THE STUDY OF EXCITATIONS IN STRONG MAGNETOELECTRIC COUPLING SYSTEMS AND MULTIFERROIC MATERIALS

A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS
IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF PHILOSOPHY OF SCIENCE IN CONDENSED MATTER PHYSICS

BY: SHEGAW ENYEW MULUYE

ADDIS ABABA UNIVERSITY, ADDIS ABABA, ETHIOPIA

JANUARY, 2015

Abstract

Electric charge is not the only possible property for the interaction of atoms or materials with other elementary excitations. The spin is a fundamental quantum mechanical property inherent to elementary particles. Atoms are composed of positively charged core and extended cloud of electrons prone to induce polarizations which in turn complement interactions with external fields. Multiferroic Magnetoelectrics find new applications in magnetic as well as electric devices. The coupling of magnetic and electric degrees of freedom offers additional functionalities arising from the quantum mechanical interactions of the charges,spins and lattice vibrations. The interactions of magnetic and lattice phenomena are treated to formulate the model Hamiltonian and analyzed through the double time Green function. The spectrum of excitation is found to depend on the excitation wave vector and the spectral broadening explains the interaction that exists between the two domains. The density fluctuations of electromagnetic domains and the lattice vibration modes can be due to the the exchange interaction and consequently, explained by the damping Green function. In particular case, the interaction phenomena of phonons and magnones have been studied in ferroelectric-ferromagnetic multiferroics making use of the equation of motion method to understand the magnetizations and polarizations which indicate the cross coupling of magnetic and electric properties(existence of multiple ferroic orders) opening a new route towards alternating switching for practical applications,and appreciable results are obtained in broad agreement with experimental findings.

ADDIS ABABA UNIVERSITY

DEPARTMENT OF PHYSICS

The undersigned hereby certify that they have read and recommend to the college of Natural Science for acceptance of the thesis entitled " THE STUDY OF EXCITATIONS IN STRONG MAGNETOELECTRIC COUPLING SYSTEMS AND MULTIFERROIC MATERIALS" by SHEGAW ENYEW MULUYE in partial fulfillment of the requirements for the degree of Doctor of philosophy.

Date: January, 2014

External Examiner: Prof. K. N. Pathak _____

Internal Examiner: Dr. Chernet Amente _____

Research Supervisor: Prof. P. Singh _____

Examining Committee: Dr. Belayneh Mesfin _____

Acknowledgment

It is only by the grace of God that I have completed this doctoral dissertation. From the very beginning, there have been enormous obstacles, ups and downs to overcome, but with strong dedication and passion, my long cherished dream has become true.

I would like to express my sincere gratitude to my advisor Prof.Pooran Singh for giving me the opportunity to work on this challenging and exciting field and for his faith, guidance and support throughout the course of my PhD study and research. I benefit a lot from his guidance during my study including the discussion we held, the intelligent suggestions he made on my research, his patience on correcting my papers, and helpful instruction on my presentations and seminars. I deeply appreciate all his invaluable help and affection.

I would like to thank Addis Ababa University, Physics department on providing favorable playgrounds to my study. I would also like to thank all the staff members who have contributed directly or indirectly for the fulfillment of my research work. It will always be a good memory to work with them. Further more, I would like to express my gratitude to my colleagues whom I always contend and also share whatever they have at their hands. And also I would like to thank my uncle Adane Abeje for his invaluable support professionally and material wise since the beginning to the end of my PhD study. Extending my thanks, I have tremendous respect to my uncle, Zemen Mirtu whose technical support guided me to be at this position now.

Finally, but the most important acknowledgement, to my parents: My father Enyew Muluye who gave me an opportunity as a matter of chance to start my education from the very beginning where most of other brothers and sisters of mine were not lucky to pursue. And my mother, Teje Birhane who took the lions share of my greatest achievement in every aspect where her courages and dedications inspired me to work hard for the better future. I would also like to thank all my elders and littles, for their wholehearted love, unconditional support, understanding, patience and encouragement when I was in challenge, sad and depressed.

Last, but not the least, I would like to thank my families standing on my side all the time providing technical supports when I was depressed and impatient turning up with passion and delightedness and hence special thanks must be given to them. Otherwise, I would not come after without these help.

Contents

List of Figures

List of Tables

Acronyms

ME	Magnetoelectrics
SQUIDS	Superconducting quantum interference devices
MF	Multiferroic
FM	Feromagnetism
FE	Ferroelectrics
CO	Charge ordering
CDW	Charge density wave
SDW	Spin density wave
AFM	Anti-ferromagnet
AFE	Anti-ferroelectric
emu	Electromagnetic unit

Chapter 1

Introduction

The common feature of all materials is the existence of several competing interactions manifested in their phase diagrams [1]. Electrons in solid state matter interact with each other in several ways. Notable consequences of these enigmatic electron-electron interactions include diverse electronic ground states like magnetism, superconductivity, and ferroelectricity. Of particular interest are systems in which properties can be tuned as a function of external control parameters like temperature, pressure, and magnetic or electric fields. The complex electronic structures and competing interactions in the transition metal oxide compounds are potentially interesting for technological applications since the competitions include the charges,spins, orbitals and the lattice degrees of freedom which can ultimately lead to giant responses with very small external stimuli. The thesis deals with different aspects of competing interactions between elementary excitations. In particular, we focus on a theoretical aspects of materials rich in properties of magnetoelectricity, multiferroism, and electromagnons mostly very well known to display cross-correlations between magnetic properties, electric properties and mechanical stresses. In the ME composite systems, coupling is strain-mediated, that is, the strain induced in one component, either by magnetostriction in the ferromagnetic or by the piezoelectric effect in the ferroelectric, is transferred to the other component, altering the polarization or magnetization which has been activated theoretically [2]. A ferroelectric crystal possesses a spontaneous polarization that can be reversed or reoriented by applying an electric field, whereas a ferromagnet exhibits a spontaneous and switchable magnetization [3,4]. It is difficult to combine ferroelectricity and magnetism in conventional cases because of mutual exclusive original

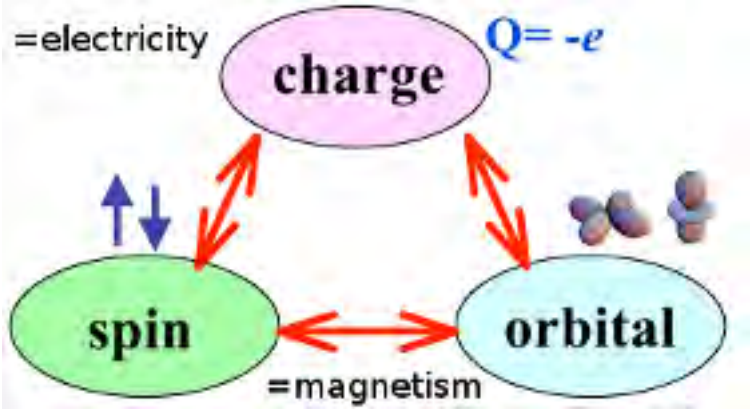

Figure 1.1: The interplay of charge, spin and orbital degrees of freedom along with the lattice degree of freedom determines exotic physical properties of the crystal

driving mechanism of ferroelectrics that requires empty d-shell transition ions, and the driving mechanism of ferromagnetism which requires a partly field d-shells. However, in multiferroics, in general, require different mechanisms of electric polarization than in prototypical ferroelectrics which allow the coupling with ferromagnetism [5]. The dynamic counter part of magnetic and electric properties realizes the existence of hybridized magnon-polaron modes, and these multiferroic materials that exhibit collective mode of excitations have been attracting enormous interest recently for fundamental reasons and for possible applications, such as memory elements, optical switches, and magnetic sensors beyond the existing ones [6]. Particularly, magnetoelectrics and multiferroics are examples of the broader class of multifunctional materials that merge several useful features in the same substance and display new phenomena that are more than just the sum of the individual parts [7]. An ever-increasing interest of multi-functional materials both for research purposes and technological aspirations coiled the focus towards multiferroics. The theoretical backgrounds and experimental endeavors helped the field to envisage fast, huge memory and multifunctional devices in the electronics industry. Prominently, in the spintronics world where the spin and the charge degrees of freedom play independent roles so as to manipulate spin and electronic properties separately. These features of the composite multiferroics can be considered as an exclusive means to point out the coexistence of coupled order parameters. The existence of simultaneous order parameters in some naturally occurring compounds is very weak to be used in wide ranges of applications and also

very rare due to several constraints. The comparatively few number of single phase(naturally found) multiferroics put sever limitations to the researchers not to proceed further on the same track. However, the possibility of the coupled order parameters in synthesized compounds of different strengths have triggered the spirit onto composite ferroelectric- ferromagnetic multiferroics providing magnetically ordered phases and electrically active states besides the elastic responses. Such composites have rich phase diagrams, not only because they have the properties of their parent compounds, but also interactions between the magnetic and electric orders lead to additional functionalities such as the four state logic devices [8]. The general principle underlying on the quantum mechanical description of the interacting particles with the surrounding environment is on the pursuit of small perturbation that leads to elementary excitations. In the composite systems of FE-FM nano-structured materials, coupling is inevitable so long as there is magneto(electro) striction effects that can be shared from one component to the other and, consequently, modifies the magnetizations and polarizations of the system. The physics of these materials is full of surprises and undoubtedly give rise to challenging phenomena at this time and in the future the new science of multiferroics will certainly spark out if concerted efforts brought together.

Outline of the thesis

In Chapter 2 basic principles of theory of magnetoelectric and multiferroic materials are explained. We first discuss a phenomenological approach to the magnetoelectric effect, and then turn to the microscopic mechanisms that give rise to ferroelectricity in frustrated magnets where competing interactions between spins result in states without inversion symmetry. This chapter is concluded with an introduction to dipole excitations of spin waves, or electromagnons which are common themes in the Chapters 3-5.

In the third chapter a theoretical model Hamiltonian is set considering the elementary quasiparticle excitations that can be described making use of the magnons and quantum of electromagnetic field(photon) which represents strongly correlated systems of ferroelectromagnets and is treated theoretically using the double time Green function. In this particular study we observed the fluctuations of the number densities in the imaginary component of the Green func-

tion characterized by the damping terms. The subsequent damping in the magnetic excitations and electromagnetic fields verify the interaction between the two domains.

The fourth chapter mainly deals with the mutually excluding phenomena, magnetism and electricity tending to play crucial roles for the upcoming technology though coupled excitations. In this part we consider the multiferroic system described theoretically on the Heisenberg exchange interaction model. Whereas, in the fifth chapter the focus was on magnetically induced multiferroic mainly the ferroelectric-ferromagnetic collinear chains of atoms Prostrate to induce electromagneons. In this case, hybridization of magnonic and phononic quasi-particles excitations are the conspicuous points and theoretically discussed through the motion equation method.

In the last chapter we look at the executive summary of the whole work and the findings are presented accordingly with the contention of experimental results and, the outlooks are also projected to whether the future is in line of this field or not.

Chapter 2

Magnetoelectricity

Magnetic materials are currently used for a wide range of practical applications including magnetic memory, and magnetic field sensors and actuators.Whereas, ferroelectrics, are used not as such in narrow boundary as magnetic ones. Although these properties, on the exclusion of one over the other,have their own vast theories and invaluable practical device applications their tendency of coexistence has recently become a blooming of plethora of scientific findings. The ability to control magnetism with an electric field has drawn wide research interest due to the potential it holds in lowering the power consumption of magnetic devices and extremely lower magnetic sensing even beyond the Superconducting quantum interference devices (SQUIDS)[9]. In this Chapter we introduce to magnetoelectricity and the phenomenological approaches to explain the coupling between magnetic and electric properties. In particular, we discuss simple Landau phenomenological theory, which describes the induction of electric polarization in collinear and non-collinear magnetic states, and vice versa. We consider various microscopic mechanisms which will lead to magnetoelectric interactions that ultimately can give rise to dynamical magnetoelectric effects.

2.1 Magnetoelectricity Phenomenological Perspectives

The evolution of magnetoelectrics is traced back to the electromagnetic interactions with solid and liquid dielectric and magnetic materials. In the solids,where the current distribution is a function of the radial position,i.e $j(r)$ about a certain origin, the magnetic dipole associated

with this continuously moving charge system is of the form:

$$\vec{m} = \frac{1}{2c} \int \vec{r} \times \vec{j}(r) d^3\vec{r} \tag{2.1}$$

For discrete charge system of particles, of charge q_i at position r_i with velocity v_i, $j(r) = \sum_i q_i v_i \delta(r - r_i)$ where the dipole moment is defined as,

$$\vec{m} = \frac{1}{2c} \sum_i q_i \vec{r_i} \times \vec{v_i} \tag{2.2}$$

The magnetic dipole moment, about an origin also defines the vector potential given by

$$\vec{A(r)} = \frac{\vec{m} \times \vec{r}}{r^3} \tag{2.3}$$

From which the magnetic field is defined as

$$\vec{B(r)} = \vec{\bigtriangledown} \times \vec{A(r)} \tag{2.4}$$

Thus,on the definition of the magnetic field $\vec{H} = \vec{B} - 4\pi\vec{M}$ and the electric field E, one can proceed to the constitutive relations. The constitutive relations in the theory of electromagnetic interaction are expressed as functions of the fields in the given material.

The macroscopic displacement and magnetic field inductions $\vec{D}$ and $\vec{B}$ are related to the macroscopic electric field $\vec{E}$ and magnetic field $\vec{H}$, as well as the magnetization, $\vec{M}$, and polarization, $\vec{P}$. The most general causal linear time-domain relationships between the displacement and electric fields and induction and magnetic fields are

$$D(\omega) = \varepsilon_0 E(\omega) + P(\omega) \tag{2.5}$$

$$B(\omega) = \mu_0 H(\omega) + \mu_0 M(\omega) \tag{2.6}$$

While the current density is defined as a function of the electric field E and magnetic field H,

$$J = J(E, H) \tag{2.7}$$

The linear response relations defining the polarization and magnetizations in non-magnetoelctrics and non-chiral dielectric and magnetic materials can be described in terms of the macroscopic fields with respect to the electric and magnetic susceptibility.

However, in some materials, such as magnetoelectrics, magnetic and electric responses are found to couple each other, i.e, having correlation between electric dipole moments and spins to induce magnetoelectric effect. In the discovery of magnetoelectrics, it is believed that two possible independent events have contributed. The first one is the magnetization of moving dielectric material in an electric field [10] followed by the converse effect, polarization of this moving dielectric in the magnetic field [11]. The second vital event is the observation of intrinsic correlation between magnetic and electric properties in some natural crystals where symmetry has got recognition to be the key issue in the search for ME behaviors [12]. And hence, the constitutive relations must be modified so as to incorporate the cross-coupling magnetic and dielectric properties. In such cases, it is often quite interesting to write as

$$D(\omega) = \varepsilon E(\omega) + \eta_1 H(\omega) \tag{2.8}$$

$$B(\omega) = \mu H(\omega) + \eta_2 E(\omega) \tag{2.9}$$

The η's are the order parameters, which describe the spatial distribution of the two phases. The term "magnetoelectrics" was coined by P. Debye in 1926, and gets its name from the fact that magnetic and electric properties are coupled to each other [13].

The magnetoelectric effect is the phenomena of mutually inducing magnetizations and electric polarizations by applied electric and magnetic fields. In more general terms the magnetoelectrics effect, not only happens on the expense of the magnetic and electric properties but also, highly correlated with elasticity of the material. Thus, the idea of magnetoelectric effect in materials can be conceptualized as shown by the following schematic diagram.

The potential interest of these materials quests for thorough studies, in particular on the symmetric considerations. According to L. D. Landau and E. M. Lifshitz, the magnetoelectric effect is odd with respect to time reversal and vanishes in materials without magnetic structure, i.e, time-asymmetric in magnetically ordered states [16]. Such violation of time-reversal symmetry can extrinsically occur through application of an external magnetic field or movement as in the historic experiment conducted by Rontgen or intrinsically in the form of long-range magnetic ordering. Dzyaloshinskii was the first to show violation of time-reversal symmetry explicitly for a particular system (antiferromagnetic Cr_2O_3) [17], which was soon followed by experimental confirmation of an electric-field-induced magnetization and a magnetic- field-

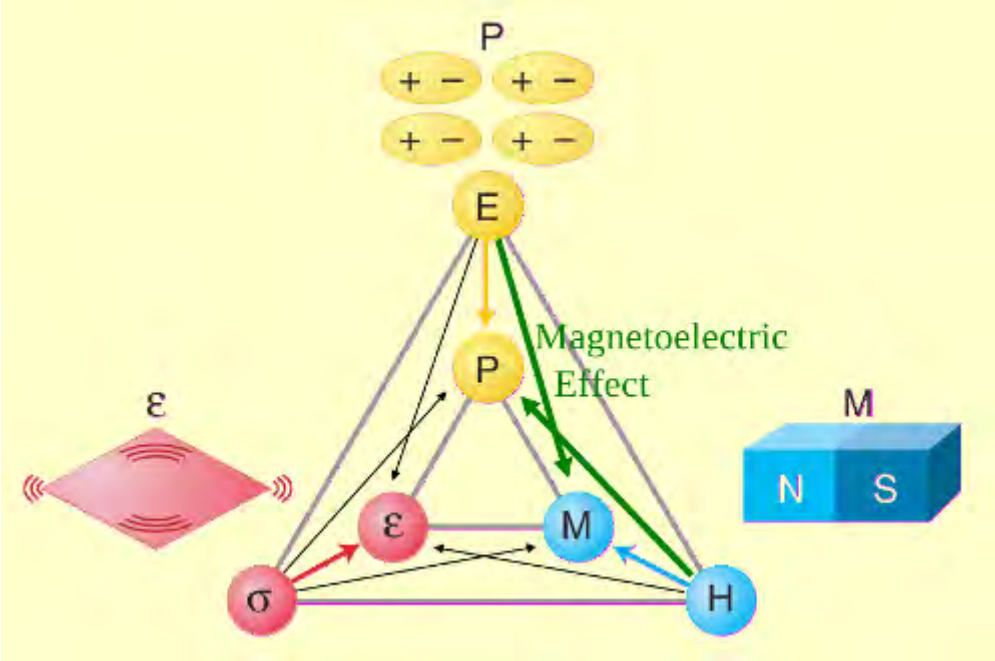

Figure 2.1: The diagram shows how the magnetoelectric effect is peeved from the three pillars, electric field, magnetic field and stress [14,15].

induced polarization in the same material [18,19]. This was the bench mark in the history of magnetoelectrics in the research for new ME materials and to step this field forward. Later, numerous single phase ME materials were reported. These single phase materials have a linear ME effect, caused by a direct coupling between dipole and spin moments on the atomic scale as well as introduction of strain effects about high dimensional compounds.

In most general forms, in the Landau phenomenological theory the magnetoelectrics (ME) effect from the free energy expansion is expanded in the following form,

$$F(E,H) = F_0 - P_i^s E_i - M_i^s H_i - \tfrac{1}{2}\varepsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2}\mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2}\beta_{ijk} E_i H_j H_k - \frac{1}{2}\gamma_{ijk} H_i E_j E_k - \ldots \quad (2.10)$$

Where E and H are electric fields and magnetic fields, respectively. The spontaneous polarizations and magnetizations are obtained upon differentiating the free energy with respect to the fields

$$P_i(E,H) = -\frac{\partial F}{\partial E_i} = P_i^s + \varepsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2}\beta_{ijk} H_j H_k + \gamma_{ijk} H_i E_j - \ldots \quad (2.11)$$

and the magnetization is

$$M_i(E,H) = -\frac{\partial F}{\partial H_i} = M_i^s + \mu_0\mu_{ij}H_j + \alpha_{ij}E_i + \beta_{ijk}E_iH_j + \frac{1}{2}\gamma_{ijk}E_jE_k - ... \qquad (2.12)$$

The P^s and M^s denote the spontaneous polarizations and magnetizations, whereas ϵ and μ are the electric and magnetic susceptibilities. The tensor α corresponds to induction of polarization by a magnetic field or of magnetization by an electric field which is termed as the linear ME effect. For instance, it can only be nonzero for materials that simultaneously break time reversal symmetry and spatial inversion symmetry. The most common source of time asymmetry in Mott insulators is spin ordering. The magnetoelectric coupling appears if the spin ordering breaks inversion symmetry. The components of the linear electromagnetic coupling parameter are constrained by thermodynamics stability criteria and is bounded by an appropriate diagonal elements of dielectric permittivity and magnetic permeability parameters related to

$$\alpha_{ij} \leqslant \frac{\sqrt{\epsilon_{ii}\mu_{jj}}}{4\pi}$$

It is supplemented by higher-order ME effects, nonlinear ME susceptibilities like those parametrized by the tensors β and γ. These linear and non-linear magnetoelectric susceptibility parameters characterize the performance of magnetoelectric materials. In most cases, interest arises to know about the linear magnetoelectric coefficient, as magnetoelectric effect is linear in most compounds. This coefficient basically quantifies the dependence of polarization on magnetic field or of magnetization on the electric field. In case of multiferroics, although many linear magnetoelectric effects are expected because these materials often possess large susceptibility and permeability respectively.

The values of ME coupling parameter for single phase materials has always been found to be very small, on the order of several mV/cm.Oe. This small ME effect makes it hard for them to be useful for devices applications. However, more recent investigations have been reported that improved multiferroic and ME properties in epitaxial layers of ME thin films such as $BiFeO_3$ grown on $SrTiO_3$, and in self-assembled multiferroic nanostructures such as $CoFe_2O_4$ nanopillars embedded in a $BaTiO_3$ matrix on $SrTiO_3$ substrates can exhibit better enhancement and potentially useful for integrated microelectronic materials that have the promise of reading a spin state as a direct voltage. Unfortunately, the electronic configurations

which favor polarization are antagonistic to those that favor magnetization, and vice versa. This is simple to conceptualize, i.e, the d^n electronic configuration is favorable to spin alignment, but is not very distortable; whereas d^0 is very distortable, but has no spin.

An ME effect involves both magnetic and electric properties and hence it seems hard to maintain both space-time symmetric operations, consequently leading to complexity on the behaviors of the materials.

2.2 Microscopic Mechanism of Magnetoelectric Effect

To estimate the magnitude of coupling coefficient it is necessary to understand the underlying microscopic mechanism driving magnetoelectric behaviors in different crystals. Perhaps, there will not be a fundamentally unique mechanism best describing the ME effect in materials exhibiting such property. It is because of the fact that compounds of different compositions, stoichiometry and morphology are prone to be magnetoelectric. Some commonly relevant interaction mechanisms are discussed in the following subsections.

2.2.1 Single-ion Anisotropy

In most cases, an appreciable magnetoelectric coupling has been observed in ferrites, rare earth manganites, and in general, in iron group metallic compounds and perovskite classes, about which exchange interactions can play dominate roles in determining the spin orientations. Thus, it turns out that the spins prefer particular directions, indeed, the magnetization direction. The exchange interactions, the shape of the crystal structure and other active interactions responsible for locking crystalline magnetization cause the magnetic anisotropy. In the crystals of these type, where the spins of 3d electrons and their orbits, as of iron groups, and 4f electron spins and their orbits in rare earths are prominent figures in strong spin-orbit couplings, the magnetic anisotropy is accounted from these strong coupling. Of course, the mechanism of anisotropy differs in every crystal as to the nature of quantum mechanical interactions existing in it. To be specific, we consider anisotropy arising from the situation related to spin-orbit interactions that can be caused by direct coupling between orbit and lattice, or in more vigorous cases that the

spins are not coupled directly to the lattice but the orbit is likely to feel the lattice. Magnetic moments arise from spins and orbits of the electrons integrated with the lattices and hence an external electric field may change the local symmetry seen by magnetic ions and affect both the strength of the anisotropy and the direction of the easy axes while moving the ions relative to one another. At the lattice site "i" of several atoms with many electrons each, the ionic anisotropy is proportional to the square of the total spin, i.e, single-ion anisotropy $\propto (S_i^{\nu})^2$ [20].

Thus, single-ion anisotropy(single ion excitation) can couple an external electric field to spins of magnetically ordered compounds.

2.2.2 Magnetic Exchange Interactions

The magnetic phenomena in solids is sparked by the electrons, due to their spins and associated magnetic moments. Electronic states decisively responsible for magnetic properties may be tightly bound to core electrons (highly localized) or free to move (itinerant) in the vicinity of atoms and within the lattice cells. Localized magnetism occurs due to the interaction between sufficiently localized and tightly bound inner electron shells of atoms/ions by the lattice sites in which wavefunction overlap is signatory for antecedent interaction. Whereas, itinerant magnetism occurs because of delocalized electrons very commonly in metallic elements and compounds with excess free electrons which can be shared by the entire crystal. Spontaneous magnetization due to electron-electron interactions called the magnetic interaction happens as a consequence of interaction between any two or more electrons. This, in fact, may lead to dipolar

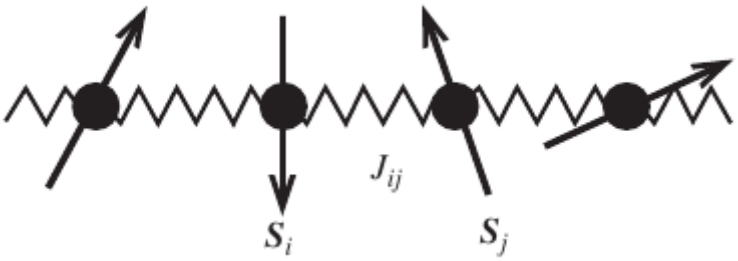

Figure 2.2: This illustration depicts the exchange interaction between the spins [21].

interactions (interaction between magnetic dipoles). On the other hand, the main interaction be-

tween localized spins is an "exchange interaction" due to the Pauli's exclusion principle which prohibits any two electrons of the same spin state taking the same place. Usually, exchange interaction is stronger than the dipolar interactions that least explains extremely strong spontaneous magnetization as compared to the exchange contribution [22].

The symmetric and antisymmetric spacial states of the electrons are correlated with spin wave functions at which the Hamiltonian is easily described by solely the spin degrees of freedom. For instance, if we have many atoms in a lattice and if there exists an exchange coupling between the spins of the atoms, the interaction Hamiltonian can be expressed in the following form,

$$H = -\sum_{\alpha\beta} J_{\alpha\beta} S_\alpha . S_\beta \tag{2.13}$$

In real many body particle system several electrons involve to determine the physical properties of the system. Whence, there may be several electrons on the same atom and the exchange coupling between the electrons of this atom is

$\sum_{\alpha\beta} J_{\alpha\beta} S_\alpha . S_\beta = \sum_{kl} J_{kl} \sum_{ij} S_{ki} . S_{lj} = \sum_{kl} J_{kl} (\sum_i S_{ki}) . (\sum_{lj} S_{lj})$

$$H = -\sum_{kl} J_{kl} S_k . S_l \tag{2.14}$$

Here, S_k and S_l denote the total spins on each atom while the exchange integral J depends upon the particular pairing of spins that are interacting to each other. This is the Heisenberg exchange interaction, the simplest form of spin–spin interaction. In general, exchange may be anisotropic, short-range $(J_{ij} = J\delta_{j,i\pm1})$ or long-range, and even may contain higher order terms. Exchange interactions in magnetoelectrics act like electric polarization dependent magnetic exchange interactions. Because, in these materials electric polarization is feasible event while magnetic exchange interactions exist. On the interaction schemes of electrons associated with their spins in the crystals, the exchange interaction can be classified in different forms. The most common studied types are:

2.2.2.1 Direct Exchange Interaction

When the magnetic ion cores are next to each other on the lattice sites having no other electrons to mediate their interaction, the overlap of electron clouds can have a direct interaction to

determine the magnetic configurations of the spins so that their magnetic moments can either, align in parallel or anti-parallel orders to determine the over all magnetic behavior of the crystal system. In the Heitler–London theoretical approximation [20], it has been predicted that the exchange interaction energy is of the same order of magnitude as the electrostatic interaction energy between two atoms and that this interaction depends on the overlap of the wave functions of the atoms. Since the overlap, characterized by the exchange integral, seems to die out exponentially, it is quite straight forward to expect that the direct exchange interaction between any two atoms is rather short range in character.

2.2.2.2 Superexchange Interaction

Direct exchange interaction is not the only one interaction mechanism between magnetic ions. Now a days, large number of artificial compounds are being synthesized through doping and even through direct mixing of different components. As a result, one component may have intrinsic magnetic dipole moment whereas, the others are non magnets. Even though, the wave functions of the magnetic ions hardly overlap, such crystals could have measurable spontaneous magnetization. This, in fact, can occur through the mediation of non magnetic ions considered to be in between the magnetic ions. The magnetic ions with non overlapping wave functions are allowed to interact on the expense of non magnetic ions sitting in between. We could have also a superexchange interaction arising from double exchange interactions where the atoms have mixed valencies and is very common in ferrites and manganites classes of crystals. Thus, an interaction of such kind is termed as superexchange interaction.

It is useful to get a physical picture of the spin-dependent energy through the Heisenberg model, which quite appreciably explains the spin interaction regardless of the type of the exchange. In considering two interacting atoms, usually, we had a parallel spin case and an antiparallel spin case by the Pauli exclusion principle, in which the parallel spins require an anti-symmetric spatial wave function, whereas the antiparallel ones require symmetric spatial wave function. Both of which, the symmetric and anti-symmetric spin configurations are considered as possible mechanisms of magnetoelectric coupling at different orders.

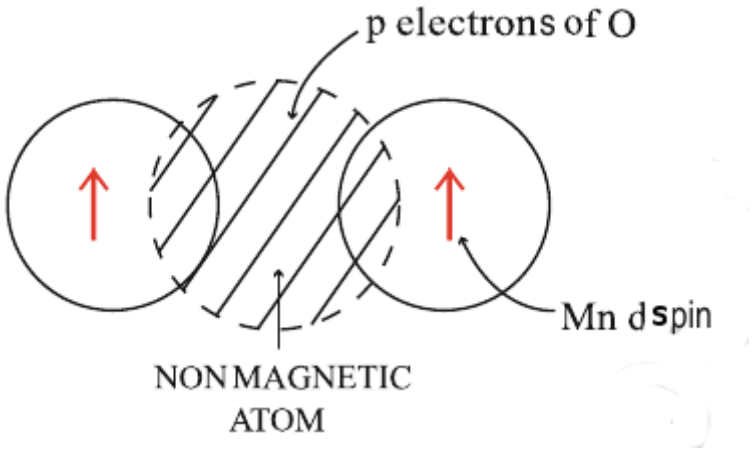

Figure 2.3: Schematic illustration of superexchange interaction between magnetic ions intermediated by nonmagnetic ion, such as the Manganese and Oxygen spin interaction in MnO [23].

A. Symmetric Superexchange Interaction

In the microscopic models the spin-lattice coupling results from exchange interactions between spins, such as the Heisenberg exchange interaction that depends on the relative positions of the ions. Heisenberg exchange is the strongest interaction between spins since it is predictable that the direct overlap of the wave functions at the short range proximity of well localized states is very likely and is predominantly common in transition metal oxides, this type of exchange is likely to be the strongest source of magnetoelectric coupling. Collinear spin configuration that breaks inversion symmetry can induce polarization via a mechanism based on isotropic Heisenberg exchange and magnetostrictive coupling of spins to a polar lattice mode. This interaction mechanism is proposed to account the rare earth manganite classes (RMn_2O_5)

The spin-lattice coupling, polarization, is proportional to the scalar product of spins $S_1 \cdot S_2$, symmetric in nature, arising from superexchange interaction of the spins. Opposite movement of differently charged ions and changes of the electron wave functions of the magnetic ions accompanied by non magnetic ions in the crystal tends to modify the orbital overlap and, consequently, the exchange integrals and energies. The exchange coupling parameter between the spins strongly depends on the bond angle of the nearby magnetic ions. Also, the coupling strength depends on the ionic positions and orientations too. Thus, it can couple lattice dis-

tortion with the spins providing a route towards the electrical manipulation of the magnetic properties. The following illustration shows an insight of the symmetric superexchange interaction which is $\propto r_{ij}(S_i^{\alpha}S_j^{\beta} + S_i^{\beta}S_j^{\alpha})$

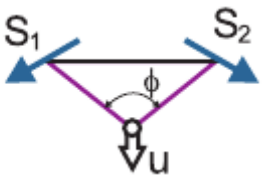

Figure 2.4: The illustration of the symmetric exchange interaction as predicted by Heisenberg to account for interaction of magnetic ions in the vicinity of non magnetic ions.

B. Antisymmetric Superexchange Interaction

According to the spin current model, spontaneous polarization is induced by neighboring canted spin interactions where the spatially antisymmetric configuration causes the electronic wave function to be modified upon reducing the relative charge concentration in the region between the atoms raising the kinetic energy, eventually, modifying the exchange integral. Spin canting is a common manifestation of the so-called Dzyaloshinskii–Moriya contribution leading to an antisymmetric superexchange interaction i.e $\propto r_{ij}(S_i^{\alpha}S_j^{\beta} - S_i^{\beta}S_j^{\alpha})$. In more rigorous forms, the DM interaction of neighboring magnetic ions with the ligands mediating superexchange interaction between them is

$$H_{DM} = \sum_{ij} D_{ij} \cdot (S_i \times S_j)$$

Here λ is the spin-orbit coupling constant, the DM vector is $D_{ij} \cdot \lambda x \times r_{ij}$ and x is the distance between the ligand and the line of action of magnetic ions. The magnetoelectric effect for a simple geometrical spin structure, the spontaneous polarization is defined by the following relation

$$P = -\sum_{ij} r_{ij} \times (S_i \times S_j) \tag{2.15}$$

Where r_{ij} denotes the vector connecting the two magnetic ions.

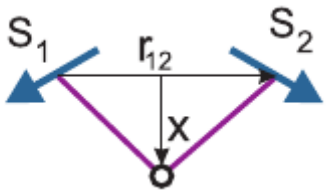

Figure 2.5: A schematic notation of DM interaction between the spiral magnetic ion configuration mediated by the non magnetic ions.

2.2.2.3 Indirect Exchange Interaction

The way electrons interact within the crystal varies as to the constituents in it. The direct overlap of the wave functions may not be always possible and even not responsible for the physical properties of the system. However, unlike the superexchange interaction, the magnetic ions may interact each other on the presence of the third atom with conduction electrons. This situation is more common and very important in metals and metallic compounds where excess free electrons are there. The Ruderman, Kittel, Kasuya, Yosida, (RKKY) interaction is important for rare earths where localization (sufficiently well shielded from the environmental influence by outer, filled shells, and remains localized) is strongly predominant. This is an interaction that happens between the conduction electrons with the localized moments associated with the 4f electrons. Since the spins cause the localized moments, the conduction electrons can mediate an indirect exchange interaction between the spins.

2.2.2.4 Itinerant Exchange Interaction

It happens to be true in some cases that an exchange interaction between delocalized (quasi-free) electrons can also show spontaneous magnetization. The conduction electrons are free to wonder in the crystal and in the meantime scattering is expected which can have a preponderant influence on the magnetic properties of the material. The magnetic response of alkali metals with considerably high free conduction electrons is smaller than that of the transition metals of moderately localized electron systems. It is due to the fact that the later have high density of orbitals and is accounted for the better magnetic susceptibility responses [24] The theoretical explanation of the exchange interaction in such cases seem to be rather difficult so long as the

electrons are mobile, where the Heisenberg exchange interaction is very effective on localized electron systems scarcely describes such interaction. But, it is likely to be explained on the basis of Hatree-Fock approximation and this is not the point of interest for the mechanism of magnetoelectric effect as it is expected not to be worthwhile.

2.2.3 Strain Driven Magnetoelectric Effect

Magnetoelectric effects are also observed through mechanical effects. Unlike the discussions above, the mechanical properties of ferromagnetic and ferroelectric gives rise to the coupling of magnetic and electric properties when components are brought together. In addition to direct couplings, there may be instances of indirect coupling mediated by strain in the multiphase materials. For instance, if we take ferroelectric material, it is all the time piezoelectric; i.e, when there is a stress applied on it, quite often, its polarization changes. And also, conversely, if an electric field is applied/removed the ferroelectric material becomes strained and changes the polarization. Similarly, since all ferromagnetics are magnetostrictive, an application of magnetic field/removal of the field stresses it and changes the magnetization of the material .Conversely, if a stress is imposed on a ferromagnet the magnetization changes as well. Therefore, while these components are coupled, i.e, when the magnetostrictive material and the electrostrictive materials are combined, the strain on one component transforms to the other and induces the perspective effects where the crucial role is played by f-electrons in establishing the spin-driven FE [25].

This is likely to arise in two phase systems where two components are coupled via strain. However, ME coupling is not restricted only on multiphase materials, more recently, strain mediated ME effect is observed even in single phases, such as in $SrMnO_3$ and $EuTiO_3$.

Inhomogeneous magnetoelectric interaction leads to ferroelectricity. It can be seen in: Spiral multiferroics, micromagnetic structures; micro domains,and magnetic vortexes. Any magnetic structure (material) even in centrosymmetric ones can develop ferroelectricity.

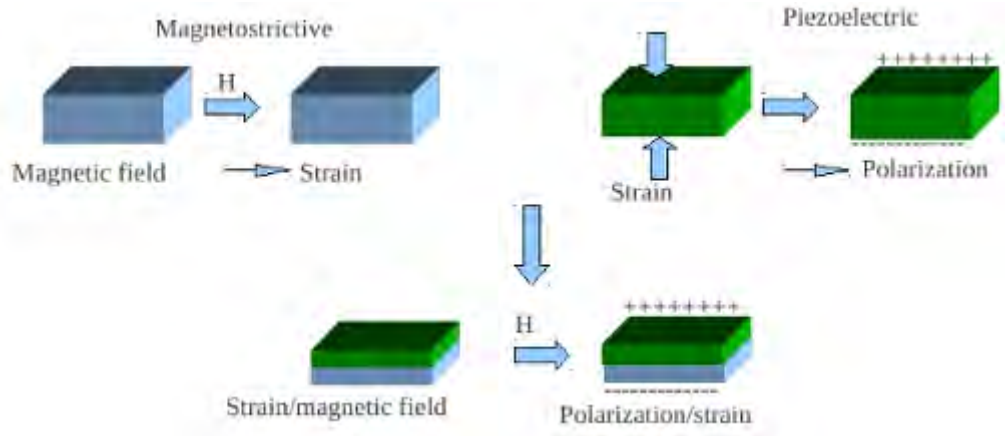

Figure 2.6: This schematic illustration indicates the strain mediated coupling of ME effect. The strain on ferromagnet passes over to the ferroelectric component to induce polarization.

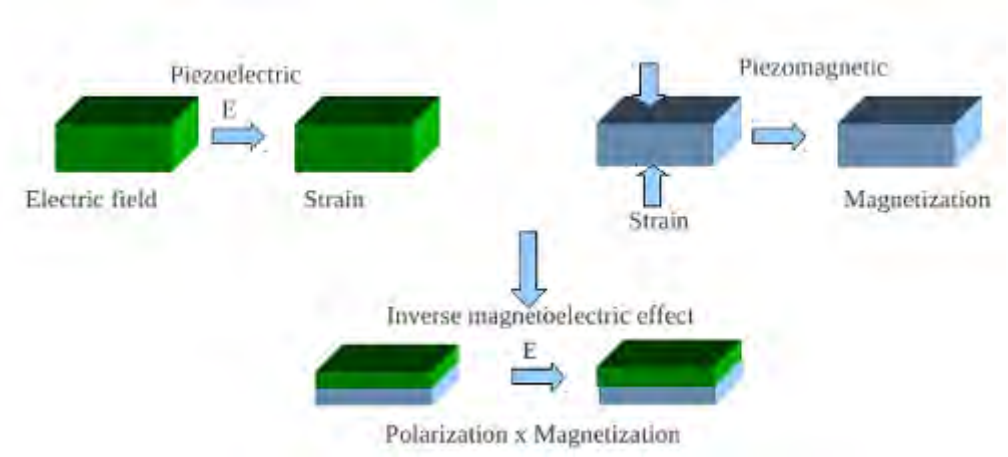

Figure 2.7: The diagram shows the converse ME coupling as a result of electric field in the elctrostrictive one and the stress is transfered to magnetostrictive component while to change the magnetization of ferromagnetic material [26].

2.2.4 Zeeman Energy

When ever an external magnetic field is applied to any crystal, the spectral lines tend to split into several components(closely spaced lines). This splitting into spectral lines was observed by Pieter Zeeman. It is analogous to the Stark effect where the spectral lines break into components on the application of an electric field which has an effect on the polarization thereby altering the spin-orbit coupling strength and magnetic anisotropy constant. The Zeeman splitting is

attributed to the interaction of the magnetic field with the magnetic dipole moments at the macroscopic scales associated with the spin and orbital angular moments. It turns out to be true that while there is an external magnetic field, the magnetic dipole moments give rise to a torque imposed by the external field. Therefore, the energy associated is described as

$$H = H_0 + V_m$$

Where H_0 is the the unperturbed Hamiltonian and V_m is the perturbation energy due to the field. Eventually, the perturbed energy is expressed as

$$V_m = -\mu.B$$

Here, μ denotes the magnetic moment, the electronic and nuclear components, while B is the external field. Often, the nuclear component is neglected as it is very small compared with other contributions. This is, of course, based on the mass differences of the electron and the nucleus that it is approximated to be smaller order of magnitude. The electronic contribution of the magnetic moment, as it is defined by the electronic spin and the orbital motion can be written as

$$\mu = -\mu_B g \frac{J}{\hbar}$$

The term μ_B is the Bohr magneton while J is the total electronic angular momentum and is the sum of spin angular momentum, S, and the orbital angular momentum, L. Thus, the total magnetic moment becomes,

$$\mu = -\frac{\mu_B}{\hbar}(g_l L + g_s S)$$

The terms g_l and g_s are called the spin-g-factor or gyromagnetic ratio and the Lande-g factor, respectively. To be specific, the eigen value of the Lande g-factor has an expression of the form

$$g = \frac{3}{2} + \frac{1}{2}\frac{s(s+1)-l(l+1)}{j(j+1)}$$

The treatment of Zeeman effect describes the phenomenon when the magnetic field is small enough that the orbital and spin angular momenta can be considered to be coupled. However, when there is a crystal field interaction, while it is quite ”real”, that breaks the spin-orbit coupling, the net orbital angular momentum has to be zero(L=0). Therefore, one can conclude

that the Zeeman interaction can be valid for magnetoelectric phenomena nevertheless spin orbit coupling picture comes to be broken. That is even at larger magnetic field Zeeman interaction plays well so as it splits the electronic states, consequently affects the magnetic behavior.

2.3 Ferroelectrics

Despite the fact that the theory of electricity has spanned long before the new ages of magnetoelectricity and multiferroism, its application still remains subtle in any field of study. The dielectric and magnetic properties of a medium are characterized by the response functions, the dielectric permittivity $\epsilon(\omega)$ and the magnetic permeability $\mu(\omega)$. When a dielectric insulator is placed in an external field, it induces polarization. The field may be static or time-varying and the response may also be linear or nonlinear. The resulting polarization that can be related to the dielectric constant occurs due to the interaction between the field and the electrons and lattice ions. The electric field interacting with these electrons and lattice ions tend to distort the electronic clouds around the atoms or relatively moves the charged ions with respect to one another. It is this polarity which we refer as electric dipoles. These dipoles upon reconfiguration into small regions of different states each with random polarization directions undergoing structural phase transition determines the macroscopic electrical properties of the crystal.

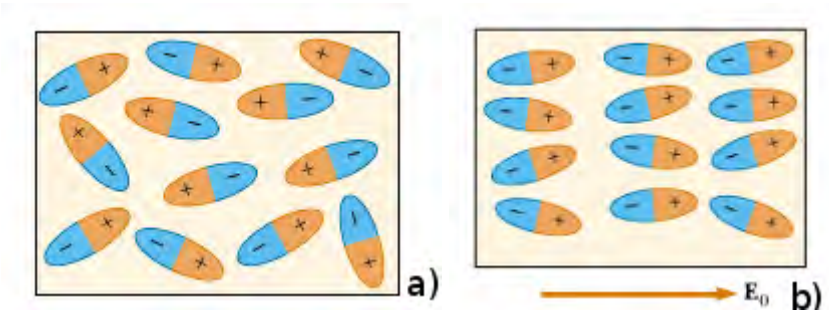

Figure 2.8: The above illustrations indicate the polarization in dielectric crystal. In a) the dipoles in the polar crystals are randomly oriented. But if an external field E_o, is applied these dipoles align them selves in the direction of the field as shown by figure b.

Roughly, the polarization in simple terminology for simple systems can be classified as [23]

a) Electronic polarization: The bound electrons about the core lattice may displace relative

to it and hence induces a polarization.

b) An ion relative to its equilibrium position may displace and give rise to polarization.

c) The orientation of any intrinsic permanent dipoles as a result of the electric field on the absence of thermal disorder can induce polarization.

These polarizations dramatically change phase when ever any external perturbation is imposed on a system. Generally, several properties change accompanied by structural phase transition, of which ferroelectric transition is marked by the spontaneous dielectric polarization in the crystal. Therefore, polarization in ferroelectric crystals, since they belong to polar crystals, is attributed from the displacements of the charged individual ions from their equilibrium positions and the polarization of the ions themselves resulting from the displacement of the electrons relative to the nucleus under the influence of an external applied field. However, ferroelectricity may even exist in the absence of an external electric field, while it is because of the permanent intrinsic electric dipole moments whose center of positive charge does not coincide with the center of negative charges [24].The spectacular feature of ferroelectrics is that the spontaneous polarization can be reversed by an applied electric field; the polarization is dependent not only on the current electric field but also on its history, yielding a hysteresis loop.

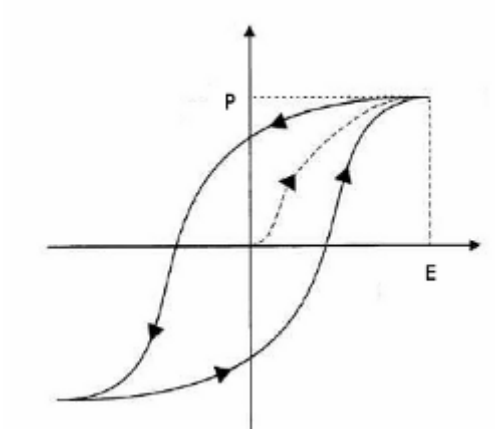

Figure 2.9: Ferroelectric polarization and the hysteresis curve.

Ferroelectric phase transitions are often characterized by either displacive (such as $BaTiO_3$) or order-disorder phases. Below the curie temperature, the barium titanate exhibits structural deformation whereby the electric dipole moments tend to orient in parallel all the way [24]. In barium titanate, a typical ferroelectric of the displacive type, the transition can be understood in

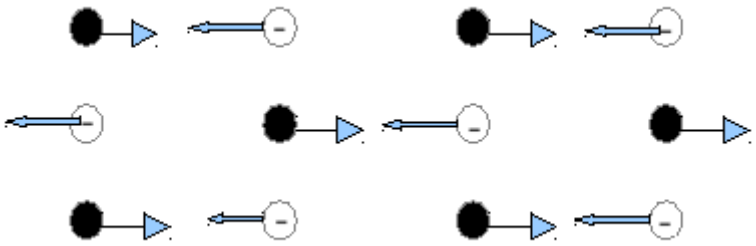

Figure 2.10: The relative displacement of pair of atoms in unit cell of a polar crystal inducing polarization.

terms of a polarization catastrophe, in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increases faster than the elastic restoring forces. This leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moments. The ionic displacement in barium titanate concerns the relative position of the titanium ion within the oxygen octahedral cage.

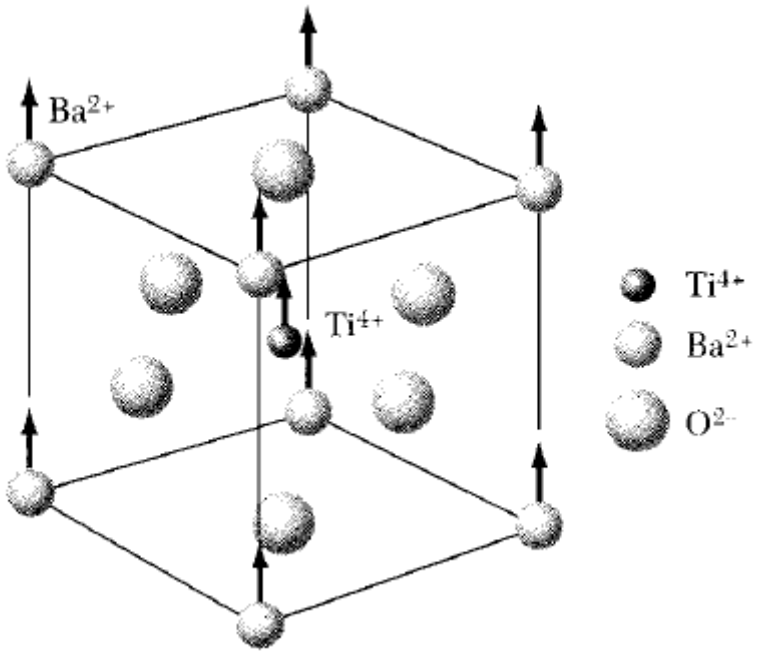

Figure 2.11: The displacive ferroelctric polarization in $BaTiO_3$.

The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the strength of the dipoles (in other words, a

change in the spontaneous polarization). In this regard, atoms in crystals have energies viable to the temperature changes. The variation in temperature modifies the crystal structure and, consequently the properties. Some ferroelectric materials are very sensitive to the changes corresponding to temperature and thus, the polarization changes upon heating or cooling the crystal. This phenomenon is called the pyroelectricity. Whereas, an application of an external stress does affect the structure as well and so do the polarization. All ferroelectrics are polar and also piezoelectric that stress imposes a change on the electrical properties.

2.4 Ferromagnetism

In the classical model of atoms electrons are believed to move in circular orbits around the massive central nucleus while it is spinning about its own axis. An orbiting electron experiences an orbital magnetic dipole moment. However, though all electrons execute orbital motion, it does not mean that all materials possess net orbital angular moment. The electrons belonging to those, whose orbital motions are canceled by another orbitals of opposite direction contribute either null or very small net magnetizations, which eventually be the reason that all materials are not magnetic.

In addition, an electron behaves itself as a tiny magnet since it has an intrinsic dipole moment associated with its quantum mechanical state the ”spin”. This fundamental property of an electron allows it to be in two possible states, either up or down in the field. This alignment of the spins into a particular direction tends to give an overall magnetic behavior of the material. Depending on the magnetic properties materials are classified as diamagnetic, paramagnetic, ferro(anti-ferro)magnetic, and ferrimagnetic. In some materials, such as diamagnetics and paramagnetics, the induced magnetization is proportional to the applied field whereas in others, nonlinear relations exist as characterized by the hysteresis curves. In some crystalline materials permanent dipole moments are there and found to be in the form of microscopic regions within which all moments align in the same direction. Thus, if weak external field is applied, this dipoles remain aligned to give rise to the macroscopic ferromagnetic character of the crystal even after the removal of applied field. Some of the examples of elements that show spontaneous magnetization or in other words exhibiting ferromagnetism are: The transition or

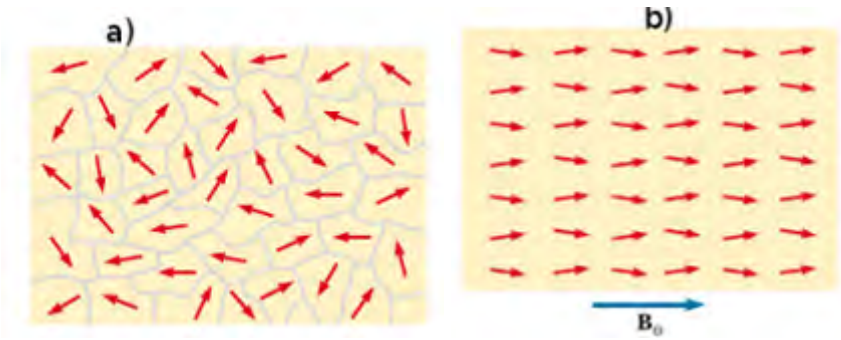

Figure 2.12: The figures show the magnetic dipole moments. The dipoles in the absence of field oriented randomly as depicted in figure a, and when external field is imposed, the microscopically ergodic dipoles restructure themselves to align in the direction of the field as indicated in figure above b.

iron group elements (e.g. Fe, Ni, Co), the rare earth group elements (e.g. Gd or Dy), and many compounds and alloys that are the playgrounds for research and investigation purposes.

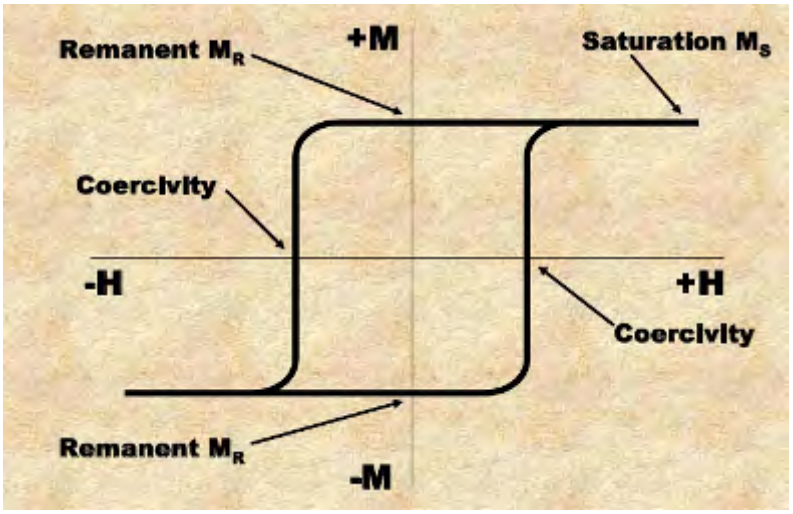

Figure 2.13: The above illustration shows the magnetic hysteresis curve of the ferromagnetic material.

2.5 Multiferroism

After the first observation of magnetoelectric effect by Rontgen in 1888 subsequent progressive investigations have been made and found to trigger research activities. Particularly, around

1960s, experimental endeavors successfully ensure the magnetoelectric effect, i nspite of being the coupling strength of the apparently different properties was very small in magnitude. The experimental result obtained on Cr_2O_3 has twinkled a spirit of attention on various materials exhibiting this extraordinary effect that can attribute for practical applications and also remarkably for fundamental understanding from theoretical view points. This new emerging science has opened a new route towards the magneto-electric switching on the expense of the cross coupling of the polarization and magnetization parameters. The progress on the field, later showed some more materials such as Ti_2O_3, Boracites, phosphates, Ba,Bi, and Ga ferrites, perovskites and others. The research interest in the 1960's and 1970's was so hot, and gradually went down till the 1990's. However, a resurgence comes on while the field of study, "multiferroism" with new terminology evolves out. The field of multiferroics is strongly tied with the birth of magnetoelectrics and has passed ups and downs too. For the success of multiferroics growth different scenarios have been forwarded. Of the most remarkable reasons, the rareness of materials with coexisting of magnetoelectric coupling and in the absence of ferroelectricity in magnetic systems, the theory of the induction on the expense of magnetism take the lead [27,28].

The term Multiferroic was coined by H. Schamid in 1994 for the first time and served till today. Although considerable motivations and an initial burst of interest arose until 2000, research in the field remains some how static due to material specific reasons. However, in 2003 very great discoveries re-enforced the renaissance of the multiferroic studies. The first one is the discovery of most popular multiferroics thin film, $BiFeO_3$ with an enhanced coupling particularly in thin film form better than the bulk sample [29]. The second and third belongs to the experimental investigation of the novel class of multiferroics, in which the the magnetic and ferroelectric properties do not coexist, but magnetism can lead to ferroelectricity and hence coupling is possibly true. Magnetically induced polarization is, of course, very small so as to be used for practical applications, but opened new route towards another way of multiferroism. This surmountable evidence was observed in compounds of $TbMnO_3$ by Tokura and Kimura and latter on, a similar effect was confirmed on $TbMn_2O_5$ by another researcher, Cheong [30,31]. The first ever found multiferroic material with simultaneous ferroelctric and ferromagnetic coupled ordered states was Nickel Iodine boracite $Ni_3B_7O_{13}I$. Subsequently,

while research was carried on various materials have been found with coupled ordered states. Multiferroics are materials which possess more than one type of primary ordered states in a single phase material.

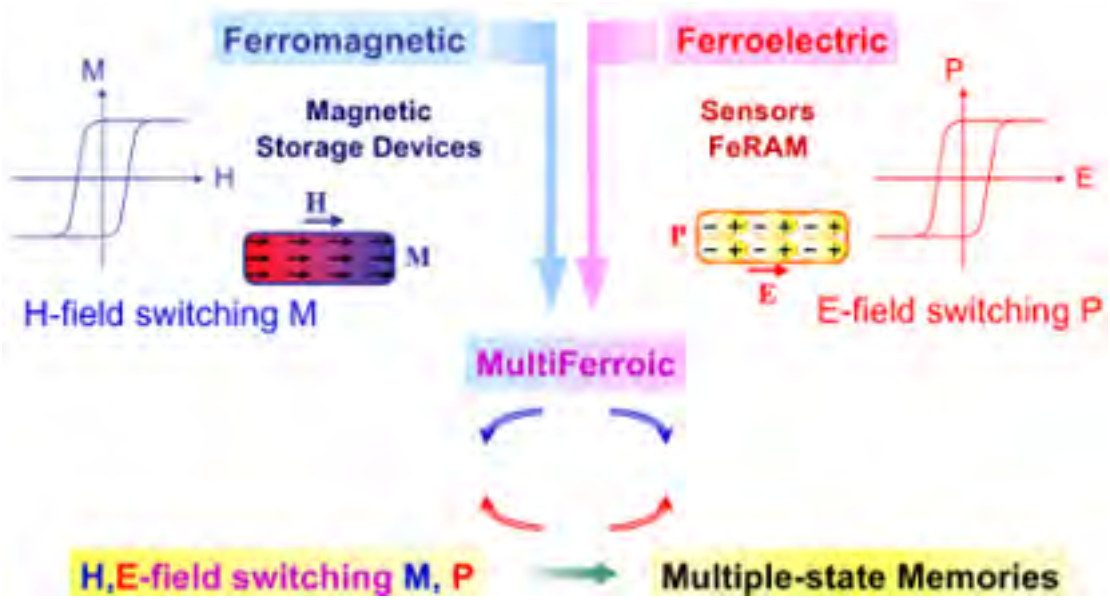

Figure 2.14: The illustration shows very common primary ferroic orders in multiferroics accessible for switching of multi-state functionalities [6].

Ferroics are in general characterized by large change in the properties of the material at the instant of phase transition, which can most likely be accompanied by symmetry breaking. To list some of the common ferroic orders; the coupling of electric charge associated with the electric field is the ferroelectric ordering, the coupling of magnetic dipole moments associated with the magnetic field is another ordering type which we call it the ferromagnetic, whereas, the coupling of the mechanical stress with the strain is the ferroelastic ordering [32] In addition, there is also another proposed ordering mechanism, associated with the coupling of magnetic field with the magnetic toroidal moment that arises from arrangement of magnetic vortexes in an ordered state, called ferrotoroidicity. Conventionally, multiferroics, as pointed out by many researchers, can be considered to be the coupling of ferroelectric and ferromagnetic ordering states, though recently, antiferromagnetic, and rarely ferrimgnetic couplings are also taken into account. The key milestone on the discovery of coexisting ferroic orders of various states emanate from the birth of magnetoelectricity. Multiferroic materials with the coupled orders of multiple ferroic

states ,for instance, the ferroelectric, ferromagnetic and the ferroelastic states have got great attention now a days in condensed matter physics research due to the paramount applications they have in these days technology. There is a prediction to be used in the electronics industry as integrated components or else in spintronics, and even for the future generation technological era for variety of applications in energy saving and massive information transfer at very fast rates. It is due to the fact that these materials have great opportunities to integrate multiphase states that can serve for multiple purposes.

Today, huge number of compounds are found to be electrically polarizable and magnetically polarizable. But, ferroelectric and ferromagnetic materials are uniquely defined by having strictly ordered electric dipole moments and magnetic dipole moments. Magnetoelectrics, on the other hand, are described regardless of the coupling of ordered electric dipoles and magnetic moments, i.e, these classes are characterized by simultaneous electric and magnetic polarization. Beyond which there is another possibility of the orderings to be coupled in very few materials which we will deal with in detail as multiferroics. Some of the compounds which

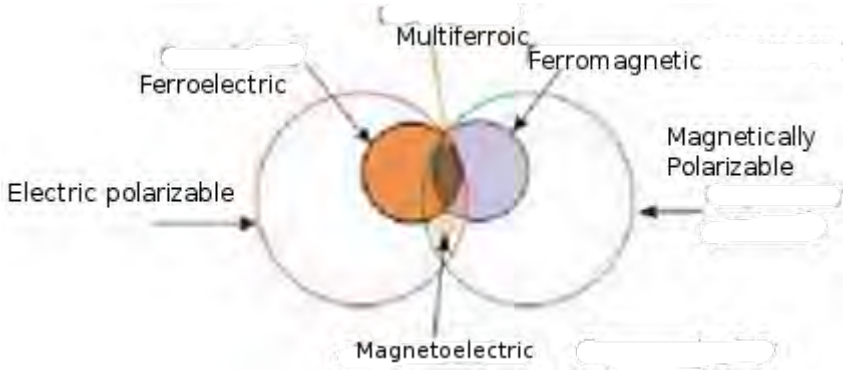

Figure 2.15: Classification of materials into different types based on the order parameters coupling scheme [7].

exhibit multiferroism, as the need arises from their multiple state functionality and from the fundamental physics in the theoretical point of view, are either rare earth manganites or ferrites or transition metal perovskite oxides. The examples are $TbMnO_3$, $TbMn_2O_5$, $HoMn_2O_5$, $LuFe_2O_4$, $BiFeO_3$, $BiMnO_3$ and $YMnO_3$. There are also some non-oxide multiferroics such as $BaNiF_4$ and spinel chalcogenides, e.g, $ZnCr_2Se_4$. Multiferroics have also been named as magnetoelectric multiferroics.

The promising way to get enhanced magnetoelectric coupling and hence multiferoics too is just while the internal electromagnetic field is quite strong. This is, however, achieved by having components with strong dielectric function and magnetic permeability. The strongest dielectric coefficient is found in ferroelectrics materials, while the strongest magnetic permeability is displayed in ferromagnetc materials. Consequently, ferromagnetics and ferroelectrics are prime candidates to display giant magnetoelectric effect and multiferroism as well. The general characteristics of the hysteresis loop of the coexisting ferroic orders can be shown by the illustration.

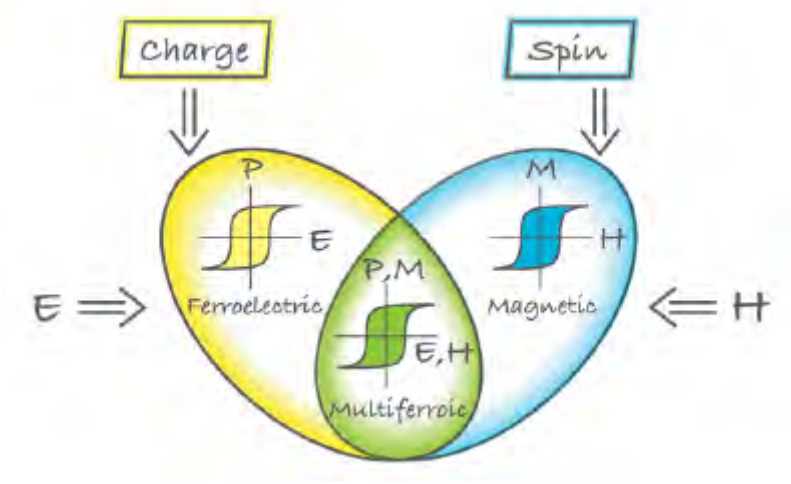

Figure 2.16: The hysteresis loop of coexisting ferroc states [34].

As mentioned before, in conventional definition, multiferroic is closely related to the coupling of ferroic orders. Thus, it is essentially related to the symmetry analysis in one way or another. It is very interesting that the property of each ferroic state is characterized by the behavior it has under space and time inversion. In the material classes under consideration, the coexistence of simultaneous ferroic orders require the violation of both time(temporal) and space inversion symmetries. Because, we know that ferroelectricity is invariant under time inversion symmetry, while ferromagnetism is invariant under space inversion symmetry.

In ferroelectrics and ferromagnetics the symmetric argument can be easily shown by the illustration hereunder. Most of the actively studied multiferrroics lie into complex oxides; compounds which are composed of two or more transition metals and oxygen, and extends to non-oxides such as $BaNiF_4$ and spinel chalcogenides, e.g, $ZnCr_2Se_4$, and recently, "PZTFT" [33].

	Space invariant	Space variant
Time invariant	Ferroelastic	Ferroelectric
Time variant	Ferromagnetic	Ferrotoroidic

Table 2.1: The symmetry relations of the ferroic states.

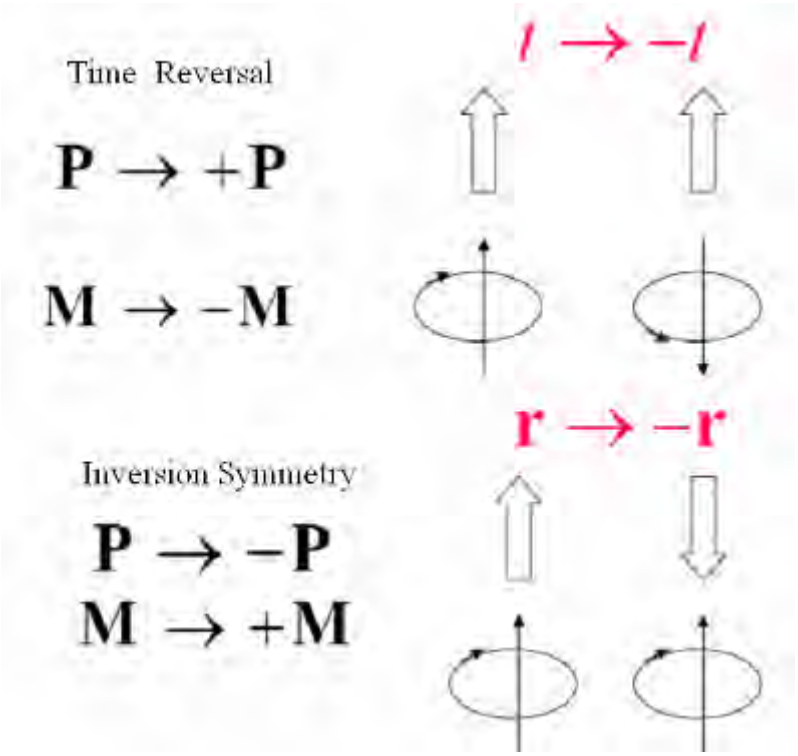

Figure 2.17: The violation of time and space symmetry while both ferroelectric and ferromagnetics are combined in to one component.

2.5.1 Types of Multiferroics

Multiferroics are classified based on either the driving mechanism or the structural compositions. The microscopic origin of magnetism is basically the same mostly in all magnetic materials. However, the situation is very different in materials showing electric polarization. That is, the mechanism of how electric properties arise from is very intricate and wide range, and whence multiferroism mechanisms are different accordingly.These can essentially be divided into two classes the single-phase(usually referred as type-I) and composite(also called

as type-II)[34].

A. Type-I Multiferroics

In this category, ferroelectricity and magnetism have different origins and even occur at different temperatures, usually, well above room temperature. Although, the possibility at high temperature is a positive feature, the small value of coupling order parameter is a sever limitation.

In the following subsections we point out some mechanisms of ferroelectricity which will eventually lead to multiferroism.

1. Multiferroics Perovskites

It is a family name of a group of materials having mineral name of calcium titanate ($CaTiO_3$) exhibiting a structure of the type ABO_3 (where A is a large cation, B is a much smaller cation and O is oxygen; anion) as indicated in the figure. The general principle how ferroelectricity in the perovskites happens is mainly due to the off-center shifts of the transition metal ion, i.e, the B site ion.

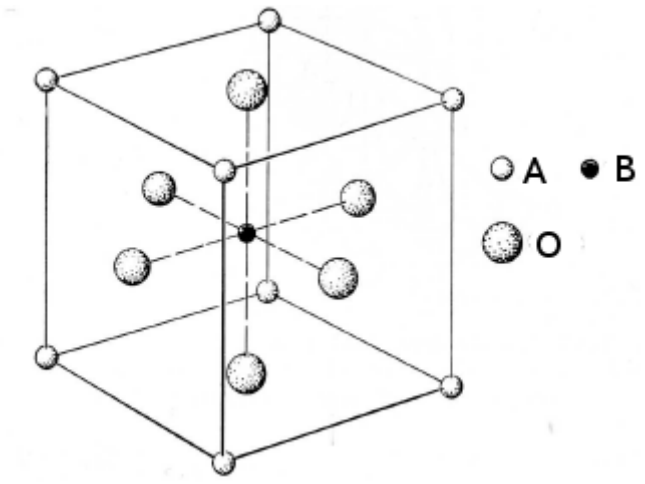

Figure 2.18: The crystal structure of prototype perovskite.

2. Ferroelectricity Caused by Lone pairs

In the perovskite crystals structures unbounded pair of electrons which do not participate in the chemical bonding can lead to ferroelectricity causing hybridization of orbitals between the A site and O site ions allowing structural distortion, which consequently, helps to displace (second-order Jahn-Teller distortion effect) the partially filled B site ions responsible for magnetic properties. Thus, FE and magnetism can be seen in one compound and this mechanism is responsible for compounds of the form $BiRO_3$ (where R =Fe,Mn and Cr), and Some of which are $BiFeO_3$ and $BiMnO_3$

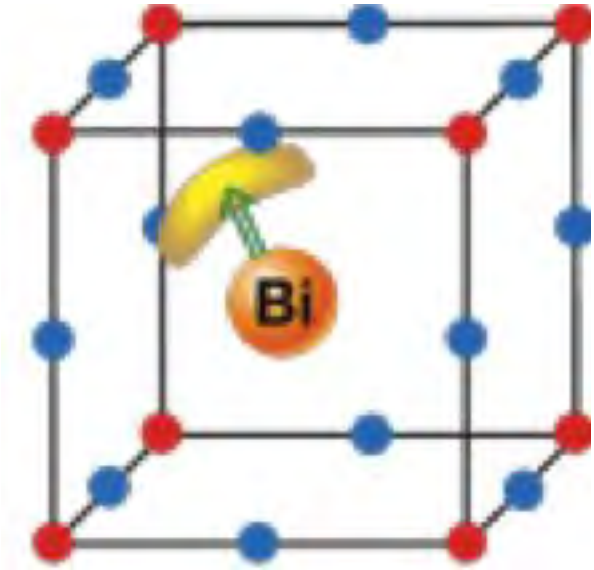

Figure 2.19: The role of lone pairs in a typical perovskite, BFO (Bismith ferrite). The ordering of lone pairs of Bi^{+3} takes the leading role for polarization [34].

3. Ferroelectricity due to Charge Orderings

Crystal structures with different charges, multi-valence ions would have different bond lengths and/ or inequivalent bond strengths that can be indispensable for having materials of various properties. Some of the multiferroics where the charge ordering is considered as a relevant FE mechanism are: the perovskite manganites of $(PrCa)MnO_3$, magnetites (Fe_3O_4), $LuFe_2O_4$ (very strong ferroelectric frustration) and some other organic structures. In this system of ferroelectricity the charge ordering may be of site-centered and bond-centered, or their combinations.

The figure delineates the simple visualization of the mechanism. The charge ordering being it

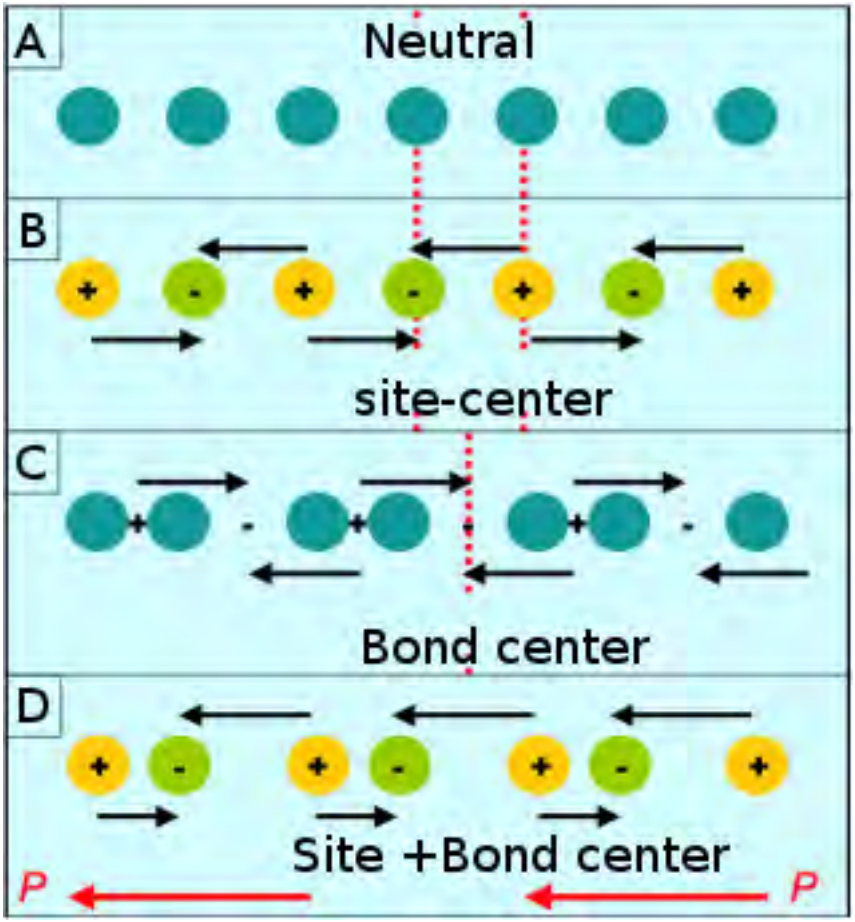

Figure 2.20: The charge ordering mechanism either in the site centered or bond centered and also the combination of the two to induce polarization. Thus, when the magnetic ordering is there one can observe their coexistence [35].

hot issue and not yet well understood can be one of the recent studied mechanism. The event of inequivalent sites and bonds may be of different origins, like the crystallographic structures, and the spontaneous charge ordering (CO) below the phase transition temperature, i.e, the very-wey transition commonly shown in prototypical mineral magnetite Fe_3O_4. In the above figure, "A" indicates the homogeneous crystal charge at every site. While "B" shows the presence of charge ordering at inequivalent sites(site-centered ordering). Whereas "C", shows equivalent sites, while the bonds are varied i.e, bond centered and often quite weak, however, if the bond is so strong it can lead to CDW. Finally in "D" combined effects, i.e, charge ordering due to site

center and bond center orderings leading to symmetry breaking and hence the development of dipole can be realized [36].

4. "Geometric" Ferroelectrics

Another very interesting class of how ferroelectric ordering comes about is realized in the $YMnO_3$.In this case,the ferroelectric appears to be seen not on the displacement of Mn^{+3} ion, but it is due to the strong bond between Y-O, indeed, responsible for dipole formation, that has a tendency to tilt the rigid MnO plane [37]. Temperature dependent studies through

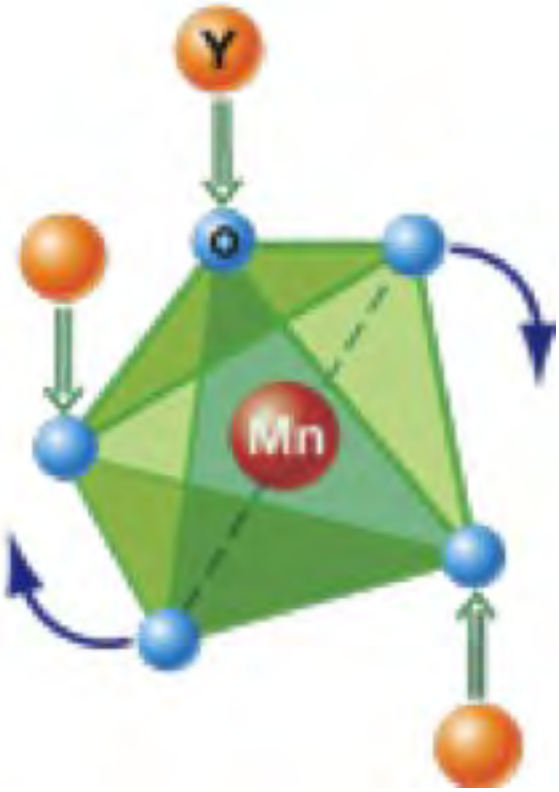

Figure 2.21: The induction of polarization on the expense of the geometric feature of the $RMnO_3$ (Ho, Er, Tm, Yb, Lu, Sc, and Y) classes of materials [38].

Raman scattering verified that the phonon peaks have shown a shift which can be regarded as a result of the interplay of the spin-lattice coupling in these materials. These Hexagonal manganites are in general known to have improper ferroelectricity which could co-exist with the magnetic long range orders. Despite these material classes have the same form of the usual

Table 2 classification of Ferroelectrics

Mechanism of inversion symmetry breaking		Materials
Proper	Covalent bonding between $3d^0$ transition metal (Ti) and Oxygen	$BaTiO_2$
	Polarization of $6s^2$ lone pair of Bi or Pb	$BiMnO_2$, $BiFeO_3$, $Pb(Fe_{2/3}W_{1/2})O_3$
Improper	Structural transition, "Geometric ferroelectrics"	K_2SeO_4, Cs_2CdI_4, Hexagonal $RMnO_2$
	Charge ordering, "Electronic ferroelectric"	$LuFe_2O_4$
	Magnetic ordering , "Magnetic ferroelectrics"	Orthorhombic $RMnO_2$,RMn_2O_5, $CoCr_2O_4$

Table 2.2: The classification of ferroelectric materials.

perovskites,hexagonal manganites are quite different in crystal and electronic structures. Even though, the magnetic ion has no significant attributes to the polarization the specific geometry plays the leading role on the dipole to be created while bonded with the R(small rare earths) ions. The displacement of the B site ion is Not Jahn-Teller type however, FE is caused by a rotation of rigid Mn–O polyhedra. The drawbacks in these classes of materials are the ferroelectric and magnetism are of different nature and hence their coupling is weak.

As well discussed so far, magnetism, especially in multiferroic compounds is related to the localized electrons, mostly, the characteristics of transition metal and rare earth elements. The spontaneous electric polarization, in other words, ferroelectricity requires absence of inversion symmetry. This ferroic ordering is expected to be seen into two possible ways. The "proper" ferroelectrics and "improper" ferroelectrics [39]. In proper ferroelectrics, the main driving force towards the polar state was associated with the electronic pairing. In conventional ferroelectric materials, the polarization arises when nonmagnetic cations shift away from the center of their surrounding anions that leads to a displacement, or non-centrosymmetricity, between positive and negative charges giving rise to the electric dipole moment. $BaTiO_3$ is best known perovskite (ABO_3) ferroelectric material due to the displacement of transition metal ion, i.e, Ti imposed by the covalent bonding with the oxygen ion. In prototypical perovskite structures the geometric centers of A,B, and O ions coincide, resulting in non-polar lattice. But, when polarized, the A and B ions are displaced from their geometric centers with respect to O ions to

induce net polarization. The displacement can occur due to changes in the crystal lattice structure caused by different stimuli. A change in the average polarization corresponds to a change in the position of the ferroelectric ions which can in turn change the position of the magnetic ions, altering the exchange interaction between nearest neighbors. Usually, the displacive type of ferroelectrics require empty d-shells. This, in fact, tends to reduce the possibility that contradicting magnetism to happen together which enforces the demand of partially filled d-shell and also meet the centrosymmetric orientation. Although, the realties seem to be very disparate, primary ferroelectric orders coexist along with magnetism.

On the other hand, the induced polarization in improper ferroelectrics involves a more complex lattice distortion or other accidental orderings with no ionic displacements. Some of the mechanisms of spontaneous symmetry breaking related to structural and other related changes are indicated in table 2. According to the phenomenological theory suggestion spacial modulation and frustrations of the magnetization, is required to have improper ferroelectricity. X Wan et.al have predicted that indirect magnetic exchange interaction, just considering the simplest antiferromagnetic (AFM) insulator MnO, showed the induction of ferroelectricity. In general, as it has been pointed out, the particular subject of interest is to look on the specific mechanism that leads us to have both temporal and spacial symmetry breaking which meets the requirement of MF.

In general, different behaviors between the magnetic and nonmagnetic ions in perovskite structures can be understood as a consequence of the competitive interactions between FE and magnetism and hence the question of d^0 and d^n becomes the central topic to explain multiferroism.

B. Type-II Multiferroics: Magnetic Multiferroics

In conventional ferroelectric materials, uneven displacement, or noncentrosymmetricity, between positive and negative ions gives rise to the electric dipole moment. But in magnetic materials, unlike the former case, the magnetic cation that tends to sit exactly at the center of the surrounding anions, in centrosymmetric positions, interacting with the surroundings are expected to play the role to have the dipole moments.

In this section, emphasis is given on the ferroelectricity induced due to magnetism. In this regard, several proposed mechanisms have been forwarded to describe the ultimate reasons how FE could occur in line with magnetic orderings. Jia and coworkers systematically investigated magnetically induced ferroelectricity in Motti insulator transition metal oxides strictly into three main mechanisms: The first is based on the exchange striction where ferroelectric polarization is due to the change of a materials' physical dimensions in response to changing the magnetization. This is attributed from the crystallographic deformations induced by changing bonding as a result of magnetic ordering which in turn is because of magnetic frustrations. The second belongs to the spin-current (or vector spin chirality) mechanism(flow of magnetic dipole; spin current produces the electric field perpendicular to the direction of the velocity and spin polarization). And lastly, the third type is the d-p hybridization mechanism. In this case it predicts spontaneous symmetry breaking in some crystal structures of noncollinear magnetic structures attributed by the spin-orbit interaction [40]. It is interestingly different from the way ferroelec-

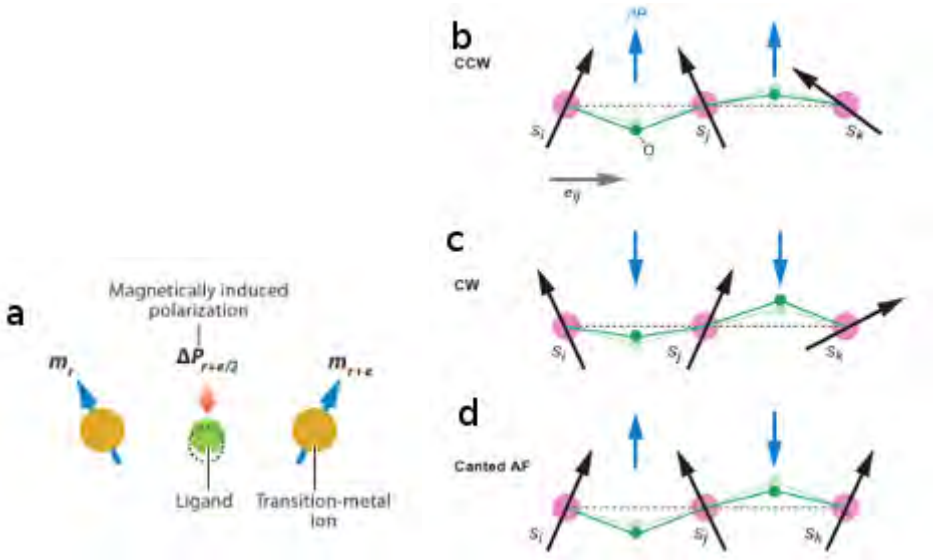

Figure 2.22: Induction of Ferroelectricity by spin-current structures just in conjugation of electronically driven or lattice driven interactions.The microscopic spin current mechanism ($S_i \times S_j$) induced between noncollinear spin states results electric polarization in $TbMnO_3$. It also describes how the polarization changes its direction while the helicity of the spiral changes subsequently [40,41,42,43,44,45].

tricity exists in type-I materials. Here, it appears to be true that the spontaneous polarization sets

at the same temperature that the magnetic ordering do exist. Certainly, it means that ferroelectricity turns out to be the consequence of magnetic ordering phenomena [46], unlike the type-I where their orderings are at very different temperatures. In 2003, Kimura et al, reported the presence of spontaneous polarization in the magnetized state of the $TbMnO_3$ that has various interesting and remarkably variable magnetic structures at different temperatures. Afterwards, similar observations followed in $TbMn_2O_5$ and subsequently variety of other materials have also been investigated such as $Ni_3V_2O_8$ and $MnWO_6$ showing this effect. Magnetic spin structure which are responsible for the appearance of FE can be either a non-collinear spiraling cycloid type or a collinear type [47]. Nevertheless, it is worthwhile to imagine that magnetic structures are not as so simple in these types of crystal structures [31].

Magnetically induced ferroelectricity in type-II multiferroics can mainly grouped into:

A) Spiral type-II Multiferroics:

These belong to spiral magnetic structures of different spin orientations, i.e, canted antiferromagnetic states examined to produce electric polarizations [48].

This is clearly shown by the illustration below. It is theoretically considered in the inverse DM interaction where noncollinear spiral spin magnetic structures are also possible routes for ferroelectricity and experimental evidences to confirm the spin-current mechanism which helps for FE induction have been observed in $RMnO_3$ (R = Tb, Dy, Gd, and others), in such a way that the direction of electric polarization is found to be controlled by changing the direction of cycloid plane with the external magnetic field [49].

B) Collinear type-II multiferroics: There might happen in some cases that the spin-current model can not well explain the scenario of how electric dipoles induced (i.e in the case when $S_i \times S_j = 0$). In other wards, non-spiral spin states (where magnetic moments are coupled to parallel or antiparallel to their nearest neighboring) can also give rise to spontaneous polarizations [50]. Another magnetic structure that has a remarkable contribution for the ferroelectricity based on magnetic ordering is the collinear spin structure. In one dimensional array of magnetic moments, the configuration of spins can also lead to electric dipoles. This can happen due to the magnetic exchange striction interaction between the nearest neighbors, next nearest neighbors and to the long range-order interactions of the spins depending on the magnetic structure where a periodic modulation of symmetric exchange interactions accompanied by the lattice distortion

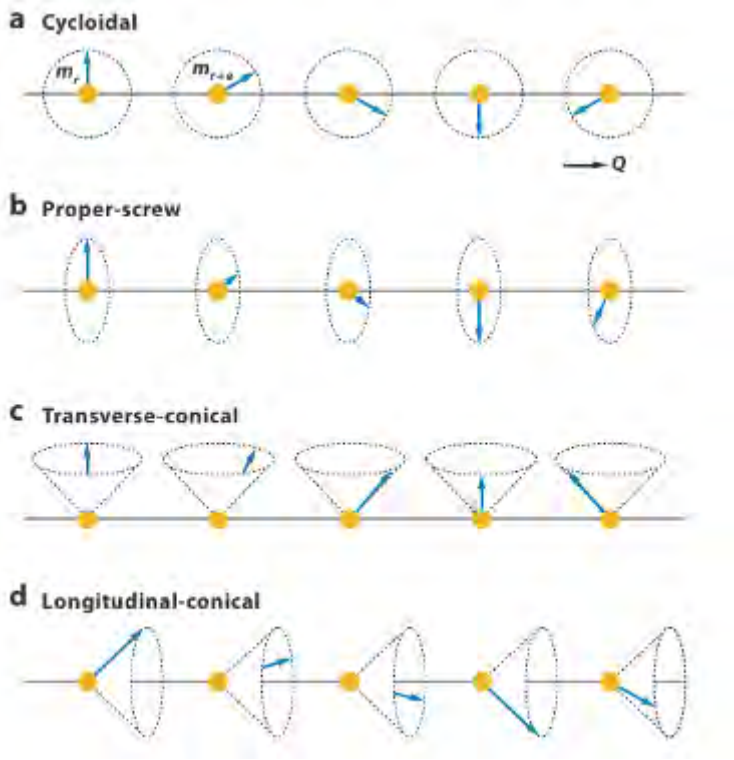

Figure 2.23: Illustrations depicting spiral spin configurations which can be considered as possible sources of ferroelctricity [40].

in the system as a whole enhanced the ferroelectricity phenomenon in general. However, this requires a detail investigation of somehow relevant crystallographic and magnetic structures for better understanding of the mechanism. The major challenges here are that the coupling of order parameters occur at low temperatures and also the complex magnetic ordering structure is the result of magnetic frustrations which, of course, has an impact on the magnetic states to be stable.

2.5.2 Flexomagnetoelectric Effect

Besides, from these major categories of multiferroics based on the microscopic mechanism in which the ordered states couple to each other, recently, large number of materials coming to join the zoo and attracting much more attentions while they exhibit extraordinary couplings. An alternative method of achieving high degree of coupling between ferroic orders is attained through the mixing of ferroelectric and ferromagnetic materials in deferent forms, such as combining

the two phases either in the form of composites of epitaxial layers, and [51,52,53] laminates [54,55,56,57,58,59].

To date, magnetic inhomogeneity structure and ferroelectric inhomogeneity can be taken as another way of look at for multiferroism. The magnetoelectric coupling can appear due to the coupling between the inhomogeneous order parameters. This effect literally called flexo-magnetoelectric effect is best described by the dynamics of domains and domain walls, and vortexes [60,61,62,63,64,65] that include much of the physics in the multiferroics world as of every material having domains of technological merits for imminence and immense data manipulation and processing [65,66,67,68,69,70,71,72]. As a major challenge in this approach is that the coupling requires high perfection of the interfacing contacts between the compartments of different orders.

2.6 Electromagnons

In magnetic solids electrons as we are well aware play substantive and key roles in determining the specific properties of the system, and particularly, the magnetic phenomena tightly rely on the quantum nature of the spins and their associated magnetic moments. On the other hand, the physics of solids begin from the crystals and the low-energy arrangement of atoms and ions within these crystals are so often periodic. It seems that nature has provided a gift to all matter to be in the lowest energy state; the ground state. However , maintaining equilibrium states and linear elasticity fails due to real interactions and the nature of the crystal. In qualitative aspects, one can consider the microscopic deformation of lattice points with an amplitude comparable to inter-atomic separation which can be attributed from the vibration of crystalline lattices. Most interactions in solids involve elementary excitations as observed in spectroscopic measurements and their frequency ranges are also in the energy scale ranges of the interaction. The prominent excitations are the magnetic ones also called magnons and the second belongs to the excitation of elastic lattice vibration, the phonons [73].

In recent years, the evolution of multiferroics has come to be the focus of attention because of the fertility of the subject on modulating these aforementioned zoos of excitations on the same platform.

2.6.1 The Spin Wave Theory

The complex magnetic structures found in multiferroics result from the geometrical spin frustration and the presence of more than one type of magnetic ions in the crystal structure. To have an insight of the detailed behaviors of the system, modeling is an essential step since finding the solution of full Schrodinger equation is quite cumbersome in complex structures of solids. However, in magnetic insulators Heisenberg model is proven to be useful in describing magnetic properties [74]. The relevant magnetic interaction in ideal cases, i.e, a system which is supposed to be free from anisotropy, where the atoms or ions are arranged in regular lattice positions each of them carrying a total spin S is written as

$$H = -\sum_{ij} J_{ij} S_i . S_j - g\mu_B B \sum_i S_i^z \tag{2.16}$$

Where J_{ij} is the measure of magnetic exchange interaction between the spins at sites i and j, and can be positive(negative) for FM(AFM) interactions, B is the magnetic field pointing in the z-direction. To solve the Hamiltonian, we restrict ourselves into a particular type of magnetic interaction, for convenience, and is in fact the simplest, we consider the ferromagnetic interaction. The ground state in this case corresponds to spin configurations in which all the spins align in the same direction,i.e, along the magnetic field. And also, we specify the possible number of nearest neighbors (the coordination number) z, of the total number of N lattice points. The spin deviation states can be produced by the spin operators upon changing the ground states. Thus, the spin raising and lowering operators are defined as,

$$S_i^{(\pm)} = S_i^x \pm i S_i^y$$

The spin commutation relation leads to satisfy the condition

$$[S_i^-, S_j^+] = 2S_i^z \delta_{ij}$$

The exchange interaction between the spins breaks up the degeneracy and induce band such that this band can be described in terms of the quantized energy levels considering the quasi-particle excitations. In this regard, to deal with such a system based on the elementary excitations we can transform the spin operators into bosonic operators using the Holstein Primakoff transformation

$$S_i^+ = a_i (2S)^{\frac{1}{2}} \sqrt{1 - \frac{a_i^\dagger a_i}{2S}} \tag{2.17}$$

$$S_i^- = a_i^\dagger (2S)^{\frac{1}{2}} \sqrt{1 - \frac{a_i^\dagger a_i}{2S}} \tag{2.18}$$

$$S_i^z = S - a_i^\dagger a_i \tag{2.19}$$

The Boson operators $a_i^\dagger$ and a_i satisfy the usual commutation rule $[a_i, a_{i'}^\dagger] = \delta_{ii'}$ and the Hamiltonian to the lowest order becomes,

$$H \approxeq E_0 - JS \sum_{ij} [a_i^\dagger a_j + a_j^\dagger a_i - a_j^\dagger a_j - a_i^\dagger a_i] \tag{2.20}$$

Where $E_0 = -\frac{NZ}{2} JS^2 + NBg\mu_B S$ is the ground state energy of the spin system. The intermediate Hamiltonian is diagonalized choosing the suitable linear combinations such that taking the Fourier transforms and introducing new operators spanned by the wave number k, in momentum space,

$$a_k^\dagger = \frac{1}{\sqrt{N}} \sum_{i'} a_{i'}^\dagger exp(ik.i') \tag{2.21}$$

$$a_k = \frac{1}{\sqrt{N}} \sum_{i'} a_{i'} exp(-ik.i') \tag{2.22}$$

Therefore, for the Green function defined by these operators, i.e, $G(k, k'; t) = \ll a_k^\dagger(t), a_{k'}(0) \gg$ its equation of motion in the Fourier transform becomes

$$[\hbar\omega - E(k)] G(k, k'; \omega) = -\delta_{kk'} \tag{2.23}$$

Where this results to a very interesting expression usually termed as the magnons or spin waves characterizing the magnetic excitation. In magnetic materials the spin waves have been studied through inelastic neutron scattering measurements and provided a very direct way to understand the excitation phenomena related to it.

$$E(k) = g\mu_B B + JS \sum_{\triangle} [1 - cos(k.\ \triangle)] \tag{2.24}$$

$\triangle$ is the nearest neighboring lattice vector. Therefore, this equation describes the spin waves or magnons that are usually understood in the framework of semiclassical description and can be visualized as small oscillations of classical spin vectors around their equilibrium positions in the ground state spin structure.

2.6.2 Lattice Vibration Theory

A solid is an interacting system of particles. These interacting particles in general are of two types, i.e, the lattice ions and valence electrons. The valence electron region is the broadest electron cloud portion and whereas the lattice ion is composed of the atomic nuclei plus the core electrons which are strongly bounded and highly localized electron clouds to the vicinity of the nucleus. An ensemble of lattice ions vibrate even when a single ion deforms about an equilibrium position or collied with other particles to microscopic scales which have vibrational effects to the whole crystalline lattices in the solid. The local lattice effect transformed into collective lattice vibration modes has to be quantized as phonons(traveling waves in solids) [75].

The study of this quantized lattice vibration enables to an understanding of how the crystal interacts with, such as mechanical and electromagnetic forces and others to explain the physical properties accordingly. To deal the motion of such subsystem of ions we denote the total energy functional as a function of arbitrary location u^i of the ions.

$$\varepsilon(u,^1 u^2, ...u^N) \tag{2.25}$$

The Taylor expansion of this energy at very small lattice deviation becomes

$$\varepsilon = \varepsilon_c + \sum_{\alpha l} \frac{\partial \varepsilon}{\partial u^l_\alpha} u^l_\alpha + \frac{1}{2} \sum_{\alpha\beta l l'} u^l_\alpha \phi^{ll'}_{\alpha\beta} u^{l'}_\beta + ... \tag{2.26}$$

Here α and β are cartesian indices running for basis unit vectors. Whereas u^l is the deviation vector of the ion from the ground state location R^l. The potential matrix function to the second order is $\phi^{ll'}_{\alpha\beta} = \frac{\partial^2 \varepsilon}{\partial u^l_\alpha \partial u^l_\beta}$. Let's introduce the phonon raising and lowering operators to evaluate the specific Hamiltonian comprising the kinetic and potential terms in the second quantization formalism. We used the notation c and $c^\dagger$ the annihilation and creation operators of phonons respectively.

$$c = \sqrt{\frac{M\omega}{2\hbar}} R + i \sqrt{\frac{1}{2\hbar M\omega}} P \tag{2.27}$$

$$c^\dagger = \sqrt{\frac{M\omega}{2\hbar}} R - i \sqrt{\frac{1}{2\hbar M\omega}} P \tag{2.28}$$

Thus, the particle position and momentum operators are obtained as

$$R = \sqrt{\frac{\hbar}{2M\omega}} (c + c^\dagger) \tag{2.29}$$

$$P = i\sqrt{\frac{\hbar M\omega}{2}}(c^{\dagger} - c) \tag{2.30}$$

Analogously defining the phonon operators as

$$c_{q\nu} = \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{-iq.R^l}\epsilon_{q\nu}.[\sqrt{\frac{M\omega_{q\nu}}{2\hbar}}u^l + i\sqrt{\frac{1}{2\hbar M\omega_{q\nu}}}P^l] \tag{2.31}$$

$$c_{q\nu}^{\dagger} = \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{iq.R^l}\epsilon_{q\nu}.[\sqrt{\frac{M\omega_{q\nu}}{2\hbar}}u^l - i\sqrt{\frac{1}{2\hbar M\omega_{q\nu}}}P^l] \tag{2.32}$$

$\epsilon_{q\nu}$ is the phonon polarization unit vectors, and $\nu = 1, 2, 3$, While u^l and P^l are defined to be

$$u^l = \frac{1}{\sqrt{N}}\sum_{q\nu}[u_{q\nu}e^{iq.R^l} + u_{q\nu}^{\dagger}e^{-iq.R^l}] \tag{2.33}$$

Where

$$u_{q\nu} = \sqrt{\frac{\hbar}{2M\omega_{q\nu}}}\epsilon_{q\nu}c_{q\nu}$$

And

$$P^l = \frac{1}{\sqrt{N}}\sum_{q\nu}[P_{q\nu}e^{iq.R^l} + P_{q\nu}^{\dagger}e^{-iq.R^l}] \tag{2.34}$$

While

$$P_{q\nu} = -i\sqrt{\frac{\hbar M\omega_{q\nu}}{2}}\epsilon_{q\nu}c_{q\nu}$$

From the usual commutation relation $[P^l, R^l] = -i\hbar$, it follows that $[c_{q\nu}, c_{q\nu}^{\dagger}] = 1$ is satisfied. Then the simple model Hamiltonian describing the lattice ions energy defined by the following expression

$$H = \sum_{l}\frac{{P^l}^2}{2m} + \frac{1}{2}\sum_{ll'}u^l\phi^{ll'}u^{l'} \tag{2.35}$$

can be simplified setting the condition of symmetry $\phi(q) = \phi(-q)$ and also considering the fact that $\omega_{-q\nu} = \omega_{q\nu}$. Therefore, With these conditions, one can find

$$H = \sum_{q\nu}\frac{\hbar\omega_{q\nu}}{2}[c_{q\nu}c_{q\nu}^{\dagger} + c_{q\nu}^{\dagger}c_{q\nu}] \tag{2.36}$$

This can also be reduced to a single index notation of quantized lattice vibration energy defined by discrete frequency and the phonon number occupation.

$$H = \sum_{i}\hbar\omega_i(n_i + \frac{1}{2}) \tag{2.37}$$

2.6.3 Electromagnons Earmarked from Spin Wave and the Lattice Vibration

In the above subsections we introduce the excitation mode of lattice vibrations and magnetic excitation systems separately. But, in recently discovered magnetoelectric material system having magnetic and electric properties implicitly, collective modes of excitations become common practical quasi-particles,especially, in magnetically induced multiferroics. These materials with both polar and magnetic order parameters usually show a relatively low-symmetry crystal structure due to the absence of both time and space inversion symmetries; hence a strong interaction between the low-lying magnetic and lattice excitations can be highly expected to produce spin waves that interact with uniquely polarized light upon manifestation of electric properties from lattice vibrations, leading to rich new physics phenomena such as "electromagnons". This hybridized magnon-phonon excitation, implies that magnetic excitations are possible through electric fields and vice versa. The coupling of these properties leads to the cross-controlling of magnetism and polarizations [30,76,77].

A necessary, but not a sufficient, condition for the existence of electromagnons is the appearance of unusual symmetry breaking. Magnetically induced ferroelectricity may arise from lattice distortions and spin orderings in addition to the frustrated spin configurations. In the non-collinear spin ordering structures Dzyaloshiniskii-Moriya interaction activated by concomitant lattice and electronic distributions can be considered for the spontaneous electric polarization. Whereas, in the collinear spin orderings that can be attributed for ionic distortions and polarizations of electronic clouds, strong spin interactions can be explained by the symmetric Heisenberg exchange interaction. These magnetoelectric interactions couple the oscillations of magnetic type and polar lattices. The dynamical aspects of such collective excitation continuum of two magnon and a phonon system, indeed, results from the spin-lattice coupling process [78].

As an experimental evidence, Pimenov et al reported on the $GdMnO_3$ and $TbMnO_3$ samples that there is spectral weight transfer from the lowest frequency phonons down to the electric active modes of magnon frequency in low energy and temperature scales. There are also strong electric dipole active modes emerging from low frequency phonon modes in YMn_2O_5 and $TbMn_2O_5$ with the unique features for both families, that is, they are active only in one polar-

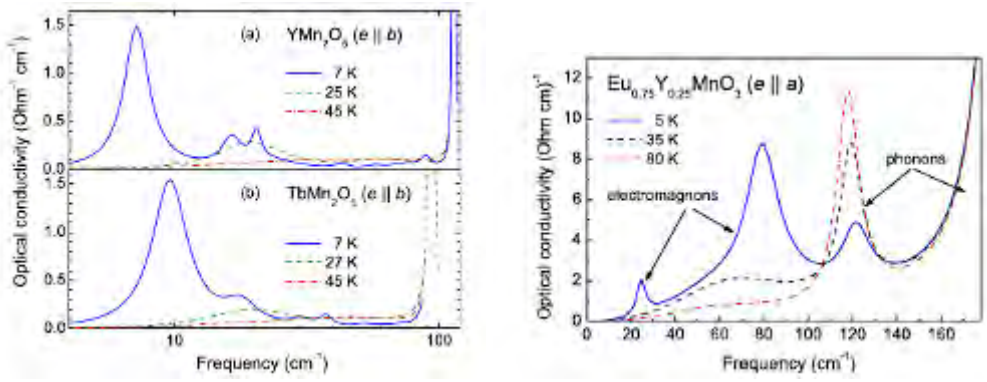

Figure 2.24: Electromagnon modes with two peaks emerging from low frequency phonon in very common and well studied multiferroic materials [78].

ization $e||a$ axis for $RMnO_3$ and $e||b$ axis for RMn_2O_5, where e is the electric field of light; well defined peaks exist only in the low-temperature magnetic ferroelectric phase. Therefore, electromagnons are obeyed by some sort of selection rules and spin excitation is susceptible to the direction of light polarization. However, this phenomenon is explained on the basis of lattice distortion accompanied by the Mn-O bonds, and not on the spiral plane orientation [79].

In the $TbMnO_3$ compound the electric polarization is switched by the magnetic field. It has been discussed thoroughly by Kimura that a magnetic field of the order of 4-8 T in the b-axis suppresses the polarization in the c-axis while inducing the a-axis polarization. This suppression is attributed to the metamagnetic phase transition. Likewise, the magnetic field in the a-axis also suppresses the c-axis polarization. The effect of magnetic fields along the c axis is distinct from that along the a and b axes. The electric polarization vanishes for all crystallographic directions by the application of a high magnetic field along the c axis. Therefore,making use of these magnetoelectric multiferroics, ferroelectric order can be either induced or suppressed by the application of a magnetic field. Furthermore, the direction of the ferroelectric polarization vector can be switched by 90^0 and 180^0 or even turned full circle by the use of magnetic fields [49,40].

The first experimental observation of collective mode excitation of magnons and phonons was performed through optical spectroscopic measurements [80] and another spectacular finding was made on $Eu_{0.75}Y_{0.25}MnO_3$ where well defined absorption peaks have been observed from mode mixing of magnetic excitations and phonons, while their strong interactions give

rise to the spectral weight lose of the phonon mode [81]. Afterwards some more investigations leading to many stimulating experimental works have been performed successfully. The possibility of electromagnonic excitation was anticipated long before their experimental observation. Nevertheless, the theoretical explanation of electromagnons is still being debated. In some rare earth manganite classes ($RMnO_3$) a reasonable theoretical description was suggested through the spin current model which predicts that the rotation of the spiral spin plane is excited by the electric field component of light and latter this has been confirmed experimentally. Another approach that accounts for the magnetic interaction leading to the electromagnons is [77,82] through symmetric exchange interactions of collinear spin orders.

Chapter 3

Interaction of Quanta of Electromagnetic Field and Magnons in Magnetoelectrics

Magnetoelectrics find new applications in magnetic as well as electrical devices. The coupling of magnetic and electric degrees of freedom offers strong electron correlations in real many-body interactions that arises from the quantum mechanical behaviors of the charges, spins and lattice vibrations. The magnetic behaviors and quantum of electromagnetic field (photon) interaction in the magnetoelectrics which represents strongly correlated systems of ferroelectromagnets has been treated theoretically using the double time Green function. The fluctuations of number densities, arising from the exchange coupling of the two domains (magnons and photons) characterized by the joint number density operators in imaginary components of the Green's function accounts for the subsequent damping in the quantum electromagnetic field and the magnonic oscillations in the time evolution which tends to measure the life time about which the excitation takes.

3.1 Introduction

Magnetoelectronics means, in the broadest possible terms, the manipulation of the electronic charge transport by the spin-degrees of freedom elucidating on the interplay between the spin, charge, and lattice correlations in the material system [83]. In the more narrow technical sense it refers to a new electronics which uses magnetoresistive properties in device applications.

In conventional materials, the electric polarization is proportional to the electric field, and the magnetization is proportional to an applied magnetic field. However, magnetoelectric materials, most of which are transition metal oxides and rare earth manganites or ferrites, show appreciable coupling of magnetizations and polarizations [84,85]. As a result, the magnetization and electric polarizations of these materials can be influenced by either of applied magnetic (or electric) field [86,87]. Particularly, the interaction effect is usually very strong in some classes of materials with simultaneous electric and magnetic orderings such as multiferroics. These materials, be it single phase or composite, exhibit new types of excitations enabling to magnonic excitations with electromagnetic quantum field, and controlling of the polar lattice vibrations (polarizations) by magnetic switches [88]. It emphasizes on two magnon absorptions because of magnetodipole and dipole exchange interaction. The coupling of spin and charge degrees of freedom becomes crucially important so as to study the fundamental mechanism of magnetoelectric phenomena in magnetoelectronics.In this study the dynamical magnetoelectric excitation is described on the basis of isotropic Heisenberg exchange interaction subjected to electromagnetic quantum field represented by the corresponding vector potential. Magnetic excitations that induce electric polarization can be excited by the electric field component of the electromagnetic quantum field, as R. Valdes et al., (2009) have pointed out in their work, which provides an insight for the cross coupling of two seemingly disparate events [89].

3.2 Formulating Mathematical Model Hamiltonian

The perovskite crystal structural compounds show many structural modifications. These families of oxides are best known to have distortions(reduced symmetry) and non-stoichiometry (lack definite proportion between constituents) that leads to various magnetic and electric properties. Particularly, transition metal ions at B site show intrigue properties because of the complex characters the transition metal ions play in coordination with the oxygen along with the atomic size effects at site A(typical to rare-earths). In this section we tried to develop a mathematical model that well describe systems of such classes of materials at low dimension. We describe a 2D system as a lattice of atoms, each of which has a single atomic level which then can be occupied by at most two electrons (of opposite spins). In the atomic limit, in the ground state,

each site is occupied and we can consider the electric dipole interaction of lattice ions (dipoles induced by the centro-symmetric distortion, typical to perovskite classes due to their crystal structure) with valence electron cloud that gives rise to an interacting system of electromagnetic wave modes characterized by the vector potential and the localized electronic spins that leads us towards the Heisenberg model of exchange interaction. We have added to the Hamiltonian a Zeeman term, in order to take account of the interaction of the local moments with the applied and/ or intrinsic magnetic field. The electron spin couples to applied and/ or intrinsic electric field through spin exchanges and spin-orbit interactions, particularly, in this study the John Teller lattice distortion can play pivotal role to conceive of the quantum electromagnetic field [90,91,92]. The model Hamiltonian can be written as.

$$\hat{H} = -\sum_{ij} J_{ij}\vec{S}_i.\vec{S}_j - g\mu_B \sum_i \hat{B}_i.\vec{S}_{iz} - \mu \sum_i \hat{E}_i.\vec{S}_{iz} + D\sum_i S_{iz}^2 \tag{3.1}$$

The parameters μ and D are electric field-spin coupling(spin stiffness) and (single-ion anisotropies: anisotropy arising from spin-orbit coupling of ion) magnetic anisotropy. The anisotropy in magnetism is possible since the magnetic structure can not be uniform in every lattice points of the crystal and also the orbital moments,especially, contributed by the f electron orbitals of the rare-earth ions substantially changes the characters of the elementary excitations providing the polarization-spin couplings [91,93]. For material medium,the quantized electromagnetic field described by Fourier series expansion of the complex transverse field vector potential A, obeying the coulomb (transverse or radiation) gauge $\bigtriangledown.\hat{A} = 0$ that requires the condition $\hat{e}_{k\sigma}.k = 0$ and $\hat{e}^*_{k\sigma}.k = 0$, is expressed in terms of time-dependent bosonic annihilation and creation field operators $c_{k\sigma}$ ($c^\dagger_{k\sigma}$) based on the Heisenberg picture [94]. Whereas, $\hat{e}_{k\sigma}(\hat{e}^*_{k\sigma})$ is the polarization unit vector ($|\hat{e}_{k\sigma}| = |\hat{e}^*_{k\sigma}| = 1$) which, obviously, is orthogonal to k; accordingly, there exist two linearly independent orientations corresponding to two independent planes of polarization.

$$\hat{A}(r,t) = \sum_{k\sigma} \sqrt{\frac{\hbar}{2\omega V\epsilon'}}(\hat{e}_{k\sigma}c_{k\sigma}e^{ik.r} + \hat{e}^*_{k\sigma}c^\dagger_{k\sigma}e^{-ik.r}) \tag{3.2}$$

Here the field operators are to be obtained from Maxwell's equations in the absence of source (no real or displacement current); the magnetoelectrics are insulating dielectrics materials and lack free charges. That is, source and sink free and thus divergence free. Therefore, we can find the field expressions from the divergences:

$\nabla.D = 0$ and $\nabla.B = 0$ then it follows that,

$$\hat{E} + \frac{\partial \hat{A}}{\partial t} = - \nabla \phi$$

With zero gradient, the field operators are obtained to be

$$\hat{E}(r,t) = -\frac{\partial \hat{A}}{\partial t} = i \sum_{k\sigma} \sqrt{\frac{\hbar\omega}{2V\epsilon'}} (\hat{e}_{k\sigma} c_{k\sigma} e^{ik.r} - \hat{e}^*_{k\sigma} c^\dagger_{k\sigma} e^{-ik.r}) \tag{3.3}$$

$$\hat{B} = \nabla \times \hat{A} = i \sum_{k\sigma} \sqrt{\frac{\hbar}{2\omega V\epsilon'}} (k \times \hat{e}_{k\sigma} c_{k\sigma} e^{ik.r} - k \times \hat{e}^*_{k\sigma} c^\dagger_{k\sigma} e^{-ik.r}) \tag{3.4}$$

Where V is the volume of the system, and ϵ' is the dielectric constant of the system under consideration while σ takes values transverse to the propagation of the quantum field. The transverse nature of the electromagnetic field restricts us to chose σ in particular sets. The field operators are reduced to the following forms for real polarization unit vectors and to some specific easy axis of magnetization, +z-direction [95,96].

$$\hat{E} = i \sum_{k\sigma} \varepsilon \hat{e}_{k\sigma} (c_{k\sigma} e^{ik.x} - c^\dagger_{k\sigma} e^{-ik.x}) \tag{3.5}$$

$$\hat{B} = i \sum_{k\sigma} \xi \hat{e}_{k\sigma} (c_{k\sigma} e^{ik.x} - c^\dagger_{k\sigma} e^{-ik.x}) \tag{3.6}$$

Where $\varepsilon = \sqrt{\frac{\hbar\omega}{2V\epsilon'}}$ and $\xi = \sqrt{\frac{\hbar\omega\mu'}{2V}}$ are electric and magnetic field amplitudes. The symbol μ' denotes the magnetic permeability. The Hamiltonian is solved using these operators and the spin variables transformed into magnon operators.

$$\mu \textstyle\sum_i \hat{E}_i.\vec{S}_{iz} = i\mu \sum_{k\sigma i} \varepsilon \hat{e}_{k\sigma} (c_{k\sigma} e^{ik.x_i} - c^\dagger_{k\sigma} e^{-ik.x_i}).(S - N^{-1} \textstyle\sum_{k',k''i} e^{i(k'-k'').x_i} b^\dagger_{k'} b_{k''}) \hat{z}$$

Where $b_{k's}$ are Heisenberg operators and the z-component of the spin at i^{th} site is defined by $S_{iz} = S - N^{-1} \sum_{k',k''i} e^{i(k'-k'').x_i} b^\dagger_{k'} b_{k''} \hat{z}$, and we have, [1] [2]

$$\mu \textstyle\sum_i \hat{E}_i.\vec{S}_{iz} = i\mu \sum_{k\sigma i} \varepsilon (c_{k\sigma} e^{ik.x_i} - c^\dagger_{k\sigma} e^{-ik.x_i}) S \hat{e}_{k\sigma}.\hat{z}$$
$$- i\mu N^{-1} \textstyle\sum_{k,k',k''\sigma i} \varepsilon [e^{i(k+k'-k'').x_i} c_{k\sigma} b^\dagger_{k'} b_{k''} - e^{-i(k-k'+k'').x_i} c^\dagger_{k\sigma} b^\dagger_{k'} b_{k''}] \hat{e}_{k\sigma}.\hat{z}$$

Summing over i, at $k = -(k' - k'')$ and $k = -(-k' + k'')$, then it becomes

$$\mu \sum_i \hat{E}_i.\vec{S}_{iz} = (i\mu \sum_{k\sigma} \varepsilon N (c_{k\sigma} - c^\dagger_{k\sigma}) S - i\mu \sum_{,k',k''\sigma} \varepsilon [c_{-(k'-k'')\sigma} b^\dagger_{k'} b_{k''} - c^\dagger_{(k'-k'')\sigma} b^\dagger_{k'} b_{k''}]) \hat{e}_{k\sigma}.\hat{z} \tag{3.7}$$

[1] In this chapter, $c(c^\dagger)$ denotes the photon operator with the wave vector k.

[2] Whereas, the $b(b^\dagger)$ stands for magnonic operators of the corresponding wave vector k'.

Similarly,

$$g\mu_B \sum_i \hat{B}_i.\vec{S}_{iz} = ig\mu_B \sum_{k\sigma i} \xi \hat{e}_{k\sigma}(c_{k\sigma}e^{ik.x_i} - c^{\dagger}_{k\sigma}e^{-ik.x_i}).(S - N^{-1}\sum_{k',k''i} e^{i(k'-k'').x_i} b^{\dagger}_{k'}b_{k''})\hat{z}$$

$$g\mu_B \sum_i \hat{B}_i.\vec{S}_{iz} = (ig\mu_B \sum_{k\sigma} \xi N(c_{k\sigma} - c^{\dagger}_{k\sigma})S - ig\mu_B \sum_{,k',k''\sigma} \xi[c_{-(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''} - c^{\dagger}_{(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''}])\hat{e}_{k\sigma}.\hat{z} \tag{3.8}$$

Finally, the Hamiltonian becomes

$$\begin{aligned} H = &-\sum_{i\delta} J_{i,i+\delta}[S^2 - \tfrac{S}{N}\sum_{k',k''}(e^{i(k'-k'')x_{i+\delta}}b^{\dagger}_{k'}b_{k''} + e^{i(k'-k'')x_i})b^{\dagger}_{k'}b_{k''} \\ &+ \tfrac{S}{N}\sum_{k',k''} e^{-i(k'-k'')x_i}e^{ik''\delta}b_{k'}b^{\dagger}_{k''} + \tfrac{S}{N}\sum_{k',k''} e^{i(k'-k'')x_i}e^{-ik''\delta}b^{\dagger}_{k'}b_{k''}] \\ &- (ig\mu_B \sum_{k\sigma} \xi N(c_{k\sigma} - c^{\dagger}_{k\sigma})S - ig\mu_B \sum_{,k',k''\sigma} \xi[c_{-(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''} - c^{\dagger}_{(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''}])\hat{e}_{k\sigma}.\hat{z} \\ &- (i\mu \sum_{k\sigma} \varepsilon N(c_{k\sigma} - c^{\dagger}_{k\sigma})S - i\mu \sum_{,k',k''\sigma} \varepsilon[c_{-(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''} - c^{\dagger}_{(k'-k'')\sigma}b^{\dagger}_{k'}b_{k''}])\hat{e}_{k\sigma}.\hat{z} \\ &+ D(NS^2 - \frac{2S}{N}\sum_{k',k''} e^{i(k'-k'')x_i}b^{\dagger}_{k'}b_{k''}) + o(h) \end{aligned} \tag{3.9}$$

We restrict ourselves to the condition that the exchange interaction term existing in the next-nearest neighbors and farther neighbors tends to decay exponentially. This equation can be simplified for z-nearest neighbors of the total atoms of N and isotropic Heisenberg nearest neighbor exchange interaction $J_{i,i+\delta} = J\delta_{i,i+\delta}$ that could determine either ferromagnetic(FM) or anti-ferromagnetic (AFM) character of the system. This Hamiltonian, re-arranging on the bilinear operator terms and neglecting the higher order terms can be reduced to the following form

$\hat{H} = H_1 + H_2 + H_3 + H_4$

Where,

$$H_1 = -JNzS^2 + DNS^2 \tag{3.10}$$

$$H_2 = -ig\mu_B \sum_{k\sigma} N\xi(c_{k\sigma} - c^{\dagger}_{k\sigma})S - i\mu \sum_{k\sigma} N\varepsilon(c_{k\sigma} - c^{\dagger}_{k\sigma})S \tag{3.11}$$

$H_3 = -\sum_{k',k''}[2JzS(\gamma_{k'} - 1) + 2DS]\delta_{k'k''}b^{\dagger}_{k'}b_{k''}$

$$H_3 = -\sum_{k'}[2JzS(\gamma_{k'} - 1) + 2DS]b^{\dagger}_{k'}b_{k'} \tag{3.12}$$

$$H_4 = ig\mu_B \sum_{k'k''\sigma} \xi(c_{-(k'-k''),\sigma}b^{\dagger}_{k'}b_{k''} - c^{\dagger}_{(k'-k''),\sigma}b^{\dagger}_{k'}b_{k''}) + i\mu \sum_{k'k''\sigma} \varepsilon(c_{-(k'-k''),\sigma}b^{\dagger}_{k'}b_{k''} - c^{\dagger}_{k'-k'',\sigma}b^{\dagger}_{k'}b_{k''}) \tag{3.13}$$

The 1^{st}, 2^{nd} and 3^{rd} terms of the Hamiltonian $\hat{H}$ suggest the ground state energies of magnonic and quantum electromagnetic field modes. However, the last equation contains an interaction term of the two operators. The elastic scattering process of interaction in the first order is shown in the following illustration.

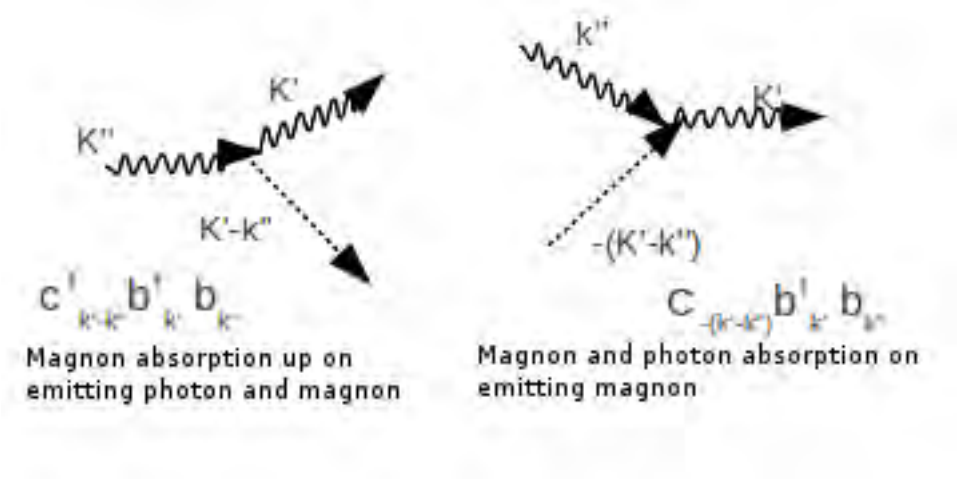

Figure 3.1: The electromagnetic field mode(photon)-magnon scattering process in the first order. The wavey line stands for magnons and the broken line represents photons.

Therefore, the Hamiltonian can be set as:

$$\hat{H} = \sum_{k\sigma} \epsilon_k c^{\dagger}_{k,\sigma} c_{k,\sigma} + \sum_{k'} \Omega_{k'} b^{\dagger}_{k'} b_{k'} + \sum_{kk'k''\sigma,(k'-k''=k)} (A_k + B_k)(c_{-k,\sigma} b^{\dagger}_{k'} b_{k''} - c^{\dagger}_{k,\sigma} b^{\dagger}_{k'} b_{k''}) \quad (3.14)$$

Where $\epsilon_k = \mu NS|\varepsilon|^2 + g\mu_B NS|\xi|^2$ is the quantized electromagnetic field energy and $\Omega_{k'} = 2JzS(\gamma_{k'} - 1) + 2DS$ is the quantized magnon energy, while the variables $A_k = ig\mu_B\xi$, and $B_k = i\mu\varepsilon$ are described as the coupling parameters. The operators $c_{k\sigma}(c^{\dagger}_{k,\sigma})$ and $b_{k'}(b^{\dagger}_{k'})$ satisfy the motion equation

$$i\frac{dc_{k\sigma}}{dt} = [c_{k\sigma}, \hat{H}] = \epsilon_k c_{-k\sigma} - \sum_{kk'} (A_k + B_k) b^{\dagger}_{k'-k} b_{k'} \quad (3.15)$$

$$i\frac{dc^{\dagger}_{k,\sigma}}{dt} = -\epsilon_k c^{\dagger}_{k,\sigma} - \sum_{kk'} (A_k + B_k) b^{\dagger}_{k'+k} b_{k'} \quad (3.16)$$

$$i\frac{db_{k'}}{dt} = [b_{k'}, \hat{H}] = \Omega_{k'} b_{k'} + \sum_{kk'\sigma} (A_k + B_k)(c_{-k\sigma} - c^{\dagger}_{k,\sigma}) b_{k'-k} \quad (3.17)$$

$$i\frac{db^{\dagger}_{k'}}{dt} = -\Omega_{k'}b^{\dagger}_{k'} - \sum_{kk'\sigma}(A_k + B_k)(c_{-k\sigma} - c^{\dagger}_{k,\sigma})b^{\dagger}_{k'+k} \tag{3.18}$$

Introducing the Green functions for the magnonic and quantized photon fields.

$$G_{k'}(t-t') = \langle\langle b^{\dagger}_{k'}(t); b_{k'}(t')\rangle\rangle \tag{3.19}$$

$$G_k(t-t') = \langle\langle c^{\dagger}_{k\sigma}(t); c_{k\sigma}(t')\rangle\rangle \tag{3.20}$$

The motion equations are, respectively,

$$i\frac{dG_{k'}}{dt} = i\frac{d}{dt}\langle\langle c^{\dagger}_{k\sigma}(t); c_{k\sigma}(t')\rangle\rangle = -\delta(t-t') + \Omega_{k'}G_{k'} + \sum_{k\sigma}(A_k + B_k)\langle\langle(c_{-k\sigma} - c^{\dagger}_{k,\sigma})b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle \tag{3.21}$$

$$i\frac{dG_k}{dt} = -\delta(t-t') + \epsilon_k G_k + \sum_{k'}(A_k + B_k)\langle\langle b^{\dagger}_{k'+k}b_{k'}; c_{k\sigma}\rangle\rangle \tag{3.22}$$

To decouple these equations having the set of operators of more than one kind, it is possible to construct mixed Green functions of the form

$$\Gamma_1 = \langle\langle c_{-k\sigma}b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle \tag{3.23}$$

$$\Gamma_2 = \langle\langle c^{\dagger}_{k\sigma}b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle \tag{3.24}$$

Thus, equations 3.21 and 3.22 are respectively,

$$i\frac{dG_{k'}}{dt} = -\delta(t-t') + \Omega_{k'}G_{k'} + \sum_{k\sigma}(A_k + B_k)(\Gamma_1 - \Gamma_2) \tag{3.25}$$

$$i\frac{dG_k}{dt} = -\delta(t-t') + \epsilon_k G_k + \sum_{k'}(A_k + B_k)\Gamma_3 \tag{3.26}$$

Where Γ_3 is also defined as $\Gamma_3 = \langle\langle b^{\dagger}_{k'+k}b_{k'}; c_{-k\sigma}\rangle\rangle$. Furthermore, the motion equations for the mixed terms are

$$i\tfrac{d\Gamma_1}{dt} = (\epsilon_k - \Omega_{k'+k})\Gamma_1 - \textstyle\sum_{k'}(A_k + B_k)\langle\langle b^{\dagger}_{k'-k}b_{k'}b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle -$$

$$\sum_{k\sigma}(A_k + B_k)\langle\langle c_{-k\sigma}(c_{-k\sigma} - c^{\dagger}_{k\sigma})b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle \tag{3.27}$$

$$i\tfrac{d\Gamma_2}{dt} = -(\epsilon_k + \Omega_{k'+k})\Gamma_2 - \textstyle\sum_{k'}(A_k + B_k)\langle\langle b^{\dagger}_{k'+k}b_{k'}b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle -$$

$$\sum_{k\sigma}(A_k + B_k)\langle\langle c^{\dagger}_{k\sigma}(c_{-k\sigma} - c^{\dagger}_{k\sigma})b^{\dagger}_{k'+k}; b_{k'}\rangle\rangle \tag{3.28}$$

$$i\frac{d\Gamma_3}{dt} = (\Omega_{k'} - \Omega_{k'+k})\Gamma_3 - \sum_{k\sigma}(A_k + B_k)\langle\langle(c_{-k\sigma} - c^\dagger_{k,\sigma})b^\dagger_{k'+k}b_{k'}; c_{k,\sigma}\rangle\rangle + \sum_{k\sigma}(A_k + B_k)\langle\langle b^\dagger_{k'+k}(c_{-k\sigma} - c^\dagger_{k,\sigma})b_{k'-k}b_{k'}; c_{k,\sigma}\rangle\rangle \tag{3.29}$$

The above equations contain higher order Green functions which can be decoupled taking operators at the same time domain following Zubarev [74,97,98] as follows

$$\langle\langle b^\dagger_{k'-k}b_{k'}b^\dagger_{k'+k}; b_{k'}\rangle\rangle = \langle b^\dagger_{k'-k}b_{k'}\rangle\langle\langle b^\dagger_{k'+k}; b_{k'}\rangle\rangle\delta_{k'-k-k'} = n_{k'-k}G_{k'} \tag{3.30}$$

$$\langle\langle c_{-k\sigma}(c_{-k\sigma} - c^\dagger_{k\sigma})b^\dagger_{k'+k}; b_{k'}\rangle\rangle = \langle c_{-k\sigma}c^\dagger_{k\sigma}\rangle\langle\langle b^\dagger_{k'+k}; b_{k'}\rangle\rangle\delta_{-k-k}\delta_{-\sigma-\sigma} = -(1 + m_k)G_{k'} \tag{3.31}$$

$$\langle\langle b^\dagger_{k'+k}b_{k'}b^\dagger_{k'+k}; b_{k'}\rangle\rangle = \langle b_{k'}b^\dagger_{k'+k}\rangle\langle\langle b^\dagger_{k'+k}; b_{k'}\rangle\rangle\delta_{k'-k-k'} = (1 + n_{k'+k})G_{k'} \tag{3.32}$$

$$\langle\langle c^\dagger_{k\sigma}(c_{-k\sigma} - c^\dagger_{k\sigma})b^\dagger_{k'+k}; b_{k'}\rangle\rangle = \langle c^\dagger_{k\sigma}c_{-k\sigma}\rangle\langle\langle b^\dagger_{k'+k}; b_{k'}\rangle\rangle\delta_{k+k}\delta_{\sigma-\sigma} = m_k G_{k'} \tag{3.33}$$

$$\langle\langle(c_{-k\sigma} - c^\dagger_{k,\sigma})b^\dagger_{k'+k}b_{k'}; c_{k,\sigma}\rangle\rangle = \langle b^\dagger_{k'+k}b_{k'}\rangle\langle\langle -c^\dagger_{k,\sigma}); c_{k,\sigma}\rangle\rangle\delta_{k'+k-k'} = -n_{k'-k}G_k \tag{3.34}$$

$$\langle\langle b^\dagger_{k'+k}(c_{-k\sigma} - c^\dagger_{k,\sigma})b_{k'-k}b_{k'}; c_{k,\sigma}\rangle\rangle = -\langle b^\dagger_{k'+k}b_{k'-k}\rangle\langle\langle c^\dagger_{k,\sigma}; c_{k,\sigma}\rangle\rangle\delta_{k'+k-k'+k} = -n_{k'}G_k \tag{3.35}$$

Where the number operators are defined as $n_{k'} = \langle b^\dagger_{k'}b_{k'}\rangle$ and $m_k = \langle c^\dagger_{k\sigma}c_{k\sigma}\rangle$. Now using these decoupled terms, the set of equations of Green functions can be written as

$$i\frac{dG_{k'}}{dt} = -\delta(t - t') + \Omega_{k'}G_{k'} + \sum_k(A_k + B_k)(\Gamma_1 - \Gamma_2) \tag{3.36}$$

$$i\frac{dG_k}{dt} = -\delta(t - t') + \epsilon_k G_k + \sum_k(A_k + B_k)\Gamma_3 \tag{3.37}$$

$$i\frac{d\Gamma_1}{dt} = (\epsilon_k - \Omega_{k'+k})\Gamma_1 - \sum_{kk'}(A_k + B_k)[n_{k'-k} - 1 - m_k]G_{k'} \tag{3.38}$$

$$i\frac{d\Gamma_2}{dt} = -(\epsilon_k + \Omega_{k'+k})\Gamma_2 - \sum_{kk'}(A_k + B_k)[n_{k'+k} + 1 + m_k]G_{k'} \tag{3.39}$$

$$i\frac{d\Gamma_3}{dt} = (\Omega_{k'} - \Omega_{k'+k})\Gamma_3 + \sum_{kk'}(A_k + B_k)[n_{k'-k} - n_{k'}]G_k \tag{3.40}$$

Introducing the Fourier components of these functions

$$G_{k'}(t) = \int_{-\infty}^{\infty} G_{k'}(E)e^{-iEt}dE \tag{3.41}$$

$$G_k(t) = \int_{-\infty}^{\infty} G_k(E) e^{-iEt} dE \tag{3.42}$$

$$\Gamma_1(t) = \int_{-\infty}^{\infty} \Gamma_1(E) e^{-iEt} dE \tag{3.43}$$

$$\Gamma_2(t) = \int_{-\infty}^{\infty} \Gamma_2(E) e^{-iEt} dE \tag{3.44}$$

$$\Gamma_3(t) = \int_{-\infty}^{\infty} \Gamma_3(E) e^{-iEt} dE \tag{3.45}$$

We obtained the following

$$\Gamma_1(E) = -\sum_{kk'} (A_k + B_k) \frac{n_{k'-k} - 1 - m_k}{E - (\epsilon_k - \Omega_{k'+k})} G_{k'}(E) \tag{3.46}$$

$$\Gamma_2(E) = -\sum_{kk'} (A_k + B_k) \frac{n_{k'+k} + 1 + m_k}{E + (\epsilon_k + \Omega_{k'+k})} G_{k'}(E) \tag{3.47}$$

$$\Gamma_3(E) = \sum_{kk'} (A_k + B_k) \frac{n_{k'-k} - n_{k'}}{E - (\Omega_{k'} - \Omega_{k'+k})} G_k(E) \tag{3.48}$$

Making use of $\Gamma_1(E)$, $\Gamma_2(E)$, $\Gamma_3(E)$ and the delta function of the form $\delta(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-iE(t-t')} dE$ we find the solutions for the Green functions $G_{k'}(E)$ and $G_k(E)$

$$E - \Omega_{k'} - \sum_{kk'} |A_k + B_k|^2 [\frac{1 + m_k - n_{k'+k}}{E - (\epsilon_k - \Omega_{k'+k})} - \frac{n_{k'-k} + 1 + m_k}{E + \epsilon_k + \Omega_{k'+k}}] G_{k'}(E) = -\frac{1}{2\pi} \tag{3.49}$$

$$E - \epsilon_k - \sum_{kk'} |A_k + B_k|^2 \frac{n_{k'-k} - n_{k'}}{E - (\Omega_{k'} - \Omega_{k'+k})} G_k(E) = -\frac{1}{2\pi} \tag{3.50}$$

In a condensed matter context relevant to electrons moving in a material, the self-energy represents the potential felt by the electron due to the surrounding medium's interactions with it: for example, the fact that electrons repel each other means that a moving electron polarizes (causes to displace) the electrons in its vicinity and this in turn changes the potential the moving electron feels; these and other effects are included in the self-energy. We define new operators $g_{k'}(E)$ and $l_k(E)$, we see that the entire influences of the particles interaction are contained in these new operators which are complex-valued functions of energies and wavevectors of the quasi-particles. The energy corrections of the quasi-particles of the system which we referred here the polarization operators(in other words the self-energies of the process) in which the two bosonic quasi-particles take part in the interacting system.

$$g_{k'}(E) = \sum_{kk'} |A_k + B_k|^2 [\frac{1 + m_k - n_{k'+k}}{E - (\epsilon_k - \Omega_{k'+k})} - \frac{n_{k'-k} + 1 + m_k}{E + \epsilon_k + \Omega_{k'+k}}] \tag{3.51}$$

$$l_k(E) = \sum_{kk'} |A_k + B_k|^2 \frac{n_{k'-k} - n_{k'}}{E - (\Omega_{k'} - \Omega_{k'+k})} \tag{3.52}$$

These functions are termed as the magnon polarization and quanta of electromagnetic field polarization functions,equivalently, defined as the self energy operators modifying the poles of Green functions and broadens the spectral functions. Thus, in terms of these operators the Green functions become,

$$G_{k'}(E) = -\frac{1}{2\pi} \frac{1}{E - \Omega_{k'} - g_{k'}(E)} \tag{3.53}$$

$$G_k(E) = -\frac{1}{2\pi} \frac{1}{E - \epsilon_k - l_k(E)} \tag{3.54}$$

The polarization operators are complex quantities signifying the energy shift (real part;singularities in the real axis) and life time (imaginary part) of the excitation of the system for some finite damping functions. The operators are expressed as

$$g_{k'}(\omega \pm i\epsilon) = g_{k'}(\omega) \mp \alpha_{k'}(\omega) = \sum_{kk'} |A_k + B_k|^2 [\frac{1 + m_k - n_{k'+k}}{\omega - (\epsilon_k - \Omega_{k'+k}) \pm i\epsilon} - \frac{n_{k'-k} + 1 + m_k}{\omega + \epsilon_k + \Omega_{k'+k} \pm i\epsilon}] \tag{3.55}$$

$$l_k(\omega \pm i\epsilon) = l_k(\omega) \mp \alpha_k(\omega) = \sum_{kk'} |A_k + B_k|^2 \frac{n_{k'-k} - n_{k'}}{\omega - (\Omega_{k'} - \Omega_{k'+k}) \pm i\epsilon} \tag{3.56}$$

These equations can be simplified using the Dirac identity,

$$\frac{1}{x \pm i\epsilon} = \frac{p}{x} \mp i\pi\delta(x) \tag{3.57}$$

where p is the principal value. Therefore,

$$G_{k'}(\omega + i\epsilon) - G_{k'}(\omega - i\epsilon) = -\tfrac{1}{2\pi}(\tfrac{1}{\omega - \Omega_{k'} - g_{k'}(\omega) - i\alpha_{k'}(\omega)} - \tfrac{1}{\omega - \Omega_{k'} - g_{k'}(\omega) + i\alpha_{k'}(\omega)})$$

$$G_{k'}(\omega + i\epsilon) - G_{k'}(\omega - i\epsilon) = -\frac{i\alpha_{k'}(\omega)}{\pi(\omega - \Omega_{k'} - g_{k'}(\omega))^2 + (\alpha_{k'}(\omega))^2} \tag{3.58}$$

The damping parameter, $\alpha_{k'}(\omega)$ is defined to be

$$\alpha_{k'}(\omega) = \pi \sum_{kk'} |A_k + B_k|^2 [(n_{k'-k} + 1 + m_k)\delta(\omega + (\epsilon_k + \Omega_{k'+k})) - (1 + m_k - n_{k'+k})\delta(\omega - (\epsilon_k - \Omega_{k'+k}))] \tag{3.59}$$

Similarly,

$$G_k(\omega + i\epsilon) - G_k(\omega - i\epsilon) = -\tfrac{1}{2\pi}(\tfrac{1}{\omega - \epsilon_k - l_k(\omega) - i\alpha_k(\omega)} - \tfrac{1}{\omega - \epsilon_k - l_k(\omega) + i\alpha_k(\omega)})$$

$$G_k(\omega + i\epsilon) - G_k(\omega - i\epsilon) = -\frac{i\alpha_k(\omega)}{\pi(\omega - \epsilon_k - l_k(\omega))^2 + (\alpha_k(\omega))^2} \tag{3.60}$$

Whereas, $\alpha_k(\omega)$ is

$$\alpha_k(\omega) = -\pi \sum_{kk'} |A_k + B_k|^2 [n_{k'-k} - n_{k'}] \delta(\omega - (\Omega_{k'} - \Omega_{k'+k})) \tag{3.61}$$

3.3 Spectral Representations of Time Correlation Functions

The analytical properties of the Fourier transform of Green function are determined by those of the correlation function. The Green function and correlation functions are related by

$$G_{AB}(t) = \frac{-i}{\hbar}\theta(t)\langle [F_{AB}(t) \mp F_{BA}(-t)]\rangle \tag{3.62}$$

The time correlation function between two operators A and B is defined

$$F_{AB}(t) = \frac{1}{Z(\beta)} Tr[e^{-\beta H_o} A(t)B(0)] = \langle A(t), B(0)\rangle \tag{3.63}$$

Transforming a function from the time domain to the frequency domain provides information about the energies of excitations. Thus, in this work the Fourier transform of the above time correlation function that is the spectral density function $J(\omega)$ that can be normalized as a probability function is given by

$$J(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F_{AB}(t) e^{-i\omega t} dt \tag{3.64}$$

The spectral density function as it is either the quantum state of resolution of a particle with a given energy or the energy resolution of a particle in a given quantum state, enlightens how the excitation occurs at the time of interaction. The spectral function is related to the density of states. For instance, for non-interacting electrons the spectral function is given by a Dirac delta function, $J(k, \omega) = 2\pi\delta(\epsilon_k - \omega)$.

In many-body systems, as there would be different possible interactions,the spectral function changes, line broadening is observed due to energy exchange [94]. Therefore, defining in the Heisenberg representation the operators averaged over the grand canonical ensemble lead to the time correlation function for magnonic operators when the times are different and hence we write,

$\langle b_{k'}(t')b^{\dagger}_{k'}(t)\rangle = \frac{1}{Z(\beta)} Tr(e^{-\beta H} b_{k'}(t')b^{\dagger}_{k'}(t))$

$\langle b_{k'}(t')b^{\dagger}_{k'}(t)\rangle = \frac{1}{Z(\beta)} \sum_{nm} \langle n|b_{k'}(0)|m\rangle\langle m|b^{\dagger}_{k'}(0)|n\rangle e^{-\beta E_n} e^{\frac{i(E_n - E_m)(t'-t)}{\hbar}}$

Then, interchanging the indices

$$\langle b_{k'}(t')b^{\dagger}_{k'}(t)\rangle = \frac{1}{Z(\beta)}\sum_{nm}\langle m|b_{k'}(0)|n\rangle\langle n|b^{\dagger}_{k'}(0)|m\rangle e^{-\beta E_m}e^{\frac{i(E_m-E_n)(t'-t)}{\hbar}} \tag{3.65}$$

Similarly,

$$\langle b^{\dagger}_{k'}(t)b_{k'}(t')\rangle = \frac{1}{Z(\beta)}\sum_{nm}\langle n|b^{\dagger}_{k'}(0)|m\rangle\langle m|b_{k'}(0)|n\rangle e^{-\beta E_n}e^{\frac{i(E_m-E_n)(t'-t)}{\hbar}} \tag{3.66}$$

Now if we let

$E_m - E_n = \hbar\omega_{mn}$ that leads to $E_n = E_m - \hbar\omega_{mn}$. Then,

$$\langle b_{k'}(t')b^{\dagger}_{k'}(t)\rangle = \frac{1}{Z(\beta)}\sum_{nm}\langle n|b^{\dagger}_{k'}(0)|m\rangle\langle m|b_{k'}(0)|n\rangle e^{-\beta E_n}e^{-\beta\hbar\omega_{mn}}e^{i\omega_{mn}(t'-t)} \tag{3.67}$$

And

$$\langle b^{\dagger}_{k'}(t)b_{k'}(t')\rangle = \frac{1}{Z(\beta)}\sum_{nm}\langle n|b^{\dagger}_{k'}(0)|m\rangle\langle m|b_{k'}(0)|n\rangle e^{-\beta E_n}e^{i\omega_{mn}(t'-t)} \tag{3.68}$$

The time correlation functions are expressed as

$$\langle b^{\dagger}_{k'}(t)b_{k'}(t')\rangle = \int_{-\infty}^{\infty} J(\omega)e^{-i\omega(t-t')}d\omega \tag{3.69}$$

$$\langle b_{k'}(t')b^{\dagger}_{k'}(t)\rangle = \int_{-\infty}^{\infty} J(\omega)e^{\beta\hbar\omega_{nm}}e^{-i\omega(t-t')}d\omega \tag{3.70}$$

Where $J(\omega) = \frac{\sqrt{2\pi}}{Z(\beta)}\sum_{nm}\langle m|b_{k'}(0)|n\rangle\langle n|b^{\dagger}_{k'}(0)|m\rangle e^{-\beta E_n}\delta(\omega-\omega_{mn})$. These time correlation expressions are related to the retarded and advanced Green functions(double time Green function). The retarded and advanced Green functions can be considered as one analytic function having two branches; upper and lower half planes in the complex plane with singularity on the real axis. Therefore, using the definitions of the Green functions

$$G_r(t,t') = -i\theta(t-t')\langle[b^{\dagger}_{k'}(t), b_{k'}(t')]\rangle_r \tag{3.71}$$

And

$$G_a(t,t') = i\theta(t'-t)\langle[b^{\dagger}_{k'}(t), b_{k'}(t')]\rangle_a \tag{3.72}$$

And also, taking the Fourier transforms,

$G_r(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G_r(t,t')e^{iE(t-t')}dt$

$G_r(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} -i\theta(t-t')\langle[b_{k'}^{\dagger}(t), b_{k'}(t')]\rangle_r e^{iE(t-t')}dt$

$$G_r(E) = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega(e^{\beta\hbar\omega_{nm}}-1)J(\omega)\int_{-\infty}^{\infty}\theta(t-t')e^{i(E-\omega)(t-t')}dt \tag{3.73}$$

To evaluate this equation we use the steep function,

$$\theta(t-t') = \int_{-\infty}^{t} e^{\epsilon(t-t')}\delta(t-t')dt \tag{3.74}$$

Where the condition $\epsilon \to 0 \quad (\epsilon > 0)$ is satisfied and also the delta function is given by

$$\delta(t-t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ix(t-t')}dx \tag{3.75}$$

Which leads to the steep function to be

$$\theta(t-t') = \frac{-1}{2\pi i}\int_{-\infty}^{\infty}\frac{e^{-ix(t-t')}}{i\epsilon + x}dx \tag{3.76}$$

Therefore the retarded Green function becomes,

$G_r(E) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} d\omega(e^{\beta\hbar\omega_{nm}}-1)J(\omega)\frac{1}{(E-\omega)+i\epsilon}$

$$G_r(\omega) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} dE(e^{\beta E}-1)J(E)\frac{1}{(\omega-E)+i\epsilon} \tag{3.77}$$

Using the same procedure the advanced Green function is found to be

$G_a(E) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} d\omega(e^{\beta\hbar\omega_{nm}}-1)J(\omega)\frac{1}{E-\omega-i\epsilon}$

$$G_a(\omega) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} dE(e^{\beta E}-1)J(E)\frac{1}{(\omega-E)-i\epsilon} \tag{3.78}$$

$G_r(\omega+i\epsilon) - G_a(\omega-i\epsilon) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} dE(e^{\beta E}-1)J(E)[\frac{1}{(\omega-E)+i\epsilon} - \frac{1}{(\omega-E)-i\epsilon}]$

Since $\delta(x) = \frac{1}{2\pi i}(\frac{1}{x-i\epsilon} - \frac{1}{x+i\epsilon})$

$G_r(\omega+i\epsilon) - G_a(\omega-i\epsilon) = \frac{-1}{2\pi}\int_{-\infty}^{\infty} dE(e^{\beta E}-1)J(E)(-2\pi i)\delta(\omega-E)$

$$G_r(\omega+i\epsilon) - G_a(\omega-i\epsilon) = i(e^{\beta\omega}-1)J(\omega) \tag{3.79}$$

This expression, equated with the previous one for magnonic operators, leads to

$$i(e^{\beta\omega}-1)J(\omega) = -\frac{i\alpha_{k'}(\omega)}{\pi(\omega-\Omega_{k'}-g_{k'}(\omega))^2 + (\alpha_{k'}(\omega))^2} \tag{3.80}$$

The spectral density function of magnon variable that gives information on the excitation energies is non-negative and is obtained as

$J_{k'}(\omega) = \frac{-\alpha_{k'}(\omega)(e^{\beta\omega}-1)^{-1}}{\pi(\omega-\Omega_{k'}-g_{k'}(\omega))^2+\alpha_{k'}^2(\omega)}$

This also indicates that $\alpha_{k'}(\omega) \leqslant 0$ [98] and at very small damping term,the polarization operator suggests singularity at $\omega - \Omega_{k'} - g_{k'}(\omega) = 0$ and the spectral density function leads to be delta function.

$$J_{k'}(\omega) = \frac{-\alpha_{k'}(\omega)(e^{\beta\omega}-1)^{-1}}{\pi(\omega-\Omega_{k'}-g_{k'}(\omega))^2+\alpha_{k'}^2(\omega)} \tag{3.81}$$

In the same way the spectral density of quanta of electromagnetic mode is obtained as

$$J_k(\omega) = \frac{-\alpha_k(\omega)(e^{\beta\omega}-1)^{-1}}{\pi(\omega-\epsilon_k-l_k(\omega))^2+\alpha_k^2(\omega)} \tag{3.82}$$

The magnon and quanta of electromagnetic mode distributions are thus obtained from the correlation functions.

$\langle b_{k'}^{\dagger}(t)b_{k'}(t')\rangle = \int_{-\infty}^{\infty} J_{k'}(\omega)e^{-i\omega(t-t')}d\omega$ and setting $t = t'$, i.e, the thermal average occupancies.

$$n_{k'} = \int_{-\infty}^{\infty} \frac{-\alpha_{k'}(\omega)(e^{\beta\omega}-1)^{-1}}{\pi(\omega-\Omega_{k'}-g_{k'}(\omega))^2+\alpha_{k'}^2(\omega)}d\omega \tag{3.83}$$

$$m_k = \int_{-\infty}^{\infty} \frac{-\alpha_k(\omega)(e^{\beta\omega}-1)^{-1}}{\pi(\omega-\epsilon_k-l_k(\omega))^2+\alpha_k^2(\omega)}d\omega \tag{3.84}$$

The spectral density functions seem to have step maxima at $\omega = \tilde{\Omega}_{k'}$, and $\omega = \tilde{\epsilon}_k$ when the damping parameters $\alpha_{k'}(\omega)$ and $\alpha_k(\omega)$ approaching to zero. Now taking the power series expansions of the polarization operators and using some approximations,

$\frac{-\alpha_{k'}(\omega)}{\pi(\omega-\Omega_{k'}-g_{k'}(\omega))^2+\alpha_{k'}^2(\omega)} \approxeq \frac{-\tilde{\alpha}_{k'}(\tilde{\Omega}_{k'})[1-\frac{dg_{k'}}{d\omega}|_{\omega=\tilde{\Omega}_{k'}}]^{-1}}{\pi(\omega-\tilde{\Omega_{k'}})^2+\tilde{\alpha}_{k'}^2(\tilde{\Omega}_{k'})}$

$\frac{-\alpha_k(\omega)}{\pi(\omega-\epsilon_k-l_k(\omega))^2+\alpha_k^2(\omega)} \approxeq \frac{-\tilde{\alpha}_k(\tilde{\epsilon}_k)[1-\frac{dl_k}{d\omega}|_{\omega=\tilde{\epsilon}_k}]^{-1}}{\pi(\omega-\tilde{\epsilon_k})^2+\tilde{\alpha}_k^2(\tilde{\epsilon}_k)}$

Where

$\tilde{\alpha}_{k'} = -\alpha_{k'}(\tilde{\Omega}_{k'})[1-\frac{dg_{k'}}{d\omega}|_{\omega=\tilde{\Omega}_{k'}}]^{-1} = \delta(\omega-\tilde{\Omega}_{k'})$

$\tilde{\alpha}_k = -\alpha_k(\tilde{\epsilon}_k)[1-\frac{dl_k}{d\omega}|_{\omega=\tilde{\epsilon}_k}]^{-1} = \delta(\omega-\tilde{\epsilon}_k)$

and using the conditions

$\frac{dg_{k'}}{d\omega} \ll 1, \qquad \frac{dl_k}{d\omega} \ll 1$

So that the distribution function equations can be reduced to the magnon and quantum of electromagnetic mode upon approximating the damping terms and ignoring very small terms.

Thus, it turned out to be

$$n_{k'} = (e^{\beta\tilde{\Omega}_{k'}} - 1)^{-1} \;\; ; \qquad m_k = (e^{\beta\tilde{\epsilon}_k} - 1)^{-1} \tag{3.85}$$

Here $\Omega_{k'}$ and ϵ_k are elementary excitation energies.

3.4 The Polarization Response Functions $g_{k'}(\omega)$ and $l_k(\omega)$

The real parts of these operators signify the physical energy shift corresponding to the interaction under consideration. However, the inverse of the imaginary parts are expected to measure the excitations or dressed particles (also called quasi-particles) lifetime [99].

The availability of empty state of one species or occupancy of the other while the real crystal system interaction takes place as a result of the dynamism of matter is indicated in the number density operations. An interaction always involves many quasi-particles. The specific feature of ME is that they involve different quasi-particles,such as the magnons , the photons and the phonons, including some others. In recent years it is evidenced that magnetoelectrics are known to having excitations described by the magnetic modes, the magnons, and excitation modes described by the quantized electromagnetic modes called photons. This is a blue print to handle one excitation state with another. Theoretically the strong magnetoelectric interaction which very often studied happens in materials containing the ligands and observed that the magnon-photon interaction is crucially becoming the lesson of researchers in light of the merging of two magnons that give rises to a THz photon(conversion of magnon laser into THz photon laser) which has immense technological benefits in the field of medicine and molecular imaging. In more simpler terms the exchange interaction system may allow scattering of the electromagnetic modes with the magnons and vice-versa. This phenomenon just obeying the conservation laws, can be seen through momentum and wave vector exchanges as depicted in figure 3.1.

3.4.1 The Magnon Polarization Operator

The magnon polarization operator we have defined is written as

$$g_{k'}(\omega \pm i\epsilon) = \sum_{kk'} |A_k + B_k|^2 [\frac{1 + m_k - n_{k'-k}}{\omega - (\epsilon_k - \Omega_{k'+k}) \pm i\epsilon} - \frac{n_{k'+k} + 1 + m_k}{\omega + (\epsilon_k + \Omega_{k'+k}) \pm i\epsilon}] \tag{3.86}$$

$g_{k'}(\omega + i\epsilon) = \sum_{kk'} |A_k + B_k|^2 [\frac{1+m_k-n_{k'-k}}{\omega-(\epsilon_k-\Omega_{k'+k})+i\epsilon} - \frac{n_{k'+k}+1+m_k}{\omega+(\epsilon_k+\Omega_{k'+k})+i\epsilon}]$

This is a Lindhard function and making use of the Dirac identity it can be expressed in terms of real and imaginary parts [100].

$$Reg_{k'}(\omega + i\epsilon) = p \sum_{kk'} |A_k + B_k|^2 [\frac{1 + m_k - n_{k'-k}}{\omega - (\epsilon_k - \Omega_{k'+k})} - \frac{n_{k'+k} + 1 + m_k}{\omega + (\epsilon_k + \Omega_{k'+k})}] \tag{3.87}$$

Where p denotes the principal part and for small k, such that, $k' + k \longleftrightarrow k' - k$ the above equation becomes

$$Reg_{k'}(\omega + i\epsilon) = p \sum_{kk'} |A_k + B_k|^2 2 \frac{\epsilon_k(1 + m_k) - (\omega + \Omega_{k'+k}) n_{k'+k}}{(\omega + \Omega_{k'+k})^2 - \epsilon_k^2} \tag{3.88}$$

This equation, as it is the energy expression, is related to the energy shift. Hence, we can see that there is a singularity at some energy values restricted by the condition

$$(\omega + \Omega_{k'+k})^2 - \epsilon_k^2 = 0$$

This also leads to the condition $\omega = \pm\epsilon_k - \Omega_{k'+k}$. Moreover, one can also see that

$$Reg_{k'}(\omega + i\epsilon) = Reg_{k'}(\omega - i\epsilon)$$

Where as the imaginary part is

$$\begin{aligned} Img_{k'}(\omega + i\epsilon) = -i\pi \sum_{kk'} |A_k + B_k|^2 [(1 + m_k - n_{k'-k}) \delta(\omega - (\epsilon_k - \Omega_{k'+k})) - \\ (n_{k'+k} + 1 + m_k) \delta(\omega + (\epsilon_k + \Omega_{k'+k}))] \end{aligned} \tag{3.89}$$

$$Img_{k'}(\omega + i\epsilon) = i\alpha_{k'}(\omega) \tag{3.90}$$

and

$$\begin{aligned} Img_{k'}(\omega - i\epsilon) = i\pi \sum_{kk'} |A_k + B_k|^2 [(1 + m_k - n_{k'-k}) \delta(\omega - (\epsilon_k - \Omega_{k'+k})) - \\ (n_{k'+k} + 1 + m_k) \delta(\omega + (\epsilon_k + \Omega_{k'+k}))] \end{aligned} \tag{3.91}$$

In the imaginary part the modulus; the coupling term (time independent amplitude)is traditionally called the "matrix element", reflects how strong the interaction is that arises from the interaction of the local quantum field environment. The imaginary function obtained above explicitly implies the intensity while it is integrated in the frequency domain, i.e,

$I = \int_0^\infty Img_{k'}(\omega)d\omega$

Now, focusing on the rate of transition for positive energy shifts and at some peak values of the oscillating field frequency and magnon frequency, the following function can be evaluated and reduced [101].

$$\alpha_{k'}(\omega) = \pi \sum_{kk'} |A_k + B_k|^2 [(n_{k'+k} + 1 + m_k)\delta(\omega + (\epsilon_k + \Omega_{k'+k})) - (1 + m_k - n_{k'+k})\delta(\omega - (\epsilon_k - \Omega_{k'+k}))] \tag{3.92}$$

The above expression is readily simplified by defining the spectral densities such as

$\rho^+(kk'\omega) = (n_{k'+k} + 1 + m_k)\delta(\omega + (\epsilon_k + \Omega_{k'+k}))$ and

$\rho^-(kk'\omega) = (1 + m_k - n_{k'+k})\delta(\omega - (\epsilon_k - \Omega_{k'+k}))$. Therefore,

$$\alpha_{k'}(\omega) = \pi \sum_{kk'} |A_k + B_k|^2 [\rho^+(kk'\omega) - \rho^-(kk'\omega)] \tag{3.93}$$

A transition rate depends upon the strength of the coupling between the initial and final state of a system and upon the number of ways the transition can happen (i.e, the density of the final states). The width of the smeared-out region as a result of interaction between these two bosonic quasi-particles is determined by the damping terms associated with the imaginary part of the polarization operators. Hence, the magnonic damping term describes the probability of the photon-magnon transition (absorption or emission), or the rate at which the quasi particles interact and change their initial and final states. This transition rate is also called the decay probability. It is related to the inverse of mean lifetime of excitation corresponding to the given momentum and energy and is also proportional to the density of final states [94]. It is credible to take positive energy transfer, i.e, $\omega{>}0$ which also admits the possible excitation energies and the allowed wavevector ranges, i.e, $\epsilon_k > \Omega_{k'+k}$ and hence the damping term is reduced to the well known Fermi Golden equation. It states that, to first-order in perturbation theory, the transition rate depends only the square of the matrix element of the operator between initial and final states and includes, via the δ function, an energy-conservation condition. Here, in this case the transition rate is proportional to the joint density of states as it is clearly seen by the equation, i.e, the decay rate strongly dependence on the magnonic and electromagnetic mode excitations [18]. Thus, it becomes

$$\alpha_{k'}(\omega) = -\pi \sum_{kk'} |A_k + B_k|^2 \rho^-(kk'\omega) \tag{3.94}$$

This equation is non-zero only when the condition $\omega = \epsilon_k - \Omega_{k'+k}$ is satisfied. The oscillating frequency ω is not a sharply defined term due to several reasons such as the life times of excitations, quantum mechanical fluctuations , and the interaction in practical situations in the many-body system (for instance, electron-electron, electron-phonon,phonon-magnon, magnons and electromagnetic modes etc.) but there exists a peak value as defined so far. Therefore, considering these facts and assuming homogeneous broadening (all quasi-particles or molecules behave the same) accounted on the life times of the initial and final states , the ideal delta functions become a broadened profile which tend to be a Lorentzian shape [102,103]. The spectral function for a finite width of frequencies can be recast in the following form

$$\alpha_{k'}(\omega) = \int_{-\omega}^{+\omega} (-\pi \sum_{kk'} |A_k + B_k|^2 (1 + m_k - n_{k'-k}) \delta(\omega' - (\epsilon_k - \Omega_{k'+k}))) g(\omega - \omega') d\omega' \quad (3.95)$$

Consequently,

$$\alpha_{k'}(\omega) = -\pi \sum_{kk'} |A_k + B_k|^2 (1 + m_k - n_{k'-k}) g(\omega - (\epsilon_k - \Omega_{k'+k})) \quad (3.96)$$

The delta function is replaced by the normalized generalized distribution function $g(\omega - (\epsilon_k - \Omega_{k'+k}))$ which corresponds to the frequency centered at $\epsilon_k - \Omega_{k'+k}$.

We approximate this final expression on the assumptions based on the line widths of the quantum fields and the excitation spectrum line width. In practical reasons, as there are interactions in many-body system, the line width of the excitation spectrum is expected to be wider. As a result, the above expression becomes

$$\alpha_{k'}(\omega) \cong -\pi \rho(\omega) \langle (A_k + B_k)^2 \rangle_{ave} \quad (3.97)$$

where $\rho(\omega)$ is the final joint density of state and is Lorantzian in character. The damping term is also related to the life time of excitation of the quasi-particles.

$$\alpha_{k'}(\omega) = \frac{1}{\tau} \quad (3.98)$$

where τ measures the life time of the excitation.

To observe the frequency and momentum functionality we use the quantized field energy $\epsilon_k = \hbar\omega_k$ where $\omega_k = c|k|$ and the quantized magnon energy at long wavelength limit is

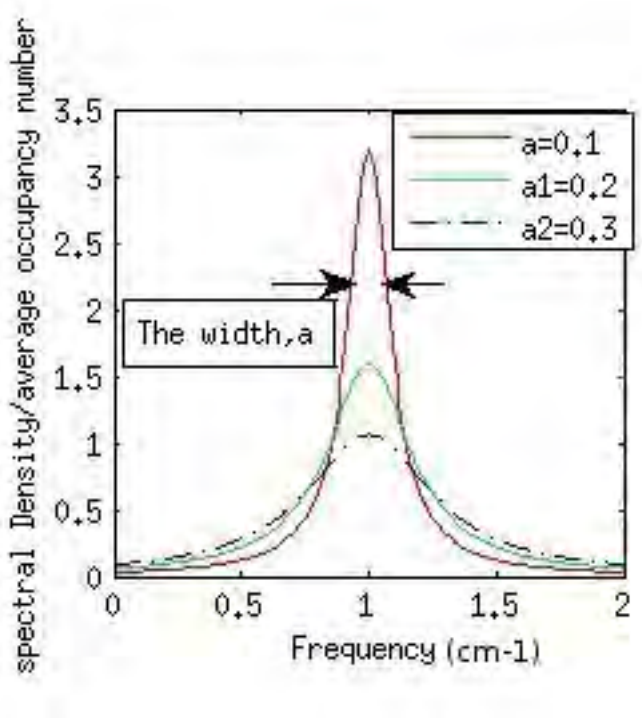

Figure 3.2: The figure depicts the spectral density function per average magnon occupancies, $\frac{J_{k'}(\omega)}{n_{k'}(\omega)}$. It is indicated that the spectral function with the frequency range of ω between 0 to 2 and at a central frequency roughly corresponding to the term $\Omega_{k'} - g_{k'}(\omega) = 1$ shows a line broadening depending on the damping factor, which we take arbitrarily small values to the order of 0.1, 0.2, and 0.3.

proportional to k'^2 as it has been shown in the quantization of spin waves. The dispersion is $\hbar\omega = (2JSa^2)k'^2$ for $\beta = (2JSa^2)$ and introducing the momentum shift argument, we see that [24],

$$\Omega_{k'-k} = \beta(k' - k)^2 = \beta k'^2 - 2\beta|k|.|k'|cos(\theta_{kk'}) + \beta k^2$$

Where $\theta_{kk'}$ is the angle between two propagating vectors. The ω dependency on the wave vectors is thus,

$$\omega = |k| + 2\beta|k|.|k'|cos(\theta_{kk'}) - \beta k'^2 - \beta k^2 \tag{3.99}$$

This expression predicts that the final density of state frequency can easily be related to the elctromagnetic mode vibration and the magnon wavevectors, and even it depends also on the

angles the wavevectors make each other. It is easy to look at different possible ways the frequency depends.

Case 1: For some specific wavevectors, but, $k > k'$ and variable angle $\theta_{kk'}$

Case 2: For very small wavevector values, but, $k = k'$ and variable angle $\theta_{kk'}$, in this particular case it proceeds to give

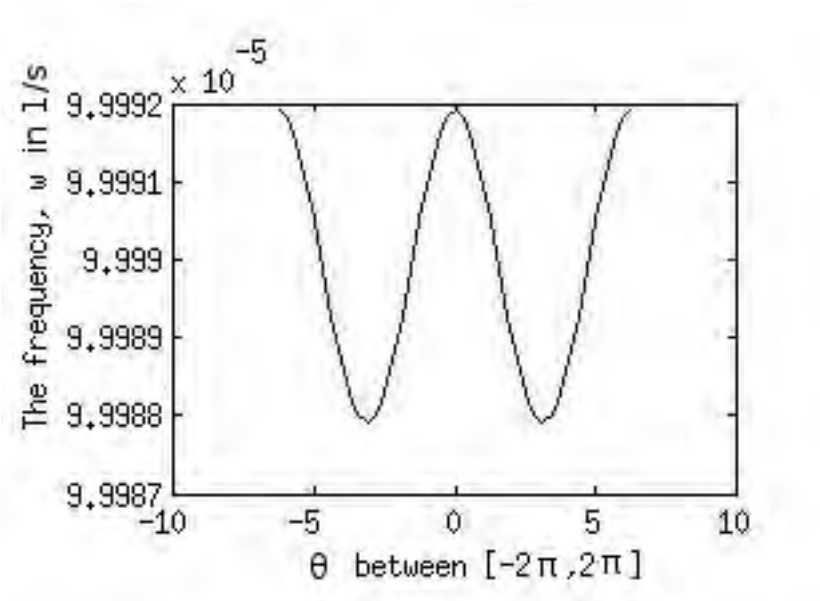

Figure 3.3: The frequency versus θ graph. This figure indicates that ω can have maximum and minimum values for different orientation angles of the vectors. In this particular instance, taking some arbitrary values of k's, such that $k > k'$, we obtained that ω_{max} corresponds to $\theta = 2\pi n$ for $n = 0, \pm 2, \pm 4, ...$, and $\omega_{min} = n\pi$ for $n = \pm 1, \pm 3, \pm 5, ...$

$\omega = |k|(1 + 2\beta|k|(cos\theta_{kk'} - 1))$

Case 3: For different wavevectors, k and k' and fixed angle $\theta_{kk'}$

3.4.2 The Polarization Operator of the Electromagnetic Mode

The polarization operator of the electromagnetic mode, of course, it does not include the two types of the number densities and we are less interested on it, but still plays very important role and marks realistically what is going on at the time of the process. This polarization operator indicates that the damping of this mode is determined on the expense of the density of states of

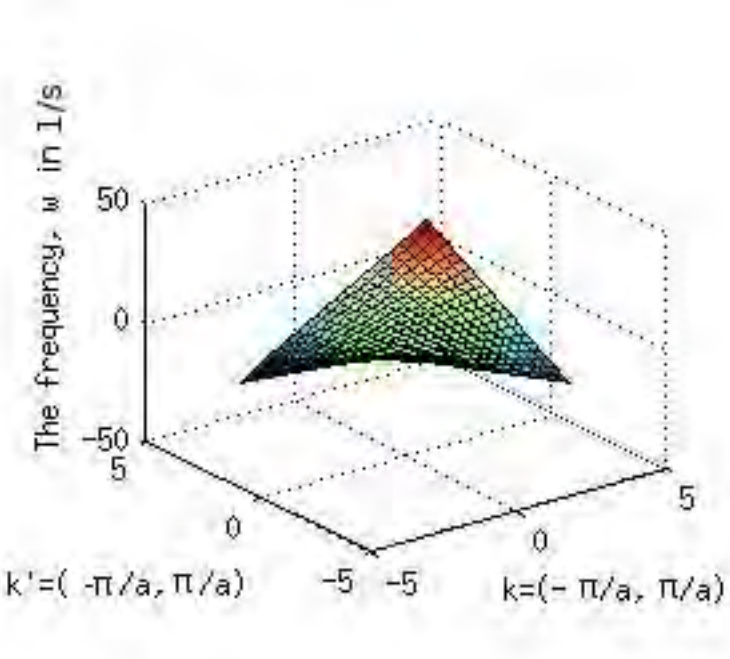

Figure 3.4: This figure indicates the frequency dependency on wavevectors. It illustrates the variations of ω at an angle $\theta = 0$ where "a" is the lattice parameter.

the magnons while there is an interaction in the two bosonic operators. The operator in terms of the number densities is expressed as

$$l_k(\omega \pm i\epsilon) = \sum_{kk'} |A_k + B_k|^2 [\frac{n_{k'-k} - n_{k'}}{\omega - (\Omega_{k'} - \Omega_{k'+k}) \pm i\epsilon}] \tag{3.100}$$

$$l_k(\omega \pm i\epsilon) = l_k(\omega) \mp i\pi \sum_{kk'} |A_k + B_k|^2 (n_{k'-k} - n_{k'}) \delta(\omega - (\Omega_{k'} - \Omega_{k'+k})) \tag{3.101}$$

The real part is

$$Rel_k(\omega \pm i\epsilon) = p \sum_{kk'} |A_k + B_k|^2 \frac{n_{k'-k} - n_{k'}}{\omega - (\Omega_{k'} - \Omega_{k'+k})} = l_k(\omega) \tag{3.102}$$

But the imaginary part is $Iml_k(\omega \pm i\epsilon) = \pm i\alpha_k(\omega)$ Where

$$\alpha_k(\omega) = -\pi \sum_{kk'} |A_k + B_k|^2 (n_{k'-k} - n_{k'}) \delta(\omega - (\Omega_{k'} - \Omega_{k'+k})) \tag{3.103}$$

This last equation can be evaluated following the same argument we employed in the above section. It also leads us to conclude that if our system is purely dominated by magnonic excitations, i.e, for $k \to 0$ the damping term vanishes which rightly leads to the case where there is no fluctuations or interactions in general.

3.5 Conclusions

The presence of coupled magnetic and electric moments in the transition and/ or rare-earth metal oxides, often refers perovskites and characterized by strong electron correlations as well as a rich variety of crystallographic, electronic and magnetic phases [104,105,106,107], offer opportunities to consider the fields with their associated vector potentials in a material system. In this case, we treat the two dimensional magnetoelectrics samples. The magnetoelectric interactions that we discussed in this work are real many-body interaction system which arises from the quantum mechanical behavior of constituents of materials [108]. The magnetic behaviors and lattice vibrations(distortions) somehow natural consequences of the materials have been taken to be the basis of our model Hamiltonian. Since our system is an interaction system, we exploit a double time Greens function that have poles on the real axis which corresponds to the energy shift of excitations and analytically continuous on the complex energy plane for finite damping functions.

The imaginary functions describe some sorts of damping, while their peaks are to be the thermally averaged excitation values. The spectrum of excitation energy as it is found to depend on wavevectors varies broadly, accordingly and our predictions suggest the real interaction processes. The fluctuations of number densities, arising from the exchange coupling of the two domains [109], characterized by the joint number density operators in imaginary components of the Greens functions accounts for the subsequent damping in the quantum electromagnetic field and to the magnonic oscillations in the time evolution which tends to measure the life time about which the excitation can take place.

Chapter 4

Magnetization and Polarization Studies in Multiferroics

In multiferroic thin film system the magnetic field tends to play a role to stabilize the spins in preferred orientations and induces a coupling of magnetism and ferroelectricity that opens a route to switch magnetization with electric polarization and vice-versa. In this chapter we study the magnetization and polarization of multiferroics.

4.1 Introduction

It is straight forward to relate electric polarization to applied electric field and the magnetic polarization to an external magnetic field. Being abide with the laws of electromagnetism, several discussions and predictions have been made on the correlation between magnetic and electric properties of real crystals [12,13,17,110] until the first effect has been observed on antiferromagnetic Cr_2O_3 [18,19]. Afterwards, however, comprehensive studies on magnetoelectric effects showed a decline considerably, and later, more recently for the last three and more decades, enormous progress has been made both theoretically and experimentally not only on the fundamental physics behind it but also for scientific research interests [111,112]. Manipulation of magnetization by other means than magnetic field is a challenging task, which leads to the resurgence of magnetoelectric phenomenon that brings about new vision to wards the mutual control of one over the other [113]. It is hard to get coupled order of ferromagnetism and ferroelec-

tricity in real crystals due to the fact that ferromagnetic ordering primarily needs partially filled d-orbitals and, on the other hand ferroelectricity is favored by empty d-orbitals. The cross-link of properties on materials usually put complexity to understand the behavior of the materials, but it can open an important degree of freedom to tune the order parameters. Multiferroics materials that maintain the right symmetry of ferroic phase (materials that combine two or more of the primary ferroic order parameters in one phase) are found to be very excellent classes of materials that showed strong magnetoelectric coupling [6,93,114]. These recently emerging materials are classified as: a) Type-I, where the order parameters appear on single phase, and b) Type-II, if the order parameters exist in different components of composite materials [115,116]. In both cases the origins of spontaneously induced order parameters are different, while on the later, it is predominantly due to the magnetism of the composites. Moreover, the temperature range over which the multiferroic behavior is observed varies from system to system [34,117]. The underlying microscopic mechanism to explain the dynamic magnetoelectric coupling in multiferroics is still under debate, however, two possible mechanisms are responsible and best explained experimental results successfully. The inverse Dzyaloshinskii–Moriya (IDM) interaction mechanism is also termed as the spin-current mechanism. In most recently discovered oxide multiferroics it accounts that the ferroelectric polarization is expressed as,

$$P_e \sim e_{ij} \times S_i \times S_j$$

where e_{ij} is the lattice vector connecting both neighboring spins S_i and S_j at sits i and j. In this equation, it is easy to observe the spin order and the static electric polarization related in the magnetic cycloid [118]. Counterclockwise spin spiral of $TbMnO_3$ promoting an upward directed electric polarization by forced oxygen displacements as shown in figure 4.1 below. The second important approach that explained the magnetoelectric coupling in multiferroics system is the Heisenberg superexchange interaction. This model deals with the excitation conditions for the electro-active excitations in spiral magnets on account of the contribution of the free energy proportional to the superexchange interaction $S_i \cdot S_j$ is considered as the playground to explain the coupling of order parameters. Heisenberg model is based on the uniquely defined condition that an application of a homogeneous electric field, independent of the spin spiral tends to induce a modulation of the exchange coupling along the other crystallographic axis

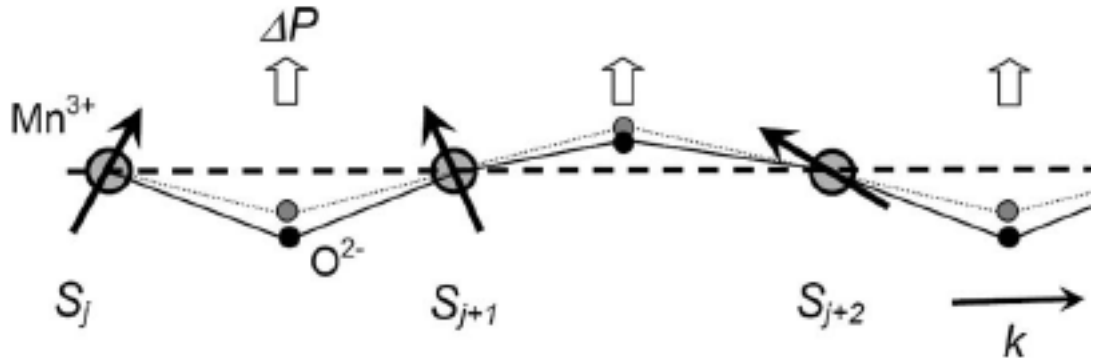

Figure 4.1: In $TbMnO_3$ structure forced oxygen displacement as a result of spin ordering is responsible for the induced electric polarization as shown by the diagram.

perpendicular to the field [78,89,119]. In this paper we extend the Heisenberg superexchange interaction mechanism in the spiral magnetic system to investigate the magnetoelectric coupling in this fascinating field which shows an interplay of various orders.

4.2 Model Hamiltonian

The multiferroics ground state can be modeled as a quasi-2D thin film as depicted in figure 6, of [78,120] so that spin chains can be studied on a plane. We consider a crystal lattice in which the spin degree of freedom is relevant to the model [67,73,121]. An effective model Hamiltonian that presents a frustrated spin interaction is defined as,

$$H = -\sum_{ij} J_{ij}\vec{S}_i.\vec{S}_j - g\mu_B H\sum_i S_{iz} - \mu E\sum_i S_{iz} + D\sum_i S_{iz}^2 \tag{4.1}$$

Where $S_i(S_j)$ is spin operator at sites $i(j)$. The isotropic exchange coupling term J_{ij} is a function of distance between neighboring spins defined by $J_{ij} = J(R_i - R_j)$. In the minimum energy bond length the magnetic coupling between nearest neighbors is ferromagnetic ($J_{ij} > 0$). The constant g is the gyromagnetic ratio, and the second term of equation 1 is the effective Zeeman field with an external deriving field while in this model chosen to be parallel to the $+z$ axis to align all the spins in the same direction. Whereas, the third term includes an electric

field E that interacts with the spins in the system. The constant μ describes the coupling strength between the spins and the radiation field that is either intrinsic or extrinsic. The terms μ_B and D are the Bohr magneton and magnetic anisotropic (or spin-wave stiffness) constants, respectively [108,122]. In this model Hamiltonian the constants of motion includes the total spin operators,

$$S^2 = \sum_i (S_i)^2 \tag{4.2}$$

$$S_z = \sum_i S_{iz} \tag{4.3}$$

The ground state of a system of N identical atoms of spin S has,

$$S^2/0\rangle = NS(NS+1)/0\rangle; \qquad S_z/0\rangle = NS/0\rangle \tag{4.4}$$

The total spin at site i in the Hamiltonian has components, S_{ix}, S_{iy} and S_{iz}, and are dependent on one another with an identity $S_i.S_i = S(S+1)$. The spin problem can be transformed into a more standard many-body interaction problem by replacing the spins with boson creation and annihilation operators. Subsequently, one can use the Holstein-Primakoff transformation subjected to an approximation of small spin deviation that keeps only terms up to those linear in $< n_i > << 2S$ that is defined as,

$$S_i^+ = S_{ix} + iS_{iy} = (2S)^{1/2}(1 - \frac{a_i^\dagger a_i}{2S})^{1/2} a_i \tag{4.5}$$

$$S_i^- = S_{ix} - iS_{iy} = (2S)^{1/2} a_i^\dagger (1 - \frac{a_i^\dagger a_i}{2S})^{1/2} \tag{4.6}$$

Where a_i and $a_i^\dagger$ are boson annihilation and creation operators, respectively, and can satisfy the commutation relation, $[a_i, a_l^\dagger] = \delta_{il}$ Now, using the identity,

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

We get

$$S_z^2 = S(S+1) - S_x^2 - S_y^2$$

Substituting the expressions of, S_x^2 and S_y^2 it becomes

$$S_{iz}^2 = S(S+1) - 1/2(S_i^+ S_i^- + S_i^- S_i^+) \tag{4.7}$$

Therefore, to evaluate this equation we use the bosonic operators,

$$\begin{aligned} S_i^+ S_{i'}^- &= (2S)^{1/2}(1 - \tfrac{a_i^\dagger . a_i}{2S})^{1/2} a_i . (2S)^{1/2} a_{i'}^\dagger (1 - \tfrac{a_{i'}^\dagger . a_{i'}}{2S})^{1/2} \\ &= 2S(a_i a_i^\dagger - \frac{a_i^\dagger a_i}{S} - \frac{a_i^\dagger a_i^\dagger a_i a_i}{2S}) \end{aligned} \tag{4.8}$$

$$\begin{aligned} S_{i'}^- S_i^+ &= (2S)^{1/2} a_{i'}^\dagger (1 - \tfrac{a_{i'}^\dagger . a_{i'}}{2S})^{1/2} . (2S)^{1/2} (1 - \tfrac{a_i^\dagger . a_i}{2S})^{1/2} a_i \\ &= 2S(a_i^\dagger a_i - \frac{a_i^\dagger a_i^\dagger a_i a_i}{4S} - \frac{a_i^\dagger a_i^\dagger a_i a_i}{4S}) \end{aligned} \tag{4.9}$$

Finally, equation (4.7) becomes

$$S_{iz}^2 = S(S+1) - S(a_i a_i^\dagger - \frac{a_i^\dagger a_i}{S} + a_i^\dagger a_i - \frac{a_i^\dagger a_i^\dagger a_i a_i}{S}) \tag{4.10}$$

$$S_{iz}^2 = (S - a_i^\dagger a_i)^2 \tag{4.11}$$

For a magnetic system, the bosonic operators $a_i^\dagger$ and a_i can be transformed to the magnon variables $b_k^\dagger$ and b_k

$$b_k = N^{-1/2} \textstyle\sum_i e^{ikx_i} a_i \quad and \;\; b_k^\dagger = N^{-1/2} \sum_i e^{-ikx_i} a_i^\dagger$$

The inverse transformation is,

$$a_i = N^{-1/2} \textstyle\sum_k e^{-ikx_i} b_k \quad and \;\; a_i^\dagger = N^{-1/2} \sum_k e^{ikx_i} b_k^\dagger$$

The spin operators can be expressed in terms of spin variables

$$S_i^+ = \left(\frac{2S}{N}\right)^{1/2} \left[\sum_k e^{-ikx_i} b_k - (4NS)^{-1} \sum_{k,k',k''} e^{i(k-k'-k'')x_i} b_k^\dagger b_{k'} b_{k''}^\dagger + ...\right] \tag{4.12}$$

$$S_i^- = \left(\frac{2S}{N}\right)^{1/2} \left[\sum_k e^{ikx_i} b_k - (4NS)^{-1} \sum_{k,k',k''} e^{i(k+k'-k'')x_i} b_k^\dagger b_{k'}^\dagger b_{k''} + ...\right] \tag{4.13}$$

$$S_{iz} = S - N^{-1} \sum_{k,k'} e^{i(k-k')x_i} b_k^\dagger b_{k'} \tag{4.14}$$

The total spin operator of the system is

$$NS - S_z = NS - \sum_i S_{iz} = \sum_i a_i^\dagger a_i$$

And it follows that the total spin operators along z-direction is

$$S_z = NS - \sum_k b_k^\dagger b_k \tag{4.15}$$

Now, using the equations 4.12, 4.13, and 4.15, the model Hamiltonian can be evaluated.

$$H = -\sum_{ij} J_{ij}\vec{S}_i.\vec{S}_j - g\mu_B H \sum_i S_{iz} - \mu E \sum_i S_{iz} + D\sum_i S_{iz}^2 \tag{4.16}$$

$$\vec{S}_i.\vec{S}_j = S_{ix}.S_{jx} + S_{iy}.S_{jy} + S_{iz}.S_{jz} \tag{4.17}$$

Using the operators given by equation 4.5 and 4.6, it follows that

$$\vec{S}_i.\vec{S}_j = \frac{1}{4}(2S_i^+.S_j^- + 2S_i^-.S_j^+ + S_{iz}.S_{jz}) \tag{4.18}$$

The first term of equation 4.16 along with equation 4.18 gives

$$-\sum_{ij} J_{ij}\vec{S}_i.\vec{S}_j = -\sum_{ij} J_{ij}(S_{iz}.S_{jz} + \frac{1}{2}S_i^+.S_j^- + \frac{1}{2}S_i^-.S_j^+) \tag{4.19}$$

Upon expanding the the operators,

$$S^+ = \sqrt{2S}(a_i - \tfrac{1}{4S}a_i^\dagger a_i a_i + ...) \text{ and } S^- = \sqrt{2S}(a_j^\dagger - \tfrac{1}{4S}a_j^\dagger a_j^\dagger a_j + ...)$$

$$S_i^+ = \left(\frac{2S}{N}\right)^{1/2}\left[\sum_k e^{-ikx_i}b_k - (4NS)^{-1}\sum_{k,k',k''} e^{i(k-k'-k'')x_i}b_k^\dagger b_{k'}b_{k''} + ...\right] \tag{4.20}$$

$$S_i^- = \left(\frac{2S}{N}\right)^{1/2}\left[\sum_k e^{ikx_i}b_k^\dagger - (4NS)^{-1}\sum_{k,k',k''} e^{i(k+k'-k'')x_i}b_k^\dagger b_{k'}^\dagger b_{k''} + ...\right] \tag{4.21}$$

Similarly, S_j^+ and S_j^- can be obtained Whereas the first term of equation 4.19 making use of equation 4.14 becomes

$$S_{iz}.S_{jz} = S^2 - \tfrac{S}{N}\textstyle\sum_{k,k'} e^{i(k-k')x_j}b_k^\dagger b_{k'} - \tfrac{S}{N}\sum_{k,k'} e^{i(k-k')x_i}b_k^\dagger b_{k'}$$
$$+N^{-2}\sum_{k,k'} e^{i(k-k')(x_i+x_j)}b_k^\dagger b_{k'}b_k^\dagger b_{k'} \tag{4.22}$$

It is convenient to set a relation between two sites x_i and x_j assuming that these sites are position vectors of nearest neighbors. We put δ to be the difference of these vectors. In other words,

$x_j \rightarrow x_i + \delta$. Maintaining only the bilinear terms corresponding to the spin variables, it suffices to write

$$S_{iz}.S_{jz} = S^2 - \frac{S}{N}\sum_{k,k'}(e^{i(k-k')x_j}b_k^\dagger b_{k'} + e^{i(k-k')x_i})b_k^\dagger b_{k'} \tag{4.23}$$

The second and third terms of equation 4.19 can also be reduced to interacting system taking into account the binary terms of spin variables.

$$S_i^+ S_j^- = \left(\tfrac{2S}{N}\right)\left[\sum_k e^{-ikx_i}b_k - (4NS)^{-1}\sum_{k,k',k''} e^{i(k-k'-k'')x_i}b_k^\dagger b_{k'}b_{k''} + ...\right]$$

$$\left[\sum_{k'} e^{ik'x_j}b_{k'}^\dagger - (4NS)^{-1}\sum_{k,k',k''} e^{i(k+k'-k'')x_j}b_k^\dagger b_{k'}^\dagger b_{k''} + ...\right] \tag{4.24}$$

$$S_i^+ S_j^- = \frac{2S}{N}\sum_{k,k'} e^{-i(k-k')x_i}e^{ik'\delta}b_k b_{k'}^\dagger \tag{4.25}$$

$$S_i^- S_j^+ = \left(\frac{2S}{N}\right)\sum_{k,k'} e^{i(k-k')x_i}e^{-ik'\delta}b_k^\dagger b_{k'} \tag{4.26}$$

Then, combining equations 4.23, 4.25 and 4.26

$$S^2 - \tfrac{S}{N}\sum_{k,k'}(e^{i(k-k')x_j}b_k^\dagger b_{k'} + e^{i(k-k')x_i})b_k^\dagger b_{k'} + \tfrac{2S}{N}\sum_{k,k'} e^{-i(k-k')x_i}e^{ik'\delta}b_k b_{k'}^\dagger +$$

$$\left(\frac{2S}{N}\right)\sum_{k,k'} e^{i(k-k')x_i}e^{-ik'\delta}b_k^\dagger b_{k'} + o(h) \tag{4.27}$$

Evaluating the remaining terms of the model Hamiltonian results the following.

$$\sum_i S_{iz} = \sum_i (S - a_i^\dagger a_i)$$

$$\sum_i S_{iz} = NS - N^{-1}\sum_{k,k'} e^{i(k-k')x_i}b_k^\dagger b_{k'} \tag{4.28}$$

Similarly, ignoring higher order terms it turns out to be

$$\sum_i (S_{iz})^2 = NZS^2 - \frac{2S}{N}\sum_{k,k'} e^{i(k-k')x_i}b_k^\dagger b_{k'} \tag{4.29}$$

Where Z stands for the number of nearest neighbors. Finally, the Hamiltonian with the help of equations 4.27, 4.28 and 4.29 is,

$$H = -\sum_{i\delta} J_{i,i+\delta}[S^2 - \tfrac{S}{N}\sum_{k,k'}(e^{i(k-k')x_{i+\delta}}b_k^\dagger b_{k'} + e^{i(k-k')x_i})b_k^\dagger b_{k'}$$

$$+\tfrac{S}{N}\sum_{k,k'} e^{-i(k-k')x_i}e^{ik'\delta}b_k b_{k'}^\dagger + \tfrac{S}{N}\sum_{k,k'} e^{i(k-k')x_i}e^{-ik'\delta}b_k^\dagger b_{k'}]$$

$$-g\mu_B H(NS - N^{-1}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'})$$

$$-\mu E(NS - N^{-1}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'}) + D(NS^2 - \tfrac{2S}{N}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'})$$

$$+o(h) \tag{4.30}$$

This equation can be treated focusing on the bilinear spin variable terms and can be grouped into:

$$H = H_1 + H_2 + H_3 + H_4 + H_5 \tag{4.31}$$

Where H_1 and H_2 are quadratic and linear with S, i.e,

$$H_1 = JNZS^2 + DNS^2\,; \quad H_2 = -g\mu_B HNS - \mu ENS$$

$$H_3 = -\sum_{i\delta} J_{i,i+\delta} \tfrac{S}{N}[\sum_{k,k',i,\delta} e^{-i(k-k')x_i} e^{ik'\delta} b_k b_{k'}^\dagger + \sum_{k,k',i,\delta} e^{i(k-k')x_i} e^{-ik'\delta} b_k^\dagger b_{k'}$$
$$- \sum_{k,k',i,\delta} e^{i(k-k')x_{i+\delta}} b_k^\dagger b_{k'} - \sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'}] - \tfrac{2DS}{N}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'}$$

Summing over i and for $k = k'$, and considering an isotropic exchange coupling this reduces to

$$H_3 = -\tfrac{JNZS}{N}\sum_k(\gamma_k b_k b_k^\dagger + \gamma_{-k} b_k^\dagger b_k - 2b_k^\dagger b_k) - \tfrac{2DNS}{N}\sum_k b_k^\dagger b_k$$

Where $\gamma_k = Z^{-1}\sum_\delta e^{-ik.\delta}$. Thus, the linear term with the total spin S, is found to be

$$H_3 = -JZS\sum_k(\gamma_k(1 + b_k^\dagger b_k) + \gamma_{-k} b_k^\dagger b_k - 2b_k^\dagger b_k) - 2DS\sum_k b_k^\dagger b_k \tag{4.32}$$

Similarly, the Hamiltonian H_4 proportional to the term 1/N can be simplified as

$$H_4 = g\tfrac{\mu_B H}{N}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'} + \tfrac{\mu E}{N}\sum_{k,k',i} e^{i(k-k')x_i} b_k^\dagger b_{k'}$$

$$H_4 = g\mu_B H\sum_k b_k^\dagger b_k + \mu E\sum_k b_k^\dagger b_k \tag{4.33}$$

In this effective Hamiltonian(equation 4.31), the last term H_5, is a fourth and higher order term of spin variables. Therefore, it can be neglected without significant changes if the excitation is low. The most important point lies on equations 4.32 and 4.33. As a result,

$$H_{34} = -JZS\sum_k(\gamma_k(1 + b_k^\dagger b_k) + \gamma_{-k} b_k^\dagger b_k - 2b_k^\dagger b_k) - 2DS\sum_k b_k^\dagger b_k + (g\mu_B H + \mu E)\sum_k b_k^\dagger b_k \tag{4.34}$$

In symmetrical considerations, $\sum_k \gamma_k = 0$ therefore equation 4.34 becomes,

$$H_{34} = \sum_k (-2JZS(\gamma_k - 1) - 2DS + g\mu_B H + \mu E) b_k^\dagger b_k \tag{4.35}$$

The Hamiltonian of the system is thus written in simplified form as:

$$H = -JNZS^2 + DNS^2 - g\mu_B HNS - \mu ENS + \sum_k (-2JZS(\gamma_k - 1) - 2DS + g\mu_B H + \mu E) b_k^\dagger b_k \tag{4.36}$$

However, equation 4.35 can be written as,

$$H_{34} = \textstyle\sum_k \hat{n}_k \omega_k \text{ where}$$

$$\omega_k = -2JZS(\gamma_k - 1) - 2DS + g\mu_B H + \mu E) \tag{4.37}$$

For $|k.\delta| << 1$ and for cubic symmetry equation 4.37 can be approximated in the following manner [123] on the aproxamation of $Z(1 - \gamma_k) \approx \frac{1}{2}\sum_\delta (k\delta)^2 \approx \frac{1}{2}(ka)^2$

$$\omega_k = JSa^2k^2 - 2DS + g\mu_B H + \mu E \tag{4.38}$$

Defining terms, $\beta = JSa^2$ and $\gamma = -2DS + g\mu_B H + \mu E$ the dispersion equation of the excited system becomes,

$$\omega_k = \beta k^2 + \gamma \tag{4.39}$$

One can use this dispersion relation to find other physical quantities such as the internal energy, heat capacity, and the magnetization as well as the susceptibility of a given system. The internal energy is given as

$$U = \sum_k \omega_k \langle n_k \rangle_T \tag{4.40}$$

The specific heat capacity is given by

$$C = \tfrac{dU}{dT}$$

$$C = \tfrac{d}{dT}\tfrac{1}{(2\pi)^3}\textstyle\int d^3k \omega_k \langle n_k \rangle_T$$

$$C = \frac{d}{dT}\frac{1}{2\pi^2}\int dk k^2(\beta k^2 + \gamma)\frac{1}{e^{\frac{\beta k^2+\gamma}{\tau}} - 1} \tag{4.41}$$

Where $\tau = k_B T$

let $x = \beta k^2$

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}\int_0^\infty \frac{(x^{\frac{3}{2}} + \gamma x^{\frac{1}{2}})}{e^{\frac{x+\gamma}{\tau}} - 1})dx \tag{4.42}$$

The integral in equation 4.42 is of the form,

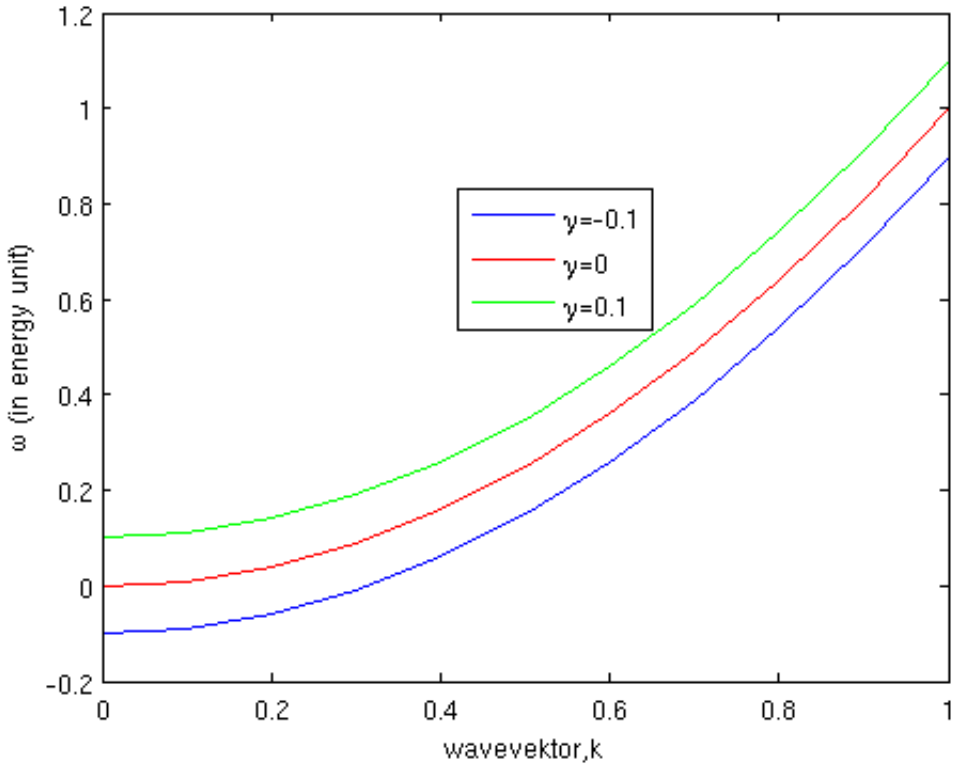

Figure 4.2: The dispersion curve in the presence of fields for different gamma values.

$$\int_0^\infty \frac{x^s}{\frac{1}{\alpha}e^{\frac{x}{\tau}}-1} = \Gamma(s+1)\tau^{s+1}\sum_{m=1}^{\infty}\alpha^m\frac{1}{m^{s+1}}$$

For $\alpha \leq 1$ the integral is

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}\left\{\Gamma(\frac{5}{2})\tau^{\frac{5}{2}}\sum_{m=1}^{\infty}e^{-\frac{m\gamma}{\tau}}\frac{1}{m^{\frac{5}{2}}} + \gamma\Gamma(\frac{3}{2})\tau^{\frac{3}{2}}\sum_{m=1}^{\infty}e^{-\frac{m\gamma}{\tau}}\frac{1}{m^{\frac{3}{2}}}\right\} \tag{4.43}$$

In the limit as $\frac{\gamma}{\tau} \ll 1$, the summation on the right side of equation 4.43 can be approximated as $\zeta(\frac{5}{2})$ and $\zeta(\frac{3}{2})$.

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}\left\{\Gamma(\frac{5}{2})\tau^{\frac{5}{2}}\zeta(\frac{5}{2}) + \gamma\Gamma(\frac{3}{2})\tau^{\frac{3}{2}}\zeta(\frac{3}{2})\right\} \tag{4.44}$$

$$C = \frac{1}{4\pi^2\beta^{\frac{3}{2}}}\left\{\Gamma(\frac{5}{2})k_B^{\frac{5}{2}}\frac{5}{2}T^{\frac{3}{2}}\frac{15\pi^{\frac{1}{2}}}{8} + \gamma\Gamma(\frac{3}{2})k_B^{\frac{3}{2}}\frac{3}{2}T^{\frac{1}{2}}\frac{\pi^{\frac{1}{2}}}{2}\right\}$$

$$C = \frac{3}{16}(\frac{k_B}{\pi\beta})^{\frac{3}{2}}\left\{\frac{25}{4}\Gamma(\frac{5}{2})k_BT^{\frac{3}{2}} + \gamma\Gamma(\frac{3}{2})T^{\frac{1}{2}}\right\} \tag{4.45}$$

$$C = \frac{75}{64(\pi\beta)^{\frac{3}{2}}}\Gamma(\frac{5}{2})k_B^{\frac{5}{2}}T^{\frac{3}{2}}(1 + \frac{4\gamma\Gamma(\frac{3}{2})}{25\Gamma(\frac{5}{2})k_BT})$$

$$C = C_o(1 + \frac{4\gamma\Gamma(\frac{3}{2})}{25\Gamma(\frac{5}{2})k_BT}) \tag{4.46}$$

$If \;\; \gamma = 0, \;\; then \; C \to C_o$

$$C_o = \frac{75}{64(\pi\beta)^{\frac{3}{2}}}\Gamma(\frac{5}{2})k_B^{\frac{5}{2}}T^{\frac{3}{2}} \tag{4.47}$$

At low temperature limit, $e^{\frac{x+\gamma}{\tau}} - 1 \simeq e^{\frac{x+\gamma}{\tau}}$. Therefore, equation 4.42 can be written as

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}\int_0^\infty (x^{\frac{3}{2}} + \gamma x^{\frac{1}{2}})e^{-(\frac{x+\gamma}{\tau})}dx$$

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}e^{-\frac{\gamma}{\tau}}\int_0^\infty (x^{\frac{3}{2}} + \gamma x^{\frac{1}{2}})e^{-\frac{x}{\tau}}dx \tag{4.48}$$

The integral in equation 4.48 can be evaluated using the following integral values,

$$\int_0^\infty x^{\frac{3}{2}}e^{-\frac{x}{\tau}}dx = \frac{\Gamma(\frac{3}{2}+1)}{(\frac{1}{\tau})^{\frac{3}{2}+1}}$$
$$\int_0^\infty x^{\frac{1}{2}}e^{-\frac{x}{\tau}}dx = \frac{\Gamma(\frac{1}{2}+1)}{(\frac{1}{\tau})^{\frac{1}{2}+1}}$$

Thus,

$$C = \frac{d}{dT}\frac{1}{4\pi^2\beta^{\frac{3}{2}}}e^{-\frac{\gamma}{\tau}}(\frac{\Gamma(\frac{3}{2}+1)}{(\frac{1}{\tau})^{\frac{3}{2}+1}} + \gamma\frac{\Gamma(\frac{1}{2}+1)}{(\frac{1}{\tau})^{\frac{1}{2}+1}}) \tag{4.49}$$

Finally the specific heat at low temperature is found to be dependent on exponential term,

$$C = \frac{e^{-\frac{\gamma}{k_BT}}}{4(\pi\beta)^{\frac{3}{2}}}(\frac{45}{32}k_B^{\frac{5}{2}}T^{\frac{3}{2}} + \frac{21}{16}\gamma k_B^{\frac{3}{2}}T^{\frac{1}{2}} + \frac{1}{2}\gamma^2 k_B^{\frac{1}{2}}T^{\frac{-1}{2}}) \tag{4.50}$$

The magnetization of the system at any arbitrary temperature which depends on the number of spin reversal is defined in terms of the spin wave occupancy.

$$M_s(T) = 2\mu_o S_z = 2\mu_o \textstyle\sum_i S_{iz}$$

$$M_s(T) = 2\mu_o(NS - \sum_k b_k^\dagger b_k) \tag{4.51}$$

The change in magnetization is

$$M_s(0) - M_s(T) = \Delta M = 2\mu_o \textstyle\sum_k \langle n_k\rangle$$

$$\textstyle\sum_k \langle n_k\rangle = \frac{1}{(2\pi)^3}\int d^3k \frac{1}{e^{\frac{\beta k^2+\gamma}{\tau}}-1}$$

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\int d^3k \frac{1}{e^{\frac{\beta k^2+\gamma}{\tau}}-1}$$

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\frac{4\pi}{2\beta^{\frac{3}{2}}}\int_0^\infty \frac{x^{\frac{1}{2}}}{e^{\frac{x+\gamma}{\tau}}-1}dx \tag{4.52}$$

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\frac{4\pi}{2\beta^{\frac{3}{2}}}\Gamma(\frac{3}{2})\tau^{\frac{3}{2}}\sum_{m=1}^{\infty} e^{-\frac{m\gamma}{\tau}}\frac{1}{m^{\frac{3}{2}}} \tag{4.53}$$

In the limit as $\frac{\gamma}{\tau} \ll 1$ the summation on the right side of this equation can be approximated as $\zeta(\frac{3}{2})$. Thus, it becomes

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\frac{4\pi}{2\beta^{\frac{3}{2}}}\Gamma(\frac{3}{2})\tau^{\frac{3}{2}}\zeta(\frac{3}{2}) \tag{4.54}$$

$$\Delta M = \frac{\mu_o}{4(\pi\beta)^{\frac{3}{2}}}\Gamma(\frac{3}{2})\tau^{\frac{3}{2}} \tag{4.55}$$

The ground state magnetization is given by $M_s(0) = 2\mu_o NS$. Finally, temperature dependent magnetization can be expressed by the following equation consistent with the experimental results [124].

$$M_s(T) = M_s(0) - \frac{\mu_o}{4(\pi\beta)^{\frac{3}{2}}}\Gamma(\frac{3}{2})(k_B T)^{\frac{3}{2}}$$

It becomes

$$M_s(T) = 2\mu_o NS - \frac{\mu_o}{4}(\frac{k_B}{\pi\beta})^{\frac{3}{2}}\Gamma(\frac{3}{2})T^{\frac{3}{2}} \tag{4.56}$$

This equation tells us that at very high temperature, the magnetization explicitly depends on the temperature no matter how the fields are large. However, in the low temperature limit the integral in equation 4.52 is approximated to be

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\frac{4\pi}{2\beta^{\frac{3}{2}}}\int_0^\infty x^{\frac{1}{2}}e^{-(\frac{x+\gamma}{\tau})}dx$$

This reduces to

$$\Delta M = \frac{2\mu_o}{(2\pi)^3}\frac{4\pi}{2\beta^{\frac{3}{2}}}e^{-\frac{\gamma}{\tau}}(\frac{\Gamma(\frac{1}{2}+1)}{(\frac{1}{\tau})^{\frac{1}{2}+1}})$$

$$\Delta M = \frac{\mu_o k_B^{\frac{3}{2}}}{4(\pi\beta)^{\frac{3}{2}}}e^{-\frac{\gamma}{k_B T}}T^{\frac{3}{2}} \tag{4.57}$$

The saturation magnetization at any arbitrary temperature is,

$$M_s(T) = 2\mu_o NS - \frac{\mu_o}{4}(\frac{k_B}{\pi\beta})^{\frac{3}{2}}e^{-\frac{\gamma}{k_B T}}T^{\frac{3}{2}} \tag{4.58}$$

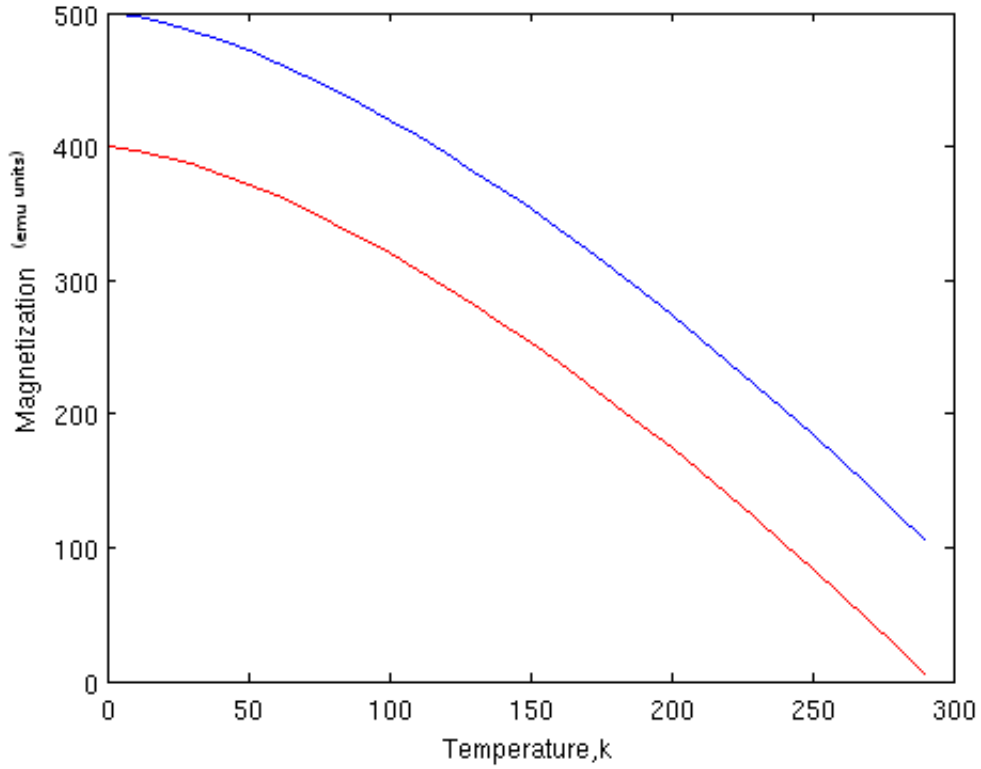

Figure 4.3: The sketch indicates the magnetization versus temperature dependence at high temperature values.

The saturation magnetization, $M_s(T) \to 0$ as $T \to T_c$, whence

$$M_s(0) = \frac{\mu_o}{4}(\frac{k_B}{\pi\beta})^{\frac{3}{2}} e^{-\frac{\gamma}{k_B T_c}} T_c^{\frac{3}{2}} \tag{4.59}$$

The critical temperature is expressed as follows,

$$T_c \ln(\frac{T_c}{\alpha}) = \frac{2}{3}\frac{\gamma}{k_B} \tag{4.60}$$

Where the constant $\alpha = \frac{8N\pi^{\frac{3}{2}} J^{\frac{3}{2}} a^3 S^{\frac{5}{2}}}{k_B^{\frac{3}{2}}}$. In the low temperature limiting case it is found that

$$\frac{M_s(T)}{M_s(0)} = 1 - e^{\frac{\gamma}{k_B}(\frac{T-T_c}{TT_c})}(\frac{T}{T_c})^{\frac{3}{2}} \tag{4.61}$$

The volume magnetic susceptibility is also defined as

$$\chi = \frac{M_s(T)}{H}$$

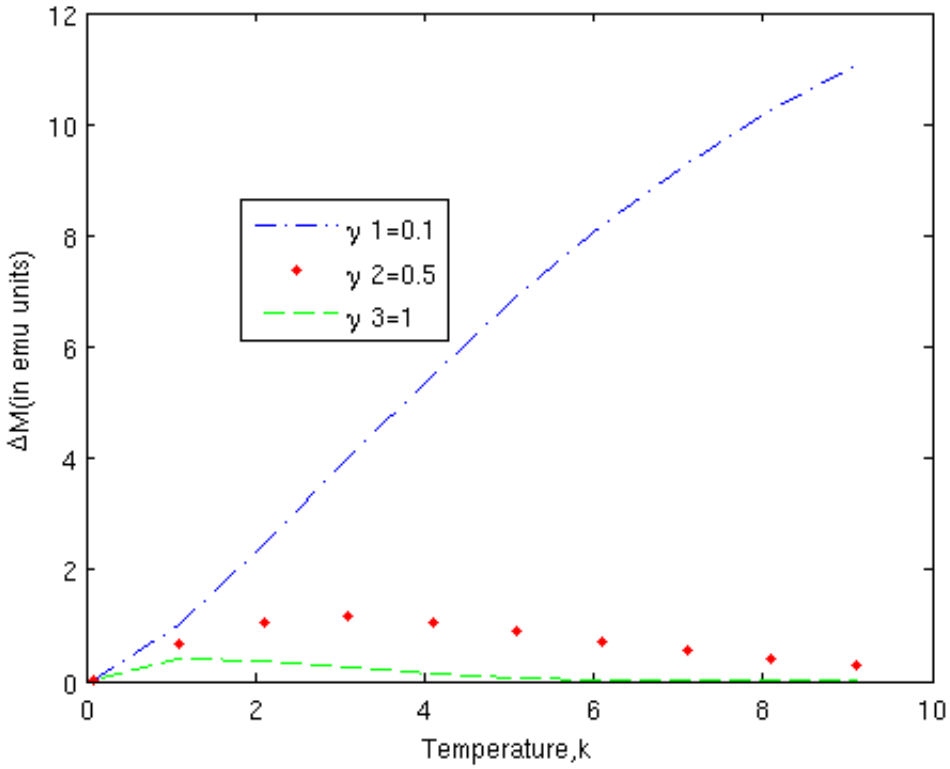

Figure 4.4: This figure shows the characteristics of the change in magnetization as a function of temperature at low temperature.

At low temperature, the volume magnetic susceptibility is found to be

$$\chi = \frac{2\mu_o NS - \frac{\mu_o}{4}(\frac{k_B}{\pi\beta})^{\frac{3}{2}} e^{-\frac{\gamma}{k_B T}} T^{\frac{3}{2}}}{H} \tag{4.62}$$

4.3 Results and Discussion

The specific heat calculation in this work shows a remarkable dependency on temperature and fields(magnetic and electric) [125,126,127]. We obtained the expression at high temperature that is linear to the γ value and is a polynomial function of fractional exponents of the temperature. $C = C_o(1 + \frac{4\gamma\Gamma(\frac{3}{2})}{25\Gamma(\frac{5}{2})k_B T})$ Where $C_o = \frac{75}{64(\pi\beta)^{\frac{3}{2}}}\Gamma(\frac{5}{2})k_B^{\frac{5}{2}}T^{\frac{3}{2}}$ is the heat capacity in the absence of fields proportional to the magnon contribution,$T^{3/2}$ [128]. However, at low temperature the specific heat function varies a bit in the form that it is an exponential function of γ and

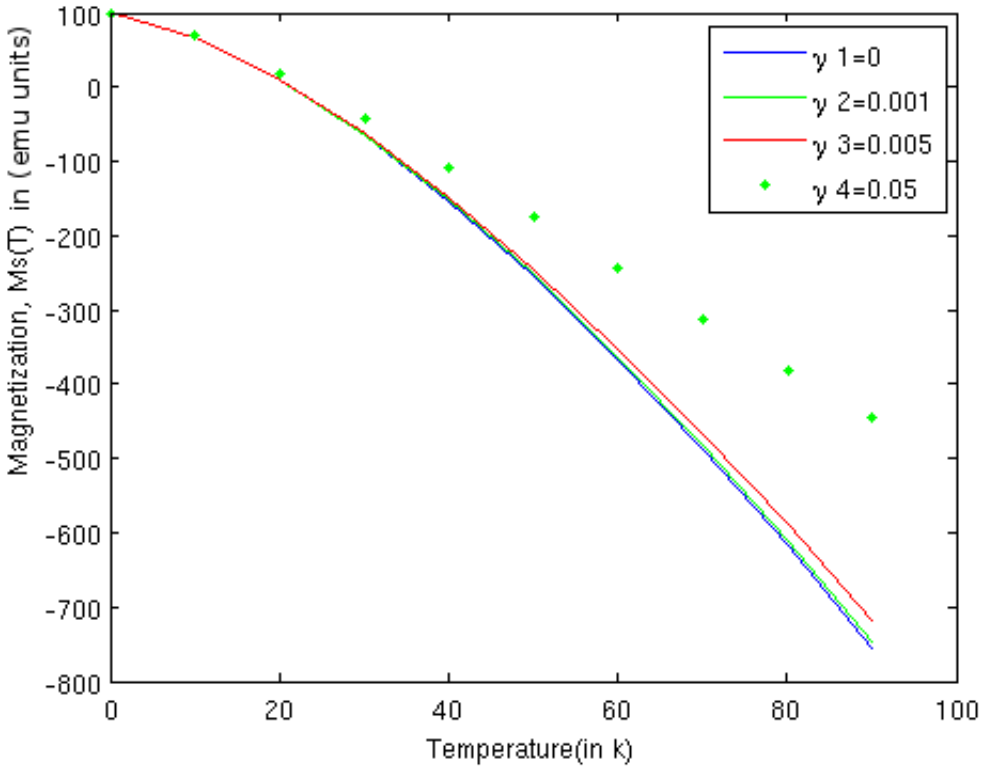

Figure 4.5: This figure shows the variation of saturation magnetization as a function of low temperature values at some specific γ values.

temperature, i.e, $\propto e^{-\frac{\gamma}{k_B T}}$.

The spin-wave dispersion function of the multiferroic thin film system is obtained as a function of the wave vector and the fields. A significant change in the dispersion relation is observed as depicted by figure 2 above at different γ values [129]. This can be used to modify the behavior of the multiferroics upon appropriate selection of the magnetic and electric field components in some orientations while the magnetic anisotropy is still kept in controlling of the ferroelectric polarization (interacting through lattice polarization field) by floping, rotation and reversals along with the dielectric anomaly. Moreover, the magnetic properties of these classes of materials are also analysed based on the spin-wave occupation number, $\sum_k b_k^\dagger b_k$. It is shown that the magnetization at low temperature is a function of the γ values as indicated by figure 4 above [130,131].

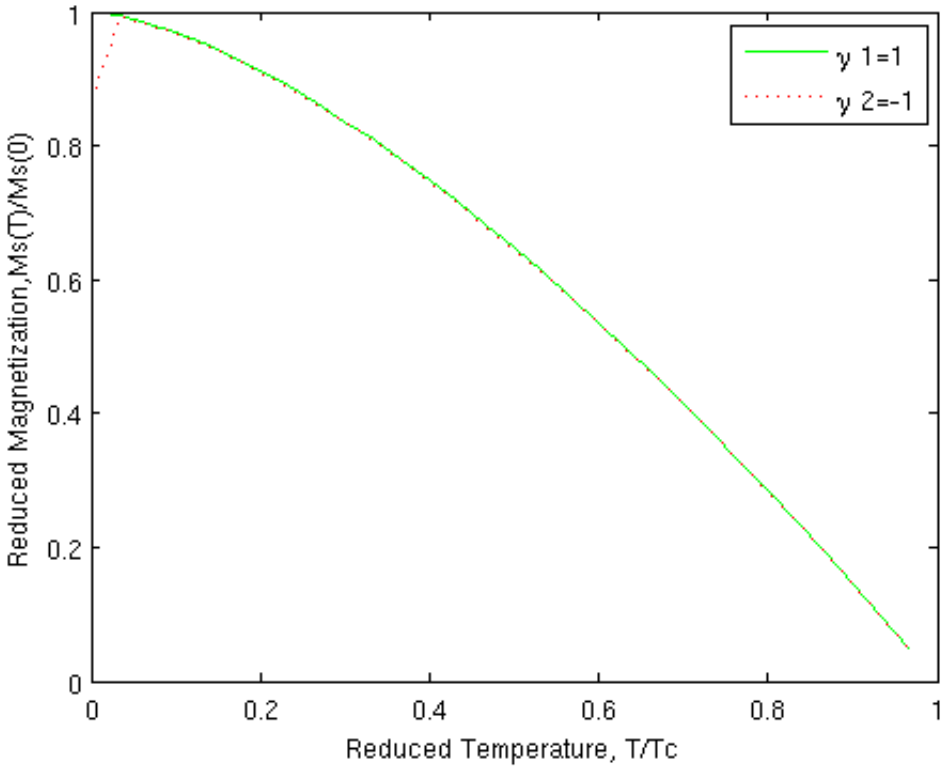

Figure 4.6: The figure depicts the reduced magnetization versus temperature plot at about $T_c = 300k$ [83].

Chapter 5

Magnon-Phonon Excitation in FE-FM Nanostructure Composite

A hallmark of magnetically induced multiferroicity, which may arise from collinear or non-collinear spin configurations, is the appearance of hybridized magnon-phonon excitation. Magnetic frustration is the characteristics of insulators and is a main source of magnetic orderings. In the nanostructures of FE-FM composites magnetic field is expected to influence the electric polarization quite strongly at low field limits. Nanocomposites of linear chain of ferroelectric-ferromagnetic crystal structure is considered.It is analyzed theoretically in the equation of motion method on the pursuit of magnonic excitations,lattice vibration excitations and their interactions leading to a new collective mode of excitations, the ”electormagnons”. In this particular work, it is observed that the magnetizations and polarizations are tunable in a given temperature ranges for some specific values of the coupling order parameter.

5.1 Introduction

Lattice vibrations are responsible for different physical properties in crystals and, magnetic excitations do the same parallelism in magnetic materials. The quest of multifunctionality of devices has become the frontal research endeavors, particularly in the spintronics world [132,133,134,135,136]. Composite materials of both ferromagnetic and ferroelectric states have been examined experimentally and showed appreciable couplings of the two phases at room

temperatures [137,138]. Nanofibers have also shown enhanced magnetoelectric responses and rich phase diagrams marking the coupling of various order parameters [139]. In this work the lattice vibrations and magnetic excitations are considered for the extraordinary couplings of the orders. To deal with this, a linear chain of lattice atoms of composite ferroelectric-ferromagnetic multiferroic is considered and discussed in the sections below with the motion equation approach to diagonalize the Hamiltonian.

5.2 Spin Wave Excitations in One Dimensional FE-FM Nanostructure

Magnetic fluctuations in insulators are associated with localized magnetic moments and these moments have the tendencies of orderings at sufficiently low temperature and support coherent magnetic waves [140]. The magnetic excitations that we will consider here are oscillations of the relative orientations of the spins in the lattices of insulating multiferoics whose quantized states are described as "magnons" [94]. Because of the magnetostricive properties of the magnetic crystals, the spin waves are expected to couple with an elastic lattice vibrations. The magnetoelastic wave propagation in the crystal of spatially variable magnetic field is studied by Schlomann and Joseph [141]. They found that the wave propagates with constant power flow (variable energy), but variable momentum and wavevector at the crossover region (where the spin waves and lattice vibrations wave numbers are comparable) and most of the energy stays in the spin wave state. However, if the field gradient is very small, most energy is converted into the elastic state. Therefore, the coupled oscillation exists for some wavevectors of the spin and lattice vibrations.

The following Hamiltonian describes the effective magnetic interaction of spin frustrated nanostructured chains of atoms whose electrons are localized and their ions are free to oscillate about the equilibrium positions. We can also suggest that the electron clouds, despite they are bounded strongly, can polarize the nearby lattices. So, it is realistic to discuss the magnetic behaviors and lattice vibrations in general.

$$H = -\sum_{ij} J_{ij}\vec{S}_i.\vec{S}_j - g\mu_B H\sum_i S_{iz} - \mu E\sum_i S_{iz} + D\sum_i S_{iz}^2 \tag{5.1}$$

The first term is the exchange energy. The second one is the Zeeman interaction, while the third and the fourth terms stand for the spin-electric interaction and anisotropic contributions, respectively [108,142].

Thus, the interaction Hamiltonian through subsequent transformations and mathematical operations followed by suitable approximations, to the bilinear order of spin operators become,

$$H = \sum_k (-2JZS(\gamma_k - 1) - 2DS + g\mu_B H + \mu E)b_k^\dagger b_k \tag{5.2}$$

Which can be written in the following form

$$H = \textstyle\sum_k \hat{n}_k\omega_k \text{ where}$$

$$\omega_k = -2JZS(\gamma_k - 1) - 2DS + g\mu_B H + \mu E) \tag{5.3}$$

For $|k.\delta| << 1$, long wavelength limit and cubic symmetry

$$Z(1 - \gamma(k)) \approx \tfrac{1}{2}\textstyle\sum_\delta (k\delta)^2 \approx \tfrac{1}{2}(ka)^2$$

So that, the excitation frequency of quasi-particles is

$$\omega_k = JSa^2k^2 - 2DS + g\mu_B H + \mu E \tag{5.4}$$

Letting the parameters $\beta = JSa^2$ and $\gamma = -2DS + g\mu_B H + \mu E$ lead to a dispersion relation of the excited system.

$$\omega_k = \beta k^2 + \gamma \tag{5.5}$$

This dispersion function, the spin excitation frequency, is a quadratic function of the wavenumber k, of the excitation shifted by the parameter γ about the origin.

5.3 The Quantization of Excited Lattice Vibration

In this section we study the basic aspects of lattice vibrations of ions well described by harmonic oscillation to obtain the Hamiltonian in the second quantization. The vibration dynamics in any

crystal system is classified in to three basic features. The first vibration type is the ion density oscillation in a relatively static electron cloud backgrounds, i.e, the ion plasma oscillation where the deriving force is the long range coulomb interaction. The second class corresponds to the slow ionic oscillation followed by the electronic clouds, the sound wave. The deriving force is the dragging of the deformed electron gas. The third one is the fast electronic plasma oscillation in a relatively static ion lattices (the electron plasma). The main focus in this section is, therefore, in the first vibration type because we consider the composites of insulating materials in which the electron clouds are localized so that the expected oscillation is nearly of ionic plasma. However, electronic cloud interacts with the lattice ions and induce polarizations and this is [143] based on the Jellium oscillation theory that treats the ion density dynamics neglecting and/ or approximation the electronic contributions in a lesser extent. We begin with a simple one dimensional quantum mechanical model consisting of linear chain of atoms of finite length L, having N ions of different masses m_1 and m_2 each interacting with the nearest neighbors. The ions execute simple harmonic oscillations (back and forth) about their equilibrium positions through a linear force constant, c. The equilibrium displacements of the masses m_1 and m_2 are v_j and u_i respectively. In a linear approximation, the left and right restoring forces of the masses being expressed as

$m_2 \frac{d^2u_i}{dt^2} = c(v_j - u_i) + c(v_{j-1} - u_i)$

$$m_2 \frac{d^2u_i}{dt^2} = c(v_{j-1} + v_j - 2u_i) \tag{5.6}$$

Whereas,

$m_1 \frac{d^2v_j}{dt^2} = c(u_{i+1} - v_j) + c(u_i - v_j)$

$$m_1 \frac{d^2v_j}{dt^2} = c(u_{i+1} + u_i - 2v_j) \tag{5.7}$$

Looking for trivial solutions for equations making use of the lattice displacement vectors of different amplitudes $\propto e^{-i\omega t}$, $v_j = ve^{i(jq.x)}e^{-i\omega t}$.

$m_2 \frac{d^2u_i}{dt^2} = c[(1 + e^{-iq.x})v_j - 2u_i]$

$$-\omega^2 m_2 u_i = c[(1 + e^{-iq.x})v_j - 2u_i] \tag{5.8}$$

Similarly,

$$-\omega^2 m_1 v_j = c[(1 + e^{iq.x})u_i - 2v_j] \tag{5.9}$$

These linear homogeneous equations have solutions if and only if the determinants vanish, i.e

$$\begin{vmatrix} \omega^2 m_2 - 2c & c(1 + e^{-iq.x}) \\ c(1 + e^{iq.x}) & \omega^2 m_1 - 2c \end{vmatrix} = 0$$

The eigen frequencies (branches of the dispersions)

$$\omega^2 = c\{(\frac{1}{m_1} + \frac{1}{m_2}) \pm \sqrt{(\frac{1}{m_1} + \frac{1}{m_2})^2 - \frac{2}{m_1 m_2}(1 - cos(qa))}\} \tag{5.10}$$

We clearly see that eigen solution is a function of the wavevector q and is periodic for any arbitrary reciprocal lattice vector G. The dispersion function at q $\rightarrow$ 0 and at q=0 have limiting values to the acoustic and optical branches. However, the point of interest is the optical component of these branches, i.e, ω_+^2, because it is the optical mode, especially the longitudinal optical component which interacts or couples so appreciably with the crystal under consideration having spontaneous dipole moments. This assumption is based on C. Kittle which he has emphasized on the way that the longitudinal optical limiting frequency is higher than the transverse branch due to electrostatic interactions of the ions. Our model strongly supports this idea since we have interacting chains of ions longitudinally. This, in other words means that the lattice vibrations have possibilities to couple with the magnetic excitations. Particularly, longitudinal optical lattice vibrations couple to the magnetic excitations on the expense of exchange interaction. And,to avoid higher order interactions, which in fact, can be neglected without affecting the whole system significantly, we consider only the harmonic approximation to the order of nearest neighbor interactions [144].

By symmetry, the force between each pair of atoms is described by the same spring constant. In the diatomic linear lattice we can think of each unit cell as containing two atoms of differing masses and it is characterized by two types of oscillating modes. One of these modes is called the acoustic mode. In an acoustic mode, we think of adjacent atoms as vibrating almost in phase. The other mode is called the optic mode. In an optic mode, we think of adjacent atoms as vibrating out of phase. As we shall show, these descriptions of optic and acoustic modes are valid only in the long wavelength limit. The longitudinal mode is, usually, the mode with

highest frequency for each wave vector in the three optic modes and also in the three acoustic modes.

To evaluate the Hamiltonian component of the lattice contribution we represent the elastic deformation of the chain by the vector operator $u_i = x' - x$. The total energy arising from the kinetic and potential terms can be expressed in terms of the local dipole moments and the intrinsic fields. The reason being that the crystal is polar and the interactions of the induced dipoles of the deformed lattice ions along with the clouds of localized electrons significantly play the role. Therefore, the quantized elastic vibration energy is associated with the electrostatic energy.

$$H_e = \sum_i p_i.E_{loc} \tag{5.11}$$

The local dipole moment is $p_i = \alpha_i E_{loc}$ where α_i is the polarizability of the i^{th} ion and for uniform polarization and local electric field,

$$H_e = \sum_i p_i.\frac{p_i}{\alpha} \tag{5.12}$$

The dipole moment is also defined in terms of the Born charge and the effective lattice displacement $p_i = e^* u_i$

$$H_e = \sum_i \frac{e^{*2}}{\alpha} u_i.u_i \tag{5.13}$$

The ionic operator can be transformed in to wave coordinate as

$$u_i = N^{\frac{-1}{2}} \sum_q Q_q e^{iq.x_i}$$

whose Fourier transform is

$$Q_q = N^{\frac{-1}{2}} \sum_i u_i e^{-iq.x_i}$$

Once again the displacement vector can be represented in terms of the phonon creation and annihilation operators

$$u_i = \sum_q (\tfrac{\hbar}{2MN\omega_q})^{\frac{1}{2}} (c_q e^{iq.x_i} + c_q^\dagger e^{-iq.x_i})$$

$$H_e = \sum_i \tfrac{e^{*2}}{\alpha} u_i.u_i = \sum_{iqq'} \tfrac{e^{*2}}{\alpha} (\tfrac{\hbar}{2MN\omega_q})^{\frac{1}{2}} (c_q e^{iq.x_i} + c_q^\dagger e^{-iq.x_i}).(\tfrac{\hbar}{2MN\omega_{q'}})^{\frac{1}{2}} (c_{q'} e^{iq'.x_i} + c_{q'}^\dagger e^{-iq'.x_i})$$

At $q = q'$, the energy expectation value tends to be

$$H_e = \sum_q \frac{e^{*2}}{\alpha} \frac{\hbar}{M\omega_q} (c_q^\dagger c_q + \frac{1}{2}) + 0 \tag{5.14}$$

It turnes out to be true to write the energy $\hbar\omega_q = \frac{e^{*2}}{\alpha} \frac{\hbar}{M\omega_q}$ which lead to

$$\omega_q = \pm\sqrt{\frac{e^{*2}}{\alpha M}} \tag{5.15}$$

This is equivalently to be written as the limiting frequency of the phonon plasma $\omega_{plasma} = \sqrt{\frac{n_o e^2}{\epsilon_o M}}$($n_o$ number density of electrons) as mentioned before that depends on the dielectric constant. The dielectric constant is related to the polarizablity of the ions. Finally, the pure electrostatic Hamiltonian can be related to the ground state energy of the free quantized lattice vibration or the phonon character plasma energy.

5.3.1 The Interaction Component of the Hamiltonian

The applications of ferromagnetism in magnetic recording and memory devices have been used long before the theoretical and experimental advances of multiferroics which could likely to be used for commercial and industrial applications. Magnetic recordings and memory devices work with a basic structural configurations in the context of magnetic arrays so that fine single domain particles or regions have magnetic moments directed to one end or another.As pointed out by C.Kittel, a single domain ferromagnetic particle of 10-100 nm size is available with only one domain and possible elongation of uniaxial crystal symmetry. Such chains of single domain fine particles of magnetic entities embedded in other solids are prone to show superparamagnetism which consequently have imminent magnetism even after the external field is removed. We propose a multiferroic crystal of ferroelectric and ferromagnetic components of a continuous linear chain of fine particles, elastically isotropic with reduced mass. The elastic deformation(associated with the magnetostrictive behavior and the spontaneous ionic displacements,the John Teller effect, and this effect is very common in multiferroics of Rare earth manganites where Mn^{3+} ions are responsible for the displacements) of such crystal can be expressed in terms of the vector operator $u = x' - x_o$ along the chain direction, while x' is the position after deformation and x_o is the equilibrium position of the atoms at a particular site (unit cell). Since

the crystal structure in this particular problem is a composite of ferroelectric components that have spontaneous polarization due to induced dipoles and ferromagnetic components which have spontaneous magnetizations due to the existence of permanent dipole moments, the composite is expected to behave differently from its parent materials. The crystals of multiferroic composites are often the compositions of magnetic insulators and ferroelectrics, which are basically insulators in general. The exchange striction depends on the relative positions of ions that is responsible to the coupling of spins to collective lattice distortions [145]. The coupling occurs,in fact, while the magnetic orders break inversion symmetry. In both cases the electrons are tightly bound to the core ions. The ferroelectric crystals are non-centrosymmetric in character, i.e, the spontaneous polarization arises from the John Tellor distortion type [131]. On the other hand, the magnetization in magnetic insulators originate from the localized electrons tightly bound to the lattice ions. Though, the electronic cloud tends to be bound strongly it can polarize the nearby lattices [146] and hence there exists an interaction of the dipole moments (deformed lattices induce dipole moments) with intrinsic fields through exchanges. Therefore, it paves the way to control magnetic properties through electric fields [130,147,]. The interaction Hamiltonian of the spin system and lattice vibration is represented by

$$H_{me} = -\lambda \sum_{i\delta} (u_i \times r_i).(s_i \times s_{i+\delta}) \tag{5.16}$$

Where λ is the spin-phonon coupling parameter, r_i position vector along chain axis, and s_i spin operator.

$$(u_i \times r_i) = (u_{iy} r_{iz} - u_{iz} r_{iy})i - (u_{ix} r_{iz} - u_{iz} r_{ix})j + (u_{ix} r_{iy} - u_{iy} r_{ix})k \tag{5.17}$$

$$s_i \times s_{i+\delta} = (s_{iy} s_{i+\delta,z} - s_{iz} s_{i+\delta,y})i - (s_{ix} s_{i+\delta,z} - s_{iz} s_{i+\delta,x})j + (s_{ix} s_{i+\delta,y} - s_{iy} s_{i+\delta,x})k \tag{5.18}$$

The position vector is along the x-axis and therefore,we have

$$(u_i \times r_i).s_i \times s_{i+\delta} = -u_{iz} r_{ix} s_{ix} s_{i+\delta,z} + u_{iz} r_{ix} s_{iz} s_{i+\delta,x} - u_{iy} r_{ix} s_{ix} s_{i+\delta,y} + u_{iy} r_{ix} s_{iy} s_{i+\delta,x} \tag{5.19}$$

To compute the above terms, we use the spin operators transformed into magnon operators.

$$s_i^+ = s_{ix} + i s_{iy} = \left(\tfrac{2S}{N}\right)^{1/2} \left[\sum_k e^{-ikx_i} b_k - (4NS)^{-1} \sum_{k,k',k''} e^{i(k-k'-k'')x_i} b_k^\dagger b_{k'} b_{k''}^\dagger + ...\right]$$

$$s_i^- = s_{ix} - is_{iy} = \left(\frac{2S}{N}\right)^{1/2}\left[\sum_k e^{ikx_i}b_k - (4NS)^{-1}\sum_{k,k',k''} e^{i(k+k'-k'')x_i}b_k^\dagger b_{k'}^\dagger b_{k''} + ...\right]$$

$$s_{iz} = s - N^{-1}\sum_{kk'} e^{i(k-k').x_i}b_k^\dagger b_{k'}$$

The lattice vibration operator is also written as

$$u_{i\sigma} = \sum_{q\sigma}\left(\frac{\hbar}{2MN\omega_{q\sigma}}\right)^{\frac{1}{2}}\left(c_{q\sigma}e^{iq.x_i} + c_{q\sigma}^\dagger e^{-iq.x_i}\right)$$

Here, σ stands for the lattice vibration polarization; $\sigma = x, y, z$. Taking the magnitude of the position $r_{ix} = Na$, and retaining the lowest terms of the operators,

$$u_{iz}s_{ix}s_{i+\delta,z} = \frac{1}{2}\left(\frac{2s}{N}\right)^{\frac{1}{2}}s\sum_{qkz}\left(\frac{\hbar}{2MN\omega_{qz}}\right)^{\frac{1}{2}}\left(e^{i(q-k).x_i}c_{qz}b_k + e^{i(q+k).x_i}c_{qz}b_k^\dagger + e^{-i(q+k).x_i}c_{qz}^\dagger b_k + e^{-i(q-k).x_i}c_{qz}^\dagger b_k^\dagger\right) + O(h)$$

At some values of q=k and q=-k,

$$\sum_{i\delta} u_{iz}s_{iz}s_{i+\delta,x} = \frac{1}{2}\left(\frac{2s}{N}\right)^{\frac{1}{2}}sN\sum_{qz}\left(\frac{\hbar}{2MN\omega_{qz}}\right)^{\frac{1}{2}}\left(c_{qz}b_q + c_{qz}b_{-q}^\dagger + c_{qz}^\dagger b_{-q} + c_{qz}^\dagger b_q^\dagger\right) + O(h)$$

The summation over δ appears only at higher order terms of the operators and has nothing to do with it here. Similarly, the other terms become,

$$\sum_{i\delta} u_{iz}s_{ix}s_{i+\delta,z} = \frac{1}{2}\left(\frac{2s}{N}\right)^{\frac{1}{2}}sN\sum_{qz}\left(\frac{\hbar}{2MN\omega_{qz}}\right)^{\frac{1}{2}}\left(\gamma_{-q}c_{qz}b_q + \gamma_{-q}c_{qz}b_{-q}^\dagger + \gamma_q c_{qz}^\dagger b_{-q} + \gamma_q c_{qz}^\dagger b_q^\dagger\right) + O(h)$$

where, $\gamma_q = z^{-1}\sum_\delta e^{iq.\delta}$ and $\gamma_{-q} = z^{-1}\sum_\delta e^{-iq.\delta}$

$$\sum_{i\delta} u_{iy}s_{ix}s_{i+\delta,y} = \frac{-i}{2}\frac{s}{N}zN\sum_{qy}\left(\frac{\hbar}{2MN\omega_{qy}}\right)^{\frac{1}{2}}\left(\gamma_{-(q-k)}c_{qy}b_kb_{q-k} - \gamma_{-(q-k)}c_{qy}b_kb_{-(q-k)}^\dagger + \gamma_{-(q+k)}c_{qy}b_k^\dagger b_{q+k} - \gamma_{-(q+k)}c_{qy}b_k^\dagger b_{-(q+k)}^\dagger + \gamma_{q+k}c_{qy}^\dagger b_kb_{-(q+k)} - \gamma_{q+k}c_{qy}^\dagger b_kb_{q+k}^\dagger + \gamma_{q-k}c_{qy}^\dagger b_k^\dagger b_{-(q-k)} - \gamma_{q-k}c_{qy}^\dagger b_k^\dagger b_{q-k}^\dagger\right) + O(h)$$

$$\sum_{i\delta} u_{iy}s_{iy}s_{i+\delta,x} = \frac{-i}{2}\frac{s}{N}zN\sum_{qy}\left(\frac{\hbar}{2MN\omega_{qy}}\right)^{\frac{1}{2}}\left(\gamma_{-(q-k)}c_{qy}b_kb_{q-k} + \gamma_{-(q-k)}c_{qy}b_kb_{-(q-k)}^\dagger - \gamma_{-(q+k)}c_{qy}b_k^\dagger b_{q+k} - \gamma_{-(q+k)}c_{qy}b_k^\dagger b_{-(q+k)}^\dagger + \gamma_{q+k}c_{qy}^\dagger b_kb_{-(q+k)} + \gamma_{q+k}c_{qy}^\dagger b_kb_{q+k}^\dagger - \gamma_{q-k}c_{qy}^\dagger b_k^\dagger b_{-(q-k)} - \gamma_{q-k}c_{qy}^\dagger b_k^\dagger b_{q-k}^\dagger\right) + O(h)$$

The γ's in th above equations are of the form $z^{-1}\sum_\delta e^{ik_1.\delta}$. The summations are also taken according to the momentum conservation principle, that is $q = k + k_1$. Then using the above results, the interaction Hamiltonian can be expressed

$$H_{me} = -\lambda N a \tfrac{1}{2}(\tfrac{2s}{N})^{\frac{1}{2}} sN \textstyle\sum_{qz}(\frac{\hbar}{2MN\omega_{qz}})^{\frac{1}{2}}[(z\gamma_{-q}-1)c_{qz}(b_q+b^{\dagger}_{-q})+(z\gamma_q-1)c^{\dagger}_{qz}(b_{-q}+b^{\dagger}_q)]-$$
$$\lambda N a \tfrac{i}{2} sz \textstyle\sum_{qy}(\frac{\hbar}{2MN\omega_{qy}})^{\frac{1}{2}}\{2\gamma_{-(q-k)}c_{qy}b_k b^{\dagger}_{-(q-k)} + 2\gamma_{-(q+k)}c_{qy}b^{\dagger}_k b_{q+k}$$
$$-2\gamma_{q+k}c^{\dagger}_{qy}b_k b^{\dagger}_{q+k} + 2\gamma_{q-k}c^{\dagger}_{qy}b^{\dagger}_k b_{-(q-k)}\} \tag{5.20}$$

This Hamiltonian has two terms, one bilinear to the operators and the other anharmonic term. The bilinear term is

$$H'_{me} = -\lambda N a \frac{1}{2}(\frac{2s}{N})^{\frac{1}{2}} sN \sum_{qz}(\frac{\hbar}{2MN\omega_{qz}})^{\frac{1}{2}}[(z\gamma_{-q}-1)c_{qz}(b_q+b^{\dagger}_{-q})+(z\gamma_q-1)c^{\dagger}_{qz}(b_{-q}+b^{\dagger}_q)] \tag{5.21}$$

And the anharmonic part is

$$H''_{me} = -\lambda N a \tfrac{i}{2} sz \textstyle\sum_{qy}(\frac{\hbar}{2MN\omega_{qy}})^{\frac{1}{2}}\{2\gamma_{-(q-k)}c_{qy}b_k b^{\dagger}_{-(q-k)} + 2\gamma_{-(q+k)}c_{qy}b^{\dagger}_k b_{q+k}$$
$$-2\gamma_{q+k}c^{\dagger}_{qy}b_k b^{\dagger}_{q+k} + 2\gamma_{q-k}c^{\dagger}_{qy}b^{\dagger}_k b_{-(q-k)}\} \tag{5.22}$$

Solving the Bilinear term of the Hamiltonian

At symmetric conditions it is easy to see that $\gamma_{-q} = \gamma_q$ and at q=k, we can reduce the interaction Hamiltonian in the following form

$$H'_{me} = -\lambda N a \frac{1}{2}(\frac{2s}{N})^{\frac{1}{2}} sN \sum_{qz}(\frac{\hbar}{2MN\omega_{qz}})^{\frac{1}{2}}(z\gamma_q-1)\{c_{qz}(b_q+b^{\dagger}_{-q})+c^{\dagger}_{qz}(b_{-q}+b^{\dagger}_q)\} \tag{5.23}$$

The expectation value of the interaction upon substituting the negative wavevector by its counter part(k=q and also k=-q), and at large coordination number where,$z\gamma_q - 1 \approx z\gamma_q$ the bilinear interaction component becomes

$$H'_{me} = -\frac{\lambda N a}{2} z s^{\frac{3}{2}} \sum_{qz}(\frac{\hbar}{M\omega_{qz}})^{\frac{1}{2}}\gamma_q\{c_{qz}b^{\dagger}_q + c^{\dagger}_{qz}b_q\} \tag{5.24}$$

The effective Hamiltonian now becomes

$$H = \sum_k \omega_k b^{\dagger}_k b_k + \sum_{q\sigma}\omega_{q\sigma}c^{\dagger}_{q\sigma}c_{q\sigma} - \frac{\lambda N a}{2} z s^{\frac{3}{2}} \sum_{qz}(\frac{\hbar}{M\omega_{qz}})^{\frac{1}{2}}\gamma_q\{c_{qz}b^{\dagger}_q + c^{\dagger}_{qz}b_q\} \tag{5.25}$$

To avoid nasty summation we take the ω_{qz} as we expect to be the limiting plasma frequency in the z-axis as a polarization direction. The summation index over z is thus to mean the polarization along z. Therefore, it is possible to rewrite

$$H = \sum_k \omega_k b^{\dagger}_k b_k + \sum_{q\sigma}\omega_{q\sigma}c^{\dagger}_{q\sigma}c_{q\sigma} - \sum_{qz}\lambda'\{c_{qz}b^{\dagger}_q + c^{\dagger}_{qz}b_q\} \tag{5.26}$$

Where $\lambda' = \frac{\lambda N a}{2} S^{\frac{3}{2}} (\frac{\hbar}{M\omega_{qz}})^{\frac{1}{2}} z\gamma_q$

The Eigenvalues and Equations of Motion Method

The Hamiltonian is diagonalized by the equation of motion method

$$i\frac{db_k}{dt} = [b_k, H] = \omega_m b_k - \lambda' c_{qz}$$

$$i\frac{db_k^\dagger}{dt} = [b_k^\dagger, H] = -\omega_m b_k^\dagger + \lambda' c_{qz}^\dagger$$

We denote, ω_m the free magnon frequency, $\omega_{qz} = \omega_p$ the z-direction lattice vibration frequencies, respectively.

$$i\frac{dc_{qz}}{dt} = [c_{qz}, H] = \omega_{qz} c_{qz} - \lambda' b_k$$

$$i\frac{dc_{qz}^\dagger}{dt} = [c_{qz}^\dagger, H] = -\omega_{qz} c_{qz}^\dagger + \lambda' b_k^\dagger$$

In the stationary states all the operators have exponential variations $\propto e^{-i\omega' t}$ as a solution and ω' being the excitation frequency.

$$(\omega' - \omega_m) b_k + \lambda' c_{qz} = 0$$

$$\lambda' b_k + (\omega' - \omega_p) c_{qz} = 0$$

These linear homogeneous equations have solutions if the determinant vanishes

$$\begin{vmatrix} \omega' - \omega_m & \lambda' \\ \lambda' & \omega' - \omega_p \end{vmatrix} = 0$$

It leads to

$$\omega'_\pm = \tfrac{1}{2}[\omega_m + \omega_p \pm \sqrt{(\omega_m - \omega_p)^2 + 4\lambda'^2}]$$

This is the dispersion of the excitation of coupled systems. At the crossover region,in which the dispersions coincide for values of $\omega_m = \omega_p$ at some particular values of q=k, the above equation reduces to

$$\omega'_\pm = \frac{1}{2}[\omega_m + \omega_p \pm 2\lambda'] \tag{5.27}$$

It clearly indicates that if the interaction exists, the two dispersions differ significantly to the order of the coupling parameter λ. Whereas, if it tends to be zero,the excitation energy approaches to either the pure magnon or pure phonon components [77]. In other words, the spin excitation modes decoupled from the lattice vibration excitation modes.

We can also rewrite it either

$$\omega'_{\pm} = \omega_m \pm \lambda'$$

Or

$$\omega'_{\pm} = \omega_p \pm \lambda'$$

Approximation of λ' on the symmetric argument

$$z\gamma_q = z.z^{-1}\sum_{\delta} e^{iq.\delta} \approx z - \tfrac{1}{2}\sum_{\delta}(q.\delta)^2 \approx z - \tfrac{1}{2}(q.a)^2$$

Where $\delta = a$. Finally,

$$\lambda' \approx \frac{\lambda N a}{2} s^{\frac{3}{2}} (\frac{\hbar}{M\omega_p})^{\frac{1}{2}} \{z - \frac{1}{2}(q.a)^2\} \tag{5.28}$$

Using the notion $q = k$ and $\omega_m = \beta k^2 + \gamma$ at the limiting optical frequency value of ω_p, the excitation frequency is,

$$\omega'_{+} \approx (\beta - \beta')k^2 + \gamma + \gamma' \tag{5.29}$$

Where $\beta' = \frac{\lambda N a}{4} s^{\frac{3}{2}} (\frac{\hbar}{M\omega_p})^{\frac{1}{2}} a^2$ and $\gamma' = \frac{\lambda N a}{2} s^{\frac{3}{2}} (\frac{\hbar}{M\omega_p})^{\frac{1}{2}} z$ such that $\frac{\beta'}{\gamma'} = \frac{a^2}{2z}$

In the same way,

$$\omega'_{-} \approx (\beta + \beta')k^2 + \gamma - \gamma' \tag{5.30}$$

In the preceding sections we consider the condition $k \to 0$, associated with the uniform mode at which the lattice vibration is supposed to be independent of the position

Computing the Magnetization

An essential part of this work is to obtain the magnetization. The saturation magnetization per unit length is calculated making use of the excitation energy.

$$M_s(T) = g\mu_B S_z = g\mu_B \sum_i \langle S_{iz} \rangle$$

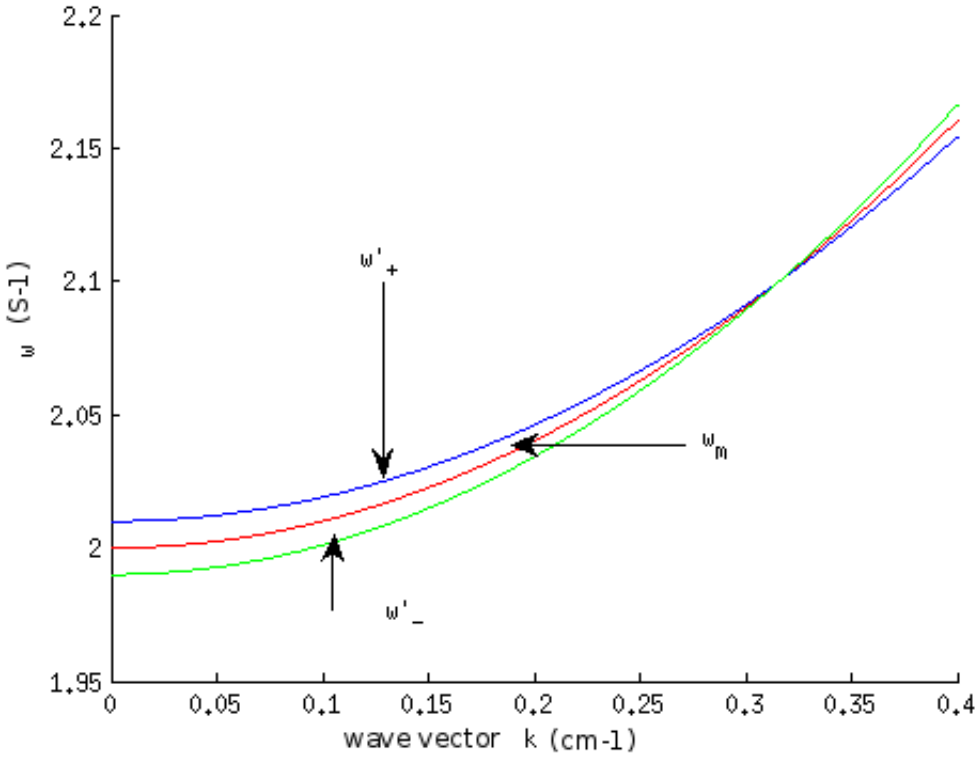

Figure 5.1: The excitation energy of the coupled system. In this plot we observe that the excitation energy is a quadratic function of the wave vector and it also deviates from the pure magnonic or phononic dispersions. It is an evidence to the electromgnon energy dispersion.

$$M_s(T) = g\mu_B \sum_i \langle S - b_i^\dagger b_i \rangle = g\mu_B NS - g\mu_B \sum_i \langle n_i(\omega') \rangle \tag{5.31}$$

Then

$$M_s(T) = M_s(0) - g\mu_B \textstyle\sum_i \langle n_i(\omega') \rangle$$

The bosonic quasi-particle occupation density at the new excitation frequency is

$$\langle n_k(\omega') \rangle = \tfrac{1}{e^{\eta\omega'}-1} \; ; \eta = \tfrac{1}{k_B T}$$

$$\textstyle\sum_k \langle n_k(\omega') \rangle = \tfrac{N}{LV^*} \int_{V^*} dk \tfrac{1}{e^{\eta\omega'}-1}$$

In one dimensional crystal, $V^* = \frac{2\pi}{L}$. As a result, it becomes

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} \int dk \frac{1}{e^{\eta\omega'} - 1} \tag{5.32}$$

This can be approximated for different conditions,such as at high or low temperature limits, and also as it is clearly seen that ω' is a function of magnetic and electric fields in addition to the wave vector.

Evaluating for the first branch, ω'_+ about $\eta \to +\infty$

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} e^{-\eta(\gamma+\gamma')} \int dk e^{-\eta(\beta-\beta')k^2} \tag{5.33}$$

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} e^{-\eta(\gamma+\gamma')} \sqrt{\frac{\pi}{4\eta(\beta-\beta')}} erf(\sqrt{\eta(\beta-\beta')}k) \tag{5.34}$$

This result is in comparison with the magnetization dependency on temperature as experimen-

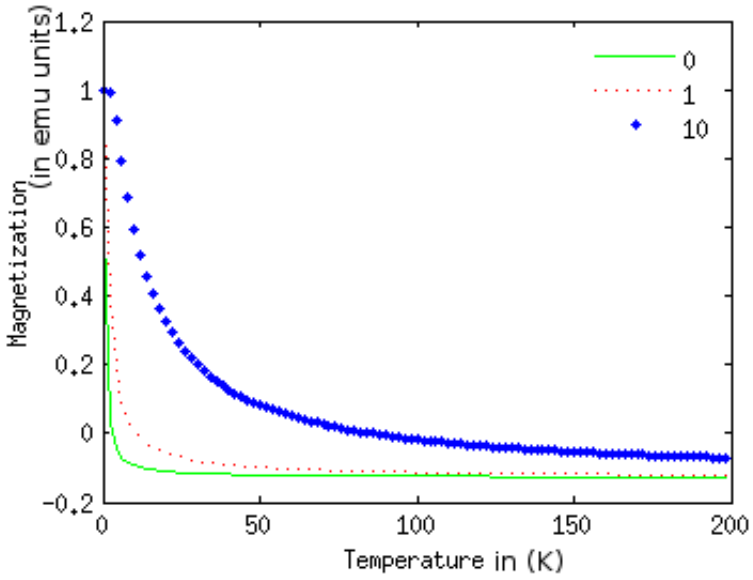

Figure 5.2: This figure shows the magnetic characteristics of the linear chain of atoms in the low temperature limits for some values of tunable parameter $\alpha' = \frac{\gamma+\gamma'}{k_B}$. The range of values given arbitrarily as, 0, 1, 10 and ensures how the relation goes on [84,87,148].

tally investigated in [87] $Bi_{1-x}Gd_xFeO_3$ ceramic compound under low field of about 0.2 T.

If the argument k goes to infinity, as it is rightly true that k has possibly run to this limit, the error function will tend to be expressed as the Gaussian integral of zero mean and half variance. In general, $erf(ax) = \pm 1$ for $ax \to \pm\infty$.

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{4\sqrt{\pi(\beta-\beta')}} e^{-\eta(\gamma+\gamma')} \sqrt{\frac{1}{\eta}} \tag{5.35}$$

In the second limit as $\eta \to 0$, i.e, $e^{\eta\omega'} \approx 1 + \eta\omega'$. Then,

$\int dk \frac{1}{e^{\eta\omega'}-1} \approx \int dk \frac{1}{\eta\omega'}$, and hence

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} \int dk \frac{1}{\eta\omega'} \tag{5.36}$$

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} \int dk \frac{1}{\eta(\beta-\beta')k^2 + \eta(\gamma+\gamma')} \tag{5.37}$$

$$M_s(T) = M_s(0) - g\mu_B \frac{N}{2\pi} \frac{1}{\sqrt{\eta(\beta-\beta')\eta(\gamma+\gamma')}} \tan^{-1}\left(\sqrt{\frac{\beta-\beta'}{\gamma+\gamma'}}k\right) \tag{5.38}$$

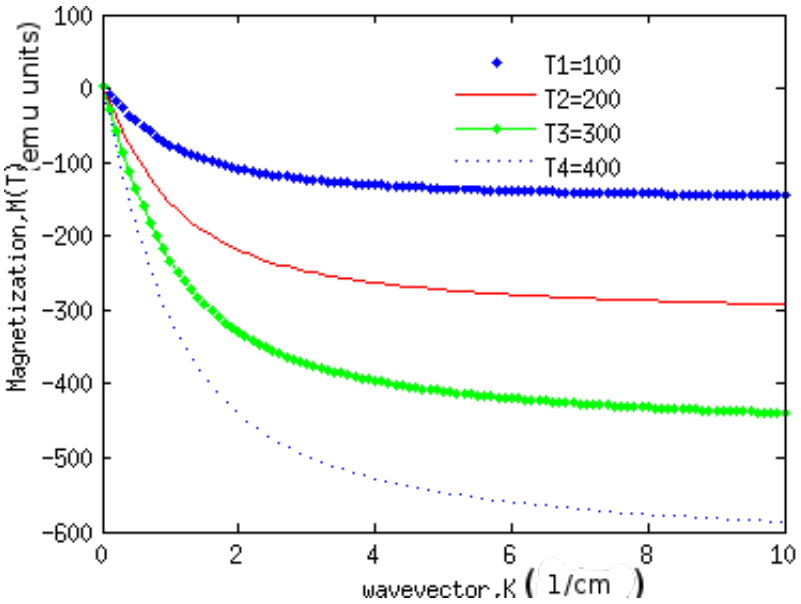

Figure 5.3: This figure characterizes the magnetization at low temperature tending to saturate about zero, while at higher temperatures, the magnetization drops exponentially with increasing wave number.

Magnetic Susceptibility Calculation

Magnetic susceptibility is defined as

$$\chi = \frac{dM}{dH}|_{H=0}$$

$$\chi = \frac{d(M_s(0) - g\mu_B \frac{N}{2\pi} \int_0^{k_{max}} dk \frac{1}{e^{\eta\omega'}-1})}{dH}|_{H=0}$$

$$\chi = (g\mu_B)^2 \frac{N}{2\pi} \int_0^{k_{max}} dk \frac{e^{\eta\omega'}}{(e^{\eta\omega'}-1)^2}|_{H=0} \tag{5.39}$$

This can also be approximated as $\eta \to +\infty$

$$\chi = (g\mu_B)^2 \frac{N}{2\pi} e^{-\eta(\gamma+\gamma')} \sqrt{\frac{\pi}{4\eta(\beta-\beta')}} erf(\sqrt{\eta(\beta-\beta')}k)|_{H=0} \tag{5.40}$$

$$\chi = (g\mu_B)^2 \frac{N}{2\pi} e^{-\eta(-2DS+\mu E+\gamma')} \sqrt{\frac{\pi}{4\eta(\beta-\beta')}} erf(\sqrt{\eta(\beta-\beta')}k) \tag{5.41}$$

The above expression, at any given wavevector k, is equivalently written as,

$\chi \propto e^{-\frac{\alpha'}{T}} \sqrt{T} erf(\frac{1}{\sqrt{T}})$ where, $\alpha' = \frac{-2DS+\mu E+\gamma'}{k_B}$

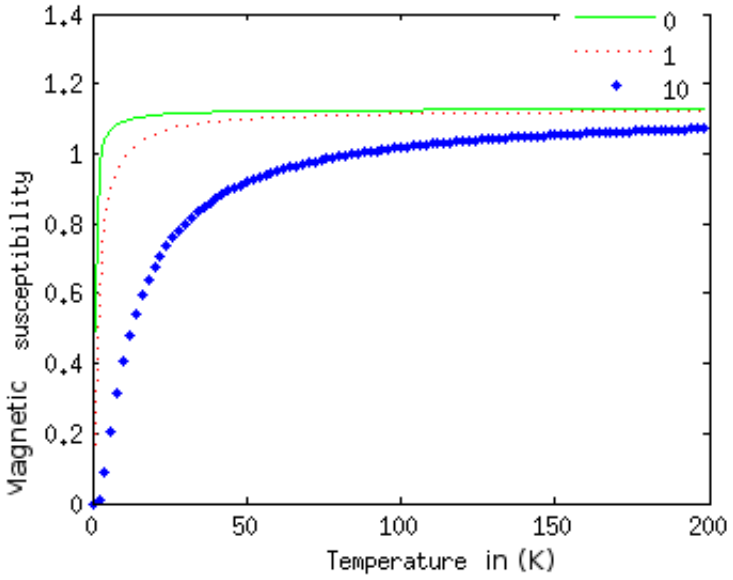

Figure 5.4: The illustration indicated above describes the susceptibility dependency at low temperatures. This figure verifies that the susceptibility tends to saturate to some value while temperature increases. Eventually, it is for $\alpha' = \frac{-2DS+\mu E+\gamma'}{k_B}$ where it does not depend explicitly on the externally applied magnetic field component.

Whereas, if $\eta \to 0$ the susceptibility becomes

$$\chi = (g\mu_B)^2 \frac{N}{2\pi} \int dk (\frac{1}{\eta\omega'} + \frac{1}{(\eta\omega')^2})|_{H=0}$$

The first term is very small and it can be neglected without affecting the result significantly as compared to the second one.

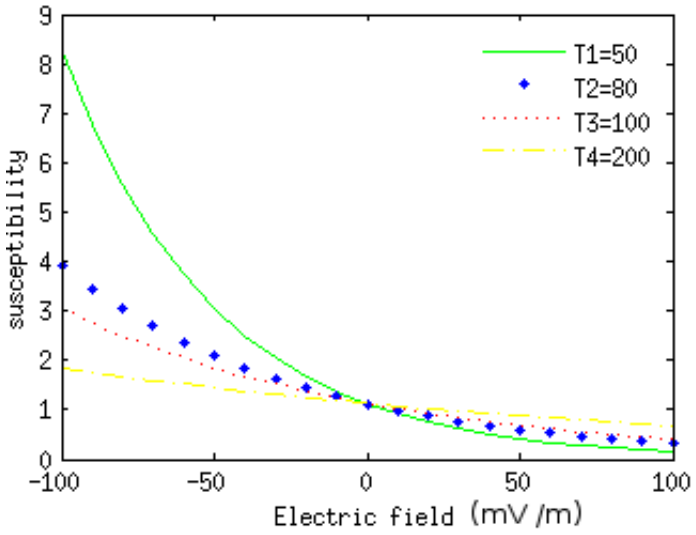

Figure 5.5: The figure herein shows how the susceptibility varies with the electric field keeping the other parameters constant at some specific low temperatures.

$$\int dk \frac{1}{\eta\omega'} = \frac{1}{\sqrt{\eta(\beta-\beta')\eta(\gamma+\gamma')}} \tan^{-1}(\sqrt{\frac{\beta-\beta'}{\gamma+\gamma'}}k)$$

$$\int dk \frac{1}{(\eta\omega')^2} = \frac{1}{2\sqrt{\eta(\beta-\beta')[\eta(\gamma+\gamma')]^3}} \tan^{-1}(\sqrt{\frac{\beta-\beta'}{\gamma+\gamma'}}k) + \frac{k}{2\eta(\gamma+\gamma')(\eta(\beta-\beta')k^2+\eta(\gamma+\gamma'))}$$

$$\chi = (g\mu_B)^2 \frac{N}{2\pi}\{\frac{1}{\sqrt{\eta(\beta-\beta')\eta(\gamma+\gamma')}} \tan^{-1}(\sqrt{\frac{\beta-\beta'}{\gamma+\gamma'}}k)+$$

$$\frac{1}{2\sqrt{\eta(\beta-\beta')[\eta(\gamma+\gamma')]^3}} \tan^{-1}(\sqrt{\frac{\beta-\beta'}{\gamma+\gamma'}}k) + \frac{k}{2\eta(\gamma+\gamma')(\eta(\beta-\beta')k^2+\eta(\gamma+\gamma'))}\}|_{H=0} \tag{5.42}$$

The Calculation of Electric Polarization

In this section, we look at the polarization of the crystal structure considered so far. We discussed the lattice distortions reasonably accounted for the electric phenomenon. The ferroelectric behaviors enable structural distortions, consequential to the ferromagnetics due to magnetostrictions. Hence, it is an essential point of interest to study about induced dipole moments. Now, it is believed that there exists charge density fluctuation $\rho(x)$ in every small local dilation of the lattice. We denote the displacement x to represent the fluctuation. The general expression for induced polarization is different from zero, i.e,

$$\int x\rho(x)dx \neq 0$$

consequently,

$$\int x\rho(x)dx = P$$

The density fluctuation operator is $\rho(x) = \sum_q \rho_q e^{iq.x}$ where the Fourier transform is $\rho_q = \sum_i \rho(x)e^{-iq.x_i}$

$$P = \int x \sum_q \rho_q e^{iq.x} dx = \sum_q \rho_q \int x e^{iq.x} dx$$

$$P = \sum_q \rho_q e^{iq.x} \frac{1}{q^2} - i \sum_q \rho_q e^{iq.x} \frac{x}{q} \tag{5.43}$$

For discrete dipoles of density fluctuation, we can also write,

$$\rho(x) = \sum_j \delta(x - x_j)$$

So that

$$\rho_q = \int \sum_j \delta(x - x_j) e^{-iq.x} dx = \sum_j e^{-iq.x_j}$$

The polarization becomes

$$P = \sum_q \tfrac{1}{q^2} \sum_j e^{iq.(x-x_j)} - i \sum_q \tfrac{1}{q} \sum_j e^{iq.(x-x_j)} x$$

At $x = x_j$, if we define the average occupation number density at j^{th} site, it can be seen that the polarization, P

$$P = \sum_q \frac{n_q}{q^2} - i \sum_q \frac{n_q}{q} x_j \tag{5.44}$$

Integrating over q space

$$P = \frac{1}{2\pi} \int dq \frac{1}{q^2} \frac{1}{e^{\eta\omega'} - 1} - i \frac{x_j}{2\pi} \int dq \frac{1}{q} \frac{1}{e^{\eta\omega'} - 1} \tag{5.45}$$

With the same approximations used above the polarization is

$$P = \frac{1}{2\pi} e^{-\eta(\gamma+\gamma')} \{ \int dq q^{-2} e^{-\eta(\beta-\beta')q^2} - i x_j \int dq q^{-1} e^{-\eta(\beta-\beta')q^2} \} \tag{5.46}$$

To evaluate these integrals, the limits of integrals are chosen to run to infinity, as it is true for the wave vector to have large value. Using this argument, the polarization becomes

$$P = \frac{1}{2\pi} e^{-\eta(\gamma+\gamma')} \{720\eta(\beta-\beta')\sqrt{\frac{\pi}{\eta(\beta-\beta'}} + ix_j \frac{1}{2}\} \tag{5.47}$$

$$P = \frac{360}{\pi} e^{-\eta(\gamma+\gamma')} \eta(\beta-\beta')\sqrt{\frac{\pi}{\eta(\beta-\beta'}} + ix_j \frac{1}{4\pi} e^{-\eta(\gamma+\gamma')} \tag{5.48}$$

Letting $x_j = a$, the lattice spacing

$$P = \frac{360}{\pi} e^{-\eta(\gamma+\gamma')} \eta(\beta-\beta')\sqrt{\frac{\pi}{\eta(\beta-\beta'}} + ia \frac{1}{4\pi} e^{-\eta(\gamma+\gamma')} \tag{5.49}$$

This can be interpreted as sum of real and imaginary components.

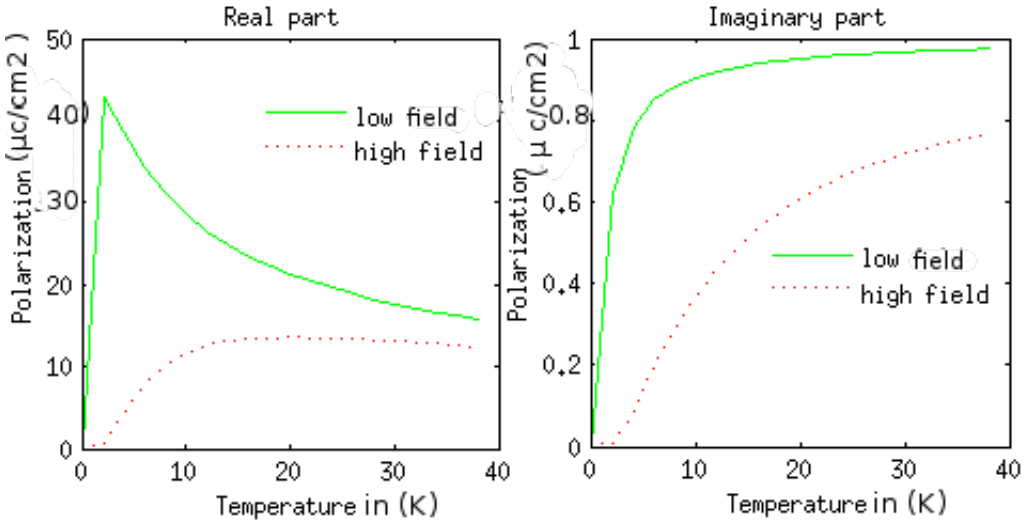

Figure 5.6: Polarization versus temperature scheme. The real and imaginary parts of the polarization are found to be dependent on the fields values. We use the approximate expression $360\sqrt{\frac{(\beta-\beta')}{\pi}} \approxeq 100$ and at some values of $\gamma+\gamma'$ =1, upper line; and $\gamma+\gamma'$ =10, lower line. The real part is significantly variable and tunable with the parameters at low temperatures [83].

On the other hand the approximate expression of the polarization as $\eta \to 0$ is

$$P = \frac{1}{2\pi}\int dq \frac{1}{q^4\eta(\beta-\beta') + q^2\eta(\gamma-\gamma')} - i\frac{a}{2\pi}\int dq \frac{1}{q^3\eta(\beta-\beta') + q\eta(\gamma-\gamma')} \tag{5.50}$$

$$P = \frac{\sqrt{(-\eta(\beta-\beta')(\eta(\gamma+\gamma'))^3)}}{4\pi(\eta(\gamma+\gamma'))^3} \log \frac{\sqrt{(-\eta(\beta-\beta')(\eta(\gamma+\gamma'))^3)} - \eta(\beta-\beta')\eta(\gamma+\gamma')q}{\sqrt{(-\eta(\beta-\beta')(\eta(\gamma+\gamma'))^3)} + \eta(\beta-\beta')\eta(\gamma+\gamma')q}$$

$$-\frac{1}{2\pi\eta(\gamma+\gamma')q} + i\frac{a}{4\pi\eta(\gamma+\gamma')} \log \frac{\eta(\beta-\beta')q^2 + \eta(\gamma+\gamma')}{q^2} \tag{5.51}$$

5.4 Conclusions

To summarize, we consider a linear chain of composites of ferroelectric ferromagnetic crystal structure where magnon-phonon interaction is responsible for the flex-ability of the magnetic and electric properties of the crystal [146,149]. This is,of course, due to the magnetostriction and electrostriction behaviors of the linear chain cooperatively inducing the new classes of collective excitation modes the "electromagnons" that can be observed at new excitation energies parametrized by the coupling order parameter. The hybrid novel excitation is a quantized quasiparticle described by the frequency ranges at the crossover region, in which the dispersions coincide for values of $\omega_m = \omega_p$ at some particular values of q=k, $\omega'_{\pm} = \omega_m \pm \lambda'$ Or $\omega'_{\pm} = \omega_p \pm \lambda'$. It indicates that if the interaction exists, the two dispersions differ significantly to the order of the coupling order parameter λ'. We find the magnetization,polarization and the susceptibilities of the model system at various temperature ranges at this new excitation frequency [150].

Whereas, if it tends to zero, the excitation energy approaches either the pure magnon or pure phonon modes.

Chapter 6

Summary and Outlook

The coexistence of various ferroic order (ferromagnetic, ferroelectric, or ferroelastic) have attracted great attention in condensed matter research due to their great potential for applications in the fields of oxide electronics, spintronics, and even the green energy devices for reducing the power consumption [151]. In the magnetoelectrics we consider electric dipoles induced by the centero-symmetric distortion, typical to perovskite classes due to their crystal structure interacting with valence electron clouds that give rise to an interacting system of electromagnetic wave modes characterized by the vector potential and the localized electronic spins in this insulating ceramics in which spin-charge coupling and spin-lattice coupling are duely considered on understanding of the strong correlation between electronic structure and magnetic ordering [152]. Thus, since the magnetoelectrics are perovskites which are most often insulators, their charges are strongly bounded and somehow strong electron correlation and localization dominates that leads us towards the Heisenberg model which decisively has a power to describe inter-atomic exchange interactions. The interaction of magnetic and lattice phenomena are treated to formulate the model Hamiltonian which is analyzed through the double time Green function. The spectrum of excitation is found to be dependent on the excitation wave vector and the spectral broadening explains the interaction that exists between the two domains. The density fluctuations of electromagnetic domains and the lattice vibration modes can be due to the the exchange interaction [153] , and consequently, explained by the imaginary damping Green function. The spectral density function of magnon variable that gives information on the excitation energies

is non-negative and is obtained as

$$J_{k'}(\omega) = \frac{-\alpha_{k'}(\omega)(e^{\beta\omega} - 1)^{-1}}{\pi(\omega - \Omega_{k'} - g_{k'}(\omega))^2 + \alpha_{k'}^2(\omega)} \tag{6.1}$$

Satisfying the condition that $\alpha_{k'}(\omega) \leqslant 0$ and at very small damping term,the polarization operator suggests singularity at $\omega - \Omega_{k'} - g_{k'}(\omega) = 0$ and the spectral density function leads to be delat function.

In most magnetoelectric multiferroics, the origins of magnetic and ferroelectric orders have no relation to each other. However, there are some magnetoelectric multiferroics for which the magnetic and electric properties persist simultaneously breaking up the inversion symmetries. Their intimation is usually very weak. But, in magnetically induced ferroelectrics where competing magnetic interactions(allowed by the spin frustration) are often favored while experimentally verified [154] ,and the coupling is expected to be strong as it is explained by the Monte Carlo simulations performed by [155].

In the FE-FM nanostructure composites our theoretical study pointed out that the energy eigen value of the coupled oscillation is characterized by the the magnonic and phononic dispersion modes with an additional coupling term as indicated by

$$\omega'_{\pm} = \tfrac{1}{2}[\omega_m + \omega_p \pm \sqrt{(\omega_m - \omega_p)^2 + 4\lambda'^2}]$$

At the crossover region,in which the dispersions coincide for values of $\omega_m = \omega_p$ at some particular values of q=k,

$$\omega'_{\pm} = \frac{1}{2}[\omega_m + \omega_p \pm 2\lambda'] \tag{6.2}$$

This theoretical result is in association with the experimental investigation performed on $GdMnO_3$ at which the change of the hybridization of electronic wave functions of the manganese and oxygen ions are interpreted considering polar atomic displacement as a possible evidence of electric polarization[156].At low temperature, the magnetization and magnetic susceptibilities have been obtained. The susceptibility is found to saturate at some specific value as temperature raises. In addition, our result also shows the electrical susceptibility as a function of the temperature and is in correspondence with experimental results of field-cooled magnetization observed in [157]. Mutual control has been identified in multiferroic systems showing the reversal of polarization upon a magnetic field reversal,and the vise-versa [158,159] , which is

very useful in practical applications having giant magnetoelectric coupling with values as large as 3700 V/cm Oe to 41700 V/cm Oe as observed experimentally on polyvinylidene fluoride (PVDF), [160,161].

The major challenge is to search for novel materials and mechanisms to realize the effective mutual control between these ferroic order parameters.

The fundamental questions underlying multiferroicity are still open and we hope that the research community will tackle these challenges and inspire new practical,paradigm-shifting multiferroics having low power consumption multifunctional devices to the coming generation in the near future.

Appendix A

For long wave length limits $\mid K.\delta \mid << 1$. In this boundary the term $e^{iK.\delta}$ is expanded in power of K to have

$$\gamma_k = z^{-1} \sum_{\delta} (1 + iK.\delta - \frac{(K.\delta)^2}{2} + ...) \tag{6.3}$$

This expression can be reduced to the following form using the approximation based on the facts that

$$\sum_{\delta} 1 = z \text{ and } \sum_{\delta} \delta = 0$$

Therefore, we will have

$$\gamma_k \approx 1 - \frac{1}{2z} \sum_{\delta} (K.\delta)^2 \tag{6.4}$$

This can be rearranged to the form which will give us

$$z(1 - \gamma_k) \approx \frac{1}{2} \sum_{\delta} (K.\delta)^2 \tag{6.5}$$

For simple cube the value of $\mid \delta \mid = a$, the lattice spacing

Appendix B

$$\begin{aligned} \int_0^\infty x^n e^{-ax^2} dx &= \frac{\frac{1}{2}\Gamma(\frac{n+1}{2})}{a^{\frac{n+1}{2}}} \qquad (n > -1, a > 0) \\ &= \frac{(2k-1)!!}{2^{k+1}a^k}\sqrt{\frac{\pi}{a}} \quad (n = 2k, \quad k \ \ integer, a > 0) \\ &= \frac{k!}{2a^{k+1}} \qquad (n = 2k+1, \quad k \ \ integer, a > 0) \end{aligned}$$

$$\int_0^\infty dq q^{-2} e^{-\eta(\beta-\beta')q^2} = 720\eta(\beta - \beta')\sqrt{\frac{\pi}{\eta(\beta-\beta'}}$$

$$\int_0^\infty dq q^{-1} e^{-\eta(\beta-\beta')q^2} = -\frac{1}{2}$$

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