoms. It is completely specified by the types and positions of the nuclei in one repeat unit (primitive unit cell) and the rules that describe the repetition (translations).

Obtaining parameters of crystal structures is a quite important issue in crystallography. Crystal structure of a material is closely related with its physical properties. Accordingly, obtaining crystal parameters of a material will help to understand its physical behavior. In material science, crystal parameters are used to classify materials. This classification helps to analyze materials effectively. Particularly, for complex cases such as perovskite like Calcium Manganites whose atomic ratios can change, such classification is quite useful to analyze physical properties.

The compound that we studied here is a complex crystal. It is a building

block of the five atoms in each unit cell; they are Calcium, Manganese, and three atoms of oxygen hence it is very crucial to know its crystal structure in order to investigate its properties for this theoretical work.

2.2 The real and reciprocal space lattice

The real space lattice is the lattice that exists periodically in the real crystal. The reciprocal lattice is essentially a map of the periodicity of the lattice in a real space of the crystal, or a spatial Fourier transform. The periodicity of the crystal structure can be considered most cleanly by dividing the structure into a lattice and basis.

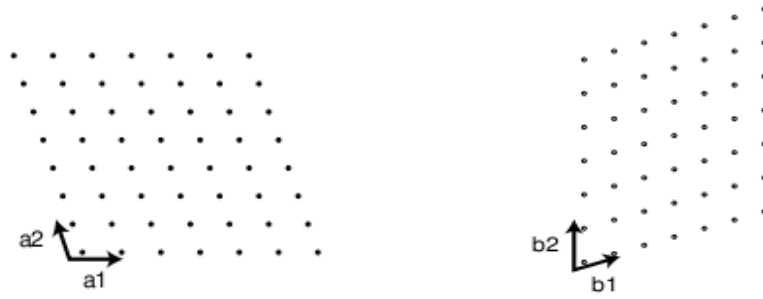


Fig 2.1 The Real and Reciprocal lattice from left to right [6]

reciprocal lattice vectors b_1 , b_2 , b_3 of the reciprocal lattice are constructed by the following definition [6]

$$\begin{aligned} b_1 &= \frac{a_2 \times a_3}{V} \\ b_2 &= \frac{a_3 \times a_1}{V} \\ b_3 &= \frac{a_1 \times a_2}{V} \end{aligned} \tag{2.1}$$

where $V = a_1 \cdot (a_2 \times a_3)$ stands for the volume of a cell in a real lattice, a_1 , a_2 , a_3 are the primitive vectors of the crystal lattice, then b_1 , b_2 , b_3 are the primitive vectors of the reciprocal lattice. Each vector defined by 2.1 is orthogonal to two axis vectors

of the crystal lattice. Thus b_1, b_2, b_3 have the property

$$b_i \cdot a_j = 2\pi \delta_{ij} \quad (2.2)$$

Where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$ points in the reciprocal lattice are mapped by the set of vectors

$$G = v_1 b_1 + v_2 b_2 + v_3 b_3 \quad (2.3)$$

Where v_1, v_2, v_3 are integers. A vector G of this form is a reciprocal lattice vector.

2.3 Brillouin zones

We can define a geometrical shape, the BZ, based on the position of these zone boundaries. The BZ is defined as the Wigner-Seitz cell in reciprocal space [7]. The Wigner-Seitz cell is defined as the smallest polyhedron enclosed by the perpendicular bisectors of the nearest neighbors to a lattice point. It gave the statement of the diffraction condition which means in the description of electron energy band theory like for the analysis of electronic energy, band structures of the crystals and of the elementary excitations of other kind. The value of the BZ is that it gives a vivid geometrical interpretations of the diffraction $2K = G \times G$. We divide both sides by 4 to obtain

$$k \cdot \left(\frac{1}{2}G\right) = \left(\frac{1}{2}G\right)^2 \quad (2.4)$$

To apply the space of k 's and G 's on reciprocal space; we select a vector G from the origin to a reciprocal lattice point and construct a plane normal to this vector G at its midpoint. This plane forms a part of a zone. An x-ray beam in the crystal will be diffracted if its wave vector K has the magnitude and direction required by Equation 2.4. The diffracted beam will then be in the direction $K-G$, with $\Delta K = -G$. Thus the BZ construction exhibits all the wave vectors K which can be Bragg reflected by the crystal.

The set of planes that are the perpendicular bisectors of the reciprocal lattice vectors is of a general importance in the theory of wave propagation in crystals. A

wave whose wave vector drawn from the origin terminates on any of these planes will satisfy the condition for diffraction [8]. The central cell in the reciprocal lattice is of special importance in the theory of solids, and we call it the first BZ. The first BZ is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

The first BZ of an oblique lattice in two dimensions and one dimension is constructed in Figures 2.2, 2.3 and 2.3

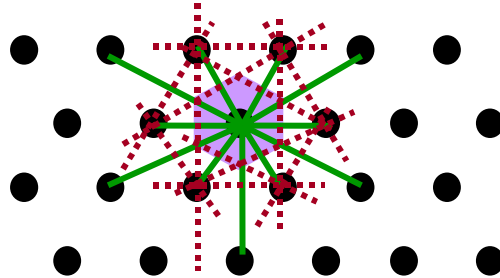


Fig 2.2 Construction of the first BZ

The zone boundaries of the linear lattice are at $K = \pm \frac{\pi}{a}$, where a is the primitive axis of the crystal lattice.

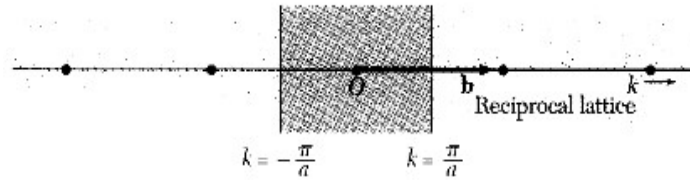


Fig 2.3 Zone boundaries of a linear lattice

First, second, third, and fourth BZ are defined as the smallest, second-smallest, third-smallest, and fourth-smallest polyhedron enclosed by bisecting planes. These constructions are illustrated in Figure 2.4.

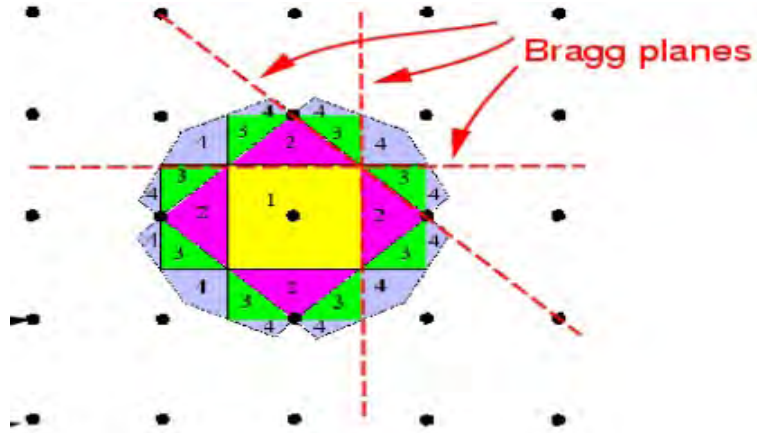


Fig 2.4 Different BZ for the oblique 2D surface

To form the Wigner-Seitz cell for this reciprocal lattice, it is necessary to go out to the boundaries to the third nearest neighbor (marked 1-3). The first, second, third, and fourth BZ are marked by yellow, pink and green colour respectively.

2.4 Plane wave basis set

Plane waves are a particular well suited set of basis functions for extended systems. Plane waves are the exact eigen functions of the homogeneous electron gas. Therefore, they are the best choice for a basis expansion of the electron wave functions for simple metals where the ionic cores can be viewed as rather small perturbations to the homogeneous electron gas [9]. They are orthonormal and energy-independent. A further advantage of plane waves is that they are not biased to any particular atom. Any region in Space is treated on an equal footing so that calculations do not have to be corrected for a basis set superposition error. Plane waves do not depend on the positions of the atoms. In practical calculations only plane waves up to a certain cutoff wave vector are included in the basis set. The convergence of the calculations with respect to the basis set size is therefore controlled by a single parameter and can be checked simply by increasing the length

of the cutoff wave vector.

2.5 k-Point Sampling

By making use of Bloch's theorem we have transformed the problem of calculating an infinite number of electronic states extended infinitely in space to one of calculating a finite number of eigen states at an infinite number of k-points which are extended over a single unit cell. At first glance this seems to be only a minor improvement since still an infinite number of calculations are needed for the different k-points. However, the electronic wave functions at k-points which are close together will be very similar. Hence it is possible to represent the wave functions of a region of k-space by the wave function at a single k-point. We thus define a regular mesh of N_{kpts} k-points and replace the integral over the BZ by a discrete sum over the chosen k-point mesh:

Several schemes to construct such k-point meshes have been proposed in the literature [10]. Within this approximation the electronic states at only a finite number of k-points are needed to calculate the charge density and hence the total energy of the solid. The error induced by this approximation can be reduced systematically by increasing the density of the k-point mesh. For insulators it turns out that usually only a small number of k-points is required to get good converged results. For increasing size of the super cell the volume of the BZ becomes smaller and smaller. Therefore with increasing super cell size less and less k-points are needed.

2.6 Brillouin-Zone sampling

In periodic boundary conditions the translational symmetry of the external

potential leads to a representation for the wave functions in the form of Bloch states. The sum on all the infinite states of the system thus becomes an integral over the first BZ, where for each wave vector there corresponds only a finite and small number of states. The kinetic energy, the band energy term and the charge density in are all defined via a full integration on the first BZ.

It was first recognized by Baldereschi [11] that the integrations over the BZ could be performed to a very high accuracy by using just a single special k-point, carefully chosen according to the point group symmetry of the unit cell lattice. This analysis has been subsequently generalized to identify a set of prescriptions for choosing relatively coarse meshes that can provide excellent accuracy in estimating the exact integrals [12,13] the existence of symmetry operators that commute with the Hamiltonian can be further exploited via the simple relations that are satisfied by the common eigen states at different but symmetry related k-points, and effectively reducing the problem to an integration over the irreducible wedge of the BZ.

CHAPTER 3

Electronic structure calculation

3 Electronic structure Methods

3.1 Introduction

Methods of Electronic structure in general can be divided into two categories: Semi-empirical methods, on the one hand, use a set of parameters and effective Hamiltonian to interpret experimental results and first principles methods, on the other hand, are parameter-free and based only on fundamental interactions between electrons themselves and between electrons and nuclei. The first-principles methods aim at solving the complicated problem of electrons moving in the electrostatic field due to the nuclei. As a first approximation, the nuclei are considered fixed and the problem becomes that of electrons only whose motion is governed by the Schrodinger equation. First principles means that the only input information required are the atomic numbers of the constituents of the system. In many cases the atomic positions are also given. This chapter is concerned with the DFT. And we will discuss the fundamental approximations to the electron-electron and electron-nuclei many-body problem to reduce it to a problem of many independent electrons which move in an effective mean field.

Since its theoretical foundation in the mid-1960's [14], DFT has demonstrated a large predictive power in the study of the ground states properties of real materials, so that it has soon become the most important tool for first principles calculations. Though exact in principle, this theoretical scheme needs some approximations to be used in practical calculations. In fact, the many body problems concerning an interacting electron system is far too complicated to be approached directly, so that it is usually treated in a simpler one body formalism which describes a fictitious non interacting electron gas with the same density of the real interacting one. In this simplified scheme the many body contributions to the electronic

interactions are usually modeled in some approximations.

The simplest of these simplified (and the first historically introduced) is the LSDA which is based on the assumption that the electronic system can be locally represented by a uniform electron gas with the same density. Using LSDA the structural, electronic and magnetic ground state properties of a large class of materials, including, for instance, nearly-free-electron-like (simple) metals, covalent semiconductors, ionic solids, and even rather complex intermetallic transition metal compounds, could be described and understood very deeply and usually within a fair agreement with experimental results.

A possible extension to the LDA method is represented by (spin-polarized) GGA approaches which, in the modeling of the effective electronic interactions, also accounts for the possible inhomogeneity of real electron systems. The introduction of this approach could solve indeed some open questions within LSDA and even improve the descriptive power of DFT calculations about the structural and the electronic properties of some real non homogeneous system as, for instance, the transition metal compounds.

However GGA functional brought out very little enlargement of the class of materials whose properties could be successfully described by DFT, so that there still remains quite a large group of systems whose study cannot be accurately addressed by standard DFT approaches: the strongly correlated materials. The reason why ordinary LDA or GGA methods are not able to correctly describe this class of materials mainly consists in the fact that their energy functionals are built treating the real interacting electron system as a (possibly homogeneous) electron gas, and thus result to be not accurate enough to deal with situations in which strong localization of the electrons is likely to occur.

3.5 Density Functional Theory

The first important conceptual advantage introduced by DFT [15] is the possibility to describe the ground state properties of a real system in terms of its ground state electronic charge density (which depends on just one spatial variable) instead of the far more complicated wave functions (which depends on the coordinates of all the electrons in the system). Dealing with the charge density allows to reformulate the problem in a mean-field-like language which is however based on an exact result. If we consider an interacting electron gas, the external potential acting on the particles determines the ground state of the system and the corresponding charge density. Thus, all the physical quantities concerning this state (like, for instance, the total energy) are functionals of the external potential. As it was first demonstrated by Hohenberg and Kohn, due to a one to one correspondence among the external potential and the ground state density, there also exists a unique universal functional $F[n(r)]$ of the ground state electron density alone such that a variational principle exists with respect to the electron density for the total energy functional.

$$E[n(r)] = F[n(r)] + \int V_{ext}(r)n(r)dr \quad (3.1)$$

where $F[n(r)]$ contains the kinetic energy and the mutual Coulomb interaction of the electrons, and $V_{ext}(r)$ represents the external potential acting on the particles. The minimization of this functional with the condition that the total number of particles, N , is preserved:

$$\int n(r)dr = N \quad (3.2)$$

directly gives the ground state energy and charge density, from which all the other physical properties can be extracted. This variational principle is very important from a conceptual point of view as it suggests a procedure to access all the interesting quantities.

Unfortunately, the universal functional $F[n(r)]$ (which is independent on

$V_{\text{ext}}(\mathbf{r})$ is not known in practice and in order to transform DFT into a useful tool, Kohn and Sham introduced a further development which consists in mapping the original interacting problem into an auxiliary non interacting one. For this fictitious system of non interacting electrons the Hohenberg and Kohn theorem also applies and the unique functional $F[n(\mathbf{r})]$ corresponds in this case to the kinetic energy of the non interacting electrons, $T_0[n(\mathbf{r})]$. The density functional $F[n(\mathbf{r})]$ for the interacting system can then be expressed as the sum of the kinetic energy of a non interacting electron gas with the same density of the real one and the additional terms describing the interparticle interaction:

$$F[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n(\mathbf{r})] \quad (3.3)$$

The second term in the right hand side of Equation 3.3 is the classical Coulomb interaction among the electrons described through their charge density (the Hartree term), whereas $E_{\text{xc}}[n(\mathbf{r})]$ is the so called exchange-correlation energy and accounts for all the many body effects which are not described in the other terms. In practice this term contains all the differences among the non interacting fictitious system and the real interacting one (here including corrections for the Coulomb interaction and for the kinetic energy also) so that what we do is confining our ignorance about $F[n(\mathbf{r})]$ into one single, hopefully small, term. This is particularly useful when we minimize the functional $F[n(\mathbf{r})]$ with the constraint given by the conservation of the total number of particle to obtain the ground state physical properties of the real system.

Minimizing the total energy with respect to the density, as stated in the second theorem gives

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0[n]}{\delta n(\mathbf{r})} + V^{\text{ext}}(\mathbf{r}) + V^H(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} = \mu, \quad (3.4)$$

Comparing the last two equations, we see that the two systems are identical if we have

$$V^{eff}(r) = V^{ext}(r) + V^H(r) + V_{xc}(r) \quad (3.5)$$

Where the exchange-correlation potential V is defined as

$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)}, \quad (3.6)$$

It then follows that by solving the single-particle Kohn-Sham equations

$$H_{KS}\psi_i(r) = [-\Delta_i + V_i^{eff}(r)]\psi_i(r) = \varepsilon_i\psi_i(r), \quad (3.7)$$

of the fictitious system one can determine the single particle density of the interacting system:

$$n(r) = \sum_{i=1}^{occ.} |\psi_i(r)|^2 \quad (3.8)$$

This is a significant simplification of the many-electron problem. The Kohn-Sham equations are similar to the Hartree ones which we know how to solve in a self-consistent manner. However, in principle the eigenvalues and eigen vectors should not be regarded to be the elementary excitations and single-electron wave functions of the real system. They correspond to the auxiliary system and should therefore be regarded as mathematical constructs which help us solve the original problem. However, comparison between the KS energy levels and experiment often works for metals and for systems where correlations are small or moderate.

In the Kohn-Sham formalism, the ground state total energy of the electronic system is given by

$$E = \sum_i^{occ.} \varepsilon_i - \int \int \frac{n(r)n(r')}{|r-r'|} dr dr' - \int n(r)V_{xc}(r)dr + E_{xc}[n], \quad (3.9)$$

where the last three terms are corrections for double counting in the sum of the eigen-values. By treating the kinetic and the electrostatic energies exactly one hope that the exchange-correlation part is only a small contribution and its approximate treatment later on should be a minor problem. While this is the case in many systems, there are so-called correlated systems where it is no longer possible to ignore the errors made in the approximate exchange-correlation. Next we will

present a local approximation to the exchange-correlation functional.

3.5.1 Approximations for the exchange-correlation energy functionals: LDA and GGA

Up to this point no approximation was introduced into the theory, but there still exists a term (the exchange-correlation energy) which, though well defined (and exact) in principle, has a very complicated expression which is not known explicitly. Some assumptions are thus needed in the definition of E_{xc} to convert the DFT in a practical tool for first principle calculations.

The simplest of these descriptions is called the LDA and is obtained assuming that the exchange correlation energy of a real system behaves locally as in a uniform (homogeneous) electron gas having the same density. The exchange correlation energy thus depends only on the local density of the system and actually reads [16]:

$$E_{xc}^{LDA}[n] = \int \epsilon_{xc}^{\text{hom}}(n(r))n(r)dr \quad (3.10)$$

where $\epsilon_{xc}^{\text{hom}}(n(r))$ is the exchange correlation energy density of the above mentioned homogeneous system. The exchange correlation potential can be easily obtained from the exchange correlation energy functional and results:

$$v_{xc}^{LDA}(r) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(r)} = \frac{\partial F_{xc}^{LDA}[n]}{\partial n} \Big|_{n=n(r)} \quad (3.11)$$

Where $F_{xc} = \epsilon_{xc}^{\text{hom}}(n(r))$. This approximation was designed to work with systems in which the electronic charge density is expected to be smooth (like, for instance, in nearly free-electron-like (simple) metals, intrinsic semiconductors and so on) but it gives indeed quite good results also with non homogeneous systems like covalently bonded materials and (some) transition metals. It typically produces good agreement with experiments about structural and vibrational properties, but usually

overestimates bonding energies and predicts shorter equilibrium bond lengths than found in experiments.

In order to overcome these and other difficulties of LDA, some extensions of the original approximation were introduced among which the GGA family is one of the most successful. Within GGA the exchange correlation energy is a functional not of the density alone, but also of its local spatial variations [17]:

$$E_{xc}^{GGA}[n] = \int \mathcal{E}_{xc}^{GGA}(n(r), |\nabla n(r)|) n(r) dr \quad (3.12)$$

Several expressions of the exchange correlation energy density have been described in different formulations of the GGA functionals. The potential corresponding to the energy functional $E_{xc}[n]$ can be expressed as:

$$v_{xc}^{GGA}(r) = \frac{\delta E_{xc}^{GGA}[n]}{\delta n(r)} = \left(\frac{\partial F_{xc}}{\partial n} - \sum_{\alpha=1}^3 \partial_{\alpha} \left(\frac{\partial F_{xc}}{\partial (\partial_{\alpha} n)} \right) \right) \quad (3.13)$$

where $F_{xc}(n, |\nabla n|) = \mathcal{E}_{xc}^{hom}(n, |\nabla n|)n$, ∂_{α} stands for the α^{th} component of the gradient and the rule of integration by parts was used to obtain the last equality. This improved approximation is actually able to cure some defects of LDA and generally produces better description of the structural properties of real materials. In particular it improves significantly the results about the binding energy of real system. It is also expected to give a better description of non homogeneous systems, like transition metals, producing correct results in some cases where LDA completely fails.

Despite the theory is exact in principle, the approximations we have to adopt for the exchange and correlation energy both in LDA and GGA introduce a mean-field like formalism which can be expected to work well for systems with rather delocalized electrons but is not sufficiently accurate when dealing with materials with localized electrons for which many body effects are expected to be more important.

3.6 The pseudopotential approximation

The pseudopotential approximation provides a rational way to isolate the fundamental role played by the valence electrons in the electronic-structure problem. In a mean-field picture, the valence electrons can be thought of as the loosely bound orbitals which are most strongly modified on formation of the chemical bonds in a molecule or the bands in a solid. And so most physical and chemical properties of crystals depend on a very good approximation only on the distribution of valence electrons. The length-scales of these orbitals are those characteristic of inter-atomic separations and chemical bond energies. In contrast, inner electrons are tightly bound around each atomic nucleus and are largely unperturbed by the environment surrounding their atom [18].

In a Hartree-Fock or Kohn-Sham mean-field picture, the higher orbitals must have features on the inner core length-scales via the orthogonality constraint to the lower orbitals. Nevertheless, it can be argued that the atomic problem can be projected for the valence electrons into an effective energy-dependent Hamiltonian, where the nuclear attraction is largely screened by a repulsive term that mimics the effects of the orthogonality constraint. The resulting potential is commonly referred to as a pseudo potential and it is much weaker and smoother than the original coulomb potential.

The modern theory of pseudopotentials builds around the key issue of transferability, constructing a pseudopotential that scatters the incoming wave function as closely as possible to the original potential over a wide range of energies.

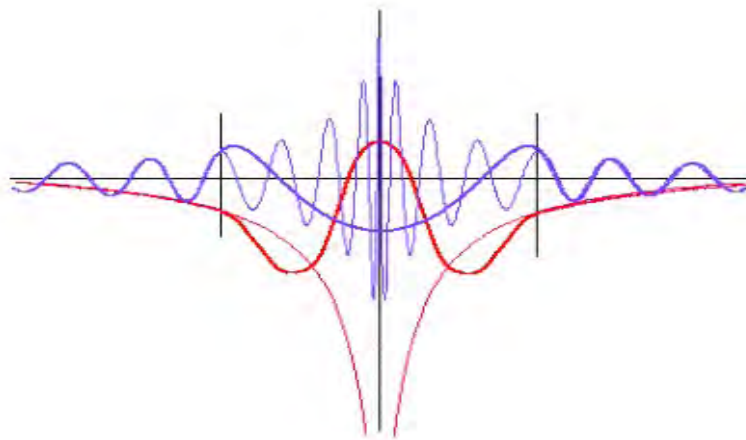


Fig 3.1 A schematic representation of the potentials (red lines) and wave functions (blue lines) for an atom. The real potential and wave function are shown with thin lines, while the pseudopotential and wave function are shown in thick lines. Thick lines outside the cutoff region (vertical black lines) the two are identical.

In the case of frozen approximation, it is just to assume that core electron to be 'frozen' and to keep the core electron distribution of the isolated atom in the crystal environment. The first advantage is that now fewer electrons have to be treated and less eigenstate of the kohn sham equations have to be calculated. The other advantage is that the total energy is largely reduced when the core electrons are removed from the calculation which makes the calculation of energy differences between atomic configurations numerically much more stable.

Very difficult to treat within a pseudopotential scheme are all elements with nodeless valence elements valence states (in particular those with 2s and 3d valence electrons). for those elements the pseudo and all electron wave functions are almost identical. Since these valence electrons are strongly localized in the core region, many plane waves are required for a good representation of their wave function which makes calculations for such elements prohibitively expensive. To circumvent this problem Vanderbilt has introduced a new type of pseudopotential, so called

ultrasoft pseudopotentials, in which the norm conserving requirement has been relaxed [19, 20]. Instead of representing the full valence wave function by plane waves, only a small portion of the wave function is calculated within the Vanderbilt ultrasoft pseudopotentials. This allows reducing substantially the plane wave cutoff energy calculations.

CHAPTER 4

Computational techniques

The computational results so far described in chapter 5 were performed on implementation of DFT using a plane wave pseudopotential within the GGA approximation and Hubbard U correction on GGA. Plane wave basis sets offer many advantages in total energy calculations for solids, including completeness, an unbiased representation, and arbitrarily good convergence accuracy. They also allow for straightforward mathematical formulation and implementation. However plane wave basis sets necessitate the use of pseudopotentials to model the electron-ion interaction and also to avoid rapid oscillations of the valence wave-functions in the region around the ion cores.

4.1 Implementation of DFT

Bloch's theorem is often stated in the statement that all eigen functions ψ_{kj} of a single particle Schrodinger equation with a periodic potential can be written as a periodic function μ_{kj} modulated by a plane wave with wave vector k has a form [21].

$$\psi_{kj}(r) = e^{ikr} \mu_{kj}(r) \quad (4.1)$$

This allows us to restrict the calculation of the eigen functions to within one unit cell. The form of the eigen functions in all other unit cells is determined by applying Equation 4.1. The values K can be restricted to within one unit cell of the reciprocal lattice. By convention this unit cell is usually taken to be the first BZ. From now on we will assume that the eigen functions are normalized with respect to a single unit cell.

$$\int |\psi_{kj}(r)|^2 d^3r = 1 \quad (4.2)$$

Since the functions μ_{kj} are periodic they can be expanded in a set of plane waves.

Together with the exponential prefactor we get:

$$\psi_{kj}(r) = \sum_G c_G^{kj} e^{i(k+G)r} \quad (4.3)$$

and the Kohn Sham equations of DFT in the notation of Bloch states:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right) \psi_{kj}(r) = \epsilon_{kj} \psi_{kj}(r) \quad (4.4)$$

To calculate the V_{eff} for Equation 4.4, construction of pseudopotential is introduced. And so pseudopotential codes calculate the electronic structure for only valence electrons. $V_{\text{pp}}(r)$ is chosen so the true function and potential match for $r > r_c$ (core radius), but so the potential is 'soft' and the wave function is smooth.

For an infinite system the effective potential ($V_{\text{eff}}(r_i)$) is the same for all valence electrons so that we have a single Schrodinger equation to solve for each electron. If we solve for the eigenfunction and eigenvalue of this Hamiltonian we obtain one electron states and energies. since the Hartree term and V_{xc} depend on $n(r)$ which again depend on V_{eff} , the problem of solving Kohn Sham equation has to be done in a self consistent manner (iterative way). Usually we will start with an initial guess for $n(r)$, then calculates the corresponding V_{eff} and solves the Kohn-Sham equations for the ψ_i . From these one calculates a new density and starts again. This procedure is repeated until convergence is reached. Let us see the algorithm of DFT using flow chart below.

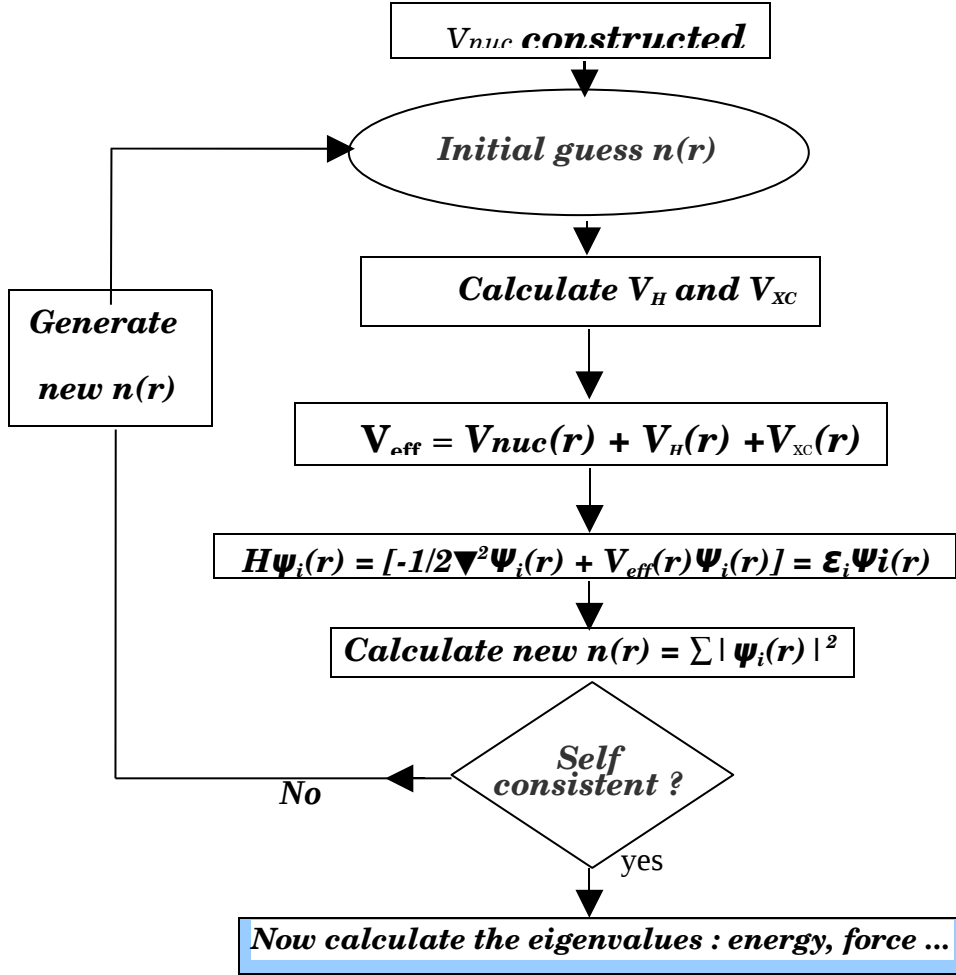


Fig. 4.1 Self consistent iteration using charge density for the calculations of different eigenvalues.

4.2 Technical Details

The total energy and band structure calculations were performed using Quantum espresso package. We study for the non spin polarized system and also extended to spin-polarized systems. We used a plane wave cut off of 30 Ry, which corresponds to around 1750 plane waves in a cubic unit cell with lattice constant of around 7.001 a.u for PM and 7.002 a.u for FM. A charge density of 300 Ry and 4x4x4 Monkhorst-Pack grid was used for all calculations.

4.3 Input file cubic and orthorhombic structure of CaMnO_3

For instance out of many of our input files let us take a counter two input files below that will enable us to calculate the total energy, total force , stress and magnetic moment for cubic PM and G-type AF respectively. Those input files contains important information about the system.

```
&control
    calculation ='scf'                outdir='./'
    prefix = 'CaMnO3 -cubic'
    pseudo_dir='/home/student/Mscthesi1/Cubic/Paramagnetic'
/
&system
    ibrav =1,                        ecutrho = 300,
    celldm(1) = 7.001,                occupations = 'smearing'
    nat = 5,                          smearing ='cold'
    ntyp = 3,                        degauss= 0.025
    ecutwfc = 30,
/
&electrons
    diagonalization='david',          mixing_beta = 0.5
    startingwfc = 'atomic+random'     conv_thr =1.0E-11
/
ATOMIC_SPECIES
    Ca  40.0      Ca.pbe-nsp-van.UPF
    Mn  54.94     Mn.pbe-sp-van_mit.UPF
    O   15.9994   O.pbe-rrkjus.UPF
ATOMIC_POSITIONS (crystal)
    Ca    0.0  0.0  0.0,              O    0.5  0.0  0.5
    Mn    0.5  0.5  0.5,              O    0.0  0.5  0.5
```

```

O      0.5  0.5  0.0,
K_POINTS automatic
4 4 4  0 0 0

```

The following input file for G type AF will be given for the software is found below.

```

&control
    calculation = 'scf',                prefix = 'CaMnO3-ortho'
    outdir='./'
    pseudo_dir = '/home/student/Mscthesis1/Orthorombic/AF'
/

&system
    ibrav = 8,                          nspin = 2
    celldm(1) = 9.979,                  starting_magnetization(2) = 0.7
    celldm(2) = 1.410,                  starting_magnetization(3) = -0.7
    celldm(3) = 0.997,                  starting_magnetization(4) = 0.7
    nat = 20,                           starting_magnetization(5) = -0.7
    ntyp = 6,                           occupations = 'smearing'
    ecutwfc = 30,                       smearing = 'cold'
    ecutrho = 300,                      degauss = 0.5
/

&electrons
    diagonalization='david',            startingwfc = 'atomic+random'
    mixing_beta = 0.5                   conv_thr = 1.0d-11
/

ATOMIC_SPECIES
Ca  40.00  Ca.pbe-nsp-van.UPF
Mn1 54.94  Mn.pbe-sp-van_mit.UPF
Mn2 54.94  Mn.pbe-sp-van_mit.UPF
Mn3 54.94  Mn.pbe-sp-van_mit.UPF

```

Mn4 54.94 Mn.pbe-sp-van_mit.UPF

O 15.999 O.pbe-rrkjus.UPF

ATOMIC_POSITIONS (crystal)

Ca	0.00	0.00	0.25	O	0.50	0.00	0.25
Ca	0.00	0.00	0.75	O	0.50	0.00	0.75
Ca	0.50	0.50	0.25	O	0.00	0.50	0.25
Ca	0.50	0.50	0.75	O	0.00	0.50	0.25
Mn1	0.50	0.00	0.00	O	0.00	0.50	0.75
Mn2	0.50	0.00	0.50	O	0.25	0.25	0.00
Mn3	0.00	0.50	0.00	O	0.25	0.25	0.50
Mn4	0.00	0.50	0.50	O	0.75	0.25	0.00
O	0.75	0.25	0.50	O	0.25	0.75	0.00
O	0.25	0.75	0.50	O	0.75	0.75	0.00
O	0.75	0.75	0.50				

K_POINTS automatic

4 4 4 0 0 0

For all input files the structure of the code is similar except in some cases.
Structure of the input file is as follows.

Those words that start with & are called Name list

&control	&system	&electrons
...	...	...
/	/	/
ATOMIC_SPECIES	K_POINTS automatic	
...	...	
ATOMIC_POSITIONS	...	

In side the name lists mentioned above, the purpose of each syntax is presented below for PM cubic structure.

In &control name list.

Calculation = 'scf': a string describing the task to be performed is self

consistent field.

Outdir = './' : input, temporary, output files are found in the current directory
that we work.

Prefix = 'CaMnO3-ortho': put input/output files inside CaMnO3-ortho folder

pseudo_dir = '/home/student/Mscthesis1/Cubic/Paramagnetic': directory
containing pseudopotential files

In & system name list

ibrav = 1 : Bravais-lattice index for cubic structure.

celldm (1) = 7.001 : the equilibrium lattice parameter for the PM configuration.

nat = 5 : the number of atoms in unit cubic cell is 5.

ntype =3 : the number of types of atoms in unit cell.

Ecutwfc = 30 : kinetic energy cutoff (Ry) for wavefunctions

ecutrho = 300 : kinetic energy cutoff (Ry) for charge density and potential

smearing= 'cold' : gaussian smearing for metals

degauss = 0.025 : value of the gaussian spreading (Ry) for BZ integration in
metals.

Nspin = 2 : spin polarized calculation, (magnetization along z axis)

starting_magnetization(2)= 0.7 : breaks the symmetry and provides a starting
point for self-consistency

In &electron name list

conv_thr = 1.0E-11 : Convergence threshold for selfconsistency

mixing_beta = 0.5: mixing factor for self-consistency

diagonalization = 'david' : Davidson iterative diagonalization with overlap
matrix

ATOMIC_SPECIES: refers the description of items of an element

ATOMIC_POSITIONS: refers the atomic position of an element in unit cell.

In the next chapter we will see the computational result in detail based on the input
files.

CHAPTER 5

Results and Discussion

5.1 Calculated parameters for Paramagnetic configuration

5.1.1 Equilibrium lattice parameter

The equilibrium parameter is the one that has the minimum energy from the curvature of the total energy vs lattice parameter graph. For PM, the calculated total energy versus for different lattice parameter in the range between 4.0 a.u and 12.5 a.u is found in Fig 5.1. We used here 30 kinetic energy cut off , 4 x 4x 4 k points mesh and 300 charge density for calculation.

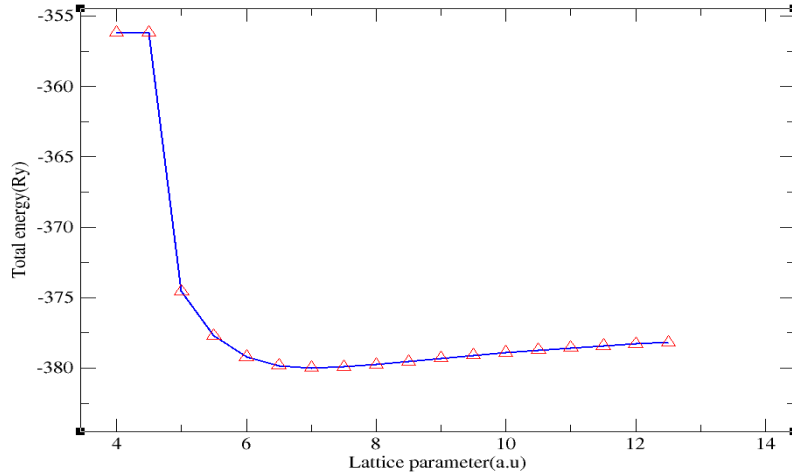


Fig 5.1 The lattice parameter vs total energy for cubic PM structure

From the curvature of the Fig 5.1 the minimum total energy is -379.983 Ry at 7.001 a.u lattice parameter. So the equilibrium lattice parameter for this magnetic configuration is found at 7.001 a.u and so this is the minimum distance between atoms in PM of CaMnO_3 .

5.1.2 Convergence of K points mesh

By using the equilibrium lattice parameter 7.001 a.u and kinetic energy cutoff

30 Ry, the total energy is calculated for different k points mesh in the BZ starting from 3 x 3 x 3 up to 14 x 14 x 14 k point mesh and the simulated graph is shown Fig 5.2. Convergence of total energy of the system is seen starting from 10 x 10 x 10 k points mesh.

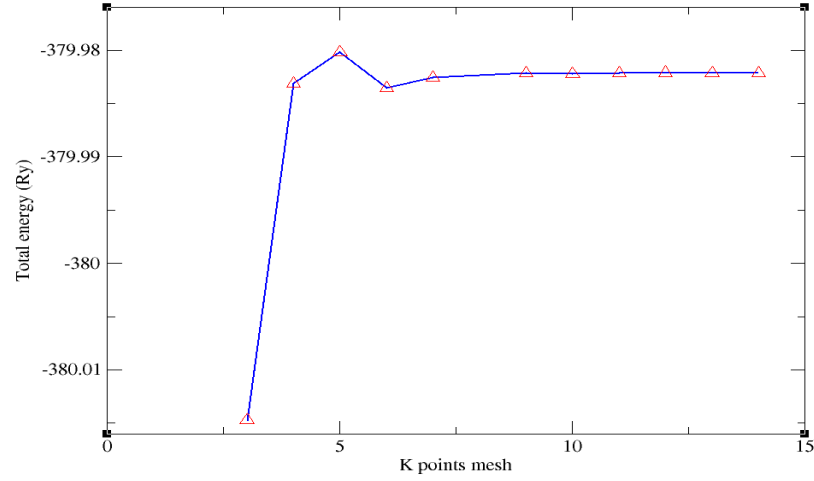


Fig 5.2 The k points mesh vs total energy for cubic PM structure

5.1.3 Convergence of charge density

By using the equilibrium lattice parameter 7.001 a.u, 30 Ry kinetic energy cutoff and 4 x 4 x 4 k points mesh, the total energy is calculated with respect to various charge density cutoff in the BZ.

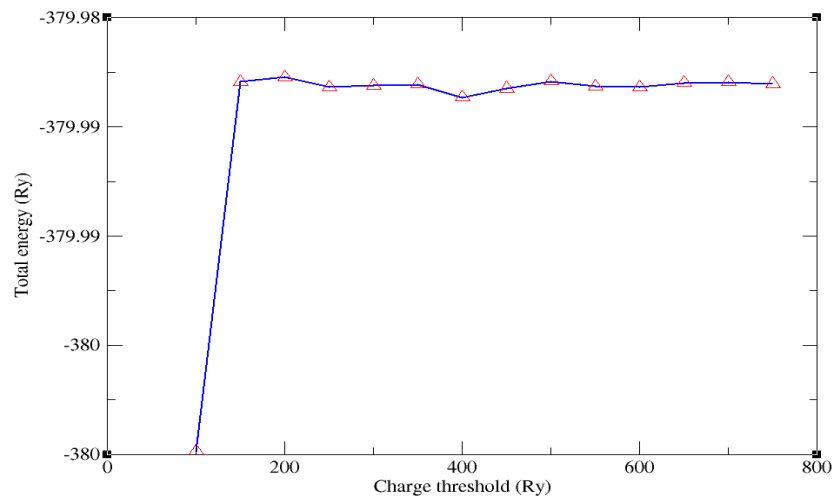


Fig 5.3 Total energy vs charge density cutoff for cubic PM structure.

It is seen from Fig 5.3 that the convergence of total energy of CaMnO_3 is achieved starting from the 500 Ry charge density.

5.2 Calculated parameters for Ferromagnetic configuration

5.2.1 Equilibrium lattice parameter

The equilibrium parameter is the one that has the minimum energy from the curvature of the parabola. The calculated total energy versus for different lattice parameter in the range between 5.0 a.u and 13 a.u is found in Fig 5.4. we used here 30 kinetic energy cutoff, $4 \times 4 \times 4$ k-points mesh and 300 charge density for FM.

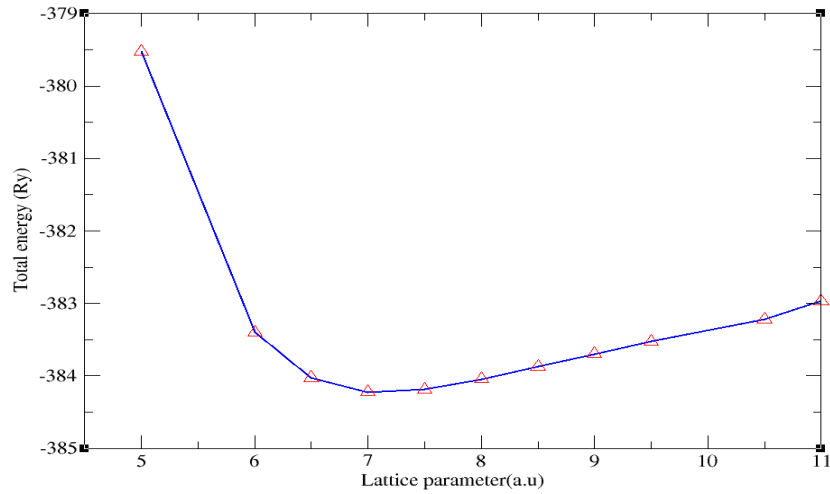


Fig 5.4 Total energy vs lattice parameter for cubic FM structure.

The curvature has a minimum total energy at -384.223 Ry. So the equilibrium lattice parameter is found at 7.002 a.u for the case of FM configuration.

5.2.2 Convergence of K points mesh

By using the equilibrium lattice parameter 7.002 a.u and kinetic energy cutoff 30 Ry, the total energy is calculated for different k-points mesh in the BZ starting from $3 \times 3 \times 3$ up to $14 \times 14 \times 14$ and the simulated result is shown Figure 5.5.

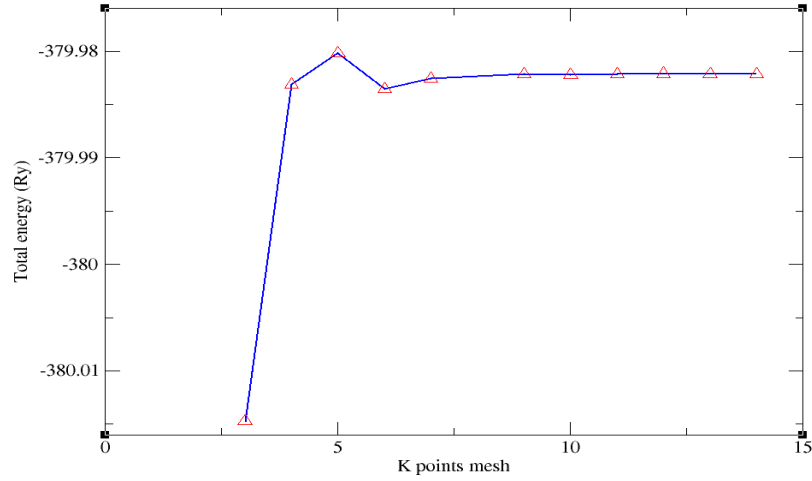


Fig 5.5 The total energy vs k point mesh for cubic FM structure.

It is clearly seen from the graph that the total energy is converged at $9 \times 9 \times 9$ k-point mesh. As we increase the k point mesh from 3.0 to 4.0 the total energy increases linearly but from 4.0 to 9.0 k points it decrease slowly. However staring from $9 \times 9 \times 9$ k points mesh the total energy of the system converged at -381.98 Ry.

5.3 Simulation of Band structure and density of state for cubic structures

5.3.1 Paramagnetic configuration

The density of state and band structure for PM structure is shown from Figures 5.6 and 5.7 respectively. We present results for CaMnO_3 in the highest possible symmetry state with cubic structure, without spin polarization (PM phase). Although this phase is experimentally inaccessible, it provides a useful reference for understanding the FM structures to be discussed later on.

Figure 5.6 and 5.7 show that the density of states and band structure for cubic PM CaMnO_3 respectively. The plotted energy range is from -8 eV to 8 eV, and the lower lying semi-core states have been omitted for clarity. The Fermi level is set to zero in both cases. The broad series of bands between -2 eV and -8 eV in the material

arises from the oxygen 2p orbitals. Along with 2p bands, t_{2g} bands of Mn hybridize below the Fermi level. The Mn 3d bands are divided into two sub bands the lower energy t_{2g} bands, and the higher energy e_g bands as a result of crystal field splitting by the octahedral oxygen anions. e_g band of Mn is found in the conduction band.

The Fermi level lies near the top of Mn 3d t_{2g} band and is in a region of high density of states. The large DOS at the Fermi level suggests that the cubic PM structure is unstable, and that a lower energy structure could be achieved by allowing spin polarization and/or structural distortion. In Figure 5.7 the corresponding band structures along with high symmetry axes of the simple cubic BZ is shown. The broad O 2p bands between -2 eV and -8 eV can be seen clearly that it overlaps with the Mn 3d bands. The bands a and b stands for the upper and lower Mn 3d bands which have a similar form each other.

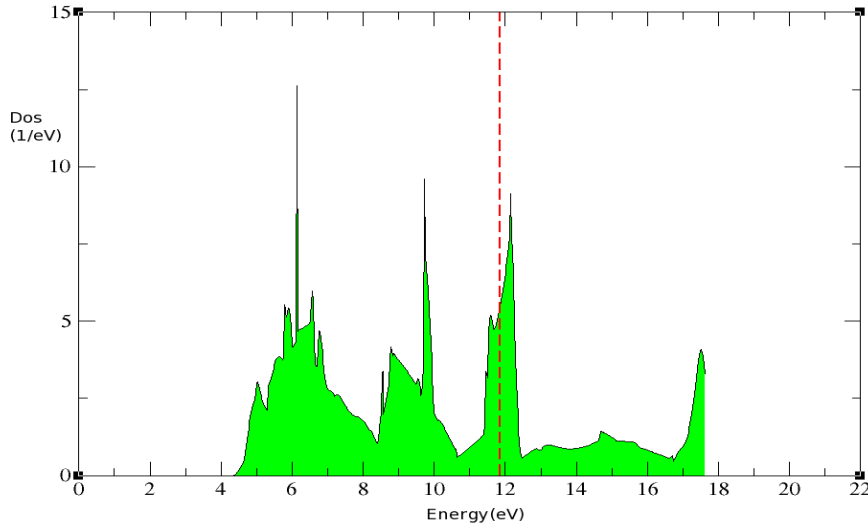


Fig 5.6 The density of state for ideal cubic PM structure in the case of un displaced atoms

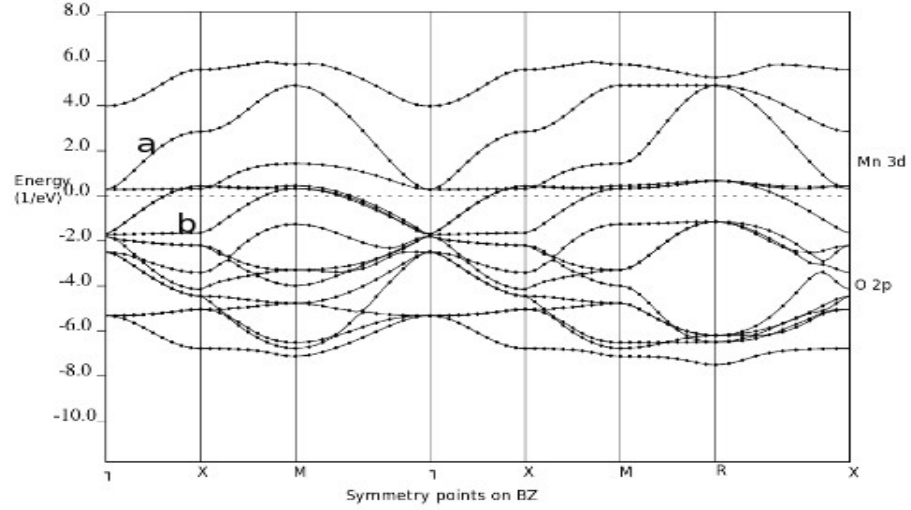


Fig 5.7 The band structure for ideal cubic PM structure in the case of undistorted atoms for total energy vs symmetry points on the BZ.

Many dots stand on the bands represent points on the BZ. In this case we used 71 k points on the BZ. The total energy ranges from -8 to 8 eV. And the number 0 tells us the Fermi energy. At Fermi level 3d orbitals of Mn are fully filled at the Fermi level. 3p, 4s and 3d orbitals of Calcium and 2s orbitals of Oxygen occupy the smallest energy and are found below -8 eV. Whereas 3d orbitals of manganese occupy the highest energy since they are dominant at Fermi level. We can see that there is no gap between the conduction band and valence band. Hence PM CaMnO_3 shows a metallic property.

We can observe that the orbitals (electrons) of the CaMnO_3 are found in the range between -8 eV and 8 eV. The highest density of state for this configuration is 6.7 1/eV whereas the least density of state is 0.5 eV. Mixing of orbitals or hybridization is also observed from -8 eV to 1 eV. The density of state in the conduction band is very less than the density of state for valence band. The Mn orbitals fully occupied the Fermi level, and the Fermi level lies at the center of the Mn orbitals. Hence there is no band gap between the conduction and valence band. Therefore the material has a characteristic of metal since there is no band gap.

Let us see some of the partial density of state for element 3d Mn and 2p O from the Figure 5.8

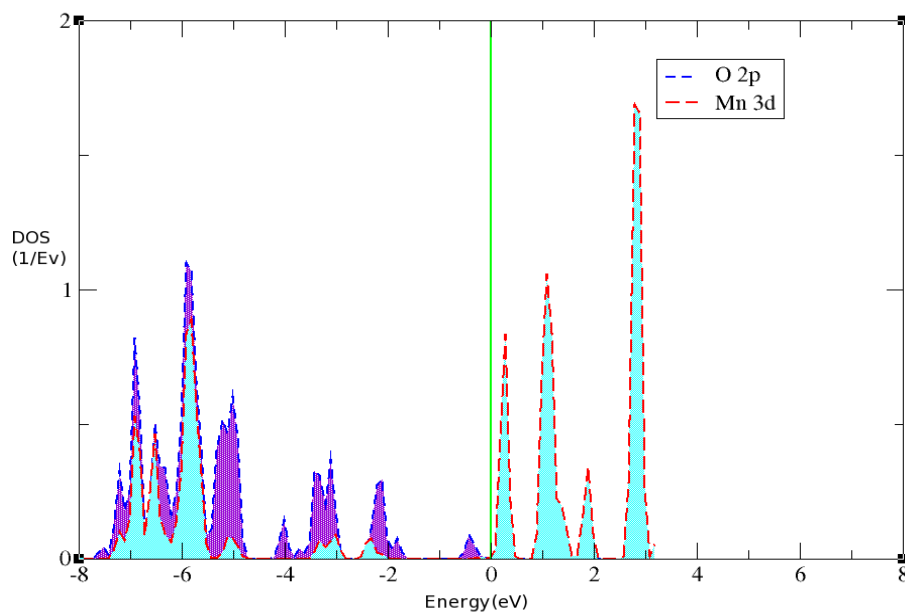


Fig 5.8 The partial density of state for 3d, 2p orbitals of Mn and O cubic PM structure.

From the partial density of state 3d orbitals of Mn atoms occupy dominantly at the Fermi level but its 3p and 4s orbital posses the smallest energy and found in the valence band below -8 eV. 2p orbital of oxygen shows a large dispersion and found dominantly on the valence band it is also found near the fermi level. Therefore a strong hybridization is clearly seen between 3d orbitals of Mn and 2p orbitals of O in the valence band. It is also seen that the O 2p is closer to the fermi energy as compared to t_{2g} up band of Mn from the valence band side.

Normally both band structure and density of state explain the properties of materials in the same way, hence one of them is the copy of the other. The similarity between the band structure with that of its density of states is shown in Figure 5.9

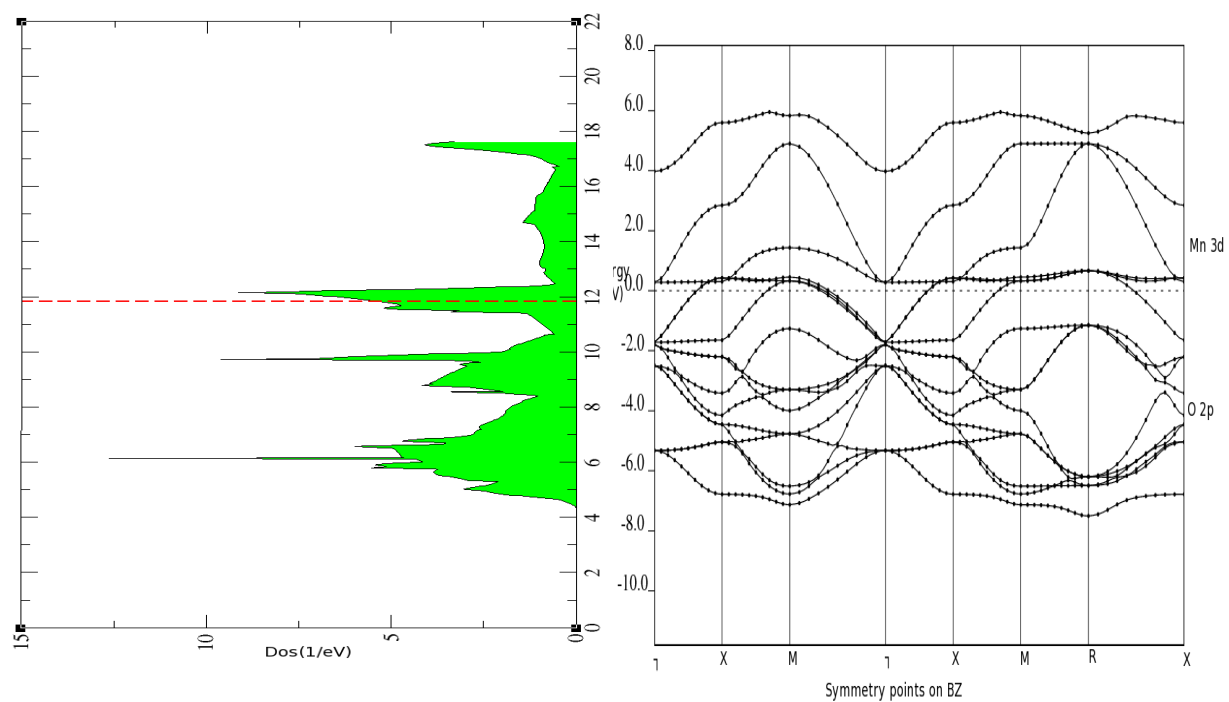


Fig 5.9 The correspondence between band structure and density of state
for cubic PM CaMnO_3

5.3.2 Ferromagnetic configuration

5.3.3.1 Undistorted atom and structure

We will discuss the band structure and density of state for undistorted atoms in the case of ideal cubic FM structure. In the case of FM the calculation is performed for both spin up and spin down electrons of the system. The majority of electrons is spin up and the minority of the electrons is spin down. And the following band structures and density of states in Figures 5.10 ,5.11, 5.12 and 5.13 represents well for both spin down and spin up of electrons.

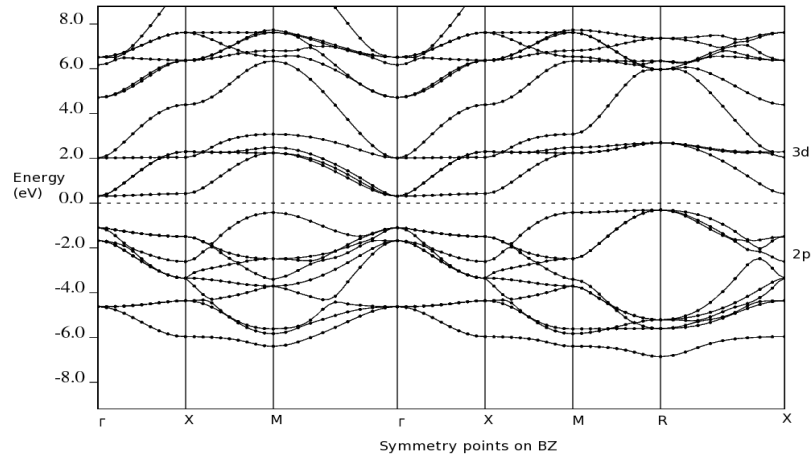


Fig 5.10 The band structure for spin down for FM cubic structure of CaMnO_3

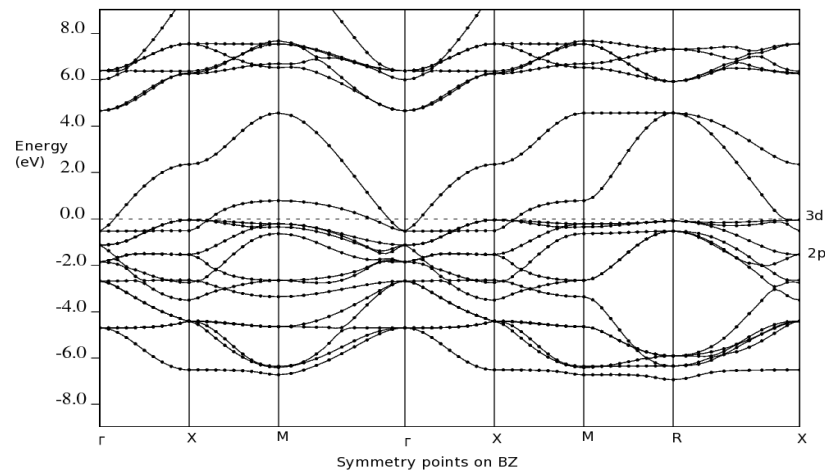


Fig 5.11 The band structure for spin up for FM cubic structure of CaMnO_3

For FM configuration the electrons are allowed to spin polarize. We find that

introduction of spin polarization reduces the energy by around 1 eV per unit cell compared with the PM. Some of the observed bands in PM calculations persist into the FM phase. From Fig 5.10 (In the case of the spin down) the Fermi energy E_f falls very near the middle of a 1.3 eV gap in the minority channel between O 2p band and Mn 3d bands. The O 2p bands are nearly 6 eV wide, with the dispersion arising from the combination of nearest neighbour O 2p - O 2p hopping and O 2p -Mn 3d hopping. From Figure 5.15 due to O 2p-Mn 3d hopping, Mn bands are 4.6 eV wide and this dispersion is seen only in the conduction band. For the majority charge carrier, the 3d bands of Mn overlaps with the O 2p bands and hybridize strongly and they form a highly conducting majority spin network.

There is a similarity between the FM and PM energy bands. First we examine the up and down-spin CaMnO_3 band structures and compare with the PM CaMnO_3 band structure. For example, the dispersion of the lowest O 2p band is identical for up and down spin, and also for PM phase. The up-spin Mn 3d and O 2p bands are strongly hybridized and there is no gap between them this is the case that is observed in PM. However, the down-spin Mn 3d are split off from the O 2p bands by a larger gap.

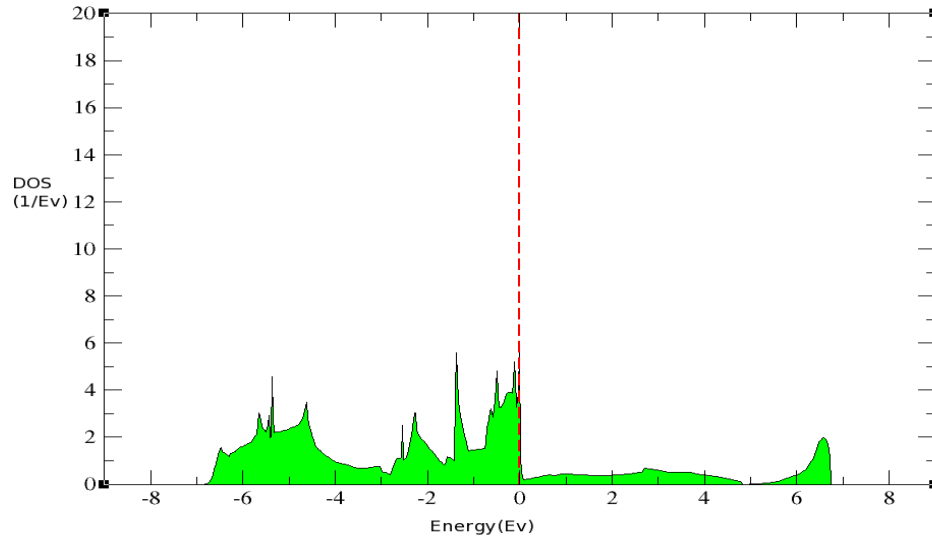


Fig 5.12 The density of state for spin up for FM cubic structure of CaMnO_3

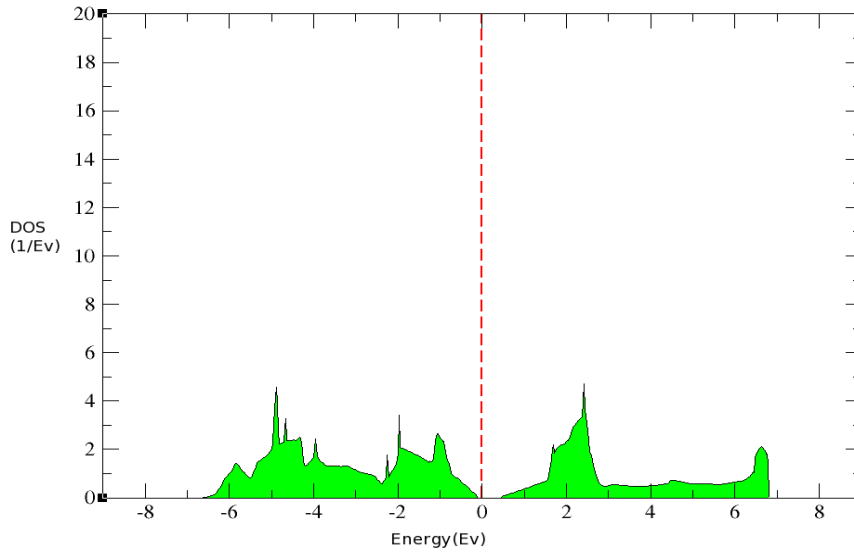


Fig 5.13 The density of state for spin down for FM cubic structure of CaMnO_3 .

From Figure 5.12 many electrons are found dominantly below the Fermi level that is in the valence band. Due the wideness of the graph in valence band, there is a strong hybridization between d and p orbitals. At the Fermi level the dominant orbital is the Mn 3d band. In the range between 0 eV and 4.5 eV the number of orbital is very less as compared to the previous interval. The highest density of state is 5.34 1/eV. Energy gap does not exit in the spin up case so there is a possibility of an electron that can jump from the valence band to the conduction band. Therefore on these majority electrons it shows that it has metallic properties.

From Figure 5.13 the splitting of 3d orbitals of Mn is observed at the Fermi level and as a result of this, energy gap is observed. Hybridization of orbitals occurred at the valence band rather than the conduction band. The highest density of state is 5.0 1/eV. The hybridization between Mn and O states decreases the electronic density of the Mn 3d band and so obtained considering a half occupied t_{2g} band. This is the cause of for the formation of band gap. Mn and O states located at the same energy values, this reflects that hybridization between 2p O states and 3d

Mn states occurred and in addition the presence of 2p states is also seen in the conduction band.

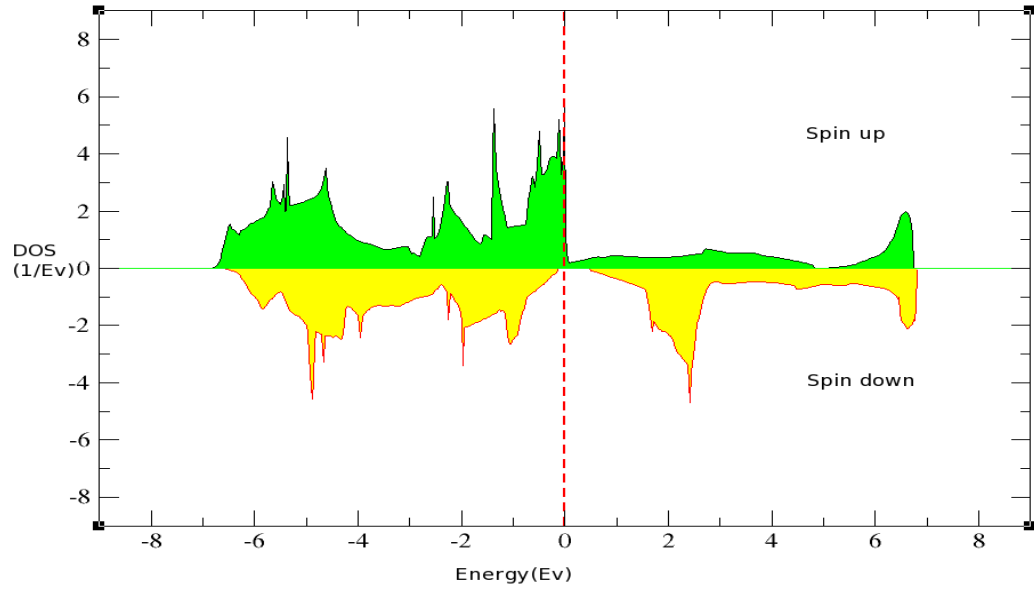


Fig 5.14 The density of state for both spin up and spin down
for FM cubic structure CaMnO_3

Fig 5.14 shows that the majority spins are represented by green colour on the positive y-axis, and the minority spins by yellow colour on the negative y-axis. In the down-spin Mn 3d band is split off from the O 2p band and a gap is there. The up spin Mn 3d hybridizes strongly with the O 2p and there is no band gap for the majority carriers. The up spin DOS at the Fermi level high, indicating that the cubic FM state has a high energy. This is consistent with the fact that the lowest energy spin polarization in structurally relaxed CaMnO_3 is AF. For this compound the Fermi level cuts through the very bottom of the down spin Mn 3d bands, and the conduction band is occupied almost entirely by up spin electrons.

The density of states in both spin up and down is quite different on a certain energy intervals. For instance in both cases the density of orbitals at Fermi level and the highest density of states is quite different. On the other hand the similarity between them is that a strong hybridization is observed in the valence band that is between 0 eV and -8 eV energy interval.

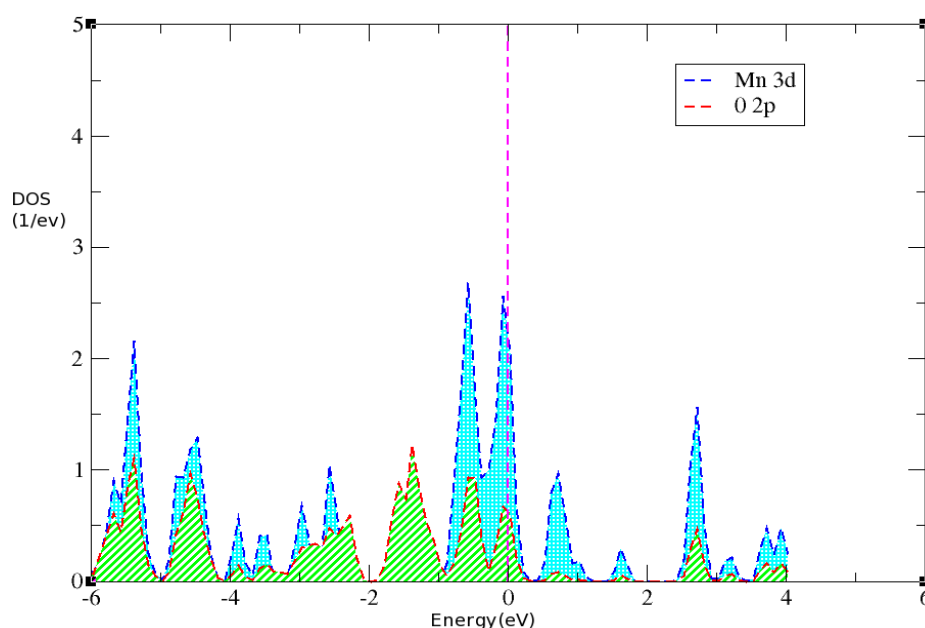


Fig 5.15 The partial density of state for 3d, 2P orbitals of Mn and O respectively for total FM cubic structure of CaMnO_3 .

4.3.3.2 Relaxed atoms and cell

The purpose of relaxing both the atoms and the cell is that the system will try to acquire a stable structure. By keeping this basic idea we relaxed the systems and got the final positions of an atom and its structure. From the Table 5.1 below the position of each atom is quite different plus the cubic structure changed in to a tetragonal structure.

After cell relaxation the cell parameters are as follows.

Element	Undistorted atomic position			For a relaxed atomic position		
	X	Y	Z	X	Y	Z
Ca	0.00	0.000	0.000	0.00389734	0.00390349	0.10341402
Mn	0.50	0.500	0.500	0.05044413	0.50444413	0.64005134
O ₁	0.50	0.500	0.000	0.49176079	-0.0084240	0.69600107
O ₂	0.50	0.000	0.500	-0.0084135	0.49174936	0.69599777
O ₃	0.00	0.500	0.500	0.49232571	0.49231408	0.16036704

Table 5.1 The atomic position for undistorted and relaxed cubic FM cubic structure

cell parameters from the output file of the relaxed structure is as follows

```
1.007981288  0.000789704 -0.003701832
0.000789691  1.007985978 -0.003705782
-0.003331300 -0.003335932  1.040038134
```

And therefore $a_1 = 1.007$ a.u , $a_2 = 1.007$ a.u and $a_3 = 1.040$ a.u and the system structure changed from the ideal cubic to tetragonal structure.

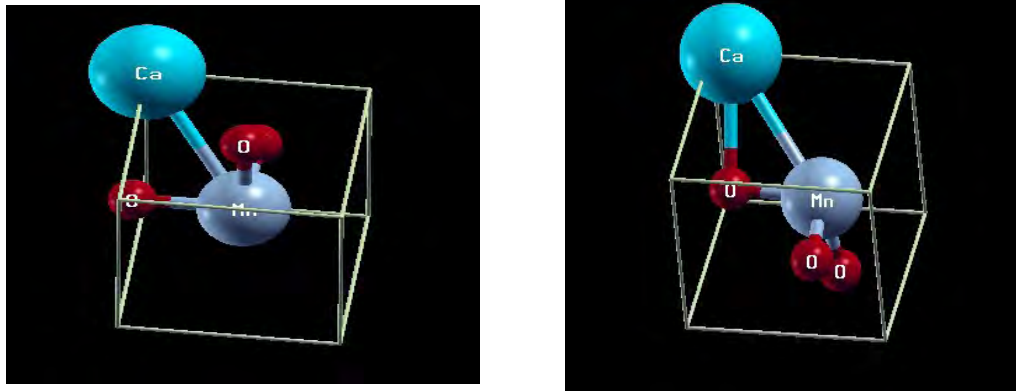


Fig 5.16 Un distorted and relaxed FM cubic structure from left to right

The band structure for this relaxed structures is as follows from the Figures 5.17 and 5.18 for spin down and up respectively.

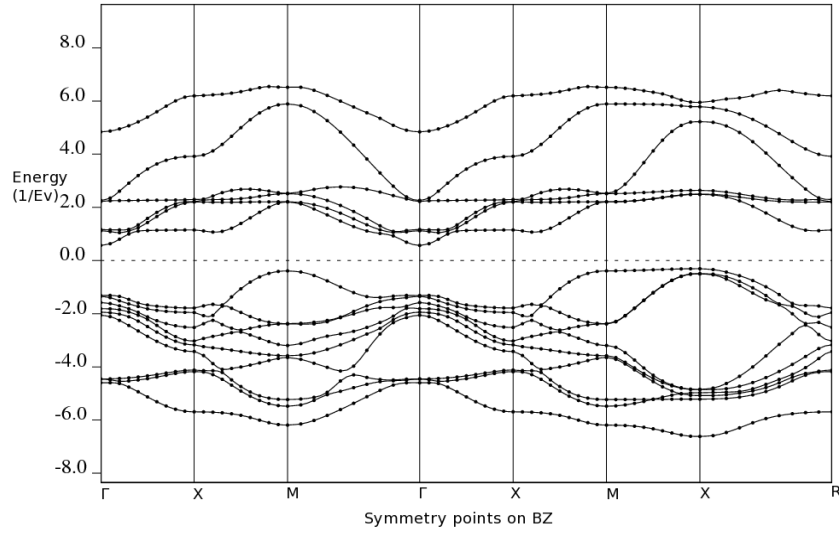


Fig 5.17 The band structure for a spin down relaxed FM cubic structure and the zero of energy set to Fermi level.

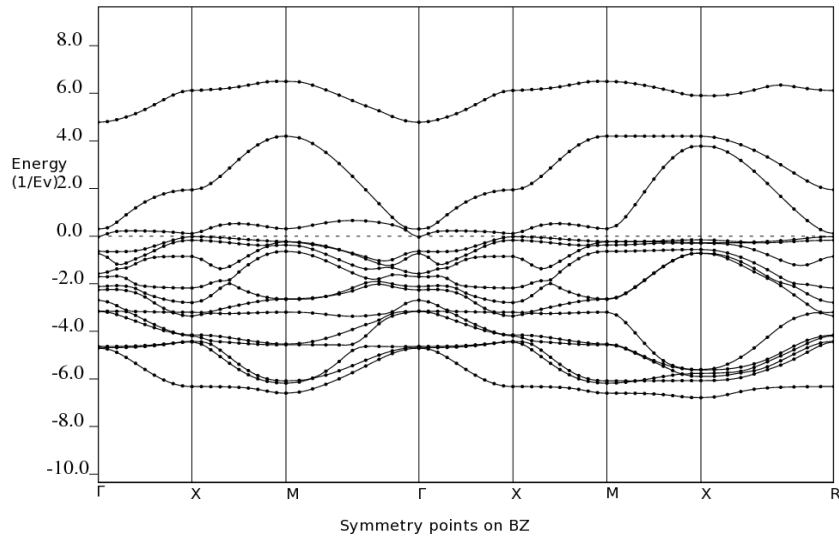


Fig 5.18 The band structure for a spin up relaxed FM cubic structure and the zero of energy set to Fermi level

For both spin down and up the effect of relaxation of the system is observed due to splitting of 3d band of Mn from 2p band of O. for spin up cases splitting effect is so small, however in spin down the effect is so high that the band gap is 1.34 eV and so it shows an insulating characteristics. Let us compare the effect of relaxation from the Figures 5.19 and 5.20.

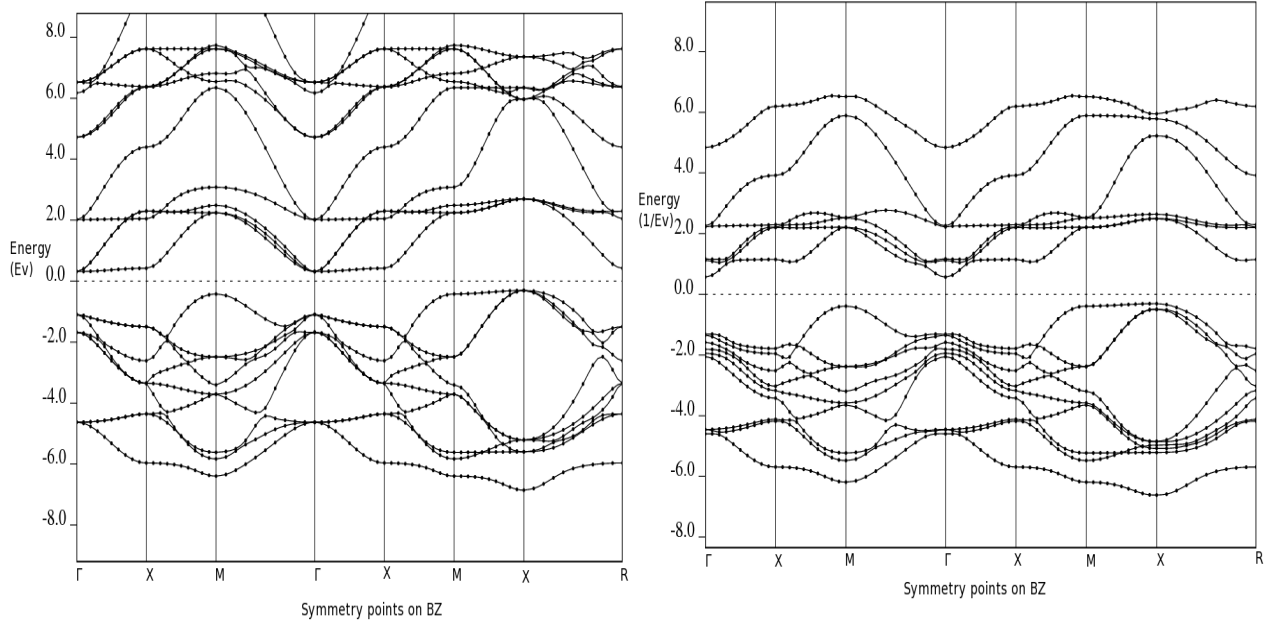


Fig 5.19 The band structure the un distorted system from the left and relaxed one from the right side in the case of spin down.

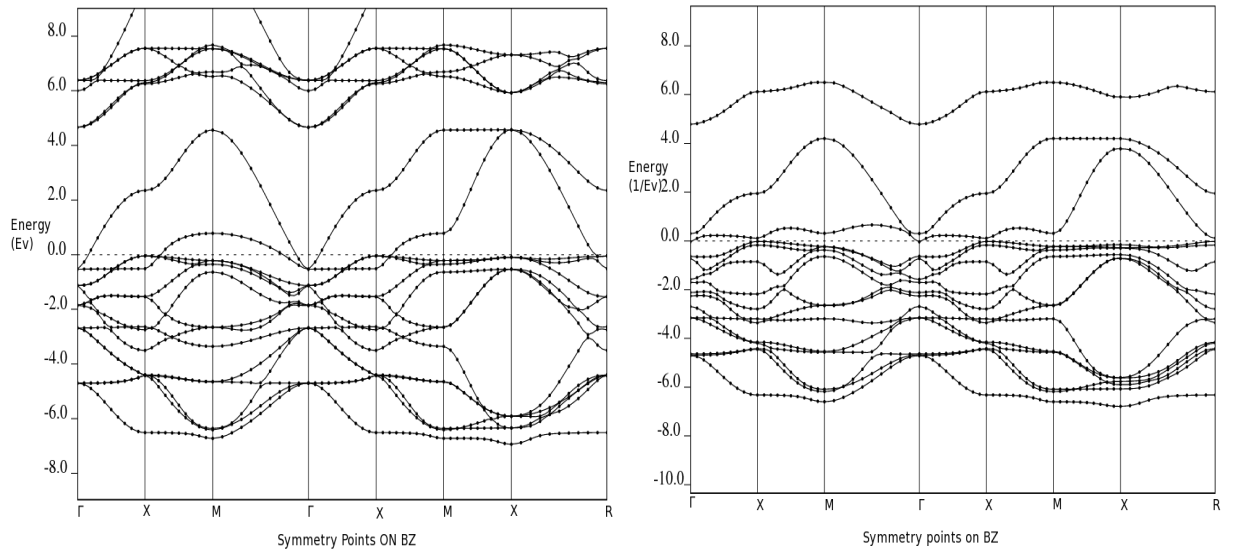


Fig 5.20 The band structure for un distorted system from the left and relaxed one from the right side in the case of spin up .

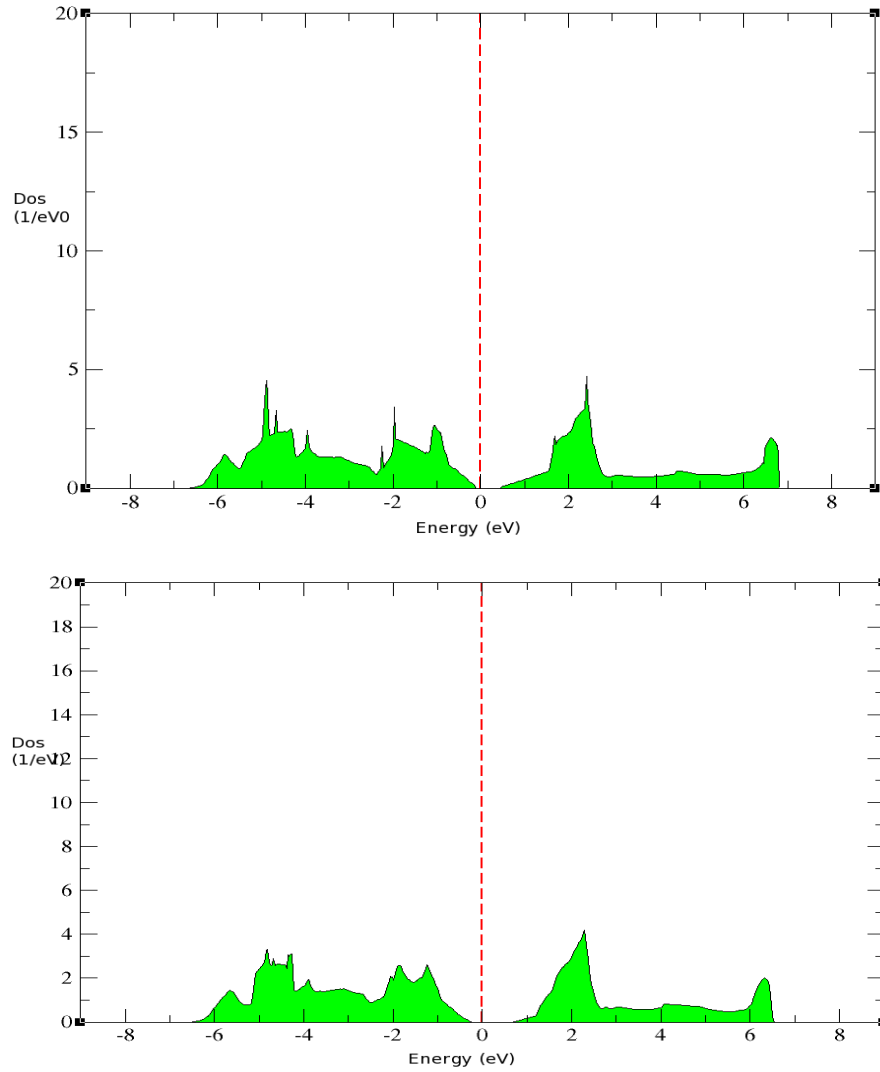


Fig 5.21 The top and the bottom density of states are the spin down for the undistorted and relaxed CaMnO_3 respectively.

From Figure 5.21 we observe that the gap in the case of relaxed one is open as compared to the undistorted one. And this shows that relaxing the system has an effect on the system and will enable us to get the correct stable structure. The similarity between the two is that the density of state is high and also a strong hybridization is found at the valence band. Whereas in the conduction band mixing of orbital is very less. On the other hand the splitting of 3d band of Mn is presented at the fermi level.

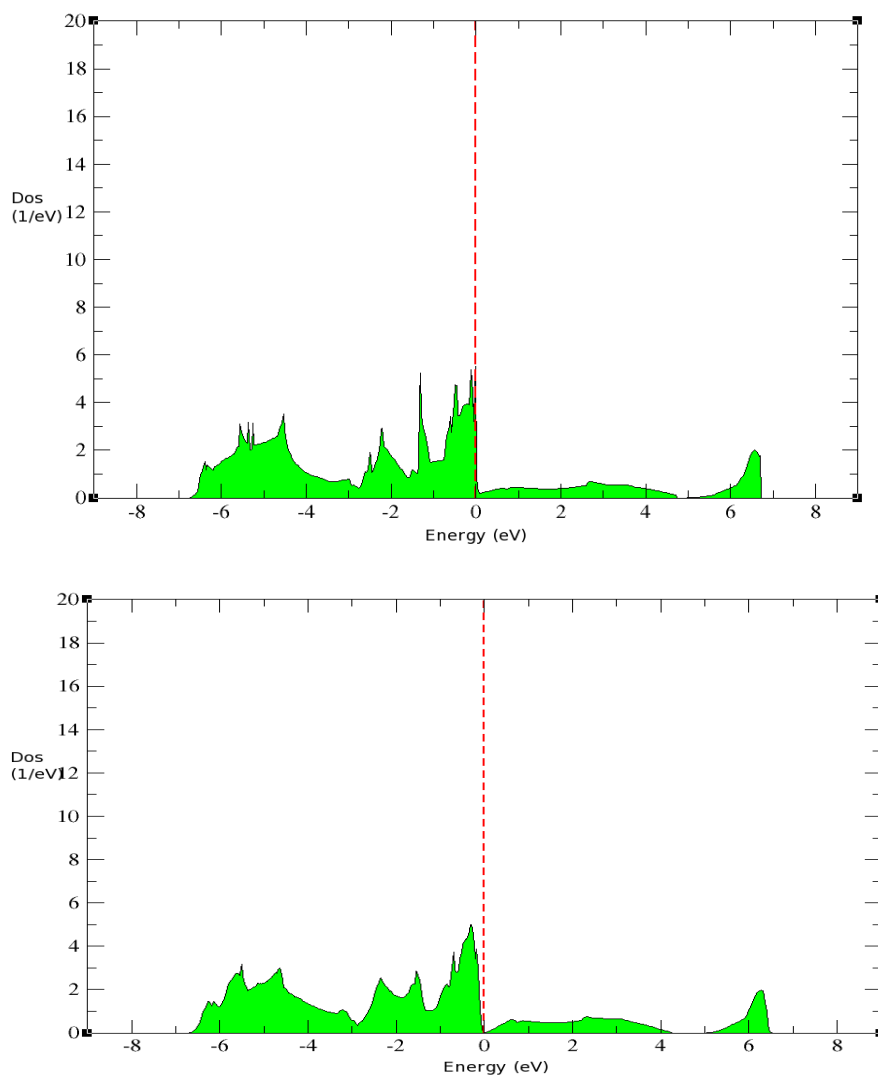


Fig 5.22 The top and the bottom density of states are the spin up for the undistorted and relaxed CaMnO_3 respectively.

Unlike the above spin down density of states in Fig 5.21, the spin up density of state showed us that Mn orbitals dominated the Fermi level and hence there is no band gap as shown from the Fig 5.22. The undistorted spin up density of state has a strong hybridization between d and p orbitals, however the d orbitals separated itself from the p orbitals little bit.

5.3.5 The effect of using GGA+U for cubic CaMnO_3

let us see the effect of Hubbard U correction on the exchange correlation functional on GGA approximation. The value of U for CaMnO_3 is 10 eV. We can clearly see that there is change in both band structure and density of states in most of the magnetic configurations.

5.3.5.1 GGA+U for undistorted paramagnetic structure

Let us see the effect of Hubbard U correction on the paramagnetic configuration.

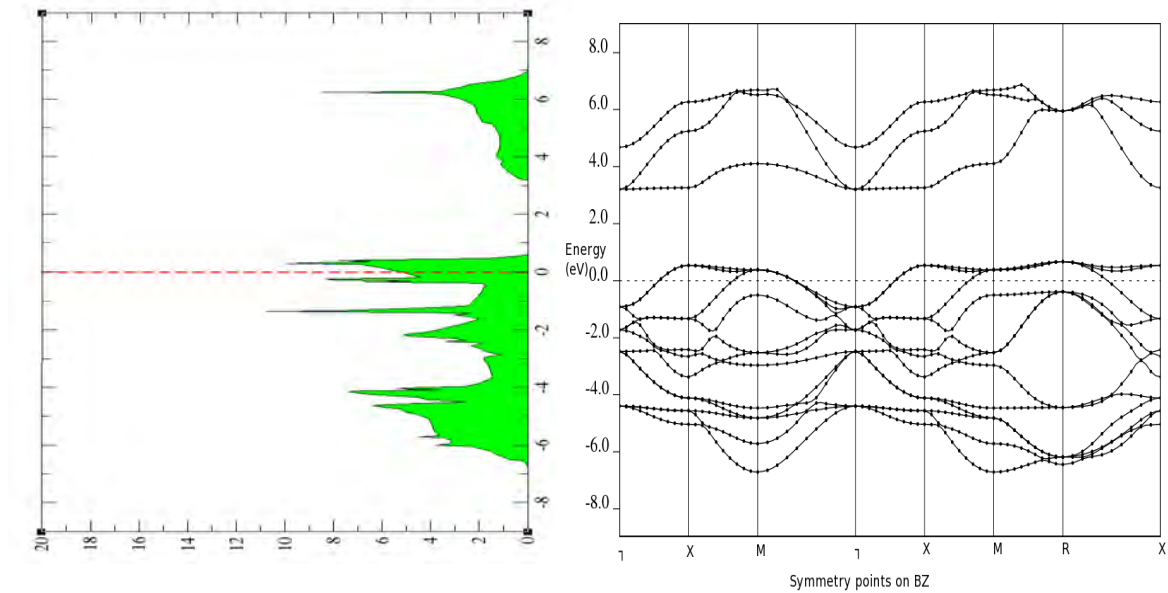


Fig 5.23 The band structure and density of states for PM CaMnO_3 using GGA+U. From the Figure 5.23 by using Hubbard correction a great gap created in the energy interval between 0.5 Ry to 3.2 Ry. The valency band consists of many orbitals plus a strong hybridization exists between 2p orbital of O and Mn orbital of t_{2g} band. On the other hand less number orbitals present at the conduction band. The theoretical calculation tells us that using U correction, it showed us an insulating gap though 2p orbital and t_{2g} orbitals are found near the fermi level in the valence band.

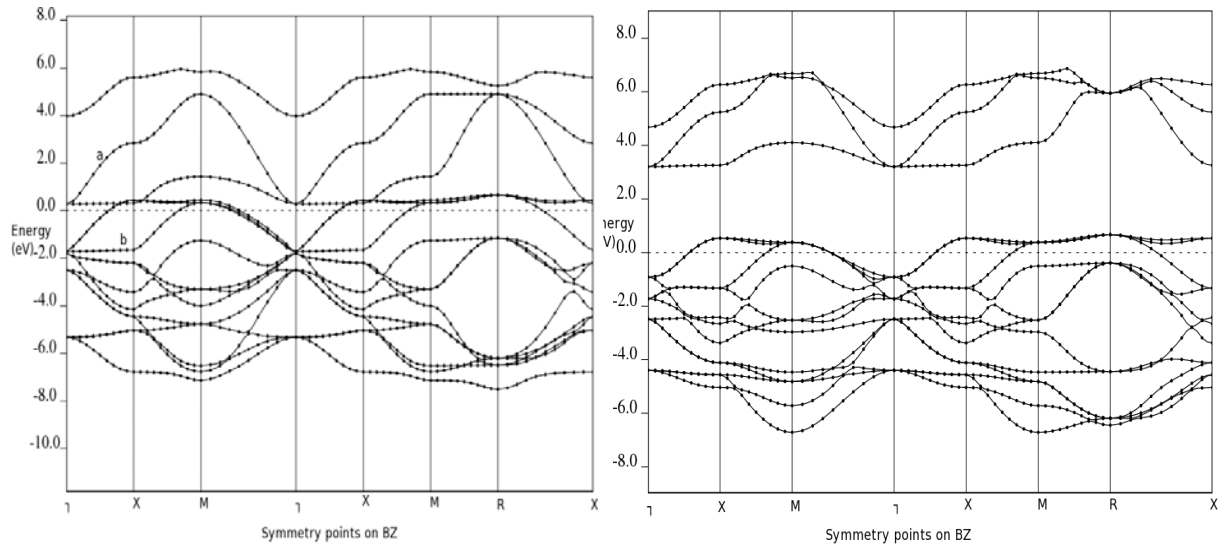


Fig 5.24 Band structure for undistorted PM cubic with GGA and with GGA+U from left to right.

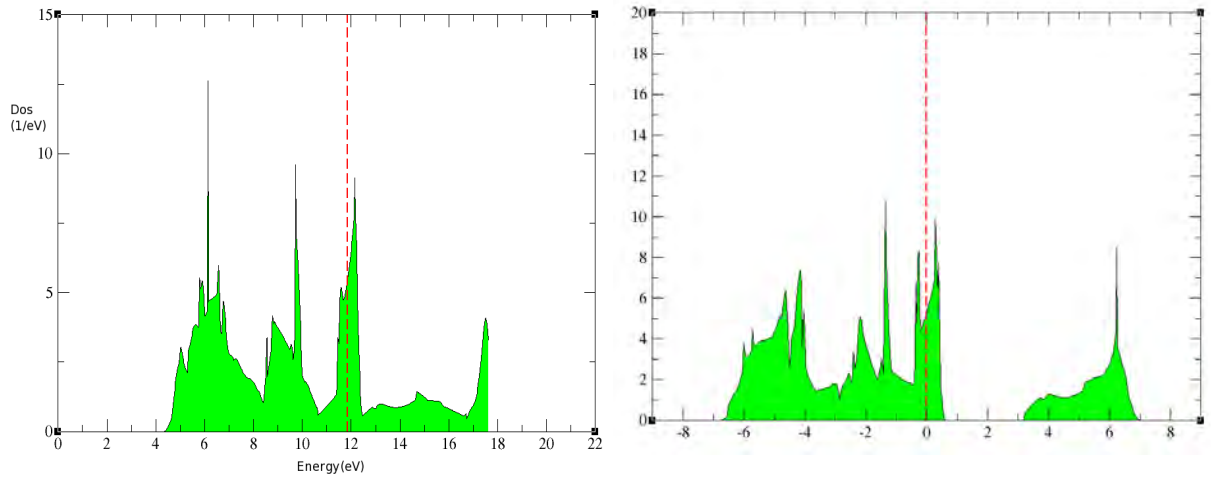


Fig 5.25 The density of state for undistorted PM cubic with GGA and GGA+U from left to right.

4.3.5.2 GGA+U for undistorted ferromagnetic structure

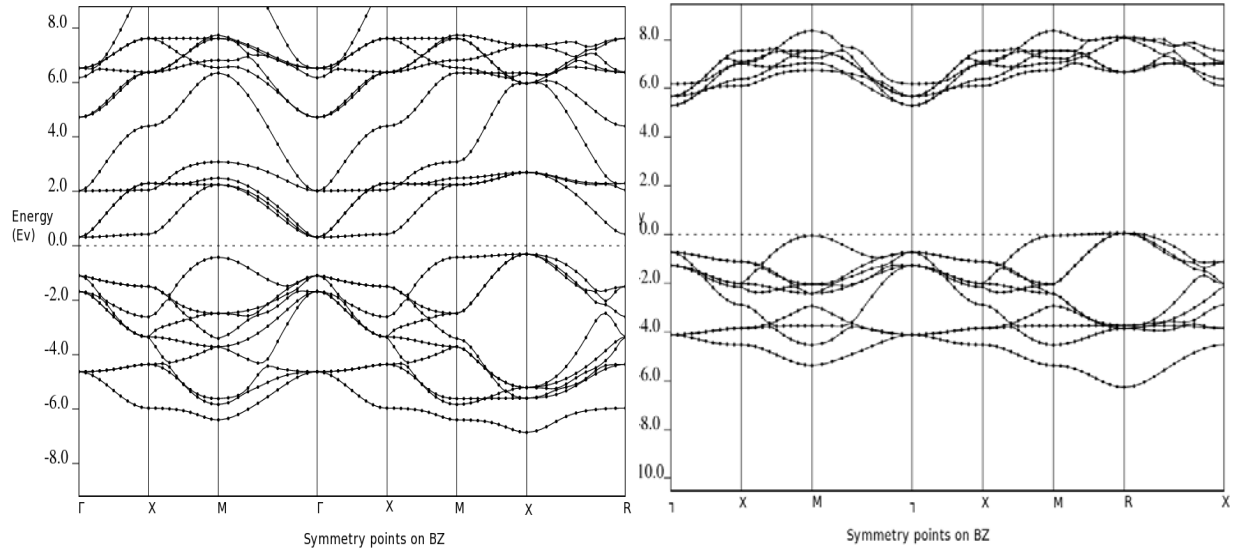


Fig 5.26 The band structure for undistorted FM cube with GGA and GGA+U from left to for spin down.

The effect of U is clearly observed for the spin down FM in Fig 5.26 is that there is a large gap which is equal to 1.2 eV. On the conduction band electrons occupy orbitals between 5.0 eV and 8.0 eV which is very small dispersion for 3d Mn compared to left one with out U. Besides this is some what seen for the case of valence band for 2p orbitals of O.

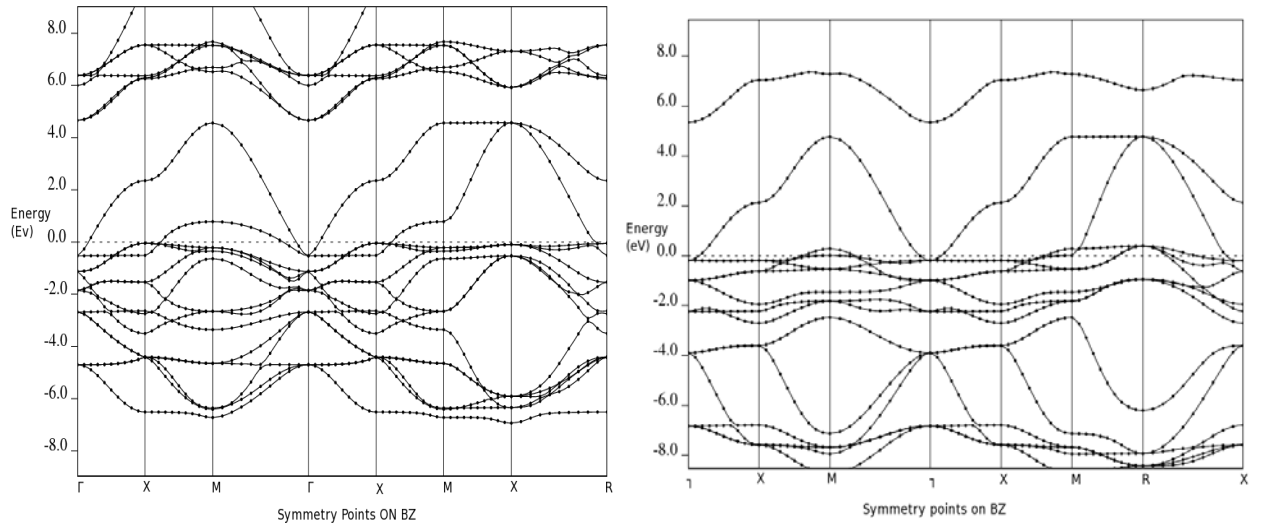


Fig 5.27 The band structure for undistorted cube FM with GGA and GGA+U from left to right for spin up.

We observe that one of the bands displaced from the end side of the Fermi level and goes to the conduction band in a small amount. The other band next to it goes from the conduction band to the valence band therefore a small amount of splitting of 3d band of Mn from the 2p bands of O the top and bottom is observed at the Fermi level by applying U terms. On the other hand the widening of bands between them or splitting of some orbitals in the region of valence band is also clearly observed as compared to non U.

Cubic structure of CaMnO_3						
	PM		FM			
Parameter	Undistorted	Undistorted +U	Undistorted	Distorted	Undistorted +U	Distorted +U
Fermi energy	11.809	10.967	11.201	10.350	10.528	9.812
Total energy	-384.16	-383.34	-384.220	-384.22	-383.752	-383.77
Equilibrium lattice Parameter(a.u)	7.00	7.00	7.002	7.002	7.002	7.002
Magnetic moment(μ_B / Mn)	—	—	2.97	2.97	3.14	3.03
Absolute magnetization(μ_B / Mn)	—	—	3.14	3.17	4.76	5.03

Table 5.2 The calculated parameters for PM and FM configuration with GGA and GGA+U

4.4 Simulation of Band structure and density of state for orthorhombic structures

The band structure and density of state in the orthorhombic structure is quite different as compared to the cubic one. The basic difference lies on the Fermi level in which the orbitals are found.

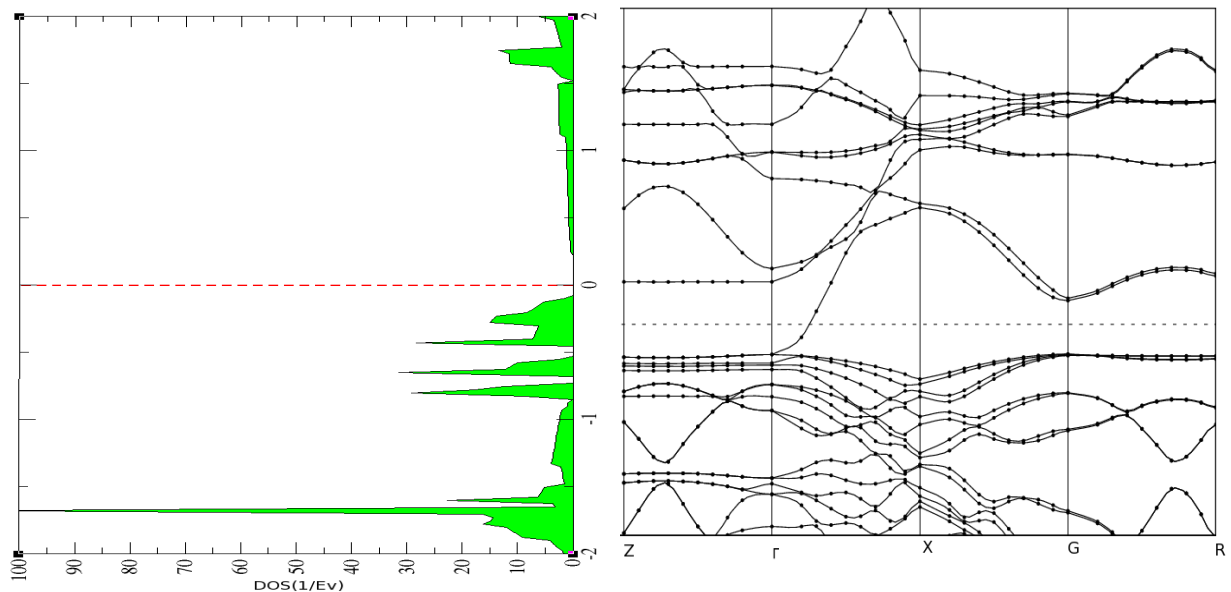


Fig 5.28 The band structure and density of states for G -AF of orthorhombic structure

from the Figure 5.28 both the total density of states and band structure are drawn for partially relaxed system. It is clearly seen that many orbitals are found in the valence band as compared to the conduction band. The separation of 3d orbital of Mn atoms is occurred at the fermi level and as a result of this a small gap of 0.51 eV of energy seen at the fermi level.

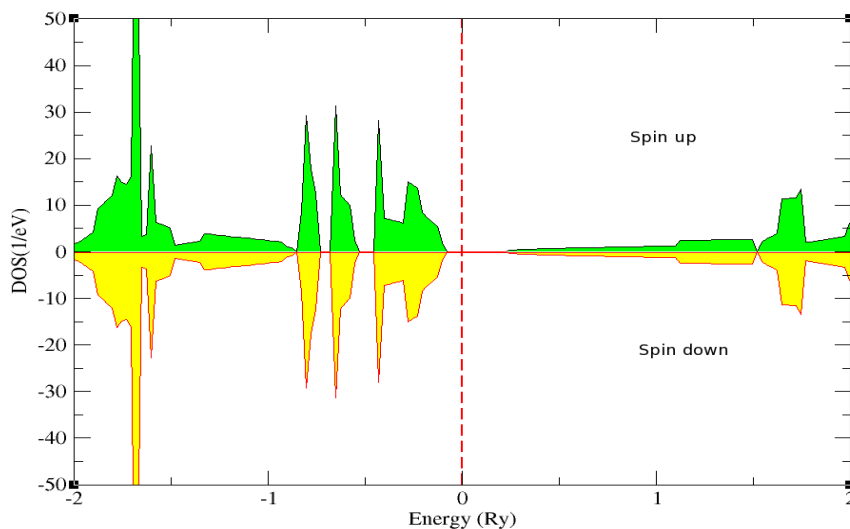


Fig 5.29 The band structure and density of states for G-AF orthorhombic structure

from Figure 5.29 it is clearly seen that in both spin up and down, the energy level in which the orbitals are found are exactly the same and the number of orbitals are also proportional. The density of state in both cases is dominant at the valence band.

	Orthorhombic structure		
Parameter	PM	FM	G-AFM
Fermi energy(ev)	11.362	10.470	10.478
Total energy(ev)	-1536.65	-1536.91	-1536.94
Total magnetization(μ_B / Mn)	—	11.88	0.0
Absolute magnetization(μ_B / Mn)	—	3.195	2.982
Relative energy(eV)	0.0	-0.262	-0.287

Table 5.3 The calculated fermi energy, total energy, total magnetization, absolute magnetization and relative energy for orthorhombic structure.

5.5 Phonon dispersion relation for cubic structure

CaMnO_3 have five atoms per unit cell, which results in 15 phonon branches, 3 acoustical and 12 optical branches. At the Γ point all phonons are three fold degenerate, so there is one acoustical phonon frequency (which is zero), and four optical frequencies.

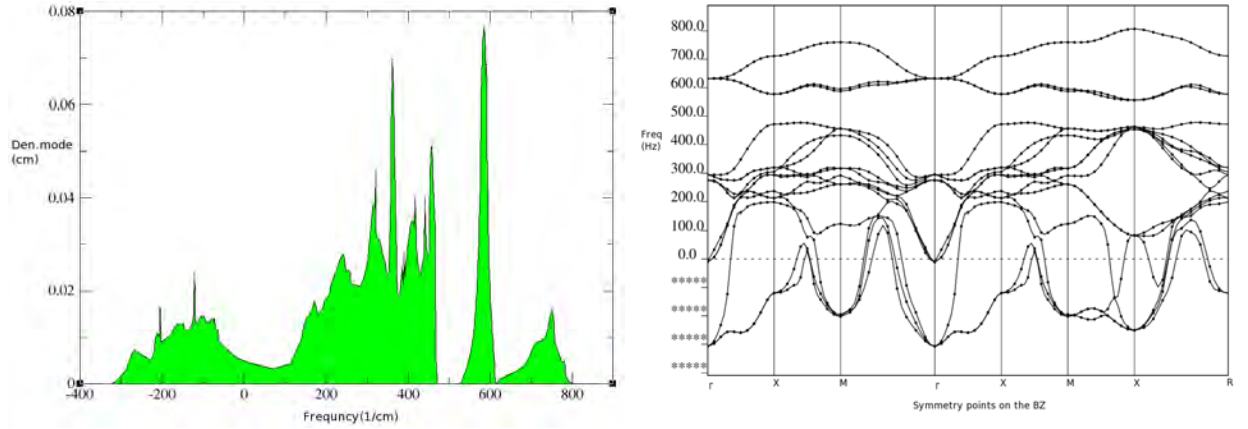


Fig 5.30 The phonon dispersion relation for undistorted PM cubic structure From Figure 5.30 at all symmetry points (wave vector) the frequency of phonon is negative. This indicates that the system at this ideal atomic position is unstable. The frequency at Γ is -330 cm^{-1} .

In order to get a stable structure all the phonon frequency must be disappear. To get at least a positive frequency at Γ we have to distort both the atoms and the cell. And let us see the phonon dispersion relation for a distorted cubic from the Figure 5.31.

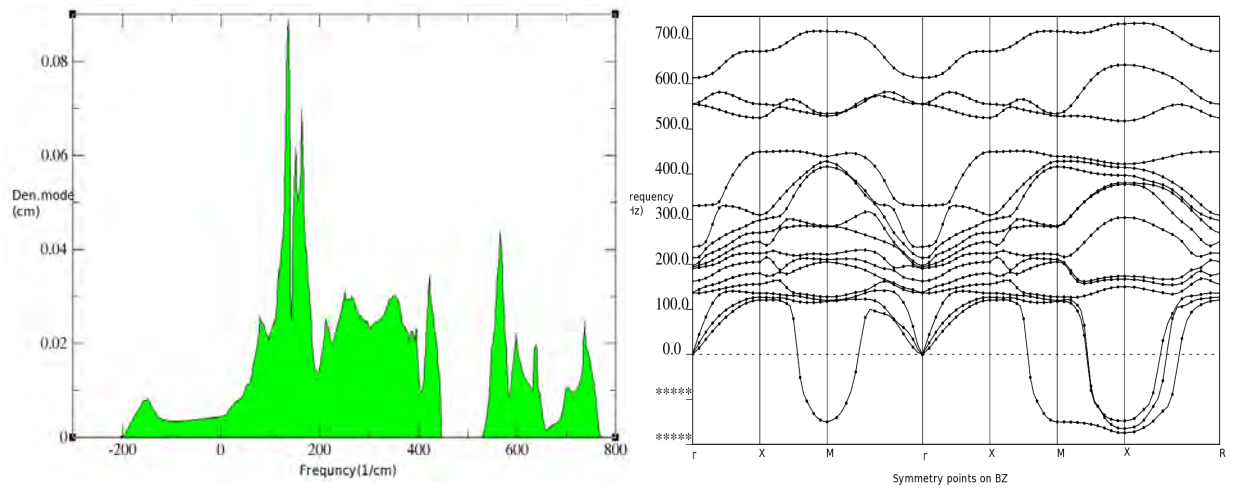


Fig 5.31 The phonon dispersion relation for distorted FM cubic structure from Figure 5.31 it is clearly seen that at Γ point the negative frequency of phonon disappear which is what we want for our 5 atoms per cell. But to remove the remaining negative frequency, we have to use super cell that contains 40 atoms. Due to computational cost we did for only for 5 atoms per cell.

5.6 Comparison of present work vs previous theoretical and experimental work

Let us see methodology (input parameters) and simulated graph for previous theoretical calculated results of CaMnO_3 . For the theoretical result-1 [22], the electronic structures and total energies were calculated with the general potential LAPW method using LSDA. The set of basis functions was supplemented with local orbitals for additional flexibility in representing the Mn 3d states, and semi core states (Ca 3s, 3p; O 2s). Self-consistency was carried out on special k-point meshes; they used 84 points in the irreducible BZ for the FM case and G-type AFM cells. The basis set was energy cutoff is 20 Ry.

For the theoretical result-2 [23], the calculations is based on DFT, within the LDA were performed using ASW method. The Ca and Mn 4s, 4p and 3d, and O 2p, 2d and 3d states were treated as valence states, and the low-lying O 2s states as core states. The calculations were performed with a grid of $6 \times 6 \times 6$ reciprocal lattice points. Convergence with respect to the number of k points was confirmed with a $10 \times 10 \times 10$ grid.

	Cubic structure					
	Theoretical-result-1		Theoretical-result-2		Present-result(Non-distorted)	
Parameter	PM	FM	PM	FM	PM	FM
Equilibrium lattice parameter (a.u)	7.353	7.353	—	—	7.001	7.002
Relative total energy (meV)	0.0	+860	—	+640	0.0	+612
Magnetic moment(μ_B / Mn)	—	2.64	—	2.67	—	2.97

Table 5.4 The previous theoretical and experimental results vs with present calculated results for different parameters for cubic structure.

	Orthorhombic structure							
Parameter	Theoretical-result-2			Present-result			Experimental-result [24]	
	PM	FM	G-AF	PM	FM	G-AF	FM	G-AF
Relative total energy(eV)	—	-0.31	-0.44	0.0	-0.262	-0.289	—	—
Magnetic moment(μ_B / Mn)	—	2.61	2.44	—	3.195	2.982	—	2.7

Table 5.5 The previous theoretical and experimental results vs with present calculated results for different parameters for orthorhombic.

Let us see the similarities between the band structures of spin down electrons of the present work with that of theoretical-result 1

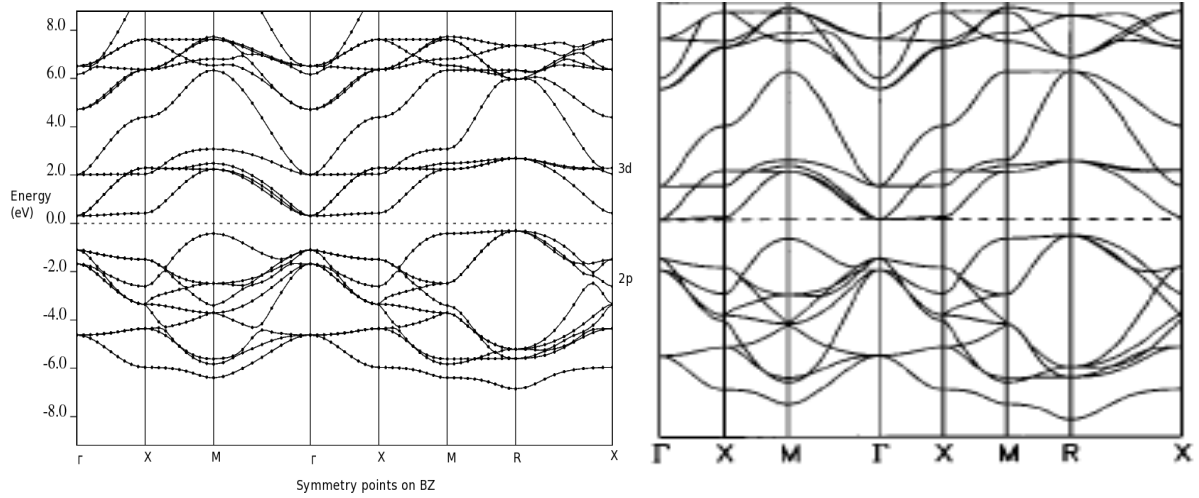


Fig 5.32 The FM cubic band structure for spin down for present work and previous theoretical result-1 work from left to right respectively.

From the Figure 5.32 in both cases it is observed that splitting of 3d band of Mn is occurred at the fermi level and t_{2g} band hybridize with that of 2p orbitals of O, any of

the band does not cross the fermi level and so band gap is created and an insulating property is observed.

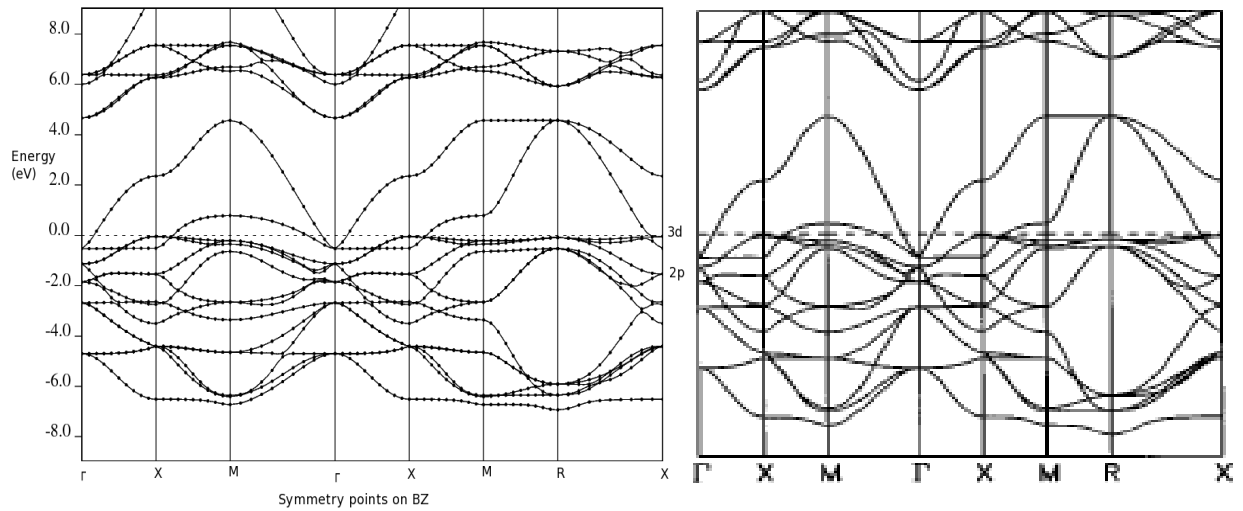


Fig 5.33 The FM cubic band structure for spin up for present work and previous theoretical result-1 work from left to right respectively.

From Figure 5.33 in both graphs we see the following similarities. two bands crosses the fermi level starting from the valence band, the 3d orbitals of Mn atoms found dominantly on the fermi level and as a result there is no band gap so it showed us a metallic property, On the conduction band the density of states is small as compared to the valence band and a strong hybridization is seen on the valence band. In general since the majority carrier (spin up) are dominant, they determine the properties of a materials so FM cubic structure of CaMnO_3 show a metallic property in both results though the material has a characteristics of insulator.

CHAPTER 6

Conclusion and Future outlook

6.1 Conclusion

Our main focus was to study the structural, magnetic and electronic properties of a strongly correlated perovskite called CaMnO_3 . The material shows a crucial properties like thermoelectric, colossal magneto resistance by doping with La etc. Due to its vital application it was studied before by different theoretician and experimentalists. Previously its properties was investigated by using DFT, LDA and LSDA based on the software called CASP package.

For this thesis the structural, magnetic and electronic properties of CaMnO_3 was determined by the implementation of DFT using GGA and GGA+U correction based on a new version of Quantum espresso package. The results, for PM cubic structure shows that the Mn orbitals fully occupied the Fermi level and this level lies at the center of the Mn orbitals that is near the top of Mn 3d t_{2g} . This shows that the fermi level is in a region of high density of states. Hence there is no band gap between the conduction and valence band. The large DOS at the Fermi level suggests that the cubic PM structure is unstable and a metallic property is observed for this magnetic configuration.

For FM cubic configuration the electrons are allowed to spin polarize and so the properties of the system is quite different for both spin down and spin up. We found that introduction of spin polarization reduces the energy by around 1 eV per unit cell compared with the PM. For the case of spin down, the down-spin Mn 3d split off from the O 2p bands and as a result of this a gap is occurred at the fermi level; However for the case of spin up, hybridization of 3d and 2p orbitals of Mn and O exists at the fermi level and so no gap is formed. Due to the fact that the spin up electrons are the majority charge carrier, they determine the nature of the

materials. Hence for this FM configuration the system shows metallic characteristic though it is accessible in experimental.

we relaxed both cubic and orthorhombic structure of the system so that the effect of structural distortion enables us to determine the ground state structure as well as the properties of a material. From our result, CaMnO_3 has G-AF insulating ground state structure. Its energy is minimum as compared to cubic structure of either FM or AM. The calculated magnetic moment of Mn for this structure is $2.9 \mu_B$ which is close to the experimental value for CaMnO_3 and the error is around 8.62 %. The calculated band gap is around 0.5 eV. This value is larger than the previous theoretical result-2 by 0.1 eV. And which is far from the experimental result [25]. So GGA calculation underestimates the band gap for this strongly correlated materials. The effect of Hubbard U is also observed for this system though it is not significant for a certain magnetic configuration. For the case of PM cubic it created a large gap because of high splitting of 3d Mn from 2p O. but for the case of FM and G-AF the level of splitting is so small that the gap is somewhat insignificant.

For this material the phonon dispersion relation was not done either on experimentally or theoretically before. And the phonon dispersion relation is done well for 5 atoms for cubic FM structure. It tells us the meta stable structure and atomic position of the atoms.

6.2 Future outlook

CaMnO_3 exhibits many interesting properties like colossal magneto resistance by doping of La element on it. The future outlook for this compounds is that it exhibits an excellent thermoelectric performance at high temperature in air and are, therefore, good candidates for thermoelectric performance oxide devices [26]. Thermoelectric materials, which have applications in refrigeration and power generation. This is a material that will maximize electrical conductivity while

minimizing thermal conductivity, which is required for good thermoelectric performance. Predictions for this materials suggest that important further improvements are on the horizon, with promising applications in the computer and other high-tech industries. According to the present invention there is provided an electrical energy storage device which consists of cathode-active material that is made up of CaMnO_3 .

The motivation of this theoretical research is due to these interesting properties. The research focuses on structural, magnetic and electrical properties of the material. We got many tangible results however due to computational cost, certain calculations are not done like phonon dispersion relation for G -type AF in the case of orthorhombic, building a super cell that contains 40 atoms for relaxing the atoms to get phonon dispersion relation for cubic structure. And therefore one can study in detail those crucial properties by having super computers.

Appendix A

Sample output file for a simple self-consistent calculation

```
Program PWSCF v.4.0cvs starts ...
Today is 7Apr2009 at 12:27:23
Ultrasoft (Vanderbilt) Pseudopotentials and PAW
Current dimensions of program pwscf are:
Max number of different atomic species (ntypx) = 10
Max number of k-points (npk) = 40000
Max angular momentum in pseudopotentials (lmaxx) = 3
bravais-lattice index = 0
lattice parameter (a_0) = 7.001 a.u.
unit-cell volume = 386.7918 (a.u.)^3
number of atoms/cell = 5
number of atomic types = 3
number of electrons = 43.00
number of Kohn-Sham states= 26
kinetic-energy cutoff = 30.0000 Ry
charge density cutoff = 300.0000 Ry
convergence threshold = 1.0E-10
mixing beta = 0.3000
the Fermi energy is 10.6098 ev
! total energy = -382.84841843 Ry
Harris-Foulkes estimate = -382.84841843 Ry
estimated scf accuracy < 1.3E-12 Ry
The total energy is the sum of the following terms:
one-electron contribution = -172.01606513 Ry
hartree contribution = 109.69924966 Ry
xc contribution = -66.34666191 Ry
```

ewald contribution = -254.18695394 Ry
 smearing contrib. (-TS) = 0.00201289 Ry
 total magnetization = 2.99 Bohr mag/cell
 absolute magnetization = 3.24 Bohr mag/cell
 convergence has been achieved in 9 iterations

Forces acting on atoms (Ry/au):

atom 1 type 1 force = -0.00004610 0.00000406 0.00009249
 atom 2 type 2 force = -0.00002248 0.00000221 0.00007819
 atom 3 type 3 force = -0.00002569 0.00000103 -0.00009491
 atom 4 type 3 force = 0.00003496 -0.00000243 -0.00004885
 atom 5 type 3 force = 0.00005932 -0.00000488 -0.00002693
 Total force = 0.000187 Total SCF correction = 0.000001

entering subroutine stress ...

total stress (Ry/bohr**3)			(kbar)	P=	-0.02
-0.00000021	0.00000001	0.00000007	-0.03	0.00	0.01
0.00000001	0.00000033	-0.00000001	0.00	0.05	0.00
0.00000007	-0.00000001	-0.00000063	0.01	0.00	-0.09

bfgs converged in 6 scf cycles and 2 bfgs steps

End of BFGS Geometry Optimization

Final enthalpy = -382.8484184335 Ry

Appendix C

Sample out put phonon file at Γ point calculation

Diagonalizing the dynamical matrix

$$q = \begin{pmatrix} 0.000000000 & 0.000000000 & 0.000000000 \end{pmatrix}$$

$$\omega(1) = 1.047275 \text{ [THz]} = 34.933550 \text{ [cm}^{-1}\text{]}$$

$$\begin{pmatrix} 0.048275 & 0.000000 & 0.048441 & 0.000000 & 0.425053 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.037698 & 0.000000 & 0.038038 & 0.000000 & 0.430262 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.049741 & 0.000000 & 0.046804 & 0.000000 & 0.456038 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.046663 & 0.000000 & 0.049777 & 0.000000 & 0.455943 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.038516 & 0.000000 & 0.038553 & 0.000000 & 0.445551 & 0.000000 \end{pmatrix}$$

$$\omega(2) = 2.110692 \text{ [THz]} = 70.405576 \text{ [cm}^{-1}\text{]}$$

$$\begin{pmatrix} -0.425576 & 0.000000 & 0.415437 & 0.000000 & 0.000612 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} -0.343352 & 0.000000 & 0.334994 & 0.000000 & 0.000614 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} -0.270904 & 0.000000 & 0.295004 & 0.000000 & 0.016415 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} -0.302481 & 0.000000 & 0.264308 & 0.000000 & -0.014859 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} -0.219623 & 0.000000 & 0.213752 & 0.000000 & 0.000712 & 0.000000 \end{pmatrix}$$

$$\omega(3) = 2.154169 \text{ [THz]} = 71.855827 \text{ [cm}^{-1}\text{]}$$

$$\begin{pmatrix} 0.406568 & 0.000000 & 0.417030 & 0.000000 & -0.053914 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.333151 & 0.000000 & 0.341523 & 0.000000 & -0.062311 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.249363 & 0.000000 & 0.298461 & 0.000000 & -0.082293 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.291231 & 0.000000 & 0.255717 & 0.000000 & -0.082747 & 0.000000 \end{pmatrix}$$

$$\begin{pmatrix} 0.227363 & 0.000000 & 0.232524 & 0.000000 & -0.074315 & 0.000000 \end{pmatrix}$$

$$\omega(4) = 4.208566 \text{ [THz]} = 140.383575 \text{ [cm}^{-1}\text{]}$$

(-0.140011 0.000000 -0.139144 0.000000 -0.552903 0.000000)

(-0.025057 0.000000 -0.024697 0.000000 0.106393 0.000000)

(0.315930 0.000000 0.165985 0.000000 0.342559 0.000000)

(0.166797 0.000000 0.314797 0.000000 0.342264 0.000000)

(0.235622 0.000000 0.233777 0.000000 0.209368 0.000000)

$\omega(5) = 4.429802 \text{ [THz]} = 147.763280 \text{ [cm}^{-1}\text{]}$

(-0.236693 0.000000 0.236737 0.000000 0.001010 0.000000)

(-0.016746 0.000000 0.016512 0.000000 -0.000229 0.000000)

(0.300929 0.000000 -0.248657 0.000000 0.098667 0.000000)

(0.248522 0.000000 -0.301285 0.000000 -0.099935 0.000000)

(0.530528 0.000000 -0.530350 0.000000 -0.000394 0.000000)

$\omega(6) = 5.093246 \text{ [THz]} = 169.893539 \text{ [cm}^{-1}\text{]}$

(-0.295613 0.000000 -0.296217 0.000000 0.316308 0.000000)

(0.062945 0.000000 0.063233 0.000000 -0.100015 0.000000)

(0.193250 0.000000 0.216753 0.000000 -0.170935 0.000000)

(0.216305 0.000000 0.193602 0.000000 -0.170715 0.000000)

(0.481826 0.000000 0.482705 0.000000 -0.121387 0.000000)

$\omega(7) = 5.682066 \text{ [THz]} = 189.534573 \text{ [cm}^{-1}\text{]}$

(-0.385939 0.000000 0.382980 0.000000 -0.000477 0.000000)

(0.453919 0.000000 -0.450012 0.000000 0.000228 0.000000)

(-0.291089 0.000000 0.043629 0.000000 -0.190840 0.000000)

(-0.044280 0.000000 0.288379 0.000000 0.191921 0.000000)

(-0.160395 0.000000 0.158380 0.000000 0.000298 0.000000)

$\omega(8) = 5.791061 \text{ [THz]} = 193.170276 \text{ [cm}^{-1}\text{]}$
 (0.294186 0.000000 0.297040 0.000000 0.124803 0.000000)
 (-0.424803 0.000000 -0.428410 0.000000 -0.046326 0.000000)
 (0.319990 0.000000 0.106638 0.000000 -0.081951 0.000000)
 (0.105999 0.000000 0.322329 0.000000 -0.080067 0.000000)
 (0.315098 0.000000 0.317370 0.000000 -0.038383 0.000000)
 $\omega(9) = 6.078261 \text{ [THz]} = 202.750303 \text{ [cm}^{-1}\text{]}$
 (-0.075208 0.000000 0.074951 0.000000 0.000106 0.000000)
 (0.037385 0.000000 -0.037298 0.000000 -0.000043 0.000000)
 (0.436166 0.000000 -0.049483 0.000000 0.356309 0.000000)
 (0.049594 0.000000 -0.434928 0.000000 -0.356412 0.000000)
 (-0.417493 0.000000 0.416340 0.000000 -0.000043 0.000000)
 $\omega(10) = 6.620125 \text{ [THz]} = 220.825075 \text{ [cm}^{-1}\text{]}$
 (-0.060103 0.000000 -0.060148 0.000000 0.096796 0.000000)
 (0.008381 0.000000 0.008501 0.000000 -0.042622 0.000000)
 (0.529055 0.000000 0.066680 0.000000 -0.043824 0.000000)
 (0.066598 0.000000 0.529592 0.000000 -0.041793 0.000000)
 (-0.451179 0.000000 -0.451842 0.000000 -0.028313 0.000000)
 $\omega(11) = 7.375378 \text{ [THz]} = 246.017773 \text{ [cm}^{-1}\text{]}$
 (-0.032279 0.000000 0.032353 0.000000 -0.000092 0.000000)
 (-0.044015 0.000000 0.044108 0.000000 0.000054 0.000000)
 (0.338068 0.000000 -0.058913 0.000000 -0.597244 0.000000)
 (0.058698 0.000000 -0.339210 0.000000 0.597320 0.000000)
 (-0.148463 0.000000 0.149085 0.000000 0.000029 0.000000)

$\omega(12) = 9.953214 \text{ [THz]} = 332.005692 \text{ [cm}^{-1}\text{]}$
 (-0.022008 0.000000 -0.021986 0.000000 -0.137687 0.000000)
 (-0.005352 0.000000 -0.005431 0.000000 0.477038 0.000000)
 (0.042605 0.000000 0.027762 0.000000 -0.611248 0.000000)
 (0.027739 0.000000 0.042682 0.000000 -0.611219 0.000000)
 (0.004899 0.000000 0.004926 0.000000 -0.003488 0.000000)
 $\omega(13) = 17.106690 \text{ [THz]} = 570.621555 \text{ [cm}^{-1}\text{]}$
 (-0.017729 0.000000 -0.016720 0.000000 -0.003141 0.000000)
 (-0.056387 0.000000 -0.053150 0.000000 -0.031580 0.000000)
 (-0.245788 0.000000 0.606694 0.000000 -0.028717 0.000000)
 (0.642437 0.000000 -0.232492 0.000000 -0.028294 0.000000)
 (-0.189481 0.000000 -0.178888 0.000000 0.166128 0.000000)
 $\omega(14) = 17.116310 \text{ [THz]} = 570.942435 \text{ [cm}^{-1}\text{]}$
 (-0.017421 0.000000 0.018384 0.000000 0.000093 0.000000)
 (-0.056060 0.000000 0.059135 0.000000 0.000907 0.000000)
 (-0.230179 0.000000 -0.653408 0.000000 -0.006981 0.000000)
 (0.618365 0.000000 0.243609 0.000000 0.008625 0.000000)
 (-0.183085 0.000000 0.193408 0.000000 -0.004789 0.000000)
 $\omega(15) = 18.907186 \text{ [THz]} = 630.680045 \text{ [cm}^{-1}\text{]}$
 (0.003263 0.000000 0.003264 0.000000 -0.005473 0.000000)
 (0.014335 0.000000 0.014365 0.000000 -0.149199 0.000000)
 (0.033059 0.000000 -0.118534 0.000000 -0.204551 0.000000)
 (-0.118359 0.000000 0.033110 0.000000 -0.204559 0.000000)

(0.034129 0.000000 0.034181 0.000000 0.927906 0.000000)

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