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INTERACTION INVOLVING ELEMENTARY EXCITATIONS
IN SOLIDS

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GOPAL CHANDRA SHUKLA M. Sc.
Solid State and Molecular Physics Group
National Chemical Laboratory
Poona - 8, India.

(October 1966)

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G. C. Shukla

SYNOPSIS

The present dissertation deals with a theoretical study of interactions involving certain elementary excitations in dielectrics and magneto-dielectrics. The oldest concept of elementary excitation came in connection with lattice wave. Owing to strong coupling between the atoms, any local disturbance is not localized but moves like a wave. In a quantum description of lattice waves we visualize the crystal as an assembly of independent harmonic oscillators which exist in certain quantum states of excitation. These excitations are referred to as phonons, characterized by a definite energy and direction of propagation.

Likewise, any local deviation from the coupled state of the spin systems (i.e. ferro-, ferri- and antiferromagnetic systems) will not remain confined in the region as a result of strong exchange forces. The corresponding propagation is called spin waves. Following the analogy of lattice waves, the spin waves too can be thought of as modes of propagation in magnetically coupled systems. When the spin waves are quantized we refer to the state of excitations in terms of a certain number of magnons. Like phonons, magnons are also field quanta.

In the first part of the thesis, the effect of electron-phonon coupling on the phase transformation, in particular ferroelectric phase transformation, is considered from

microscopic considerations. The second part is devoted to a study of interactions between spin waves (both optical and acoustic modes) quanta (i.e. magnons) and longitudinal optical phonons.

It has been recently realized that phonons may play an essential role in the ferroelectric phase transformation (i.e. in BaTiO_3). The main point in this approach is that the structure should become unstable with respect to certain vibrational modes at some temperature. This implies that the frequency of this mode should vanish at the transition temperature. However, there are several ambiguous features in these theories. It is not possible to predict the transition. Also the origin as to why the frequency becomes imaginary in the harmonic approximation is not understood.

In the present dissertation, these ad hoc aspects are done away with by starting calculations from first principles. It is conventional to assume that the electronic excited states are far removed from the ground state and are accordingly ignored in the lattice dynamics of the system. This is questionable. Hence the role of electron-phonon coupling is explicitly taken into account in constructing the microscopic Hamiltonian of the system.

With special reference to tri-ionic units (AB_2) and octahedral units (TiO_6), which are relevant to BaTiO_3 system, it is shown by means of a canonical transformation, that the odd vibrational mode becomes unstable owing to

electron-vibration coupling. This model is then extended to a three dimensional network of such units. In the study of the collective oscillations of such a system anharmonic interactions are also taken into account. The final result shows that the effective transverse optical frequency has the form

$$\omega_{\text{eff}}^2 = \left(\omega_0^2 - \frac{A^2}{|J|} - |\gamma| + \beta T \right) \quad (1)$$

where A is the matrix element connecting ground and excited states, $|J|$ the energy separation, $|\gamma|$ comes from dipole-dipole interaction and β emanates from anharmonic terms. The above expression has the desired form

$$\omega_{\text{eff}}^2 \propto (T - T_c) \quad (2)$$

The second part of the thesis deals with the interactions of optical phonons with magnons. The study has been confined to Antiferromagnetic and Ferrimagnetic crystals. The two sublattice model for antiferromagnetic spin waves and ferrimagnetic spin waves forming a b.c.c. lattice was chosen for the study. The formulation of the microscopic theory for the phonon-magnon interaction is quite alluring. The interaction mechanism of acoustic phonons and magnons have already been considered by various research workers. In the present dissertation a microscopic theory of the interaction of optical phonon and magnon is formulated. Here also the mixing of the excited orbital states with the ground states of the magnetic ions due to crystal field oscillations is taken into account.

Along with the diagonalization of the magnon part of the Hamiltonian, the one phonon interaction terms for the coupling between the longitudinal optical phonons and magnons (of all branches) are obtained. It is found that the interaction processes are quite important in the relaxation mechanism in the high temperature region i.e. ~~of the order~~ $T > 10^3 \text{K}$ ~~of Einstein temperature~~. The calculation of phonon-magnon relaxation time is reported.

PART - I

CHAPTER - 1

INTRODUCTION

Despite a considerable amount of experimental and theoretical investigation on ferroelectric crystals, our knowledge of the origin of phase transformation to the ferroelectric phase is still incomplete. The phenomenon of ferroelectricity was discovered in 1921 by Valasek¹ in an investigation of Rochelle salt. His results showed a dielectric hysteresis. Thus in analogy with ferromagnetism the above phenomenon is called ferroelectricity. The phenomenon of ferroelectricity is associated with special types of crystals, which have built in permanent electric moments. However, with slight increase in temperature, beyond the transition point, ferroelectric crystals lose their permanent moment. The important properties of ferroelectric^{2,3,4} crystals are: (a) dielectric hysteresis (b) polar point group symmetry, (c) disappearance of hysteresis at a certain point (i.e. the Curie point), (d) transition at Curie point to a state of higher symmetry i.e. transition from polar to non-polar or paraelectric phase, and (e) the dielectric constant above the Curie point follows a Curie-Weiss law, namely $\epsilon - 1 = C/T - T_c$, where ϵ , T_c refer to dielectric constant and transition temperature respectively C being a constant having the dimension of temperature. The spontaneous polarization in the ferroelectric state is associated with spontaneous electrostrictive strain in the crystal; thus the

ferroelectric state has a lower symmetry than the paraelectric or nonpolarized state. Therefore there is a change of crystal symmetry at the transition temperature. This implies that ferroelectrics have a Curie temperature above which they are non-polar. This is not an essential prerequisite because a number of ferroelectrics are known to decompose before the Curie temperature is attained.

The field of ferroelectrics is rapidly growing and a large number of ferroelectrics has been discovered with a variety of crystal symmetry. These may have simple crystal structure (e.g. BaTiO_3) or complex one as in Rochelle Salt. The nature of bonding between the constituent units also varies in different systems. This may be ionic, covalent or even intermolecular.⁵ The onset of the ferroelectric phase is connected with the ordering of permanent dipoles or to the creation of new dipoles, or pseudo-dipoles, by the displacement of the ions.

Ferroelectric crystals can be classified in various ways. The most convenient one is due to Merz.⁶ He classified them into hard and soft ferroelectrics. Hard ferroelectrics, in general, are grown at high temperature. These are mechanically hard and insoluble in water. Further they have high saturation polarization. On the other hand, soft ferroelectrics have smaller saturation polarization; perovskites and a few metal oxides having similar structures belong to former class.

The present study is confined to the ferroelectric crystals belonging to perovskite^{7,8,9} family, specially to BaTiO_3 . The name perovskite stems ^{from} after the mineral perovskite CaTiO_3 . The general formula for perovskite structure is ABO_3 . In this, A and B stand for mono- or divalent metal and tetra- or pentavalent metal ions respectively. The virgin perovskite is cubic in nonpolar state with the A atoms at cube corners, B atoms at body centres and O atoms occupying the face-centred positions. Geometrically, the A-O distance is $\sqrt{2}$ times the B-O distance. The structure can be pictured as a set of BO_6 octahedra arranged in a simple cubic pattern. These are linked together by the sharing of the oxygen atoms, wherein A atoms occupy the spaces between. The optical, mechanical and electric measurements^{10,11,12} reveal the existence of the three ferroelectric phase changes. Above 120°C , it has a cubic structure and non-polar state, between 120°C and 0°C it is polarized along the cube edge e.g. (001) direction and has a tetragonal structure. From 0°C to -70°C , it is orthorhombic, the direction of polarization being face-diagonal e.g. (011) direction. While, below -70°C it is polarized along a body diagonal e.g. (111) direction and has rhombohedral structure. In all the three cases, the mechanical deformation of the crystal is proportional to the square of the polarization and expands in the direction of spontaneous polarization and contracts at right angles to it. The crystal symmetry connected with the lowering of temperature is in succession O_h , C_{4v} , C_{2v} , C_{3v} . Barium titanate constitutes, perhaps

the most ideal system for the formulation of the theory of the ferroelectric phase transformation. Its structure is well-established and other physical properties are thoroughly studied. However, the real cause of the ferroelectric phase transformation has proved to be elusive for quite sometime. Theoretical studies on such systems have followed two main channels. The first is concerned with thermodynamic consideration and is independent of any particular crystal model. The second is atomistic and is intimately connected with the crystallographic properties as a function of temperature. It will be noted that the octahedral structure^{13,16} is of paramount importance in the understanding of various physical properties associated with perovskite and related structures. Several phenomenological theories have been proposed for the occurrence of ferroelectricity in perovskite-like systems. In these theories emphasis has been given on the various points such as (1) the occurrence of multiple minima^{22,23,24} in the free energy function, (2) the role of chemical bonding,² (3) electronic polarization.^{23,33}

The earlier theoretical studies exploited the close analogy between ferromagnetism and ferroelectricity. They were inspired by the work of P. Weiss¹⁷ who first proposed an acceptable theory of ferromagnetism though somewhat ad hoc in nature. Thus one postulates for the internal field for ferroelectric and ferromagnetic systems relations:

$$\begin{aligned} F &= E + \frac{4\pi}{3} P \quad (\text{Electric case}) \\ &= H + \frac{4\pi}{3} M \quad (\text{Magnetic case}) \end{aligned} \quad (1.1)$$

In Eqn (1.1) E and H stand for the external field, while P and M for the polarization of the sublattice per unit volume. The term $\frac{4\pi}{3}$ is called the Lorentz term. Von Hippel named it as "bootstraps" term i.e. a term by which the polarization is capable of pulling itself up by its own bootstraps. Conventionally this is a "cooperative force" term. This formula gave rise to " $\frac{4\pi}{3}$ catastrophe" i.e. many polar substances should be ferroelectric at their boiling point. This difficulty was, however, cleared by Onsager (1930) who pointed out its incorrectness for polar liquids.

The polarization in a ferroelectric crystal can be caused by one of the following three possibilities, namely (a) rotating permanent dipoles, (b) translational motion of the ion, (c) electronic distortion of atoms or ions. Early theories about rotating¹⁸ dipoles have long been forgotten. The theory by Matthias and Masons^{19,20} starts with a specific assumption for the internal field together with the idea of rotating dipoles. Thus, this is an incorrect theory. Smolenskii²¹ has also provided a different ground for its incorrectness.

Adopting the view that polarization results on account of displacive motion of the ions in BaTiO₃, Devonshire²² proposed a phenomenological theory of ferroelectric phase

transition in BaTiO₃. Various other theories also exploit the same mechanism of polarization. Among these, the significant ones are those by Slater,²³ Ginzburg,²⁴ Smolenskii²⁵ and Barret²⁶ and Shirobokov.²⁷ Instead of the oscillator²⁸ model for the potential energy of the atom, Devonshire²² assumed the form $V(r) = ar^2 + br^4$. Physically this implies that the dipole moment depends on the displacement from the equilibrium position. Further, the values of a and b are different for different ions and these were evaluated by the Born model of ionic crystal. The dipole moment is proportional to a quantity Z which represents the effective charge. The partition function and hence the Helmholtz free energy of the system is written down in terms of the constants, a, b, Z and field vector β which were given its Lorentz value $\frac{4\pi}{3}$. Thus, Devonshire expressed the free energy of the crystal per unit volume by expressing as a function of stress and polarization with the stress set equal to zero. This function must conform with O_h symmetry (non-polar state) and the most general function satisfying this condition is an arbitrary symmetric function of P_x², P_y² and P_z². Thus, free energy can be expanded in terms of polarization⁴ along as

$$\begin{aligned}
 A = & \frac{1}{2} W (P_x^2 + P_y^2 + P_z^2) + \frac{1}{4} \xi (P_x^4 + P_y^4 + P_z^4) \\
 & + \frac{1}{2} \xi_{12} (P_y^2 P_x^2 + P_x^2 P_z^2 + P_z^2 P_y^2) + \frac{1}{6} \xi (P_x^6 + P_y^6 + P_z^6)
 \end{aligned}
 \tag{1.2}$$

ξ s are the various coefficients.

In Eqn (1.2) W' is a temperature dependent function and is evaluated from experimental susceptibility data above the Curie-point. For weak field having terms upto P^4 in the expansion A, W' is given by

$$W' = \chi^{-1} = \frac{T - T_c}{C}, \quad (1.3)$$

where χ is the electric susceptibility.

The basic assumption of Devonshire's theory is that this linear relation may be extrapolated below the Curie-point T_c . Using the experimental value of Curie-point T_c , the extrapolated Curie temperature and the spontaneous polarization P_s at one temperature in the tetragonal phase, Devonshire was able to account for the characteristics of the three phase transitions including the temperature dependence of the dielectric constant and other physical properties. Although Devonshire's phenomenological theory is able to explain satisfactorily different properties of $BaTiO_3$ with a comparatively small number of expansion parameters, it is an approximation in the sense that a finite number of terms are used in the free energy. Secondly, the same free-energy expansion for both the cubic and tetragonal phase is used. Also, the assumed complete ionic character of $BaTiO_3$ is doubtful. Various investigations including x-ray as well as infra-red spectra reveal that $BaTiO_3$ has an intermediate character i.e. it is neither purely ionic nor purely covalent.^{2,29-32} Slater introduced two modifications over Devonshire's theory, namely, (1) he took into account polarization of ions by distortion, (2) he used the values of the internal field at the ion sites

determined from electronic calculations based on the actual arrangements of ions rather than the Lorentz value of $\frac{4\pi}{3}$ for all positions. Barret carried out a quantum mechanical treatment following Slater's work. Wigner³³ and Jayne's³⁴ theory proposes an electronic model for ferroelectrics built of oxygen octahedra. On the supposition that excited electronic states lie close to the ground state, crystal field mixing was considered on account of dipole moment operator, a step in the right direction.

In 1957, W. Kanzig pointed out in his review article entitled "Ferroelectrics and Antiferroelectrics" that the field had become broader rapidly but not deeper. Since that time, a number of studies on the properties of BaTiO₃ type ferroelectric crystal, ^{has} been made which explore the possibilities of relating, these properties in terms of Born von Karman theory of lattice dynamics.

The present broad understanding is an outcome of the theoretical studies by Cochran,³⁵ Anderson,³⁶ Landauer et al³⁷ and Ginzburg.²⁴ They incorporated the concept of time-varying polarization, instead of static one, and its relation to lattice dynamics. A great many physical properties of a crystal involve in some way the frequencies of the normal modes of vibration of the system e.g. elastic constants, specific heat, dielectric constants etc. Experimental techniques i.e. x-ray, slow neutron-scattering as well as Mössbauer effect are important tools to verify the effects of lattice vibrations.

The condition for the stability of the crystal against small deformations, requires the reality of all the normal mode frequencies. The limit of stability against a particular mode of vibration is inferred as the corresponding frequency tends to zero. This suggests that ferroelectric phase transition in certain crystals can be associated with such an instability or near-instability. Thus the ferro-electric phase-transformation is a problem in lattice dynamics. Cochran noted that the anomaly of the dielectric constant should be related to the anomaly of the transverse optical mode in the case of ferroelectric phase transformation. According to Lyddane-Sachs-Teller³⁸ (LST) formula

$$\frac{\epsilon}{\epsilon_0} = \frac{W_{L_0}^2}{W_{T_0}^2} \quad (1.4)$$

where ϵ_0 , ϵ stand for static dielectric constant at zero frequency and dielectric constant at high frequency respectively. W_{T_0} and W_{L_0} refer respectively to transverse and longitudinal optical frequencies.

This formula was extended by Cochran³⁵ to ionic crystals of a more complicated nature i.e. $BaTiO_3$. The coefficients of the dynamical matrix are assumed to vary with the temperature in such a way that the transverse optical frequency vanishes at the transition temperature as $T \rightarrow T_c$. This arises from LST³⁸ relation and of the Curie-Weiss law for ϵ , namely,

$$\alpha \frac{1}{T-T_c} \implies w_{T_0}^2 \propto (T-T_c) \quad (1.5)$$

Various other suggestions³⁹⁻⁴² have been put forward for the temperature dependence of optical mode and consequently verified by experimental⁴³⁻⁴⁷ work. In the next section we present the salient features of lattice dynamics.

LATTICE DYNAMICS

The problem of lattice dynamics⁴⁸⁻⁵⁰ involves the motion of very large, but finite, number of particles about a set of ordered points. The network of these points describes the crystal lattice and classically each particle is assumed to be at rest at its corresponding lattice point at the absolute zero of temperature. These particles (ions or atoms) are never quiescent but execute small oscillations. The collective oscillations of such a system i.e. Lattice dynamics of crystalline solids, was first correctly formulated by Born and Von Karman. They assumed a number of approximations, namely adiabatic (Born-Oppenheimer approximation) and harmonic approximations. The former is related with the separation of electronic and nuclear motion. As the nuclei are 10^3 to 10^5 times heavier than the electrons, their velocities are much smaller compared to the velocities of the electrons. This in turn implies that electrons are unable to notice the speed of the nucleus and the nuclei can be assumed to have arbitrarily fixed configuration relative to

electronic motion. Therefore it is a fair approximation to treat the electronic motion and nuclear vibration separately. This is the celebrated Born-Oppenheimer approximation. For its validity the phonon energy ($\hbar\omega_p$) has to be very small compared to electronic excitation energy ($\hbar\omega_e$) namely $\hbar\omega_p \ll \hbar\omega_e$.

On the otherhand, harmonic approximation restricts the Taylor series development of the nuclear displacements upto quadratic terms. Deviation from adiabatic approximation implies electron-phonon interaction, while deviation from harmonic approximation implies phonon-phonon interaction.

In the standard method of lattice dynamics in the harmonic approximation, the Hamiltonian of the lattice system has the form

$$H = \Phi_0 + \frac{1}{2} \sum_{\mathbf{k}\alpha} M_{\mathbf{k}} \delta R_{\alpha}^2(\mathbf{k}) + \frac{1}{2} \sum_{\substack{\mathbf{k}\alpha \\ \mathbf{l}'\mathbf{k}'\beta'}} \Phi_{\alpha\beta}(\mathbf{k} \mathbf{l}' \mathbf{k}' \beta') \delta R_{\alpha}(\mathbf{k}) \delta R_{\beta}(\mathbf{l}' \mathbf{k}') \quad (1.6a)$$

with

$$\Phi_{\alpha\beta}(\mathbf{k} \mathbf{l}' \mathbf{k}' \beta') = \frac{\partial^2 \Phi}{\partial (\delta R_{\alpha}(\mathbf{k})) \partial (\delta R_{\beta}(\mathbf{l}' \mathbf{k}'))} \quad (1.6b)$$

where $M_{\mathbf{k}}$ is mass of the \mathbf{k}^{th} kind of atom, $\delta R_{\alpha}(\mathbf{k})$ is the α^{th} - cartesian component of the displacement of the \mathbf{k}^{th} atom in the \mathbf{l}^{th} unit cell, $\alpha = x, y, z$. $\Phi_{\alpha\beta}(\mathbf{k} \mathbf{l}' \mathbf{k}' \beta')$ is the

coupling parameter i.e. the second derivative of the nuclear-nuclear potential function $\bar{\Phi}(\underline{R}, l-l')$ evaluated at equilibrium position in the absence of zero-point fluctuation. Sometimes, the derivatives are evaluated at the mean positions at T. In this way the coupling parameters are temperature dependent and this approximation is known as pseudo-harmonic approximation. With the use of periodic boundary condition, the Hamiltonian gives a set of coupled equation as⁴⁹

$$w^2 \delta R_\alpha(k) = \sum_{k'\beta} D_{\alpha\beta}(\hat{k}, \hat{k}') \delta R_\beta(k') \quad (1.7)$$

where

$$D_{\alpha\beta}(\hat{k}, \hat{k}') = \frac{1}{\sqrt{M_\alpha M_\beta}} \sum_l \bar{\Phi}_{\alpha\beta}(\hat{k}, \hat{k}', l) \exp(-2\pi i \hat{k} \cdot \underline{x}(l)) \quad (1.8)$$

where $\delta R_\alpha(k)$ is time-independent displacement and $D_{\alpha\beta}(\hat{k}, \hat{k}')$ define the dynamical matrix of order $3r \times 3r$ as there are r atoms in the primitive cell. The necessary condition that these equations have a solution is that

$$\left| D - w^2 I \right| = 0 \quad (1.9)$$

where I is a unit matrix of order $3r \times 3r$. On account of the hermitian character of the dynamical matrix all the roots are real. The $3r$ functions $w_j^2(\hat{k})$ for each value of \hat{k} may be thought as the components of a multivalued function $w(\hat{k})$.

It can be easily shown that 3 frequencies or modes vanish with the vanishing of the wave vector (\hat{k}). Such modes constitute the acoustic modes. The remaining $3r-3$ modes do not vanish with the vanishing of the wave vector and are called the optical modes. For a "general" \hat{k} vector which cannot be transformed into itself by any point group symmetry of the crystal (except identity transformation) all the $3r$ modes are different.⁸⁶ In case the wave vectors lie along the symmetry axis or symmetry planes^{the} dynamical matrix can be factorized and equivalently a few of its modes are degenerate. Further, neglecting the constant term, the Hamiltonian (1.5) can be rewritten as

$$H = \frac{1}{2} \sum_l \frac{p_l \cdot p_l}{M} + \frac{1}{2} \sum_{ll'} \delta_{R_l} \cdot \Lambda_{ll'} \delta_{R_{l'}} \quad (1.10)$$

Here we have supposed that masses of all the atoms are same. p_l etc. are the momenta conjugate to the displacement δ_{R_l} satisfying the commutation relation

$$[\delta_{R_l}, p_{l'}] = i\hbar \delta_{ll'}, \quad [\delta_{R_l}, \delta_{R_{l'}}] = [p_l, p_{l'}] = 0 \quad (1.11)$$

Let us introduce the following normal coordinate transformation

$$\begin{aligned} \delta_{R_l} &= \frac{1}{\sqrt{NM}} \sum_{q,p} q_{qp} \epsilon_{pq} e^{-iq \cdot R_l^0} \\ p_l &= \frac{\sqrt{N}}{\sqrt{M}} \sum_{q,p} p_{qp} \epsilon_{pq} e^{iq \cdot R_l^0} \end{aligned} \quad (1.12)$$

where \underline{q} is the propagation vector and p the branch index.

The hermiticity of δR_1 and P_1 gives

$$\epsilon_{\underline{q}p}^+ = \epsilon_{-\underline{q}p}, \quad P_{\underline{q}p}^+ = P_{-\underline{q}p} \quad \text{and} \quad \left(\begin{array}{l} \epsilon_{\underline{q}p} = \epsilon_{-\underline{q}p} \\ \epsilon_{p\underline{q}} = \epsilon_{-p\underline{q}} \end{array} \right) \quad (1.13)$$

The cyclic boundary conditions are used. Also restricting ourselves to the first Brillouin Zone (B.Z.) we can write

$$\sum_{\underline{q}1} e^{i(\underline{q}-\underline{q}') \cdot R_1^0} = \Delta(\underline{q}-\underline{q}'-k) = N \delta_{\underline{q}\underline{q}'}$$

Then H_L is transformed to

$$H_L = \frac{1}{2} \sum_{\underline{q}p} \left(P_{\underline{q}p}^+ P_{\underline{q}p} + w_{\underline{q}p}^2 \epsilon_{\underline{q}p}^+ \epsilon_{\underline{q}p} \right) \quad (1.14)$$

where

$$w_{\underline{q}p}^2 = \frac{\Lambda_{\underline{q}p}}{M} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \quad (1.15)$$

$$\Lambda_{\underline{p}q} = \epsilon_{\underline{p}q} \sum_{\Pi'} \Lambda_{11'} e^{-i\underline{q} \cdot (R_1^0 - R_1^{0'})} \epsilon_{\underline{q}p}$$

$\epsilon_{\underline{p}q}$ etc. are the eigenvectors of the dynamical matrix

$$\sum \Lambda_{11'} e^{-i\underline{q} \cdot (R_1^0 - R_1^{0'})}$$

With the help of the relation (1.11) and (1.13) it can be shown that

$$\left. \begin{aligned} \left[\underline{Q}_{qp}, \underline{P}_{q',p'} \right] &= i\hbar \delta_{qq'} \delta_{pp'} \\ \left[\underline{Q}_{qp}, \underline{Q}_{q',p'} \right] &= \left[\underline{P}_{qp}, \underline{P}_{q',p'} \right] = 0 \end{aligned} \right\} \quad (1.16)$$

Now, introduce the Boson creation and annihilation operators b_{qp}^+ and b_{qp} through the relations

$$\underline{Q}_{qp} = i \sqrt{\frac{\hbar}{2W_{qp}}} (b_{qp}^+ - b_{qp}), \quad \underline{P}_{qp} = \sqrt{\frac{\hbar W_{qp}}{2}} (b_{qp} + b_{qp}^+) \quad (1.17)$$

These operators satisfy the commutation relations

$$\left. \begin{aligned} \left[b_{qp}, b_{q',p'}^+ \right] &= \delta_{qq'} \delta_{pp'} \\ \left[b_{qp}, b_{q',p'} \right] &= \left[b_{qp}^+, b_{q',p'}^+ \right] = 0 \end{aligned} \right\} \quad (1.18)$$

Finally, making use of these second quantization representations, we get the lattice Hamiltonian as

$$H_L = \sum_{qp} \hbar w_{qp} (b_{qp}^+ b_{qp} + \frac{1}{2}) \quad (1.19)$$

with $n_{qp} = b_{qp}^+ b_{qp}$ the occupation number operator.

This has only positive integers as its eigenvalues. The physical interpretation of (1.19) implies that the Hamiltonian consists of a system of non-interacting quanta known as "Phonons" each having an energy $\hbar\omega_{\mathbf{q}\rho}$ and a propagation vector \mathbf{q} .

A few authors have carried out measurements on BaTiO_3 to see the temperature dependence of the soft mode as manifested by some physical properties. It is well known that the temperature dependence of the dielectric constant is related to nonlinear effects. That is, the dielectric constant of a perfectly harmonic lattice does not depend upon the temperature. In the earlier theories i.e. phenomenological theories of Devonshire, Slater and related ones, the observed temperature dependence of the dielectric constant was developed at constant volume as a result of the anharmonic interaction between the ions. Silverman⁵¹ developed a theory of temperature dependence of the dielectric constant in which in addition to this assumption of nonlinearity, he considered the collective motion of ions i.e. lattice dynamics of the system rather than of individual ions. Further, as the temperature dependence of the soft optical mode is $\omega_T^2 \propto (T - T_c)$, it implies that below T_c (i.e. $T < T_c$) the system is unstable. Following Born he assumed that the electronic excited state is far removed from the ground state. He formulated the potential function for nuclear coordinates which includes the harmonic instabilities. The Hamiltonian for the paraelectric phase of the system was taken to consist of

seven terms. The first two terms are harmonic contribution to the energy from optical and longitudinal modes other than the unstable optical mode. ^{3rd} Third term arises as a contribution of the unstable optical mode. ^{3rd} Fourth term owes its origin to linear electric moment. The fifth term arises on account of second order electric moment and third order potential which ~~and~~ besides the coefficient ~~it~~ has the form

$$\sum_{\underline{q}} (b_{\underline{q}}^o + b_{-\underline{q}}^{o*}) (b_{\underline{q}}^a + b_{-\underline{q}}^{a*}) (b_o^{o_r} + b_o^o)$$

Further, last two terms arise from third order electric moments and fourth order potential. By no means, it is clear to the author ^{as to} ~~that~~ how the ~~retains~~ ^{is retained} fifth term in the Hamiltonian, ~~because~~, It has been pointed out by Anderson "only quantities having zero total momentum (i.e. uniform through the crystal) have finite averages". This forbids the existence of these terms which do not satisfy such conditions. Also there are other difficulties ~~also~~ present in this theory. Firstly, this theory is unsuited to give a dissipative effects ~~of~~ of the frequency dependent effects. Secondly, the very assumption that electronic excited state is far removed from ground state is unreasonable. This has been demonstrated by Sinha and Sinha.⁵²

Recently Cowley⁸⁷ proposed a theory for ferroelectricity which considers the anharmonic effects. According to him, the temperature variation of the phonon frequency is caused by the anharmonic character of the interatomic potential. Then his

theory is based on the usual procedure i.e. expansion of the potential function in various powers and subsequent calculations for the shift and damping of frequency using the many-body perturbation approach. However, this theory contains various drawbacks. Firstly, while the potential function has been expressed in various powers of atomic displacements, only first anharmonic terms of this expansion were considered. Secondly, in case the frequency shift is not small, perturbation method seems to be questionable. Thirdly, the theory is unable to predict the occurrence of phase transition. This deficiency is also inherent in Cochran's theory. Recently Boccara^{53,54} and Sarma have proposed a self-consistent theory for phase transition which is a problem of lattice dynamics. Their theory is macroscopic one and they suppose a given form of interatomic potential which has to manifest the prediction of transition at some temperature. For this, they formulate an effective Hamiltonian containing some unknown coefficients and then their theory runs parallel to Landau's theory of phase transition. This theory is at best phenomenological attempt in the right direction.

Finally, theories of Cochran³⁵ and Boccara and Sarma^{53,54} for ferroelectricity are, indeed, an improvement over Devonshire,²² Slater²³ and other related phenomenological theories. Nevertheless, neither the lattice dynamical nor the phenomenological theories predict the phase transition or provide a correct variation of phonon frequency with temperature. The reason behind this is that though lattice dynamical approach is in right direction, they have neglected

the influence of electronic state on the nuclear vibration of the system. When due account is taken of this effect,⁵⁵ the ad hoc supposition vanishes. This is the main theme of the first part of the present thesis.

PART - I

CHAPTER - 2

It was mentioned in chapter I that the basic mechanism of ferroelectric phase transformation in BaTiO_3 type crystal has not been understood clearly so far. Though Anderson and Cochran related it with a problem in lattice dynamics, they neglected the electronic influence on the nuclear vibrations. The usual method of calculating the structure and dynamics of a molecule consists of using the Born-Oppenheimer approximation thereby separating the full Schrödinger equation into a nuclear wave equation ~~as well as~~ and into electronic wave equation. Further, the approximate solutions of these independent equations are obtained. Jahn and Teller⁵⁶⁻⁵⁸ showed that an electronically degenerate state of a nonlinear molecule (or complex) is unstable on symmetry ground, alone (except the Kramer's two fold degeneracy) with respect to some asymmetric displacement which lifts the degeneracy. In case, the coupling between electrons and such displacements is sufficiently strong relative to the zero-point energy of the associated vibrational modes, the complex sustains a static distortion thereby occupying a new configuration of minimum energy.⁵⁹⁻⁶¹ On the otherhand, if the zero-point vibrational energy is comparable with the energy barrier separating equivalent configurations, then one gets a coupled motion of the electrons and the vibrational mode.⁶²⁻⁶⁴ This latter situation is known as dynamical Jahn-Teller effect.^{65,66} Moreover, the mixing of two or more electronic states by a linear movement of the nuclei is not

limited to degenerate electronic levels. Two close-lying nondegenerate electronic states may be strongly coupled vibronically. This pseudo Jahn-Teller effect has received less attention in the literature.⁶⁷⁻⁶⁹

Although Jahn-Teller effect reveals various interesting quantum mechanical effects, the interest will be confined to a study of the aspect which deals with the phase-transformation and in particular ferroelectric phase transformation. The first application of Jahn-Teller destabilization for octahedrally coordinated transition-metal complex was due to Van Vleck.⁵⁹ He considered an octahedral complex of the type MX_6 , where M stands for the transition-metal cation, surrounded by a regular arrangements of anions i.e. 'ligands' X. His calculations were based on an ionic model which considers the d^n configuration of M as tightly bound ^{with} and ligands providing 'crystal' field through Coulomb interaction. Generalization of this concept for the situation for a large concentration of Jahn-Teller cations in an essentially cubic crystal field leads to a cooperative transition to tetragonal symmetry. Theories of such phase transformation have been given by Finch, Sinha and Sinha,⁷⁰ Wojtowicz⁷¹ and Kanamori.⁷² However, the covalency effect between central cation and ligands are important in certain cases^{73,74} and recently Pryce, Sinha and Tanabe⁷⁵ have worked out a theory which shows the importance of this effect.

Crystal, being a gigantic molecule, the Jahn-Teller effect ought to play an important role in their phase

transformation^{76,77} and interest was shown to explain the ferroelectric phase transformation with its application by Englman⁷⁸ and Sinha and Sinha.⁵² The latter authors bring out clearly the role of pseudo Jahn-Teller effect to show how it can predict the ferroelectric phase transition in perovskite-type ferroelectrics. This has received much attention.^{55,79}

Following Sinha and Sinha⁵² let us consider the representative perovskite, namely BaTiO_3 . In the paraelectric phase it has the cubic structure with Ba^{2+} ion, Ti^{4+} ion and O^{2-} ion, occupying the center, corner and center of the edge respectively. Each Ti^{4+} ion ^{is} being surrounded octahedrally by 6 oxygen ions, while each oxygen ion by two Ti^{4+} ions lying collinearly at distance $\pm R$ and four Ba^{2+} ions and eight O^{2-} ions, as in a cubic closed packed assembly at distance $R\sqrt{2}$. Taking Z-axis along Ti-O-Ti, the four Ba^{2+} ions lie at the corners of the square in the xy plane. Further the role of large Ba^{2+} ions ^{is} to provide the overlap of the charge cloud of these ions ~~with~~ oxygen ions giving rise to a deformation of the central oxygen charge and electrons of this charge cloud try to make transition to such available orbitals which have axial symmetry and point towards the Ti^{4+} ions. Such a description automatically takes into account the covalency effect between oxygen and titanium. Further, two atomistic descriptions are possible to allow such transition for the oxygen ions. These are 1) the charge ion transfer model and 2) the excitation model. It can be shown that either model predicts the existence of two orbitals

having opposite symmetry and energies close together. These were referred ^{to as} ψ_s and ψ_a or $\phi_s(0)$ and $\phi_a(0)$ on charge transfer model and excitation model respectively. Hence a situation of near degeneracy ^{can be} was shown and the role of pseudo Jahn-Teller effect can not be ignored.

Let us analyse this in detail. In the case of excitation model, the relative energies of the excitation orbitals on the central ion are determined by the energy levels of the orbitals for a single excited electron and the crystal field due to $2Ti^{4+}$, $4Ba^{2+}$ and $8O^{2-}$ ions ~~are~~ given by

$$V_c = C_0^0 Y_0^0 + C_2^0 r^2 Y_2^0 + C_4^0 r^4 Y_4^0 + C_4^4 r^4 (Y_4^4 + Y_4^{-4}) \quad (2.1.1)$$

where Y's are the normalized spherical harmonics ^{and} ~~of~~ C's denote the constants given by

$$\left. \begin{aligned} C_0^0 &= 4 \frac{\sqrt{\pi}}{R} (q_{Ti} + \sqrt{2} q_{Ba} + 2\sqrt{2} q_O) \\ C_2^0 &= \sqrt{\frac{\pi}{5}} \frac{1}{R^3} (4q_{Ti} - \sqrt{2} q_{Ba} + 2q_O) \\ C_4^0 &= \frac{\sqrt{\pi}}{R^5} \left(\frac{4}{3} q_{Ti} + \frac{\sqrt{2}}{8} q_{Ba} - \frac{13\sqrt{2}}{48} q_O \right) \\ C_4^4 &= \frac{\sqrt{35}\pi}{24R^5} \left(q_{Ba} - \frac{q_O}{2} \right) \end{aligned} \right\} \quad (2.1.2)$$

with $q_x = (Ze)_x$ ^{where} $(Ze)_x$ denotes the charge of the ion in question and r is the radial coordinate of the electron on the central oxygen ion. Further, the crystal field

effect on the excited electron i.e. equation (2.1.1) is based on the approximation that the hole left behind (O^-) in the crystal is the source of an effective positive charge ($+Ze$). Also the excited electron has hydrogen like orbitals in the absence of the crystal field. With these approximations, the 3s, 3p and 3d orbitals lie close together and constant term in equation (2.1.1) i.e. $C_{O^+O^-}^{O^+O^-}$ which is responsible to stabilize the oxygen ion, affects all the level equally. Thus, the effect of relative splitting is evaluated with the help of other terms in equation (2.1.1). A simple straight forward calculation for the diagonal matrix elements of the orbitals 3s, 3p_x, 3p_y, 3p_z, 3d_{z²}, 3d_{x²-y²}, 3d_{xy}, 3d_{yz}, 3d_{zx} shows that the 3s orbitals remain unaffected, whereas the 3d_{z²} and 3p_z orbitals are depressed and the rest are pushed up. Denoting the energy levels of 3d_{z²} and 3p_z by $\phi_s(O)$ and $\phi_a(O)$, we observe that they lie close together within a fraction of an electron volt i.e. $\sim .5$ ev. while other orbital energies are comparatively very large and so the former situation conforms to the case of near degeneracy of electronic states.

Let us analyse, the other model i.e. charge transfer model for the case of Ti-O-Ti unit. In Ti^{++} ions the orbitals upto 3p are filled and hence the available orbitals are 3d onwards. Further, those orbitals which have the maximum overlap with oxygen are important and with the Ti-O-Ti as z axis, these suitable empty orbitals are 3d_{z²} on each Ti^{++} ion. Denoting

this by ϕ_1 and likewise on the second ion ϕ_2 , we get two molecular orbitals as a linear combination of these and are given by

$$\frac{\phi_1 + \phi_2}{\sqrt{2}} \quad (2.1.3)$$

$$\frac{\phi_1 - \phi_2}{\sqrt{2}} \quad (2.1.4)$$

The first is symmetrical and other antisymmetrical with respect to the reflection in the plane perpendicular to Ti-O-Ti bond and passing through oxygen. As the overlap between ϕ_1 and ϕ_2 i.e. $\langle \phi_1 | \phi_2 \rangle$ is negligible, both orbitals have the same energy. Now, let us consider the orbital of the oxygen ion from which an electron is transferred. On symmetry considerations we take this to be $2p_z$ and denote by (p_o) orbital. This being an odd orbital mixes strongly with the antisymmetrical orbital given by equation (2.1.4), giving rise to two orthogonal molecular orbitals

$$\psi_s = \frac{\phi_1 + \phi_2}{\sqrt{2}} \quad (2.1.5)$$

$$\psi_a = \frac{\phi_1 - \phi_2 - 2S_o p_o}{\sqrt{2(1-2S_o^2)}} \quad (2.1.6)$$

with

$$S_o = \langle \phi_1 | p_o \rangle .$$

ψ_s and ψ_a are orthogonal to each other and to p_o . Also, on account of the overlap mixing the orbital energies of ψ_a and ψ_s will be slightly different. Thus either approach shows ^{that} the two electronic state lie near enough for coupling through vibration.

It has been mentioned in the introduction that Ti-O-Ti units as well as TiO_6 octahedra are relevant for studying the ionic dielectric $BaTiO_3$. In the following section it is shown ^{as is} ~~that~~ how such units are liable to show instabilities when electron-vibration coupling is considered. Also, the study includes the lattice dynamics of such units taking cognizance of electronic as well as anharmonic interaction involved in the problem. It is shown⁵⁵ that the Jahn-Teller like terms do indeed lead to expressions suggesting instabilities of certain modes (optical) which are eventually stabilized as a result of anharmonic interactions. Furthermore the inclusion of electronic effects incorporates the covalency terms which may be necessary in the chemical bonding of the units.

2.2 Vibronic coupling in elementary units:

In this section, we consider the study of the coupling of the low-lying excited electronic states with the ground state of the elementary systems owing to certain vibrational perturbations. The calculation is confined to perovskite or WO_3 type ferroelectrics. The crystal structure of perovskite type system has already been discussed in the introduction.

Here, we shall make note of the nearest neighbour coordination of O^{2-} and M (i.e. Ti^{4+} or W^{6+}) ions. In the cubic phase we have the collinear units e.g. Ti-O-Ti with Ti-O distance same on both sides of O and in the regular octahedra. The main interest is to show that vibronic effects (electron - vibration coupling) will lead to the distortion of the units (either Ti-O-Ti or TiO_6) resulting in a dielectric dipole.

The case of triatomic unit

Let us consider the situation where we have two electronic levels for the system namely, the symmetrical state $|\psi_s\rangle$ and the antisymmetrical state $|\psi_a\rangle$. The energy separation is defined by

$$2J = E (\psi_a) - E (\psi_s) \quad (2.2.1)$$

The problem then is to consider the coupling between the states $|\psi_s\rangle$ and $|\psi_a\rangle$ owing to antisymmetrical vibration. First let us consider the static case of such a unit to evaluate the energy matrix. We follow the work of Öpik and Pryce⁶¹ for the study of near degeneracy in a triatomic linear unit (B-O-B). They showed the instability of the system in symmetrical configuration and the distortion of the system in such a way that the two B atoms move in one direction and the central atom in the opposite direction. The Hamiltonian for the present system is written as

$$H = H_{el} + H_v + H_{int}, \quad (2.2.2)$$

where H_{el} is the one-electron term for the electron in question including its kinetic and potential energies in the field of ion cores while H_v represents the vibrational energy operator for the system in the harmonic approximation and has the form

$$H_v = \frac{1}{2} \sum_i (P_i^2 + \alpha_i Q_i^2), \quad (2.2.3)$$

where Q_i are the normal coordinates and P_i the corresponding momenta, and α_i the force constant. The term H_{int} represents the electron-vibration coupling term

$$H_{int} = \sum_i V^i Q_i, \quad (2.2.4)$$

with $V^i = \left(\partial V / \partial Q \right)_0$ and involves only electronic coordinates as variables. The interest is confined to the odd vibration only which couples the electronic states

$|\psi_s\rangle$ and $|\psi_a\rangle$. Treating the normal coordinates for odd vibration Q_a as a parameter in the static approximation, the eigenvalues can be shown to be ,

$$E = \alpha_a Q_a^2 \pm \sqrt{J^2 + A^2 Q_a^2}, \quad (2.2.5)$$

with

$$A = \langle \psi_s | V^a | \psi_a \rangle \quad (2.2.6)$$

As noted by Öpik and Pryce, the lower level will have two minima, symmetrically disposed about $Q_a = 0$, if the condition

$$\alpha_a = w_a^2 \left\langle \frac{A^2}{|J|} \right\rangle, \quad (2.2.7)$$

where the reduced mass is absorbed in the definition of Q_a , is fulfilled. Then Q_a has the value at the minima

$$(Q_a^{\min})^2 = \left(\frac{A^2}{\alpha_a^2} - \frac{J^2}{A^2} \right). \quad (2.2.8)$$

Thus, it is clear from equation (2.2.8) that within the harmonic approximation the transformation from undistorted to distorted configuration will take place at $w_a^2 = \frac{A^2}{|J|}$.

Now let us analyse the vibrational problem carefully. The problem is to diagonalize the Hamiltonian (2.2.2).

It is expedient to recast the Hamiltonian (2.2.3) so that its relationship with the manifold of symmetrical state $|\psi_s\rangle$ (ground state) and antisymmetrical state $|\psi_a\rangle$ (excited state) is clear. The Hamiltonian described in terms of the manifold of electronic states $|\psi_s\rangle$ and $|\psi_a\rangle$ can be written as

$$\begin{aligned} H = & |\psi_s\rangle E_s \langle \psi_s| + |\psi_a\rangle E_a \langle \psi_a| \\ & + \frac{1}{2} (P_s^2 + w_s^2 Q_s^2) + \frac{1}{2} (P_o^2 + w_o^2 Q_o^2) \\ & + |\psi_a\rangle A_{as} \langle \psi_s| Q_o + |\psi_s\rangle A_{sa} \langle \psi_a| Q_o. \quad (2.2.9) \end{aligned}$$

The Hamiltonian (2.2.9) brings out physically the role played by symmetrical and antisymmetrical vibrations and in turn these are like the projection operators acting on the Hilbert space.

For the triatomic unit under consideration the vibrational modes of interest are the symmetrical vibration (Q_s) and antisymmetrical vibration (Q_o) mode. The electron vibration coupling terms which survive and couple the symmetrical $|\psi_s\rangle$ and antisymmetrical state $|\psi_a\rangle$ through $V^o Q_o$ where $V^o = (\partial V / \partial Q_o)_o$ and has odd parity. It is given by (2.2.6).

Let us now make use of a canonical transformation in order to remove the electron vibration coupling term occurring in first order of Q_o . The transformed Hamiltonian is given by

$$H_T = e^{-iS} H e^{iS} = H + i [H, S] - \frac{1}{2} [[H, S], S] + \dots \quad (2.2.10)$$

where S is defined by

$$S = ig \left(|\psi_a\rangle \langle \psi_s| Q_o - |\psi_s\rangle \langle \psi_a| Q_o \right) \quad (2.2.11)$$

The quantity g is so chosen that the linear term in Q_o is eliminated from the transformed Hamiltonian. This is easily done by making use of the relation

$$i [H_{el}, S] + H_{int} = 0 \quad (2.2.12)$$

This implies that

$$g = \frac{A_{as}}{(E_a - E_s)} \quad (2.2.13)$$

Thus with $A_{as} = A_{sa}$, the transformed Hamiltonian upto Harmonic and diagonal terms is

$$\begin{aligned} H_T = & |\psi_a\rangle E_a \langle \psi_a| + |\psi_s\rangle E_s \langle \psi_s| \\ & + \frac{1}{2} (P_s^2 + w_s^2 Q_s^2) + \frac{1}{2} (P_o^2 + w_o^2 Q_o^2) \\ & - \frac{|\psi_s\rangle (A_{as})^2 \langle \psi_s| Q_o^2}{(E_a - E_s)} + \frac{|\psi_a\rangle (A_{as})^2 \langle \psi_a| Q_o^2}{(E_a - E_s)} \end{aligned} \quad (2.2.14)$$

As the interest lies in the vibrational problem let us take the expectation value of the Hamiltonian with respect to

$|\psi_s\rangle$ or $|\psi_a\rangle$, Thus $\langle \psi_s | H_T | \psi_s \rangle$ gives

$$H_{\text{Vib}} = E_s + \frac{1}{2} (P_s^2 + w_s^2 Q_s^2) + \frac{1}{2} \left[P_o^2 + \left\{ w_o^2 - \frac{2(A_{as})^2}{(E_a - E_s)} \right\} Q_o^2 \right] \quad (2.2.15)$$

Thus it is obvious that the frequency of the odd vibration is modified as

$$w_o^2(\text{eff}) = \left(w_o^2 - \frac{2A_{as}^2}{(E_a - E_s)} \right) \quad (2.2.16)$$

If the average is taken with respect to the state $|\psi_a\rangle$, it is seen that the effective frequency relation will have a plus sign in place of minus sign in (2.2.16).

The analysis given above shows that if the system is in the ground state having symmetrical electronic state $(E_a - E_s) > 0$, the effective frequency of the odd vibration decreases (cf (2.2.16)). On the otherhand, when it is in the excited state E_a , the frequency will be pushed up. This is a consequence of the electron-vibration coupling incorporated in the treatment.

The electronic ground state is indeed totally symmetrical $|\psi_s\rangle$. Let us now examine the effective frequency

$$w_0^2(\text{eff}) = \left(w_0^2 - \frac{A^2}{|J|} \right) \quad (2.2.17)$$

The condition $w_0^2 < \frac{A^2}{|J|}$ makes the effective frequency imaginary which implies that instability develops in the system. It has been pointed out before that this leads to the distortion of the system in which the central atom moves in one direction and the two extreme atoms in the opposite direction. It has been already demonstrated that for the Ti-O-Ti the condition $w_0^2 < A_{as}^2 / |J|$ is obtained and one expects the instability.

We shall now consider the electron-vibration coupling in the octahedral unit ML_6 where M is the metal ion and L stands for the ligand ion.

The case of octahedral unit:

It is expedient to consider the problem with the help of a specific example. The most appropriate unit is the octahedral cluster TiO_6 with the Ti ion at the center and each oxygen ion at the corners. The various electronic configurations of the complex $(TiO_6)^{8-}$ have been discussed by Nelson⁸² following the molecular orbital approach. However, he has not considered the electron-vibration coupling which seems to us to be of central importance in the present problem. To understand this, a discussion of the one electron molecular orbitals and many electron states for the unit along with the vibrational modes will be essential. The definitions and notations used here are the same as those given by Van Vleck,⁵⁹ Öpik and Pryce⁶⁰ and Pryce, Sinha and Tanabe⁷⁵ in a different context. The two ligand ions (e.g. O^{2-}) on the $\pm x$ axis are respectively numbered 1 and 4, the two on the $\pm y$ axis 2 and 5 and the two on the $\pm z$ axis 3 and 6. If we started from the ionic picture i.e. Ti^{4+} and O^{2-} then the total number of electrons to be accounted for ^{is} as follows:

$$18(Ti^{4+}) + 6 \times 10(O^{2-}) = 78.$$

Of these, 18 (in $1s^2 2s^2 2p^6 3s^2 3p^6$) can be regarded with sufficient accuracy as completely located on Ti^{4+} centre and $6 \times 4 = 24$ are located on oxygens (in $1s^2, \frac{2}{\sigma^-}$).** The remaining

** The hybridization of 2s and 2p orbitals of the ligand ion will give two orbitals, which are designated as σ^+ and σ^- where, the former points towards the metal ion and the latter in the diagonally opposite direction.

electrons (36) would occupy orbitals which can approximately be regarded as built up from the combination of 2s, 2p orbitals on oxygen and 3d, 4s and 4p atomic orbitals on Ti^{4+} .

We shall refer to the appropriate hybrids (sp) of 2s and 2p orbitals on O^{2-} which have end on overlap with the metal ions as σ_{\pm} orbitals and the remaining 2p orbitals as π orbitals. Here σ and π respectively refer to those orbitals which have even and odd symmetry under rotation by 180° about the axis joining the metal and ligand ions. It should be noted that the bonding molecular orbitals involving the σ orbitals of the ligand are expected to be of lower energy than those involving the π orbitals because the orbital function overlaps more on to the Ti and makes use of its attractive field than the π orbitals.

Then in the increasing order of energy the molecular orbitals are given as

$$\begin{array}{l} a_{1g}^b, t_{1u}^b, e_g^b, t_{2g}^b, t_{1u}^b, t_{2u}^n, t_{1g}^n, \\ t_{2g}^a, e_g^a, a_{1g}^a, t_{1u}^a, t_{1u}^{'a} \end{array}$$

Here the superscripts, b, n and a refer to bonding, non-bonding and antibonding orbitals respectively; a_1 , e and t are the group theoretical notations of the orbitals (see Griffiths⁸³).

In the absence of electron-vibration interactions and for the regular octahedron, the ground electronic state has the configuration,

$$\left| \psi_g \left({}^1A_{1g} \right) \right\rangle \rightarrow (a_{1g}^b)^2 (e_g^b)^4 (t_{1u}^b)^6 (t_{2g}^b)^6 (t_{1u}^b)^6 (t_{2u}^n)^6 (t_{2g}^n)^6 \quad (2.3.1)$$

This accounts for all the electrons and the states upto bonding and non-bonding orbitals are completely filled. Let us now consider the excited states in which a single electron is transferred from one of the bonding or non-bonding (predominantly ligand orbitals) t_u orbitals to one of the antibonding orbitals. Group theoretically various symmetry states are possible;⁸³

$$\left\{ \dots (t_{1u}^b)^6 ; ({}^1A_{1g}) \right\rangle \rightarrow \left| (t_{1u}^b)^5 (t_{2g}^a) ; {}^1A_{2u} \text{ or } {}^1E_u, \right. \\ \left. \text{or } {}^1T_{1u} \text{ or } {}^1T_{2u} \right\rangle \quad (2.3.2)$$

$$\left\{ \dots (t_{1u}^b)^6 ; ({}^1A_{1g}) \right\rangle \rightarrow \left| (t_{2u}^b)^5 (e_g^a) ; {}^1T_{1u} \text{ or } {}^1T_{2u} \right\rangle \quad (2.3.3)$$

with a similar expression for transition from (t_{1u}^b) .

Likewise we will have

$$\left\{ \dots (t_{2u}^n)^6 ; ({}^1A_{1g}) \right\rangle \rightarrow \left| (t_{2u}^n)^5 (t_{2g}^n) ; {}^1A_{1u} \text{ or } {}^1E_u \right. \\ \left. \text{or } {}^1T_{1u} \text{ or } {}^1T_{2u} \right\rangle \quad (2.3.4a)$$

$$\left\{ \dots (t_{2u}^n)^6 ; ({}^1A_{1g}) \right\rangle \rightarrow \left| (t_{2u}^n)^5 (e_g^a) ; {}^1T_{1u} \text{ or } {}^1T_{2u} \right\rangle \quad (2.3.4b)$$

We now consider the various vibrational modes for the octahedral unit MO_6 . There are fifteen normal coordinates of vibration which belong to the following types of representations:

$$A_{1g}, E_g, T_{1u}, T_{1u}^i, T_{2g} \text{ and } T_{2u}.$$

From symmetry considerations alone we can see that the various excited electronic states can couple with the ground state $|\psi_g; {}^1A_{2g}\rangle$ via the vibrational perturbation having appropriate symmetry.

The Hamiltonian involving electron-vibration interaction for the present problem is similar to (2.2.7). The general form can be written as

$$\begin{aligned} H_{\text{vib}} = & \sum_{i,\alpha} |\psi(r_i^\alpha)\rangle E_i \langle \psi(r_i^\alpha)| \\ & + \frac{1}{2} \sum_{i,\alpha} (P_{i\alpha}^2 + W_i^2 Q_{i\alpha}^2) \\ & + \sum_{(i,\alpha)(j,\beta)(k,\gamma)} |\psi(r_i^\alpha)\rangle A_{\Gamma_i \Gamma_j}^{\alpha\beta}(\Gamma_k^Y) \langle \psi(r_j^\beta)| Q_{\Gamma_k^Y}, \end{aligned} \tag{2.3.5}$$

where Γ_i refers to the irreducible representation of the octahedral group. Thus $|\psi(r_i^\alpha)\rangle$ denotes the α^{th} base function belonging to the Γ_i irreducible representation.

$Q_{\Gamma_i^\alpha}$ likewise represents a similar vibrational mode

$$A_{\Gamma_i^\alpha \Gamma_i^\beta}(\Gamma_k^Y) = \langle \Psi(\Gamma_i^\alpha) | V(\Gamma_k^Y) | \Psi(\Gamma_j^\beta) \rangle \quad (2.3.6)$$

$$\text{and } V(\Gamma_k^Y) = \frac{\partial V}{\partial Q_{\Gamma_k^Y}} \quad (2.3.7)$$

It is clear from (2.3.7) that only those matrix elements will survive for which the corresponding products representation $\Gamma_i \times \Gamma_k \times \Gamma_j$ will contain the identity representation Γ_1 on decomposition. In the present problem we are not interested in a general situation of (2.3.5). Our interest is to see as to how this ground electronic state $|\Psi_g(^1A_{1g})\rangle$ couples with the excited states via (2.3.6). Furthermore, only low lying excited electronic states will have any significant vibronic interaction. The low lying electronic state of symmetry T_{1u} is of particular interest in the present problem. Such states, denoted by $|\Psi_u(T_{1u})\rangle$, will couple with the ground configuration $|\Psi_g(^1A_{1g})\rangle$ through the vibrational modes of symmetry T_{1u} . Of these, the mode in which the positive ion moves against two of the ligand ions in opposite directions give rise to the dipole moment. It is referred to as W_{10} mode with one of the Q's called as Q_{10} (See Koide and Pryce⁸⁴). This describes the rattling of the positive ion in the octahedron of negative ions. The importance of coupling via this mode has also been stressed by Orgel.³² We shall therefore confine our attention to the vibronic coupling of states $|\Psi_g(^1A_{1g})\rangle$ and $|\Psi_u(T_{1u})\rangle$ via the appropriate vibrational modes T_{1u} . At this stage, we must consider the explicit forms of the normal

coordinates. Since there are two representations of type T_{1u} their interactions have to be considered. This evaluation involves certain assumptions about the forces between atoms. Such calculations based on valence force and central force models have been carried out by Koide and Pryce.⁶⁴ We shall use the final results.

The ratio of the masses of oxygen and Ti i.e. $\frac{M_O}{M_{Ti}} = 3$. Thus the normal coordinates of present interest are,

$$Q_u^z (T_{1u}) = \sqrt{\frac{3}{10}} (z_3 + z_6 - 2z_M)$$

$$Q_u^y (T_{2u}) = \sqrt{\frac{3}{10}} (y_2 + y_5 - 2y_M)$$

$$Q_u^x (T_{4u}) = \sqrt{\frac{3}{10}} (x_1 + x_4 - 2x_M)$$

The corresponding derivative of the potential function (cf 2.3.7) can be easily deduced for an electrostatic interaction between the ligand point ions and an electron of the metal ion at distance r_{oi} apart, namely q/r_{oi} where $q = Ze$. The method of Van Vleck is adopted here. We get

$$V_{uz} = \left(\frac{\partial V}{\partial Q_{uz}} \right) = \sum_k \left[\frac{a z_k}{R_o^3} + \frac{b}{R_o^5} \left(z_k^3 - \frac{3}{5} z_k r_k^2 \right) + \frac{c}{R_o^7} \left\{ z_k^5 - \frac{10}{9} \left(z_k^3 - \frac{3}{5} z_k r_k^2 \right) r_k^2 - \frac{3}{7} z_k r_k^4 \right\} + \dots \right] \quad (2.3.8)$$

where R_o is the distance between the metal and ligand ion in the undistorted octahedron and

$$\begin{aligned}
 a &= q \sqrt[3]{10} \\
 b &= q \sqrt[3]{20} \\
 c &= q \sqrt[3]{189}
 \end{aligned}
 \tag{2.3.9}$$

The summation is over the k electrons of the central ion. The other components namely, V_{uy} and V_{ux} can be obtained by a cyclic permutation of (2.3.8). Although, the quantities V_{uz} etc. have been deduced on an electrostatic model, the general form is given in (2.3.8) will remain the same on other models also, apart from the change in the definitions of the coefficients a , b , and c etc. The polynomials involving electronic coordinates etc. clearly indicate that the vibronic perturbations will mix excited electronic states of T_{1u} symmetry with the ground state. Thus, within the manifold of ground electronic state $|\psi_g\rangle$ and excited states $|\psi_u^\alpha\rangle$, the Hamiltonian (2.3.5) can be written as :

$$\begin{aligned}
 H_{\text{red}} &= |\psi_g\rangle E_g \langle\psi_g| + \sum_{\alpha} |\psi_u^\alpha\rangle E_u \langle\psi_u^\alpha| \\
 &+ \frac{1}{2} \sum_{\alpha} \left(P_{(T_{1u}^\alpha)}^2 + W_{(T_{1u}^\alpha)}^2 Q_{(T_{1u}^\alpha)}^2 \right) \\
 &+ \frac{1}{2} \sum_{\alpha, i (\neq T_{1u}^\alpha)} \left(P_{i,\alpha}^2 + W_i^2 Q_{i,\alpha}^2 \right) \\
 &+ \sum |\psi_g\rangle A_{g,u^\alpha} (T_{1u}^\alpha) \langle\psi_u^\alpha| Q_{(T_{1u}^\alpha)} + \text{c.c.} \tag{2.3.10}
 \end{aligned}$$

The transformation analogous to (2.2.11) can be used now, where,

$$S(\text{oct}) = i \sum_{\alpha} G^{\alpha} \left(|\psi_u^{\alpha}\rangle \langle \psi_g| Q_{1u}^{\alpha} - |\psi_g\rangle \langle \psi_u^{\alpha}| Q_{1u}^{\alpha} \right) \quad (2.3.11)$$

with

$$G^{\alpha} = \frac{A_{g,u^{\alpha}}}{E_u - E_g}; \quad A_{g,u^{\alpha}} = A_{u,g} \quad (2.3.12)$$

Thus, the transformed vibrational Hamiltonian, after taking the expectation value over the ground electronic state, is expressed as,

$$\begin{aligned} H_{\text{vib}}(E_g) &= E_g + \frac{1}{2} \sum_{\alpha, i (i \neq T_{1u})} (P_{i,\alpha}^2 + W_{i,\alpha}^2 Q_{i,\alpha}^2) \\ &+ \frac{1}{2} \left[P_{(T_{1u})}^2 + \left\{ W_{T_{1u}}^2 - \frac{2A_{g,u^{\alpha}}^2}{(E_u - E_g)} \right\} Q_{(T_{1u})}^2 \right] \quad (2.3.13) \end{aligned}$$

Thus, we see that for the elementary octahedron also the vibronic interaction can render the effective frequency,

$$W_{\text{eff}}^2 = \left(W_{T_{1u}}^2 - \frac{2A_{g,u^{\alpha}}^2}{(E_u - E_g)} \right) \quad (2.3.14)$$

imaginary (i.e. $W_{T_{1u}}^2 < \frac{2A_{g,u^{\alpha}}^2}{(E_u - E_g)}$). This instability will lead to a distortion of the system in which the metal ions moves in either of the x, y, z directions with the movement of the two appropriate ligands in the opposite direction. This will give a permanent dipole moment. This seems to be possible in any of the three directions for the

elementary octahedron. However, as has been discussed earlier, the environment of oxygen ions in BaTiO_3 is such that only one of the directions (say z) will be preferred.

Sofar we have discussed the vibronic problem for the elementary units, namely, Ti-O-Ti and TiO_6 . In the next section we consider a lattice of such units and discuss the vibrational problem of the lattice including anharmonic terms as well as vibronic interactions in the elementary units.

2.4 COLLECTIVE OSCILLATIONS

In the previous sections, we have analysed the vibrational problem of elementary units (tri-ionic or octahedral) by taking account of the vibronic coupling caused by some specific modes. This gave rise to instability of the modes in question. Let us now consider an assembly of such units forming a lattice. In BaTiO_3 , the TiO_6 octahedra are joined by their corners. This forms a three dimensional network ~~and~~ the large holes are occupied by the Ba^{2+} ions. Of course, in BaTiO_3 ~~and~~ Ba^{2+} ions do play some role in view of the large size and overlap with oxygen ions. Perhaps in WO_3 type ferroelectrics (or from structural considerations in ReO_3) one has to consider the lattice of octahedra alone. We confine our attention to the vibrational problem of the lattice made up of these units. For N such units and including anharmonic terms the lattice Hamiltonian is

$$\begin{aligned}
 H_L = & \sum_I \sum_{\lambda} \frac{1}{2} (P_{1\lambda}^2 + W_{1\lambda}^2 Q_{1\lambda}^2) + \sum_{\lambda \neq \mu} a_{\lambda\mu} Q_{1\lambda} Q_{\mu\lambda} \\
 & + \sum b_{\lambda\mu\nu} Q_{1\lambda} Q_{\mu\lambda} Q_{\nu\lambda} + \sum c_{j\lambda\mu\nu} Q_{j\lambda} Q_{1\lambda} Q_{\mu\lambda} Q_{\nu\lambda}
 \end{aligned}
 \tag{2.4.1}$$

where the frequency, $W_{1\lambda}^2$ refers to the 1th unit and its λ th mode. $P_{1\lambda} = \dot{Q}_{1\lambda}$ and $Q_{1\lambda}$ are the normal coordinates of the 1th unit and its λ th mode. In the above, we have included the translational mode of the individual units also in order that the acoustical mode for the whole crystal is taken properly into account. For present purposes, we shall be interested in a detailed study of the modes which involve the vibronic instability (cf. equation (2.3.14)) and their interactions with the acoustic mode contained in the third and fourth order anharmonic terms.

Let us introduce the transformation to lattice wave normal coordinates, namely

$$\begin{aligned}
 Q_{1\lambda} &= \frac{1}{\sqrt{N}} \sum_{\sigma_0} e^{i\sigma_0 \cdot R_1} Q_{\sigma_0} \\
 Q_{1\mu} &= \frac{1}{\sqrt{N}} \sum_{\sigma_a} e^{i\sigma_a \cdot R_1} Q_{\sigma_a} \text{ etc} \\
 P_{1\lambda} = \dot{Q}_{1\lambda} &= \frac{1}{\sqrt{N}} \sum_{\sigma_0} e^{i\sigma_0 \cdot R_1} \dot{Q}_{\sigma_0}
 \end{aligned}
 \tag{2.4.2}$$

where $Q_{\underline{\sigma}_o}$ and $Q_{\underline{\sigma}_a}$ are lattice modes corresponding to the optical and acoustic modes of vibrations respectively;

$\underline{\sigma}_o, \underline{\sigma}_a$ are the propagation vectors and R_1 is the vector spanning the 1th unit. The Hamiltonian (2.4.1) is transferred to

$$\begin{aligned}
 H = & \sum_{\underline{\sigma}} \hbar \left(P_{\underline{\sigma}} P_{\underline{\sigma}}^* + W_{\underline{\sigma}}^2 Q_{\underline{\sigma}} Q_{\underline{\sigma}}^* \right) \\
 & + \frac{1}{\sqrt{N}} \sum_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}''} Q_{\underline{\sigma}} Q_{\underline{\sigma}'} Q_{\underline{\sigma}''} B_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}''} \Delta(\underline{\sigma} + \underline{\sigma}' + \underline{\sigma}'' - \underline{K}) \\
 & + \frac{1}{\sqrt{N}} \sum_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}''} Q_{\underline{\sigma}} Q_{\underline{\sigma}'} Q_{\underline{\sigma}''} Q_{\underline{\sigma}'''} C_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}'', \underline{\sigma}'''} \Delta(\underline{\sigma} + \underline{\sigma}' + \underline{\sigma}'' + \underline{\sigma}''' - \underline{K})
 \end{aligned} \tag{2.4.3}$$

where \underline{K} is a reciprocal lattice vector and $W_{\underline{\sigma}}^2 = W_{1\lambda}^2 + D_h$

$$\begin{aligned}
 D_h &= \sum_h a_{1,1+h} e^{-i \underline{\sigma} \cdot \underline{R}_h} \\
 B_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}''} &= \sum_{1,1+h', 1+h''} b_{1,1+h', 1+h''} e^{i(\underline{\sigma}', \underline{R}_h' + \underline{\sigma}'', \underline{R}_h'')} \\
 C_{\underline{\sigma}, \underline{\sigma}', \underline{\sigma}'', \underline{\sigma}'''} &= \sum_{1,1+h', 1+h'' 1+h'''} c_{1,1+h', 1+h'' 1+h'''} e^{i(\underline{\sigma}', \underline{R}_h' + \underline{\sigma}'', \underline{R}_h'' + \underline{\sigma}''', \underline{R}_h''')} \\
 \underline{R}_h &= \underline{R}_1 - \underline{R}_m
 \end{aligned} \tag{2.4.4}$$

The suffix s is used as a general symbol for optical (o) or acoustical (a) modes. It is convenient at this stage to

go over to the second quantization representation by using the following transformations

$$\left. \begin{aligned} Q_{\sigma_s} &= \sqrt{\frac{\hbar}{2W_{\sigma_s}}} (b_{\sigma_s}^s + b_{-\sigma_s}^{s+}) \\ P_{\sigma_s} &= i \sqrt{\frac{\hbar W_{\sigma_s}}{2}} (b_{\sigma_s}^{s+} - b_{-\sigma_s}^s) \end{aligned} \right\} \quad (2.4.5)$$

We get

$$\begin{aligned} H &= \sum \frac{\hbar W_{\sigma_s}}{2} (b_{\sigma_s}^{s+} b_{\sigma_s}^s + b_{\sigma_s}^s b_{\sigma_s}^{s+}) \\ &+ \frac{1}{\sqrt{N}} \sum \frac{(\frac{\hbar}{2})^{3/2} B_{\sigma_s, \sigma_s', \sigma_s''}}{\sqrt{W_{\sigma_s} W_{\sigma_s'} W_{\sigma_s''}}} (b_{\sigma_s}^s + b_{-\sigma_s}^{s+}) (b_{\sigma_s'}^{s'} + b_{-\sigma_s'}^{s'+}) \\ &\quad (b_{\sigma_s''}^{s''} + b_{-\sigma_s''}^{s''+}) \Delta (\sigma_s + \sigma_s' + \sigma_s'' - \underline{K}) \\ &+ \frac{1}{N} \sum (\frac{\hbar}{2})^2 \frac{C_{\sigma_s, \sigma_s', \sigma_s'', \sigma_s'''}}{\sqrt{W_{\sigma_s} W_{\sigma_s'} W_{\sigma_s''} W_{\sigma_s'''}}} (b_{\sigma_s}^s + b_{-\sigma_s}^{s+}) (b_{\sigma_s'}^{s'} + b_{-\sigma_s'}^{s'+}) \\ &\quad (b_{\sigma_s''}^{s''} + b_{-\sigma_s''}^{s''+}) (b_{\sigma_s'''}^{s'''} + b_{-\sigma_s'''}^{s''' +}) \Delta (\sigma_s + \sigma_s' + \sigma_s'' + \sigma_s''' - \underline{K}) \end{aligned} \quad (2.4.6)$$

In proceeding further, we shall be guided by some physical conditions (selection rules) and approximations. First we consider those cases where the reciprocal lattice vector involved in the momentum conservation relations (Δ functions) are zero ($\underline{K} = 0$). Thus it should be noted that only those operator products will have non-zero finite averages which

which represent processes with zero total momentum (See Anderson)³⁶ In view of the selection rules derived by Szigeti⁸⁵ the third order terms with coefficients such as $B_{0\sigma\sigma}$, $B_{00\sigma}$, $B_{\sigma\sigma\sigma}$ will not survive. Also, for a system having center of symmetry, as in the present case, $(b_0^0 + b_0^{0+})$ i.e. Q_0^0 cannot enter in odd powers (1). This implies that the coefficients $B_{0\sigma\sigma}$ should be zero.

Under these conditions the Hamiltonian (2.4.6) reduces to

$$H_R = H_a + H_0 + H_0^0 + H_1 + H_2 + H_3 \quad (2.4.7)$$

where

$$H_a = \sum \frac{1}{2} \hbar w_{\sigma}^a (b_{\sigma}^{a+} b_{\sigma}^a + \frac{1}{2}) \quad (2.4.8)$$

$$H_0 = \sum_{\sigma \neq 0} \frac{1}{2} \hbar w_{\sigma}^0 (b_{\sigma}^{0+} b_{\sigma}^0 + \frac{1}{2}) \quad (2.4.9)$$

$$H_0^0 = \frac{1}{2} \hbar w_0^0 (b_0^{0+} b_0^0 + \frac{1}{2}) \quad (2.4.10)$$

$$H_1 = \frac{1}{\sqrt{N}} \left(\frac{\hbar}{2} \right)^{3/2} \frac{B_{000a}}{w_0^0 w_{\sigma}^a} (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_{\sigma}^a + b_{\sigma}^{a+}) \quad (2.4.11)$$

$$H_2 = \frac{1}{N} \left(\frac{\hbar}{2} \right)^2 \sum \frac{C_{\sigma 00}}{w_0^0 w_{\sigma}^a} (b_0^{0+} + b_0^0) (b_0^0 + b_0^{0+}) (b_{\sigma}^a + b_{\sigma}^{a+}) (b_{-\sigma}^a + b_{-\sigma}^{a+}) \quad (2.4.12)$$

$$H_3 = \frac{1}{N} \left(\frac{\hbar}{2} \right)^2 \left[\frac{C_{0000}}{(w_0^0)^2} (b_0^0 + b_0^{0+}) (b_0^0 + b_0^{0+}) (b_0^0 + b_0^{0+}) (b_0^0 + b_0^{0+}) \right. \\ \left. + \frac{C_{\sigma 00}}{w_0^0 w_{\sigma}^0} (b_0^0 + b_0^{0+}) (b_0^0 + b_0^{0+}) (b_{\sigma}^0 + b_{-\sigma}^0) (b_{-\sigma}^0 + b_{\sigma}^0) \right] \quad (2.4.13)$$

The external field E_{ext} has not been introduced so far in our Hamiltonian. We are for the moment interested in the lattice dynamical problem without the influence of such a field. For the present our primary interest is to see the effect of interaction between acoustic modes and the long wavelength optical modes. The third order anharmonic terms (cf. Equation 2.4.11) can be eliminated, to a large extent, by using the following canonical transformation

$$H_{Tr} = e^{-iS} H_r e^{iS} = H_r + i[H_r, S] + \frac{i^2}{2} [H_r, [H_r, S]],$$

where

$$S = \frac{i}{\sqrt{N}} W_0^a G (b_0^{a+} - b_0^a) (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o), \quad (2.4.14)$$

The relevant commutation relations are

$$[H_0, S] = 0, \quad [H_a, S], S = -\frac{2}{N} W_0^{a^3} \hbar G^2 (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o)$$

$$[H_a, S] = \frac{i\hbar}{\sqrt{N}} (b_0^a + b_0^{a+}) (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o) W_0^{a^2} G$$

$$[H_1, S] = \frac{1}{N} \left(\frac{\hbar}{2}\right)^{3/2} \frac{W_0^{a^3/2}}{W_0^o} B_{00} G (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o) (b_0^{o+} + b_0^o) \quad (2.4.15)$$

The commutator $[H_0^o, S]$ is non-diagonal. The commutators of S with $[H_a, S]$, $[H_0^o, S]$ and fourth order anharmonic terms give

terms of the order $\frac{1}{N\sqrt{N}}$. These can be safely neglected. We derive the value of G from the consideration,

$$H_1 + i [H_a, S] = 0, \quad (2.4.16)$$

which gives

$$G = B_{00} \sqrt{\frac{\hbar}{2}} \frac{1}{2W_0^0 W_a^{5/2}}, \quad (2.4.17)$$

where $B_{00} = B_{00,a}$.

It may be noted that the canonical transformation used here is different from that of Silverman. In his expression, the coefficient similar to G contains a factor $\frac{1}{(W_a)^2 - (W^0)^2}$. Making use of (2.4.15) and (2.4.17) the transformed Hamiltonian reduces to

$$\begin{aligned} H_T = & \sum_{\sigma} \hbar W_{\sigma}^a (b_{\sigma}^{a+} b_{\sigma}^{a+\frac{1}{2}}) + \sum_{\sigma \neq 0} \hbar W_{\sigma}^0 (b_{\sigma}^{0+} b_{\sigma}^{0+\frac{1}{2}}) + \hbar W_0^0 (b_0^{0+} b_0^{0+\frac{1}{2}}) \\ & - \frac{1}{2N} \left(\frac{\hbar}{2}\right)^2 \frac{B_{00}^2}{W_0^0{}^2 W_a} (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) \\ & + \frac{1}{N} \left(\frac{\hbar}{2}\right)^2 \sum_{\sigma} \frac{G_{\sigma a, 0}}{W_0^0 W_a} (b_0^0 + b_0^0) (b_0^{0+} + b_0^0) (b_{\sigma}^{a+} + b_{\sigma}^{a+}) (b_{-\sigma}^a + b_{-\sigma}^{a+}) \\ & + \frac{1}{2N} \left(\frac{\hbar}{2}\right)^2 \sum_{\sigma} \frac{G_{\sigma 0, 0}}{W_0^0 W_{\sigma}^0} (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_{\sigma}^{0+} + b_{-\sigma}^0) (b_{-\sigma}^0 + b_{\sigma}^{0+}) \\ & + \frac{1}{2N} \left(\frac{\hbar}{2}\right)^2 \frac{G_{0, 0}}{(W_0^0)^2} (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) (b_0^{0+} + b_0^0) \quad (2.4.18) \end{aligned}$$

The terms involving B_{00}^2 and C_{00} do not involve any summation and are of order \hbar^2/N . Their signs are opposite and since C_{00} is expected to be positive they will largely cancel each other.

We shall thus consider the effect of the acoustic and optical modes with ($\sigma_0 \neq 0$) on the long wavelength polar mode W_0^0 by taking thermal averages as explained below. We write the diagonal part of the Hamiltonian explicitly

$$H_{T_0} = \sum \hbar w_{\sigma}^a (b_{\sigma}^{a+} b_{\sigma}^a + \frac{1}{2}) + \sum_{\sigma \neq 0} \hbar w_{\sigma}^o (b_{\sigma}^{o+} b_{\sigma}^o + \frac{1}{2}) + \frac{1}{2} \left[P_0^2 + \left(W_0^2 + \frac{2}{N} \left\{ \sum_{\sigma} C_{\sigma a, 0} \langle Q_{\sigma}^2 \rangle + \sum_{\sigma_0 \neq 0} C_{\sigma_0, 0} \langle Q_{\sigma_0, 0}^2 \rangle \right\} Q_0^2 \right) \right] \quad (2.4.19)$$

where we have introduced the variable P_0^0 and Q_0^0 etc. for convenience. We shall, however, restrict ^{our attention to} the coupling with the acoustical mode whose thermal average is given by $\langle Q_{\sigma}^2 \rangle = k_B T / W_{\sigma}^2$. Thus the effective frequency is,

$$W_{\text{eff}}^2 = \left(W_u^2 - \frac{A^2 E \cdot u}{J_{gu}} + Z a_{1,1+h} + \frac{1}{N} \sum C_{\sigma_0, 0} \frac{k_B T}{W_{\sigma}^2} \right), \quad (2.4.20)$$

where $J_{gu} = \frac{1}{2} (E_u - E_g)$ and W_u is the frequency of the optical mode of one unit (i.e. (2.2.2)). Z is the number of nearest units coupled to unit at $\underline{1}$. The term may have its origin in the electrostatic interaction between dipoles.

For a long range interaction it may have the form $-\frac{1}{2}ne^2L$ where L is the local Lorentz field parameter for $\sigma = 0$. For a cubic system, $L = 4\pi/3$ for transverse mode and $L = -8\pi/3$ for longitudinal mode. This will give a negative contribution for the transverse mode.

Our expression (2.4.20) differs from a corresponding relation of Silverman⁵¹ in many ways.⁴ First W_u^2 is positive. The instability arises because of the terms $-A_{gu}^2/|J_{gu}|$ owing to vibronic interaction. This type of terms are discussed for the first time here. The dipole-dipole interaction may also give negative contribution. In the event W_u^2 is outweighed by these negative terms, the stabilization comes from $\frac{1}{N} \sum C_{a,0} \frac{k_B T}{(W_a^0)^2}$. The expression (2.4.20) also gives the same temperature dependence as obtained by Silverman⁵⁷ although the factors are different;

$$W_{\text{eff}}^2 \propto (T - T_c)$$

2.5 DISPERSION OF THE SOFT MODE

In this section, we study the wave vector dependence of the soft optical mode. This is carried out following a simplified picture. We have seen that only fourth order anharmonic terms are significant. Thus we consider the two modes, the soft optical and the acoustic modes and their interactions. The Hamiltonian is

$$H = \frac{1}{2} \sum_a (P_{\underline{a}}^2 + W_{\underline{a}}^2 Q_{\underline{a}}^2) + \frac{1}{2} \sum_{\underline{\sigma}_0} (P_{\underline{\sigma}_0}^2 + W_{\underline{\sigma}_0}^2 Q_{\underline{\sigma}_0}^2) + \frac{1}{N} \sum_{\underline{\sigma}_0, \underline{\sigma}_a} C_{\underline{\sigma}_0, \underline{\sigma}_a} Q_{\underline{\sigma}_0} Q_{\underline{\sigma}_a} \quad (2.5.1)$$

which can be written as

$$H = \frac{1}{2} \sum_{\underline{a}} (P_{\underline{a}}^2 + W_{\underline{a}}^2 Q_{\underline{a}}^2) + \frac{1}{2} \sum_{\underline{\sigma}_0} (P_{\underline{\sigma}_0}^2 + W_{\text{eff}}^2(\underline{\sigma}_0) Q_{\underline{\sigma}_0}^2), \quad (2.5.2)$$

where now

$$W_{\text{eff}}^2(\underline{\sigma}_0) = \left(W_u^2 - \frac{A_{\underline{g}, u}^2}{|J_{\underline{g}u}|} + D_h(\underline{\sigma}) + \frac{2}{N} \sum_{\underline{\sigma}_a} C_{\underline{\sigma}_0, \underline{\sigma}_a} \langle Q_{\underline{\sigma}_a}^2 \rangle \right). \quad (2.5.3)$$

If we confine our attention to the interaction between the nearest neighbours only, then after taking the thermal average

$\langle Q_{\underline{\sigma}_a}^2 \rangle$, we get

$$W_{\text{eff}}^2(\underline{\sigma}_0) = W_u^2 - \frac{A_{\underline{g}, u}^2}{|J_{\underline{g}u}|} + 2D \sum_{\underline{\sigma}_0} (\cos(\underline{\sigma}_0^x R) + \cos(\underline{\sigma}_0^y R) + \cos(\underline{\sigma}_0^z R)) + \frac{2}{N} \sum_{\underline{\sigma}_a, \underline{\sigma}_0} C_{\underline{\sigma}_a, \underline{\sigma}_0} \frac{k_B T}{(W_{\underline{\sigma}_a}^2)^2}, \quad (2.5.4)$$

where R is the distance between two octahedra and D denotes the coefficient for the dipole-dipole interaction. For transverse oscillation it will be negative. The summation

over $\sigma_{0,a}$ in the last term of (2.5.4) is rather complicated for a general three dimensional case. We shall therefore write this result for a one dimensional chain of elementary octahedra.

Now $W_a^2 = 4 \alpha \text{Sin}^2 (\sigma_a a)$ with α as the force constant $R = 2a$, a being the distance between a metal ion and a ligand ion. Further, we get

$$\begin{aligned} \frac{2}{N} \sum_{\sigma_0, \sigma_a} C_{\sigma_0, \sigma_a} \frac{k_B T}{W_{\sigma_a}^2} &= \frac{4C}{N} \sum_{\sigma_0} \left[\sum_{\sigma_a} \text{Sin}^2 (\sigma_a a) \frac{k_B T}{\alpha \text{Sin}^2 (\sigma_a a)} \right] \times \\ &\quad \cos^2 (\sigma_0 a) \\ &= 4C \sum_{\sigma_0} \frac{k_B T}{\alpha} \cos^2 (\sigma_0 a) \end{aligned} \quad (2.5.5)$$

Finally, putting $2 D = -|\gamma|$ the one dimensional model gives

$$\begin{aligned} W_{\text{eff}}^2 &= \left[\sum_u W_u^2 - \frac{A^2}{J g u} - \gamma \sum_0 \cos^2 (\sigma_0 a) \right. \\ &\quad \left. + \sum \beta T \cos^2 (\sigma_0 a) \right] \end{aligned} \quad (2.5.6)$$

where $\beta = 4 C k_B / \alpha$

The temperature dependence of the frequency can now be written for $\sigma_0 = 0$ as

$$\begin{aligned}
 W_{\text{eff}}^2 (0) &= \beta (T - T_c) \\
 \text{where} & \\
 T_c &= \left(\frac{A_{g,u}^2}{|J_{g,u}|} + |r| - W_u^2 \right) / \beta
 \end{aligned}
 \tag{2.5.7}$$

The variation of W_{eff}^2 on σ_0 at any particular temperature is given by (2.5.6). This is given in Fig.1, for arbitrary values of the parameters involved. We get the same sort of dependence as obtained by Silverman although our functions are different from his. As in his case, the agreement with the results of Cowley⁴⁵ is reasonably good.

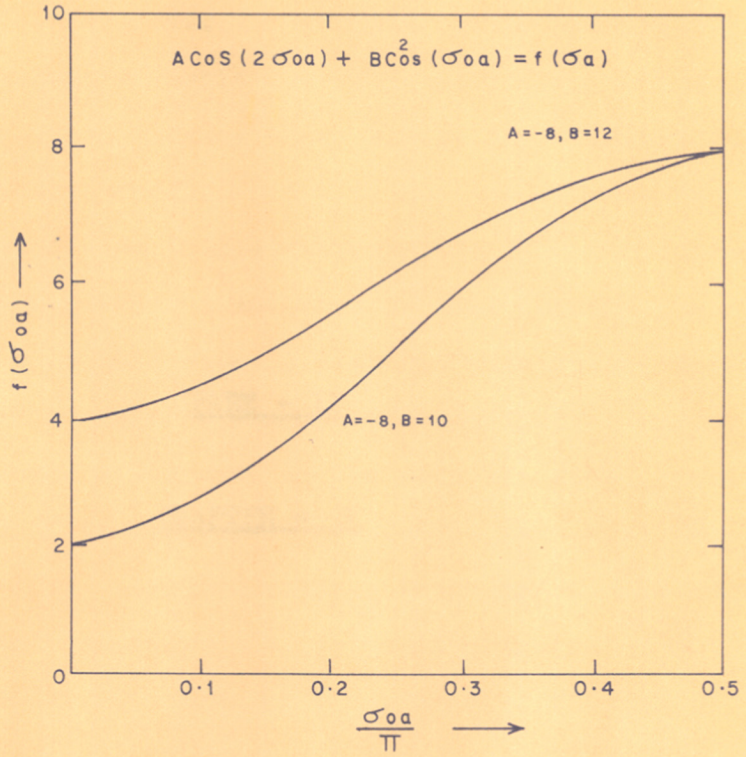


FIG.1. WAVE-VECTOR AND TEMPERATURE DEPENDENCE OF THE SOFT OPTICAL MODE WHERE $A = |\gamma|$ AND $B = \beta T$ (cf. EQUATION (2.54))

PART - II.

CHAPTER - 3.

Certain magnetically coupled crystalline solids carry permanent magnetic moment. There is growing interest in such systems, because these are of considerable importance owing to their physical properties. The ordered magnetic behaviour emanates from electrodynamic^{88,89} considerations tied up with quantum statistics of like quantum particles (electrons in this case). Various theoretical models deal with different aspects of magnetic behaviour. In spite of our considerable progress in the understanding of the importance of exchange and correlation phenomena in magnetically ordered systems (spin-systems), there is need to explore a few unsolved aspects, namely, the interaction of longitudinal optical phonon with magnons via exchange effects.

The basic concept of the quantum mechanical direct exchange interaction between two non-singlet like atoms was proposed by Heisenberg⁹⁰ in 1928. This theory springs from the Heitler-London's celebrated theory of chemical bond and it explains the ferromagnetism very well. This formed the basis of subsequent theoretical studies on ferri-, ferro- and antiferromagnetism. This model supposes a certain number of unpaired electrons present in paramagnetic atoms of the crystal. The electron spins are assumed to be localized at each lattice site. This theory clearly brings out how the ordinary Coulomb interaction among electrons leads to strong coupling between the electron spins showing exchange effect if proper

cognizance of the exclusion principle is taken. However, this theory contains two serious defects. Firstly, the simple Heitler-London description has been utilized in the formulation of the theory which does not manifest the periodicity of the lattice. Secondly, he arbitrarily assumed a Gaussian distribution of states of a given magnetic moment.

There are two approaches for the study of exchange mechanism. There are 1) determinantal method due to Slater⁹¹ and 2) spin operator method due to Dirac.^{92,93} Following Dirac, the spin dependent energy for interacting electron is given as,⁹⁴⁻⁹⁶

$$H_{ex} = \sum_{i,j} J_{ij} \underline{S}_i \cdot \underline{S}_j \quad ; \quad (3.1)$$

where \underline{S}_i stands for the spin operator for the electron in i^{th} orbital. Further, let ψ_a and ψ_b be the localized atom c orbitals satisfying the following equations :

$$\left. \begin{aligned} \left(\frac{P_i^2}{2m} - \frac{Ze^2}{Y_{ia}} \right) \psi_a(i) &= E_a \psi_a(i) \\ \left(\frac{P_j^2}{2m} - \frac{Ze^2}{Y_{jb}} \right) \psi_b(j) &= E_b \psi_b(j) \end{aligned} \right\} \quad (3.2)$$

where $\frac{P_i^2}{2m}$ or $\frac{P_j^2}{2m}$ and $-\frac{Ze^2}{Y_{ia}}$ or $-\frac{Ze^2}{Y_{jb}}$ stand for the kinetic energy and potential energy operators for the

electrons i or j and m and Ze refer to mass of the electron and charge of the ion-core respectively. Also r_{ia} , r_{jb} denote the ~~of~~ distance of the i^{th} or j^{th} electron from the ions a or b , while E_a and E_b represent the energy associated with them. In terms of these functions, the exchange integral takes the following form

$$J_{ij} = \left\langle ab \left| \frac{e^2}{r_{ij}} \right| ba \right\rangle - 2 S_{ab} \left\langle a \left| V \right| b \right\rangle \quad (3.3)$$

$$V = - \frac{Ze^2}{r_{ia}} - \frac{Ze^2}{r_{jb}}$$

with

and

$$S_{ab} = \langle a | b \rangle \equiv \int \psi_a^* \psi_b \, d\tau$$

In the case of orthogonal orbitals, the overlap integral i.e. S_{ab} vanishes and the exchange integral consists of only one term which is always positive, being the self energy of the overlap charge $e \psi_a^*(i) \psi_b(i)$. This stabilises the ferromagnetic state (the triplet state). On the other-hand, in case of non-orthogonal orbitals, the sign of J_{ij} is governed by the relative magnitude and if the second term dominates, it gives rise to antiferromagnetic coupling (stability of the singlet state). Such states exist in most of the insulators and they have total magnetic moment zero due to the anti-parallel spin alignment.

Another noteworthy contribution to the magnetic ordering, namely, the concept of ferrimagnetism was proposed

by Néel in 1948. According to him, ferrimagnets, like antiferromagnets, have sub-lattice with anti-parallel spins except that they have nonvanishing resultant magnetic moment which may be attributed to one or more of the following causes: i) unequal spins, ii) unequal g factors, iii) unequal number of atoms in the different sublattices. These substances occur in various forms and constitute an important class of magnetic materials. The present study is confined to antiferro- and ferrimagnetic insulators. Among the notable ferrimagnets, the systems $A(B_2)O_4$ ^{97,98} in which A is a divalent metal ion such as Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} , etc and B is a trivalent metal ion (i.e. Fe^{3+} , Cr^{3+}) constitutes an important class. These compounds exist in spinel structure with A and B ions surrounded by four or six oxygens in tetrahedral or octahedral positions respectively. Further the unit cell which contains eight formula unit, has cubic symmetry $(Fd\bar{3}m-O_h^7)$ ⁹⁹. In the case of inverse spinel, the A site ions and half of the B site ions exchange positions and the resulting structure is represented by $B(AB)O_4$. On the otherhand, we shall also be interested in the rutile type antiferromagnets. The general formula for such system is AB_2 where A stands for the magnetic ion (cation) and B for anion. In such system magnetic ions form a body centred tetragonal lattice. Specific examples are MnF_2 , FeF_2 , CoF_2 etc.

These magnetic systems are endowed with a definite spin ordering in the ground state at the absolute zero of temperature. With a slight increase in the temperature, spin systems are

excited, ~~over the ground state~~. These low lying spin excitations govern many physical properties of the magnetic systems. The quantized unit of spin-excitation is termed as magnon.

Magnons:

A realistic approach to the spin wave was formulated by Bloch¹⁰⁰ in 1932. He formulated the spin wave as a sinusoidal disturbance in an ordered spin system with a single spin reversal. On account of the exchange interaction the spin-excitation is not localized and its consequent motion is termed as spin wave. He showed that ferromagnets have this character. However, he neglected the interaction between the spin waves.

A alternative formulation of the spin wave was proposed by Holstein and Primakoff.¹⁰¹ They ~~essentially~~ rederived Bloch's result and spin wave interaction was also included in their treatment. This formulation of spin wave has received a wide attention because it represents a simple picture of spin wave. However, it has been criticized for its poor convergence and more rigorous treatments have followed this, namely, those due to Dyson,¹⁰² Mori¹⁰³ and Oguchi.¹⁰⁴ The Holstein and Primakoff (HP) treatment of magnons involves a series of transformations on the spin-Hamiltonian to recast it into a harmonic oscillator-Hamiltonian which, at once, provides the dispersion relation for magnons. Also the magnetization were expressed ^{as} ~~in~~ the expansion of the creation

and annihilation operators of magnons. And an expansion of the Hamiltonian in terms of these operators was formulated. The quadratic term in these operators of the Hamiltonian gave the diagonal part while those involving three or more operators exhibit transition between magnon states.

Let us consider a body centered cubic ferromagnet having for its l^{th} site, \underline{S}_l the spin operator and S the magnitude of the spin. Now, it is convenient to consider the following combination of the components of the spin operators:

$$\left. \begin{aligned} S_l^+ &= S_l^x + iS_l^y \\ S_l^z &= S - n_l \end{aligned} \right\} \quad (3.4)$$

The eigenstate of the operators n_l and S_l^z is given by

$$\psi_{n_1} \dots n_1 \dots n_N = \psi_{n_1} \quad (3.5)$$

with corresponding eigenvalues n_l and m_l respectively. The latter possess the values $S, S-1, \dots, -S$ while former takes only the integral values $0, 1 \dots 2S$, which is the measure of the difference between the Z component of the spin at the l^{th} site and its maximum value. This is termed as the spin deviation. The operators defined above are endowed with the following properties;

$$\begin{aligned}
 S_1^+ \psi_{n_1} &= \sqrt{2S} \left(1 - \frac{n_1-1}{2S} \right)^{\frac{1}{2}} (n_1)^{\frac{1}{2}} \psi_{n_1-1} \\
 S_1^- \psi_{n_1} &= \sqrt{2S} \sqrt{n_1+1} \left(1 - \frac{n_1}{2S} \right)^{\frac{1}{2}} \psi_{n_1+1} \\
 \hat{n}_1 \psi_{n_1} &= n_1 \psi_{n_1},
 \end{aligned}
 \tag{3.6}$$

with the commutation relations

$$\begin{aligned}
 [S_1^z, S_m^\pm] &= \pm S^\pm \delta_{lm} \\
 [S_1^\pm, S_m^\mp] &= 2S^z \delta_{lm}
 \end{aligned}
 \tag{3.7}$$

where δ_{lm} is the Kronecker δ -function.

Generally the study involving spin wave interactions are neatly described in terms of second quantization formulation or the number operator formalism. Thus we visualize the quasi-particles associated with the spin waves denoted by a^+ and a which represent the creation and annihilation operators for such quasi-particles. These operators are given by

$$\begin{aligned}
 a_1^+ \psi_{n_1} &= (n_1 + 1)^{\frac{1}{2}} \psi_{n_1+1} \\
 a_1 \psi_{n_1} &= (n_1)^{\frac{1}{2}} \psi_{n_1-1}
 \end{aligned}
 \tag{3.8}$$

With the aid of (3.6) and (3.8) we get

$$\left. \begin{aligned}
 S_1^+ &= (2S)^{\frac{1}{2}} \left(1 - \frac{a_1^+ a_1}{2S} \right)^{\frac{1}{2}} a_1 \\
 S_1^- &= (2S)^{\frac{1}{2}} \frac{a_1^+}{a_1} \left(1 - \frac{a_1^+ a_1}{2S} \right)^{\frac{1}{2}} \\
 \hat{n}_1 &= a_1^+ a_1 = S - S_1^Z
 \end{aligned} \right\} (3.9)$$

Use of (3.7) yields the commutation relations

$$[a_l, a_m^+] = \delta_{lm} \quad (3.10)$$

The exchange Hamiltonian for a ferromagnet given by (3.1) takes the form in terms of these operators as

$$\begin{aligned}
 H_{ex} = C + \sum_{l,j} J_{lj} S (a_l^+ a_l + a_j^+ a_j - a_l a_j^+ - a_l^+ a_j) \\
 + \text{higher order terms, with } a_l^+ a_l < 2S
 \end{aligned} \quad (3.11)$$

Owing to strong exchange forces the spin deviation will not be localized at a particular site R_l , but will have wave like motion. It was shown by Bloch and Dyson that in the case of only one spin wave, this turns out to be an exact eigenstate of the Hamiltonian. However, in case there are more than one spin wave in the lattice, their interactions make the Hamiltonian non-diagonal. Consequently, the Hamiltonian consists of two parts, one quadratic in quasi-particle operators and the other contains higher order terms.

Let us introduce the fourier transforms to the reciprocal space defined by

$$\left. \begin{aligned} a_i &= \frac{1}{\sqrt{N}} \sum_{\underline{k}} e^{i\underline{k} \cdot \underline{R}_i} a_{\underline{k}} \\ a_i^+ &= \frac{1}{\sqrt{N}} \sum_{\underline{k}} e^{-i\underline{k} \cdot \underline{R}_i} a_{\underline{k}}^+ \end{aligned} \right\} \quad (3.12)$$

where N is the number of sites in the crystal and \underline{k} , the wave-vector of the quasi-particle called magnon. The use of periodic boundary condition implies

$$\sum_{\underline{k}} e^{i\underline{k} \cdot \underline{R}_i} = N \Delta(\underline{k}) \quad (3.13)$$

where

$$\begin{aligned} \Delta(\underline{k}) &= 0 \quad \text{for } \underline{k} \neq 0 \\ &= 1 \quad \text{for } \underline{k} = 0 \end{aligned}$$

The inverse transformations are given by

$$\left. \begin{aligned} a_{\underline{k}} &= \frac{1}{\sqrt{N}} \sum_i e^{-i\underline{k} \cdot \underline{R}_i} a_i \\ a_{\underline{k}}^+ &= \frac{1}{\sqrt{N}} \sum_i e^{i\underline{k} \cdot \underline{R}_i} a_i^+ \end{aligned} \right\} \quad (3.14)$$

The operators $a_{\underline{k}}$ and $a_{\underline{k}}^+$ satisfy the commutation relation

$$[a_{\underline{k}}, a_{\underline{k}'}^+] = \delta_{\underline{k}\underline{k}'} \quad (3.15)$$

other commutators being zero. This explains that magnons are bosons. In terms of these operators, the diagonal part of the Hamiltonian is given by

$$H_D = \sum \hbar \omega_{\underline{k}} \left(a_{\underline{k}}^+ a_{\underline{k}} + \frac{1}{2} \right) \quad (3.16)$$

where $\hbar \omega_{\underline{k}}$ represents the energy of the magnon with wave vector \underline{k} and takes different expression for different systems. For a cubic ferromagnet^{105,106} it has the form

$$\hbar \omega_{\underline{k}} = 2JSZ \left(1 - \gamma_{\underline{k}} \right) \quad ; \quad \gamma_{\underline{k}} = \frac{1}{Z} \sum_{\underline{R}_n} e^{i\underline{k} \cdot \underline{R}_n} \quad (3.17)$$

where \underline{R}_n is the nearest neighbour vector.

Also for antiferromagnet¹⁰⁷ or ferrimagnet^{108,109} it has the form (in the long wavelength approximation)

$$\hbar \omega_{\underline{k}} = 2JSka \left(2Z \right)^{\frac{1}{2}} \quad (\text{antiferromagnet}) \quad (3.18)$$

and

$$\hbar \omega_{\underline{k}}^{\alpha} = k_B \Theta_C \quad k^2 \quad a^2 \quad (3.19a)$$

and

$$\hbar \omega_{\underline{k}}^{\beta} = 2J_{AB} \left| S_A - S_B \right| Z + k_B \Theta_C k^2 \quad a^2 \quad (3.19b)$$

where

$$k_B \Theta_C = \frac{4J_{AB} S_A S_B}{\left| S_A - S_B \right|}$$

for the ferrimagnetic magnon modes.

In these expressions J is a measure of exchange interaction. Z denotes ^{no of} nearest neighbours. S, S_A, S_B measure spin quantum numbers. In analogy with lattice system, the upper frequency branch i.e. (3.19b) is called optical magnon mode.

PART - II

CHAPTER - 4

A large number of crystals is known to possess long range ordering of spin-configuration. These may be ferri-, ferro- or antiferromagnetically coupled. Also certain crystals sustain the long-range ordering of the electric dipole moment configuration of the elementary cell. These may be ferro- or antiferroelectric. Further, the possibility of the coexistence¹¹⁰⁻¹¹⁵ of magnetic and electrical ordering in crystals seem plausible while retaining the separate existence of magnetic and dielectric ordering. It is well known that magnetic ordering is determined by the exchange interaction, while electric ordering owes to classical electrostatic interaction of dipoles of the elementary units. These interactions cause the displacement of ions as a whole as well as the displacements of external (valence) electrons relative to nuclei.

In such systems the paramagnetic cations, which contain localized magnetic electrons are distributed in special crystallographic positions in the matrix of diamagnetic anions, which in turn are located on special lattice points. At absolute zero of temperature these atoms lie at their equilibrium positions coupled by elastic forces. In addition to this arrangement, the magnetic ions are ordered in a particular fashion owing to direct⁹⁰, indirect^{116,117} or super-exchange forces.¹¹⁶⁻¹²²

Obviously, at a finite temperature collective modes such as lattice waves and spin waves exist in these systems.

The corresponding quasi-particles or elementary excitations are known as phonons (both acoustic and optical) and magnons (also acoustic and optical). Thus in this low temperature region, we can speak of a magnetic crystal⁸⁹ harbouring a cloud of phonons and magnons. In the harmonic approximation, both of these particles are non-interacting. However, there are processes which do indeed bring about phonon-phonon, magnon-magnon and phonon-magnon interactions.

When the crystal is not subjected to any external perturbation the totality of quasi particles find themselves in a state of equilibrium distribution which can be characterized by one temperature. It is possible to disturb this situation either by exciting the spin system or the lattice system. In the event, phonon-phonon and magnon-magnon interactions are faster than phonon-magnon interactions, the above external perturbation would lead to different equilibrium distributions of the phonons and magnon systems. One can then characterize them by two different temperatures namely, the lattice temperature T_l and the spin temperature T_s . If these temperatures differ then energy will flow from one system to another. To explain this phenomenon, an understanding of the various mechanisms of phonon-magnon interaction is essential. These interactions govern thermodynamic and transport properties of the magnetic crystals. Recently Sinha and Upadhyaya^{105,107} Joshi and Sinha,¹⁰⁹ in a series of papers, have formulated a microscopic

mechanism of phonon-magnon interactions in ferro-, ferri- and antiferromagnetic crystals. However, these studies were confined to interaction of magnons (acoustic or optical) with the acoustic phonons and the relaxation times and thermal conductivities of few systems were considered in detail in the low temperature region.¹²⁵

At somewhat higher temperatures, say above 10°K optical lattice modes will also be excited and owing to the ionic nature of the system one would expect a reasonably strong electron-optical phonon interactions. In the present study, a microscopic formulation of the mechanism of optical phonon-magnon interactions in antiferro- and ferri-magnetic ionic dielectric is proposed. Also a study of the relaxation times associated with the flow of energy from the spin systems to lattice or vice-versa is considered.

4.2 Formulation of Interaction Hamiltonian¹²⁶

Let us consider a magnetic crystal in which the paramagnetic cations are located on two otherwise equivalent sublattices which interpenetrate to form body-centered cubic lattice. Each paramagnetic cation, which carries a few localized unpaired electrons, is in turn surrounded by a given number of ligand ions (anions) in fixed geometrical configuration e.g. tetrahedral or octahedral or other arrangement as prescribed by the crystal structure of the system. Thus the nearest neighbours of each paramagnetic

ion is a diamagnetic ligand anion. However, the nearest paramagnetic ion lies on the other magnetic sublattice. The Hamiltonian for the total system is written as

$$H = H_L + H_e + H_{el} + H_{12} + H_z + H_{an} \quad (4.2.1)$$

where H_L is the lattice Hamiltonian and in the second quantization representation involving phonon creation ($b_{\underline{q}_s}^+$) and annihilation ($b_{\underline{q}_s}$) operators can be written as,

$$\begin{aligned} H_L &= \sum \hbar w_{\underline{q}_s} (b_{\underline{q}_s}^+ b_{\underline{q}_s} + \frac{1}{2}) \\ &= \sum \hbar w_{\underline{q}_a} (b_{\underline{q}_a}^+ b_{\underline{q}_a} + \frac{1}{2}) + \sum \hbar w_{\underline{q}_o} (b_{\underline{q}_o}^+ b_{\underline{q}_o} + \frac{1}{2}) \end{aligned} \quad (4.2.2)$$

where $w_{\underline{q}_s}$ is the mode branch frequency and \underline{q}_s the corresponding propagation vector. In equation (4.2.2) the acoustic and optical modes terms have been written separately; hence the suffixes a (for acoustic) and o (for optical). H_e is the one electron Hamiltonian inclusive of the kinetic energy and the potential energy operators for the situation when the atoms are in their undisplaced positions, namely,

$$H_e = \sum_i \frac{p_i^2}{2m} + \sum_{i,n} U(\underline{r}_i - \underline{R}_n^o) \dots \quad (4.2.3)$$

where \underline{R}_n^o denotes the lattice equilibrium position and \underline{r}_i is the coordinate of the i^{th} electron.

For the study of the behaviour of magnetic electrons which are localized at their respective ion cores, the unperturbed eigenfunctions ϕ_1 are the solutions of

$$\left[\frac{p^2}{2m} + U(\underline{r} - \underline{R}_1^0) + V^0 \right] \phi_{1\sigma} = E_1 \phi_{1\sigma} \quad (4.2.4)$$

where V^0 is the static crystal field of other atoms. H_{el} is the electron lattice Hamiltonian. In the present work, we are interested in the coupling with optical phonons only. Interaction processes involving acoustic phonons have been already considered by various workers.^{105,107,109}

Furthermore, the attention is confined to magnetic electrons-optical phonon interactions. For this purpose, the relevant electron-phonon coupling term involving longitudinal optical mode and an electron of atom at \underline{R}_1 can be written following Sinha and Sinha¹²³ as well as Krishnamurthy and Sinha.¹²⁴ These are electron lattice interaction potential due to crystal field oscillations and can be rewritten in a convenient form which involves the relative displacements $\delta \underline{R}_h$ between the ion n and any other l or m as follows

$$V = \sum_h \left(\frac{\partial U}{\partial \underline{R}_h} \right) \cdot \delta \underline{R}_h \quad (4.2.5)$$

where

$$\begin{aligned}
 R_n &= R_{1,m} - R_n \\
 &= \frac{-1}{\sqrt{N}} \sum_{q_0} \left(\frac{\hbar}{2m\omega_{q_0}} \right)^{\frac{1}{2}} \left(e^{i q_0 \cdot R_{1,m}} - e^{i q_0 \cdot R_n} \right) (b_{q_0}^+ - b_{-q_0}) \\
 &= \sum_{q_0} g_0 e^{i q_0 \cdot R_1} (b_{q_0}^+ - b_{-q_0}) \quad (4.2.6)
 \end{aligned}$$

with

$$g_0 = 1 \left(\frac{\hbar}{2M\omega_{q_0}} \right)^{\frac{1}{2}}$$

Further

$$\left(\frac{\partial U_{1,m}}{\partial R_n} \right) = \pm |qe^2| \left[\frac{1}{R_n^2} + \frac{2z}{R_n^3} + \frac{3}{2} \frac{(3z^2 - r^2)}{R_n^4} + \dots \right] \quad (4.2.7)$$

where R_n is the distance from metal ion at n to another ion in question. z, r stand for the coordinates of the electron at n . Also, the plus sign arises due to interaction with the cation and minus for the anion. Thus with the help of (4.2.6) and (4.2.7), (4.2.5) can be written as

$$\begin{aligned}
 V &= \sum \sum \pm |qe^2| g_0 e^{i q_0 \cdot R_1} \left[\frac{1}{R_n^2} + \frac{2z}{R_n^3} + \frac{3}{2} \frac{(3z^2 - r^2)}{R_n^4} + \dots \right] \\
 &\quad \times (b_{q_0}^+ - b_{-q_0}) \quad (4.2.8)
 \end{aligned}$$

Thus the electron optical phonon coupling form of present interest will have the form

$$H_{eL_0} = \sum_{q_0} g_0 f_h(x, y, z, R_h) e^{iq_0 \cdot R_1} (b_{q_0}^+ - b_{-q_0}) \quad (4.2.9)$$

with

$$f_h(x, yz, R_h) = \sum_{h=n} 2 \left[\frac{2z}{R_h^2} + \frac{3}{2} \left(\frac{3z^2 - r^2}{R_h^4} \right) + \dots \right] \quad (4.2.10)$$

where n stands for the nearest neighbour.

Following the earlier work on the acoustic phonons and magnon interaction the effect of H_{eL_0} is taken as perturbation on the one electron functions $\psi_{1\sigma}$. The perturbed one electron functions are then given by

$$\psi_{1\lambda} = \phi_{1\sigma} + \sum P_{\lambda 1} \phi_{\lambda\sigma} \quad (4.2.11)$$

where

$$P_{\lambda 1} = \frac{\langle \phi_{\lambda\sigma} | H_{eL_0} | \phi_{1\sigma} \rangle}{\Delta E_{1\lambda}} \quad (4.2.12)$$

and ϕ is the excited orbital connected by the perturbation H_{eL_0} and $\Delta E_{1\lambda}$ is the energy denominator. In equation (4.2.1) H_{12} is the two body Hamiltonian which is responsible for the exchange and Coulomb interaction effects. H_z and H_{an} are the Zeeman and anisotropy energies. In formulating the effective exchange interaction terms comprising

direct, indirect or transfer process, we make use of one electron orbitals of the type (4.2.11). These will give us exchange terms involving $\phi_{1\sigma}$, and other involving, in addition, one or two $\phi_{\lambda\sigma}$ and one or two phonon operators etc. Thus with this in mind the Hamiltonian (4.2.1) is rewritten as

$$H = H_L + H_m + H_{int} \quad (4.2.13)$$

where H_L is the lattice Hamiltonian given by (4.2.2) and

$$H_m = \text{Const} + 2 J_{AB} \sum_n \underline{S}_{1A} \cdot \underline{S}_{mB} - (H+H_A) g_A \mu_B \sum_l S_{1zA} - (H-H_B) g_B \mu_B \sum_l S_{mzB}, \quad (4.2.14)$$

where J_{AB} is the effective exchange integral between two neighbouring atoms at sublattice A and B respectively at absolute zero temperature. g_A, g_B, S_{1A}, S_{1B} are the spectroscopic splitting factors and spin quantum numbers at respective sites. μ_B is the Bohr magneton. For H_{int} , the attention is confined to one phonon process and it has the form

$$H_{int} = \sum_{l,m} \frac{4}{\sqrt{N}} g_0 \left(\sum_{\lambda} \frac{J_{m1}^{\lambda m} f_{\lambda 1}}{\Delta E_{\lambda 1}} \right) \sum_{q_0} e^{iq_0 \cdot R_l^0} (b_{q_0}^+ - b_{-q_0}) \underline{S}_{1A} \cdot \underline{S}_{mB} + \sum_{l,m} \frac{4}{\sqrt{N}} g_0 \left(\sum_{\lambda} \frac{J_{m1}^{\lambda m} f_{\lambda m}}{E_{\lambda m}} \right) \sum_{q_0} e^{iq_0 \cdot R_m^0} (b_{q_0}^+ - b_{-q_0}) \times \underline{S}_{1A} \cdot \underline{S}_{mB} \quad (4.2.15)$$

where $f_{\lambda\sigma}$ represent the matrix element of (4.2.10) connecting orbitals sets $\phi_{1\sigma}$ and $\phi_{2\sigma}$ with a similar definition for $f_{\lambda m}$. $J_{ml}^{\lambda m}$ etc., and the affecting exchange integral between atom l_A and m_B and involve one excited orbital e.g. $\phi_{\lambda\sigma}$. The various terms in the Hamiltonian discussed so far represent a general situation. For describing the antiferro-magnetic two sub-lattice system, it is assumed that $g_A = g_B$ and $S_{1A} = -S_{1B}$, when they are unequal, the case is for the ferrimagnets. For convenience in calculations, it is assumed that the matrix elements of the type $J_{ml}^{\lambda m} f_{\lambda l} / \Delta E_{1\lambda}$ are some parameters which are the same for all paramagnetic atoms. This is denoted by e_J . Thus the simplified form of interaction Hamiltonian can be written as

$$\frac{4}{\sqrt{N}} e_J g_0 \sum_{l,m} \sum_{q_0} (e^{q_0 \cdot R_l^0} + e^{q_0 \cdot R_m^0}) (b_{q_0}^+ - b_{-q_0}^-) S_{1A} \cdot S_{mB} \quad (4.2.16)$$

Let us now go over to the spin wave representations by making use of the following transformations

$$\left. \begin{aligned} S_{1A}^+ &= S_{1xA} + iS_{1yA} = \left(\frac{4S}{N}\right)^{\frac{1}{2}} \sum_{\underline{k}} e^{+i\underline{k} \cdot \underline{R}_1} a_{\underline{k}} \\ S_{1A}^- &= S_{1xA} - iS_{1yA} = \left(\frac{4S}{N}\right)^{\frac{1}{2}} \sum_{\underline{k}} e^{-i\underline{k} \cdot \underline{R}_1} a_{\underline{k}} \\ S_{1A}^z &= S_A - \frac{2}{N} \sum_{\underline{k}, \underline{k}'} e^{i(\underline{k} - \underline{k}') \cdot \underline{R}_1} a_{\underline{k}} a_{\underline{k}'} \end{aligned} \right\} \quad (4.2.17a)$$

$$\begin{aligned}
 S_{mB}^+ &= \left(\frac{4S}{N}\right)^{\frac{1}{2}} \sum_{\underline{k}} e^{-i\underline{k} \cdot \underline{R}_m} d_{\underline{k}}^+ \\
 S_{mB}^- &= \left(\frac{4S}{N}\right)^{\frac{1}{2}} \sum_{\underline{k}} e^{+i\underline{k} \cdot \underline{R}_m} d_{\underline{k}} \\
 S_{mB}^z &= S_B + \frac{2}{N} \sum_{\underline{k}, \underline{k}'} e^{-i(\underline{k}-\underline{k}') \cdot \underline{R}_m} d_{\underline{k}}^+ d_{\underline{k}'}
 \end{aligned}
 \tag{4.2.17b}$$

In terms of these operators, the various terms of the spin Hamiltonian (4.2.13) become

$$\begin{aligned}
 H_m &= 2 J_{AB} (S_A S_B)^{\frac{1}{2}} \sum_{\underline{k}} z \gamma_{\underline{k}} (a_{\underline{k}} d_{\underline{k}} + a_{\underline{k}}^{\dagger} d_{\underline{k}}^{\dagger}) \\
 &+ 2J_{AB} \sum_{\underline{k}} z (S_A d_{\underline{k}}^{\dagger} d_{\underline{k}} + S_B a_{\underline{k}}^{\dagger} a_{\underline{k}}) \\
 &+ (H+H_A) g_{A/B} \sum_{\underline{k}} a_{\underline{k}}^{\dagger} a_{\underline{k}} - (H-H_B) g_{B/B} \sum_{\underline{k}} d_{\underline{k}}^{\dagger} d_{\underline{k}}
 \end{aligned}
 \tag{4.2.18}$$

$$\text{where } \gamma_{\underline{k}} = \frac{1}{z} \sum_{\underline{h}} e^{+i\underline{k} \cdot \underline{R}_h}
 \tag{4.2.19}$$

$$\begin{aligned}
 \text{Hint} &= \frac{4S}{\sqrt{N}} g_0 e_J \sum_{\underline{k}} \sum_{\underline{q}_0} \left[(S_A d_{\underline{k}}^{\dagger} d_{\underline{k}-\underline{q}_0} + S_B a_{\underline{k}}^{\dagger} a_{\underline{k}+\underline{q}_0}) (1 + \gamma_{\underline{q}_0}) \right. \\
 &\left. + (S_A S_B)^{\frac{1}{2}} (\gamma_{\underline{k}+\underline{q}_0}) (a_{\underline{k}}^{\dagger} d_{\underline{k}+\underline{q}_0}^{\dagger} + a_{\underline{k}} d_{\underline{k}-\underline{q}_0}) \right]
 \end{aligned}
 \tag{4.2.20}$$

z being the number of nearest paramagnetic neighbours for a given magnetic ion and R_h^0 is corresponding distance. It is seen that H_m is not diagonal in terms of spin wave operators. In order to diagonalise this and to write the interaction

terms in the same representation we make use of the following canonical transformations

$$\begin{aligned}
 a_{\underline{k}} &= \alpha_{\underline{k}} \cosh h \theta_{\underline{k}} + \beta_{\underline{k}}^+ \sinh h \theta_{\underline{k}} \\
 a_{\underline{k}}^+ &= \alpha_{\underline{k}}^+ \cosh h \theta_{\underline{k}} + \beta_{\underline{k}} \sinh h \theta_{\underline{k}} \\
 d_{\underline{k}} &= \alpha_{\underline{k}}^+ \sinh h \theta_{\underline{k}} + \beta_{\underline{k}} \cosh h \theta_{\underline{k}} \\
 d_{\underline{k}}^+ &= \alpha_{\underline{k}} \sinh h \theta_{\underline{k}} + \beta_{\underline{k}}^+ \cosh h \theta_{\underline{k}}
 \end{aligned}
 \tag{4.2.21}$$

where $\alpha_{\underline{k}}^+$, $\alpha_{\underline{k}}$ and $\beta_{\underline{k}}^+$, and $\beta_{\underline{k}}$ now represent the creation and annihilation operators for the two types of quasi-particles corresponding to two magnon modes. In order that the non-diagonal terms in these operators vanish we must have

$$\tan h(2\theta_{\underline{k}}) = \frac{-4JAB(S_A S_B)^{\frac{1}{2}} z \gamma_{\underline{k}}}{2JAB z(S_A + S_B) + (H+H_A)g_{A/B} - (H-H_B)g_{B/B}}
 \tag{4.2.22}$$

$$\approx \frac{-2(S_A S_B)^{\frac{1}{2}} \gamma_{\underline{k}}}{(S_A + S_B)}
 \tag{4.2.23}$$

Now, let us write down the various terms of the Hamiltonian separately for the antiferro- and ferrimagnetics

Antiferromagnetic case: $(|S_A| = |S_B| = S)$

$$H(\text{antiferro}) = H_L + H_M(\text{af}) + H_{\text{int}}(\text{af})
 \tag{4.2.24}$$

where the spin Hamiltonian is now diagonal and takes the form

$$H_m^{(af)} = \sum_{\underline{k}} \hbar w_{\underline{k}}^+ (\alpha_{\underline{k}}^+ \alpha_{\underline{k}+\underline{g}}) + \sum_{\underline{k}} \hbar w_{\underline{k}}^- (\beta_{\underline{k}}^+ \beta_{\underline{k}+\underline{g}}) \quad (4.2.25)$$

where

$$w_{\underline{k}}^{\pm} = \left[(w_A + w_e)^2 - w_e^2 \gamma_{\underline{k}}^2 \right]^{\frac{1}{2}} \pm w_H \quad (4.2.26a)$$

$$w_H = \frac{g/\beta \hbar A}{\hbar}, \quad w_e = \frac{2zSJ}{\hbar}, \quad w_A = \frac{g/\beta \hbar A}{\hbar} \quad (4.2.26b)$$

$$\begin{aligned} H_{int}^{(af)} = & \sum_{\underline{k}, \underline{q}_0} \left[A_{\underline{k}\underline{q}_0}^{(af)} (\alpha_{\underline{k}}^+ \alpha_{\underline{k}-\underline{q}_0}^+ b_{\underline{q}_0}^+ - \alpha_{\underline{k}}^+ \alpha_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+) \right. \\ & + B_{\underline{k}\underline{q}_0}^{(af)} (\alpha_{\underline{k}} \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+ - \alpha_{\underline{k}}^+ \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+) \\ & \left. + C_{\underline{k}\underline{q}_0}^{(af)} (\beta_{\underline{k}} \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0} - \beta_{\underline{k}}^+ \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+) \right] \quad (4.2.27) \end{aligned}$$

where

$$A_{\underline{k}\underline{q}_0}^{(af)} = \frac{4SZ}{\sqrt{N}} e_J g_0 \left[(\gamma_{\underline{k}-\underline{q}_0} + \gamma_{\underline{k}}) \sinh(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) + (1 + \gamma_{\underline{q}_0}) \cosh(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) \right] \quad (4.2.28a)$$

$$B_{\underline{k}\underline{q}_0}^{(af)} = \frac{4SZ}{\sqrt{N}} e_J g_0 \left[(\gamma_{\underline{k}-\underline{q}_0} + \gamma_{\underline{k}}) \cosh(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) + (1 + \gamma_{\underline{q}_0}) \sinh(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) \right] \quad (4.2.28b)$$

$$C_{\underline{k}\underline{q}_0}^{(af)} = A_{\underline{k}\underline{q}_0}^{(af)} \quad (4.2.28c)$$

Ferrimagnetic case: $|S_A| \neq |S_B|$

$$H(\text{ferri}) = H_L + H_m(\text{ferri}) + H_{\text{int}}(\text{ferri}) \quad (4.2.29)$$

where, the spin Hamiltonian i.e. $H_m(\text{ferri})$ is diagonal and takes the form

$$H_m(\text{ferri}) = \sum_{\underline{k}} \hbar \omega_{\underline{k}}^{\alpha} (\alpha_{\underline{k}}^{\dagger} \alpha_{\underline{k}} + \frac{1}{2}) + \sum_{\underline{k}} \hbar \omega_{\underline{k}}^{\beta} (\beta_{\underline{k}}^{\dagger} \beta_{\underline{k}} + \frac{1}{2}) \quad (4.2.30)$$

Thus it is evident that the spin wave spectrum splits up into two branches with energies $\hbar \omega_{\underline{k}}^{\alpha, \beta}$ which are given after neglecting the external and anisotropy fields and a constant term by

$$E_{\underline{k}}^{\alpha} = \hbar \omega_{\underline{k}}^{\alpha} = \frac{4J_{AB} S_A S_B}{|S_A - S_B|} k^2 a^2 \quad (4.2.31a)$$

$$E_{\underline{k}}^{\beta} = \hbar \omega_{\underline{k}}^{\beta} = 2J_{AB} Z |S_A - S_B| + \frac{4J_{AB} S_A S_B}{|S_A - S_B|} k^2 a^2 \quad (4.2.31b)$$

where use has been made of the long wavelength approximation i.e. $\underline{k} \cdot \underline{a} \ll 1$, "a" being the lattice constant. Magnons belonging to the first branch $E_{\underline{k}}^{\alpha}$ are termed as 'Acoustic' magnons while those belonging to second branch $E_{\underline{k}}^{\beta}$ are 'optical' magnons and these have energy much higher than those of the acoustic magnons

$$\begin{aligned}
 H_{\text{int}}(\text{ferri}) = \sum_{\underline{k}, \underline{q}_0} \left[A_{\underline{k}\underline{q}_0}^{(f)} (\alpha_{\underline{k}} \alpha_{\underline{k}-\underline{q}_0}^+ b_{\underline{q}_0}^+ - \alpha_{\underline{k}}^+ \alpha_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}) \right. \\
 + B_{\underline{k}\underline{q}_0}^{(f)} (\alpha_{\underline{k}} \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+ - \alpha_{\underline{k}}^+ \beta_{\underline{k}-\underline{q}_0}^+ b_{\underline{q}_0}) \\
 \left. + C_{\underline{k}\underline{q}_0}^{(f)} (\beta_{\underline{k}} \beta_{\underline{k}-\underline{q}_0}^+ b_{\underline{q}_0} + \beta_{\underline{k}}^+ \beta_{\underline{k}-\underline{q}_0} b_{\underline{q}_0}^+) \right], \quad (4.2.32)
 \end{aligned}$$

where

$$\begin{aligned}
 A_{\underline{k}\underline{q}_0}^{(f)} = \frac{4Z}{\sqrt{N}} (e_J) g_0 \left[(\gamma_{\underline{k}-\underline{q}_0} + \gamma_{\underline{k}}) (S_A S_B)^{\frac{1}{2}} \text{Sin h}(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) \right. \\
 \left. + (1 + \gamma_{\underline{q}_0}) (S_B \text{cos h } \theta_{\underline{k}} \text{Cos h } \theta_{\underline{k}-\underline{q}_0} + S_A \text{Sin h } \theta_{\underline{k}} \text{Sin h } \theta_{\underline{k}-\underline{q}_0}) \right] \quad (4.2.33a)
 \end{aligned}$$

$$\begin{aligned}
 B_{\underline{k}\underline{q}_0}^{(f)} = \frac{4Z}{\sqrt{N}} (e_J) g_0 \left[(\gamma_{\underline{k}-\underline{q}_0} + \gamma_{\underline{k}}) (S_A S_B)^{\frac{1}{2}} \text{Cosh}(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) \right. \\
 \left. + (1 + \gamma_{\underline{q}_0}) (S_B \text{Cosh } \theta_{\underline{k}} \text{Sin } \theta_{\underline{k}-\underline{q}_0} + S_A \text{Sin h } \theta_{\underline{k}} \text{Cosh } \theta_{\underline{k}-\underline{q}_0}) \right] \quad (4.2.33b)
 \end{aligned}$$

$$\begin{aligned}
 C_{\underline{k}\underline{q}_0}^{(f)} = \frac{4Z}{\sqrt{N}} (e_J) g_0 \left[(\gamma_{\underline{k}-\underline{q}_0} + \gamma_{\underline{k}}) (S_A S_B)^{\frac{1}{2}} \text{Sin}(\theta_{\underline{k}-\underline{q}_0} + \theta_{\underline{k}}) \right. \\
 \left. + (1 + \gamma_{\underline{q}_0}) (S_A \text{Cosh } \theta_{\underline{k}} \text{Cos } \theta_{\underline{k}-\underline{q}_0} + S_B \text{Sin h } \theta_{\underline{k}} \text{Sin h } \theta_{\underline{k}-\underline{q}_0}) \right] \quad (4.2.33c)
 \end{aligned}$$

cf.

The operator forms for one phonon processes (equations (4.2.27) and (4.2.32)) are similar to those obtained earlier in the case of antiferro and ferrimagnetic crystals for magnon-acoustic phonon interactions (Upadhyaya and Sinha^{105,107} and Joshi and Sinha¹⁰⁹). The main difference arises in the form of coefficients, (cf. equation (4.2.27) and (4.2.32),) where

now we get plus signs in terms such $\alpha_{\underline{k}}^{\beta} (\gamma_{\underline{k}}' + \gamma_{\underline{k}}) \sinh(\theta_{\underline{k}}' + \theta_{\underline{k}})$ etc. This may give a different wave vector dependence for the interaction term. If we examine the operators form closely we shall see that certain terms which are unimportant for acoustic phonons, will be significant for optical phonons in view of their high energy. Thus processes such as $\alpha_{\underline{k}}^{\beta} \alpha_{\underline{k}-\underline{q}_0}^{\beta} b_{\underline{q}_0}^{\dagger}$ will be important in the case of optical phonons, whereas they are discarded for acoustic phonons in that these were not expected to conserve energy. However, the energy will be conserved for optical phonons in certain range. On the otherhand, interaction between acoustic magnons and optical phonons will be unimportant for the present case. For example, the process $\alpha_{\underline{k}}^{\beta} \alpha_{\underline{k}-\underline{q}_0}^{\beta} b_{\underline{q}_0}^{\dagger}$ involves scattering of an acoustic magnon with the emission of an optical phonon. Energetically, this process seems to be unlikely. Likewise, the third process would also be ruled out. Thus in the following, we shall consider the energy transfer effects between spin and lattice systems on the basis of the second process. The results for antiferromagnetic and ferrimagnetic crystals are given separately.

4.3 Phonon-Magnon Relaxation Time

The magnon-magnon and phonon-phonon relaxation processes are known to be much faster than phonon-magnon processes. One can therefore assume that left to its own device each system can attain equilibrium distribution in a short time. Let us start with a situation when the magnon system is at a slightly higher temperature ($T_m = T$) than the phonon (T_p). Energy will flow from the magnon to the phonon system, the optical phonons

receiving it through coupling terms formulated in the previous section. The excited phonons will come to the equilibrium by gaining energy from the spin system. According to time-dependent perturbation theory, the probability of transition from a state $|\phi_i\rangle$ with energy E_i to a state $|\phi_f\rangle$ with energy E_f is

$$W_{if} = \frac{2\pi}{\hbar} |(H_p)_{if}|^2 \delta(E_i - E_f)$$

where $(H_p)_{if}$ is the matrix element of the perturbing potential H_p between $|\phi_i\rangle$ and $|\phi_f\rangle$. Accordingly the transition probabilities for the above processes are given by

$$\begin{aligned} W(n_{\underline{k}}, n'_{\underline{k}-\underline{q}_0}, N_{\underline{q}_0} \rightarrow (n_{\underline{k}}-1)(n'_{\underline{k}-\underline{q}_0}-1)(N_{\underline{q}_0}+1)) \\ = \frac{2\pi}{\hbar} |B_{\underline{k}\underline{q}_0}^j|^2 (n_{\underline{k}})(n'_{\underline{k}-\underline{q}_0})(N_{\underline{q}_0}+1) \delta(E_{\underline{k}}+E'_{\underline{k}-\underline{q}_0} - \hbar\omega_{\underline{q}_0}) \end{aligned}$$

$$\begin{aligned} W(n_{\underline{k}}, n'_{\underline{k}-\underline{q}_0}, N_{\underline{q}_0} \rightarrow (n_{\underline{k}}+1)(n'_{\underline{k}-\underline{q}_0}+1)(N_{\underline{q}_0}-1)) \\ = \frac{2\pi}{\hbar} |B_{\underline{k}\underline{q}_0}^j|^2 (n_{\underline{k}}+1)(n'_{\underline{k}-\underline{q}_0}+1)(N_{\underline{q}_0}) \delta(E_{\underline{k}}+E'_{\underline{k}-\underline{q}_0} - \hbar\omega_{\underline{q}_0}) \end{aligned}$$

where $n_{\underline{k}}$, $n'_{\underline{k}}$, $N_{\underline{q}_0}$ respectively represent the occupation numbers of magnons associated with energies $\hbar\omega_{\underline{k}}^{(1)}$, $\hbar\omega_{\underline{k}}^{(2)}$ and optical phonon of energy $\hbar\omega_{\underline{q}_0}$. The δ -functions ensure the conservation of energy. Thus the gain in energy by the optical phonons is given by

$$\dot{Q}_{\alpha\beta} = \sum_{\underline{q}_0} \hbar\omega_{\underline{q}_0} (\dot{N}_{\underline{q}_0}) \quad (4.3.1)$$

The time rate of change of the distribution function is related to the transition probabilities of the various magnon-optical phonon processes. As explained in the last section, we shall consider only processes which are expected to conserve energy. Thus

$$\begin{aligned} \dot{Q} &= \dot{Q}_{\alpha\beta} = \sum_{\underline{k}, \underline{q}_0} \hbar \omega_{\underline{q}_0} \langle \dot{N}_{\underline{q}_0} \rangle_{\alpha\beta} \\ &= \frac{2\pi}{\hbar} \sum_{\underline{k}, \underline{q}_0} \hbar \omega_{\underline{q}_0} \sum_j |B_{\underline{k}\underline{q}_0}^{(j)}|^2 \left[(n_{\underline{k}}^{(1)})(n_{\underline{k}-\underline{q}_0}^{(2)})(N_{\underline{q}_0} + 1) \right. \\ &\quad \left. - (n_{\underline{k}}^{(1)} + 1)(n_{\underline{k}-\underline{q}_0}^{(2)} + 1)(N_{\underline{q}_0}) \right] \delta(E_{\underline{k}}^{(1)} + E_{\underline{k}-\underline{q}_0}^{(2)} - \hbar \omega_{\underline{q}_0}) \end{aligned}$$

where $n_{\underline{k}}^{(j)}$ represent the magnon occupation numbers. The above is a general expression applicable to both ferri or antiferromagnetic systems. The superscript (j) denotes either af or f according to the system under consideration. To proceed further it will be convenient to present the calculation for antiferro- and ferrimagnetic systems separately.

4.4 Antiferromagnetic case

Here the two magnon modes are degenerate in the absence of the Zeeman terms. For interaction with the optical phonons only those processes are important which involve the creation or destruction of two magnons one from each branch along with

the destruction or the creation of an optical phonon. Thus, we consider the middle term in the interaction term of equation (4.2.27). Now we substitute the appropriate Bose distribution function for magnons and phonons i.e.

$$\left. \begin{aligned} n_{\underline{k}}^{(j)} &= \left[\exp \left(\frac{E_{\underline{k}}^{(j)}}{k_B T} \right) - 1 \right]^{-1} \\ N_{\underline{q}_0} &= \left[\exp \left(\frac{\hbar \omega_{\underline{q}_0}}{k_B T} \right) - 1 \right]^{-1} \end{aligned} \right\} \quad (4.4.1)$$

Then, writing $\Delta T = T - T_p$ and expanding the terms in Taylor's series to first order in T , we get

$$\begin{aligned} \dot{Q}_{(af)} &= \frac{2\pi}{h} \frac{\Delta T}{T^2} \sum_{\underline{k}, \underline{q}_0} \frac{(\hbar \omega_{\underline{q}_0})^2}{k_B} \left| B_{\underline{k}, \underline{q}_0}^{(af)} \right|^2 e^{-\hbar \omega_{\underline{q}_0}/k_B T} \\ &\times \frac{1}{(e^{\hbar \omega_{\underline{q}_0}/k_B T} - 1)(e^{E_{\underline{k}}/k_B T} - 1)(e^{E_{\underline{k}-\underline{q}_0}/k_B T} - 1)} \delta(E_{\underline{k}} + E_{\underline{k}-\underline{q}_0} - \hbar \omega_{\underline{q}_0}) \end{aligned} \quad (4.4.2)$$

Now in the long wavelength approximation i.e. $k, \underline{q}_0 \ll \frac{1}{a}$, i.e. $\gamma_{\underline{k}} = 1 - \frac{k^2 a^2}{z}$, we get

$$\begin{aligned} B_{\underline{k}, \underline{q}_0}^{(af)}{}^2 &= \frac{8Z\hbar}{N\omega_{\underline{q}_0} M} (S e_J)^2 \left[\frac{\{k^2 + (\underline{k}-\underline{q}_0)^2\}^2 - 2q_0^2 \{k^2 + (\underline{k}-\underline{q}_0)^2 + q_0^4\}}{2k |\underline{k}-\underline{q}_0|} \right. \\ &\quad \left. + 2(q_0^2 - k^2 - (\underline{k}-\underline{q}_0)^2) \right] \end{aligned} \quad (4.4.3)$$

For the optical phonon we treat $\hbar\omega_{q_0} = k_B\theta_E$ a constant energy as is usually done. Then changing summation over \underline{k} and \underline{q}_0 to integration we get

$$\dot{Q}(af) = \frac{2\pi}{\hbar} \frac{AT}{T^2} \left[\frac{Na^3}{(2\pi)^3} \right]^2 \frac{k_B\theta_E^2 e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} \int \frac{|B_{\underline{k}q_0}^{af}|^2 d\gamma \delta(E_{\underline{k}} + E_{\underline{k}-q_0} - k_B\theta_E)}{(e^{E_{\underline{k}}/k_B T} - 1)(e^{E_{\underline{k}-q_0}/k_B T} - 1)} \quad (4.4.4)$$

where $d\gamma = d\underline{q}_0 d\underline{q}_0 \underline{k}^2 d\underline{k} \sin\theta_{\underline{k}} \sin\theta_{q_0} d\theta_{\underline{k}} d\theta_{q_0} d\phi_{\underline{k}} d\phi_{q_0}$. (4.4.5)

The dispersion relation for magnon in antiferromagnets has the form

$$E_{\underline{k}} = k_B\theta_C a k \quad (4.4.6)$$

The δ -function is expanded in the following manner to facilitate integration over the angle variable

$$\delta(E_{\underline{k}} + E_{\underline{k}-q_0} - k_B\theta_E) = \delta(k_B\theta_C a \underline{k} + k_B\theta_C a |\underline{k}-q_0| - k_B\theta_E) = \frac{1}{k_B\theta_C a} \delta(\underline{k} + |\underline{k}-q_0| - \lambda) \quad (4.4.7a)$$

where $\lambda = \frac{\theta_E}{a\theta_C}$ (4.4.7b)

(4.4.7a) simplifies to

$$\frac{1}{k_B a \theta_C} = \frac{1}{\sqrt{2kq_0}} \delta \left[\frac{k-\lambda}{\sqrt{2kq_0}} + \left(\frac{k^2+q_0^2 - \cos \theta_{kq_0}}{2kq_0} \right)^{\frac{1}{2}} \right] \quad (4.4.8)$$

Here we write

$$\cos \theta_{kq_0} = \cos \theta_k \cos \theta_{q_0} + \sin \theta_k \sin \theta_{q_0} \cos (\phi_k - \phi_{q_0})$$

and with $x = \cos(\phi_k - \phi_{q_0})$ the function becomes

$$\frac{1}{k_B a \theta_C} = \frac{1}{\sqrt{2kq_0} \sin \theta_k \sin \theta_{q_0}} \delta \left[(a-x)^{\frac{1}{2}} + d \right] \quad (4.4.9)$$

where $a = (k^2+q_0^2) / (2kq_0 \sin \theta_k \sin \theta_{q_0}) - (\cot \theta_k \cot \theta_{q_0})$

and $d = (k-\lambda) / \sqrt{2kq_0} \sin \theta_k \sin \theta_{q_0}$

The result after the integration over angular variable is

$$\dot{Q}(af) = D \iint \frac{\left| \frac{Baf}{kq_0} \right|^2 |k-q_0| k dk dq_0}{(e^{\frac{E_k}{k}} / k_B T - 1) (e^{\frac{E_{k-q_0}}{k-q_0}} / k_B T - 1)} \quad (4.4.10)$$

with

$$D = 8S^2 (e_J)^2 a^7 \cdot \frac{N}{(\pi)^3} \cdot \frac{\hbar}{Mk_B} \frac{4T}{T_C^2} \frac{\theta_E}{\theta_C} \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} \quad (4.4.11)$$

The limits are determined by δ -function. This gives

$$\left| \frac{k-q_0}{\lambda} \right| + \frac{k}{\lambda} = \lambda \quad (4.4.12a)$$

$$\text{or } q^2 - 2kq \cos\theta + 2k^2 - \lambda^2 = 0 \quad (4.4.12b)$$

Solving for q , we have

$$q = 2k \cos \theta \pm \sqrt{k^2 \cos^2 \theta + (\lambda^2 - 2k^2)} \quad (4.4.12c)$$

Only positive values of q are allowed. This implies

$$k^2 \cos^2 \theta + (\lambda^2 - 2k^2) > 0$$

$$\text{or } k^2 (\cos^2 \theta - 2) + \lambda^2 > 0$$

$$\text{or } -k^2 (1 + \sin^2 \theta) + \lambda^2 > 0$$

$$\text{or } k^2 < \frac{\lambda^2}{1 + \sin^2 \theta} \leq \frac{\lambda^2}{2} \quad (4.4.13)$$

Thus the limits of q_0 are $0 < q_0 < k$ and those of k are $0 < k < \lambda/\sqrt{2}$

Integration over q_0 yields

$$\dot{Q}(af) = D \int \frac{\left(-\frac{\lambda}{4} k^2 - 2 \lambda^3 k^3 + 4 \lambda^2 k^4 - 5 \lambda k^5 + \frac{25}{12} k^6 \right) dk}{\left(e^{E_k/k_B T} - 1 \right) \left(e^{E_{k-q_0}/k_B T} - 1 \right)}$$

(4.4.14)

Changing to the dimensional variables $\frac{E_k}{k_B T} = \eta$

we have

$$\dot{Q}(af) = \frac{D}{a^7 \theta_c^7} \int_0^{\Delta/T} \frac{(\theta_E^4 T^3 \eta^2 - 2\theta_E^3 T^4 \eta^3 + 4\theta_E^2 T^5 \eta^4 - 5\theta_E T^6 \eta^5 + \frac{25}{12} T^7 \eta^6) d\eta}{(e^\eta - 1)(e^{\xi - \eta} - 1)} \quad (4.4.15)$$

with $\xi = \frac{\theta_E}{T}$, $\frac{\Delta}{T} = \frac{1}{2} \frac{\theta_E}{T}$ and $D' = \frac{D}{(e^{\theta_E/T} - 1) a^7 \theta_c^7}$,

Integration yields

$$\begin{aligned} \dot{Q}(af) = D' & \left[\left(\frac{\theta_E}{\theta_c}\right)^4 \frac{T^3}{\theta_c^3} \cdot \frac{1}{4} \left\{ \frac{\Delta^2}{T^2} \log\left(\frac{e^{\Delta/T} - 1}{1 - e^{-\Delta/T - \xi}}\right) - \frac{2}{3} \frac{\Delta^3}{T^3} \right. \right. \\ & \left. \left. + 2 - 2e^{-\xi} - 2e^{-\Delta/T} \left(\frac{\Delta}{T} + 1\right) - 2e^{-\xi} e^{\Delta/T} \left(\frac{\Delta}{T} - 1\right) \right\} \right. \\ & - 2 \left(\frac{\theta_E}{\theta_c}\right)^3 \frac{T^4}{\theta_c^4} \left\{ \frac{\Delta^3}{T^3} \log\left(\frac{e^{\Delta/T} - 1}{1 - e^{-\Delta/T - \xi}}\right) - \frac{3}{4} \frac{\Delta^4}{T^4} \right. \\ & \left. - 3e^{-\Delta/T} \left(\frac{\Delta^2}{T^2} + \frac{2\Delta}{T} + 2\right) + 6 - 3e^{\Delta/T - \xi} \left(\frac{\Delta^2}{T^2} - \frac{2\Delta}{T} + 2\right) + 6e^{-\xi} \right\} \\ & + 4 \left(\frac{\theta_E}{\theta_c}\right)^2 \frac{T^5}{\theta_c^5} \left\{ \frac{\Delta^4}{T^4} \log\left(\frac{e^{\Delta/T} - 1}{1 - e^{-\Delta/T - \xi}}\right) - \frac{4}{5} \frac{\Delta^5}{T^5} \right. \\ & \left. - 4e^{-\Delta/T} \left(\frac{\Delta^3}{3T^3} + \frac{3\Delta^2}{T^2} + \frac{6\Delta}{T} + 6\right) + 24 \right. \\ & \left. - 4e^{-\Delta/T - \xi} \left(\frac{\Delta^3}{3T^3} - \frac{3\Delta^2}{T^2} + \frac{6\Delta}{T} - 6\right) - 24e^{-\xi} \right\} \end{aligned}$$

$$\begin{aligned}
 & - 5 \frac{\theta_E}{\theta_c} \frac{T^6}{\theta_c^6} \left\{ \frac{\Delta^5}{T^5} \log \left(\frac{e^{\Delta/T} - 1}{1 - e^{-\Delta/T}} \right) - \frac{5}{6} \frac{\Delta^6}{T^6} \right. \\
 & \quad - 5e^{-\Delta/T} \left(\frac{\Delta^4}{T^4} + \frac{4\Delta^3}{T^3} + \frac{12\Delta^2}{T^2} + \frac{24\Delta}{T} + 24 \right) + 120 \\
 & \quad \left. - 5e^{\Delta/T} \left(\frac{\Delta^4}{T^4} - \frac{4\Delta^3}{T^3} + \frac{12\Delta^2}{T^2} - \frac{24\Delta}{T} + 24 \right) - 120e^{-\xi} \right\} \\
 & + \frac{25}{12} \frac{T^7}{\theta_c^7} \left\{ \frac{\Delta^6}{T^6} \log \left(\frac{e^{\Delta/T} - 1}{1 - e^{-\Delta/T}} \right) - \frac{6}{7} \frac{\Delta^7}{T^7} \right. \\
 & \quad - 6e^{-\Delta/T} \left(\frac{\Delta^5}{T^5} + \frac{5\Delta^4}{T^4} + \frac{20\Delta^3}{T^3} + \frac{60\Delta^2}{T^2} + \frac{120\Delta}{T} + 120 \right) + 720 \\
 & \quad \left. - 6e^{\Delta/T} \left(\frac{\Delta^5}{T^5} - \frac{5\Delta^4}{T^4} + \frac{20\Delta^3}{T^3} - \frac{60\Delta^2}{T^2} + \frac{120\Delta}{T} - 120 \right) + 720e^{-\xi} \right\}
 \end{aligned}$$

For the situation $\theta_E \gg T$, we can approximate (4.5.17) as

$$\begin{aligned}
 \dot{Q}(af) = \frac{D'}{\theta^7} & \left[\frac{\theta_E^4}{\theta_c^4} \frac{T^3}{\theta_c^3} \frac{1}{4} \left(\frac{1}{3} \frac{\Delta^3}{T^3} + 2 \right) - \frac{2\theta_E^3}{\theta_c^3} \frac{T^4}{\theta_c^4} \cdot \left(\frac{1}{4} \frac{\Delta^4}{T^4} + 6 \right) \right. \\
 & + \frac{4\theta_E^2}{\theta_c^2} \cdot \frac{T^5}{\theta_c^5} \left(\frac{1}{5} \frac{\Delta^5}{T^5} + 24 \right) - \frac{5\theta_E}{\theta_c} \cdot \frac{T^6}{\theta_c^6} \left(\frac{1}{6} \frac{\Delta^6}{T^6} + 120 \right) \\
 & \left. + \frac{25}{12} \frac{T^7}{\theta_c^7} \left(\frac{1}{7} \frac{\Delta^7}{T^7} + 720 \right) \right] \quad (4.4.17a)
 \end{aligned}$$

which can be rewritten as

$$\dot{Q}(af) = \frac{D'}{\theta^7} \left[\frac{1}{4} \frac{\theta_E^4}{\theta_c^4} \left(\frac{1}{3} \frac{\Delta^3}{\theta_c^3} + \frac{2T^3}{\theta_c^3} \right) - \frac{2\theta_E^3}{\theta_c^3} \left(\frac{1}{4} \frac{\Delta^4}{\theta_c^4} + \frac{6T^4}{\theta_c^4} \right) \right]$$

$$\begin{aligned}
 & + \frac{4\theta_E^2}{\theta_c^2} \left(\frac{1}{5} \frac{\Delta^5}{\theta_c^5} + \frac{24T^5}{\theta_c^5} \right) - \frac{5\theta_E}{\theta_c} \frac{1}{6} \left(\frac{\Delta^6}{\theta_c^6} + \frac{120T^6}{\theta_c^6} \right) \\
 & + \frac{25}{12} \left(\frac{1}{7} \frac{\Delta^7}{\theta_c^7} + \frac{720T^7}{\theta_c^7} \right) \quad (4.4.17b)
 \end{aligned}$$

Further in case $T < \theta_c$, in (4.5.17b) higher powers of $\frac{T}{\theta_c}$ can be neglected and it simplifies to

$$\dot{Q}(af) = (.16)(S e_J)^2 \frac{N}{\pi^3} \left(\frac{\hbar}{Mk_B} \right) \frac{\Delta T}{T^2} \frac{\theta_E^8}{\theta_c^8} \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (4.4.18)$$

Thus

$$\dot{Q}(af) = \frac{(.16)S^2 (e_J)^2 \left(\frac{\hbar N}{Mk_B} \right) \Delta T}{\pi^3} \frac{\theta_E^8}{\theta_c^8} \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (4.4.19)$$

Now the relaxation frequency $1/\tau_{sp}$ is given by

$$\frac{1}{\tau_{sp}(af)} = \frac{\dot{Q} \left(\frac{1}{C_S} + \frac{1}{C_{La}} + \frac{1}{C_{Lo}} \right)}{\Delta T}, \quad (4.4.19)$$

where C_S , C_{La} , C_{Lo} are respectively the specific heat contribution arising from the spin system, acoustic lattice and optical lattice modes. These have the following expressions. For the Einstein model the optical mode specific heat is given by

$$C_{Lo} = Nk_B \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (4.4.20a)$$

and the Debye model for acoustic mode gives

$$C_{La} = 234 Nk_B \left(\frac{T}{\Theta_D} \right)^3, \quad (4.4.20b)$$

where Θ_D is the Debye temperature.

$$C_s = 4Nk_B \left(\frac{T}{\Theta_c} \right)^3 \quad (4.4.20c)$$

These expressions are valid in the low temperature regions.

Now C_s is much smaller than C_{Lo} and C_{La} . Thus we get the form with $\frac{1}{c_s} \gg \frac{1}{c_{Lo}} > \frac{1}{c_{La}}$ for the study of optical interaction,

$$\frac{1}{\gamma_{sp}^{(af)}} = \frac{4 \times 10^{-2}}{\pi^3} \left(\frac{h}{Mk_B^2} \right) \frac{S(e_J)^2}{\pi^3} \frac{\Theta_E^8}{\Theta_c^5} \frac{1}{T^5} e^{-\Theta_E/T}, \quad (4.4.21)$$

4.5 Ferrimagnetic Case

For two sublattice ferrimagnets, we have two magnon modes, which are referred to as 'acoustic' (cf. equation (4.2.31a)) and 'optical' (cf. equation (4.2.31b)) modes. In the magnon-optical phonon interaction terms (cf. equation (4.2.32)), we ignore the role of acoustic magnons. Thus the necessary terms involve pure optical or optical-acoustic magnon operators. The explicit forms of the coefficients $B_{kq_0}^{(f)}$ and $C_{kq_0}^{(f)}$ under the long wave length approximation are given by

$$\left| B_{\underline{k}q_0}^f \right|^2 = B a^2 (k^2 - |k - q_0|^2) \quad (4.5.1)$$

where

$$B = \left(\frac{64\hbar}{NMw q_0} \right) \frac{4S_A S_B}{|S_A - S_B|^2} (S_A^2 + 3S_B^2) (e_J)^2 \quad (4.5.2)$$

$$\left| A_{\underline{k}q_0}^f \right|^2 = \left| C_{\underline{k}q_0}^f \right|^2 = C a^2 (k^2 + |k - q_0|^2), \quad (4.5.3)$$

where

$$C = \frac{64\hbar}{NMw q_0} \frac{32S_A^2 S_B^2 (S_A^2 + S_B^2)}{|S_A - S_B|^4} (e_J)^2 \quad (4.5.4)$$

Let us now consider the calculation for the process involving (4.5.1) i.e. middle term of (4.3.22). The expression for the heat flow is given by

$$\dot{Q}_{\alpha\beta}(f) = \frac{2\pi}{\hbar} \frac{T}{T^2} \left(\frac{Na^3}{8\pi^3} \right)^2 k_B \theta_E^2 \int \frac{\left| B_{\underline{k}q_0}^f \right|^2 e^{\theta_E/T} d\tau \delta(E_{\underline{k}}^\alpha + E_{\underline{k}-q_0}^\beta - k_B \theta_E)}{(e^{\theta_E/T} - 1)(e^{E_{\underline{k}}^\alpha/k_B T} - 1)(e^{E_{\underline{k}-q_0}^\beta/k_B T} - 1)} \quad (4.5.7)$$

where $E_{\underline{k}}^{(\alpha)}$ and $E_{\underline{k}}^{(\beta)}$ are given by (4.2.31a) and (4.2.32b) respectively.

As before δ -function is removed by integration over the angle variable. Further, from the energy conservation relation we get the relation

$$k^2 + |k - q_0|^2 - \frac{2}{\lambda} = 0 \quad (4.5.8)$$

where

$$\lambda^2 = \frac{1}{a^2} \left(\frac{\theta_E}{\theta_C} - \gamma \right) \quad \left. \vphantom{\lambda^2} \right\} \quad (4.5.9)$$

$$\gamma = 4 \frac{|S_A - S_B|^2}{|S_A S_B|} \quad \left. \vphantom{\gamma} \right\}$$

The limits of integration over q_0 and k are thus taken with the help of (4.5.8). The significant range is given by

$$0 < q_0 < k \quad \text{and} \quad 0 < k < \lambda/\sqrt{2}$$

Integration over q_0 gives

$$\dot{Q}_{\alpha\beta}(f) = G \int \frac{k^3 (\lambda^2 - 2k^2) dk}{\frac{E_k^\alpha/k_B T}{(e^{-1})} \frac{E_k^\beta/b_B T}{(e^{-1})}} \quad (4.5.10)$$

where

$$G = \frac{1}{4\hbar} \frac{\theta_E^2}{\theta_C} \frac{\Lambda T}{T^2} \frac{(Na^3)^2}{8\pi^3} \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} \quad (4.5.11)$$

Making use of the dimensionless variable

$$\eta = \frac{\theta_C a^2 k^2}{T}$$

we get

$$\dot{Q}_{\alpha\beta}(f) = G \left(\frac{T}{\Theta_C} \right)^2 \frac{1}{2a^4} \int_0^{\Delta T} \frac{\left(\lambda - \frac{2T\eta}{\Theta_C a^2} \right) \eta d\eta}{\eta (e^{-1}) (\xi - \eta)^{-1}} \quad (4.5.12)$$

with

$$\frac{\Delta}{T} = \frac{2 a^2 \Theta_C}{2T} \quad \text{and} \quad \xi = \frac{\Theta_E}{T}$$

It is clear from the δ -function condition that the energy conservation condition is satisfied for $\Theta_E > \Theta_C$ and $\left(\frac{\Theta_E}{\Theta_C} - r \right) > 0$.

Further, the role of the optical phonon will be important at somewhat elevated temperatures. Thus we consider the range, say $10^\circ\text{K} < T < \Theta_C$. Integration yields,

$$\dot{Q}_{\alpha\beta}(f) = \left(\frac{\hbar}{Mk_B} \right) \frac{\Delta T}{T^2} \frac{N}{\pi^3} \frac{\Theta_E}{\Theta_C} \frac{4S_A S_B (S_A^2 + 3S_B^2)}{|S_A - S_B|^2} \cdot \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \left[\frac{1}{2} \frac{\Delta^2}{\Theta_C^2} \left(\frac{\Theta_E}{\Theta_C} - r \right) - \frac{2}{3} \frac{\Delta^3}{\Theta_C^3} + \frac{T^2}{\Theta_C^2} \left\{ \left(\frac{\Theta_E}{\Theta_C} - r \right) - \frac{4T}{\Theta_C} \right\} \right] \quad (4.5.13)$$

In the situation $T < \Theta_C$ the second term in the bracketted expression can be neglected.

This gives

$$\dot{Q}_{\alpha\beta}(f) = \frac{\hbar}{Mk_B} \frac{\Delta T}{T^2} \frac{N}{\pi^3} \frac{S_A S_B (S_A^2 + 3S_B^2)}{8 |S_A - S_B|^2} \frac{\Theta_E}{\Theta_C} \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \left(\frac{\Theta_E}{\Theta_C} - r \right)^3 \quad (4.5.14)$$

For the situation $\theta_E > \theta_C$ which is under consideration here, the scattering of optical phonons with the pure acoustic and optical magnon modes involving two magnon Raman processes will not conserve energy. That this is so even for the optical modes can be seen from the interaction terms, namely,

$$\sum_{\underline{k}, \underline{q}_0} c_{\underline{k}, \underline{q}_0}^f \left(\beta_{\underline{k}} \beta_{\underline{k}-\underline{q}_0}^+ b_{\underline{q}_0} + \text{C. C.} \right) \quad (4.5.15)$$

The corresponding energy conservation condition demands

$$2JZ |S_A - S_B| + k_B \theta_C |\underline{k} - \underline{q}_0|^2 a^2 - 2JZ |S_A - S_B| - k_B \theta_C k^2 a^2 - \hbar \omega_{\underline{q}_0} = 0$$

i.e. $a^2 (|\underline{k} - \underline{q}_0|^2 - k^2) = \frac{\hbar \omega_{\underline{q}_0}}{k_B \theta_C} = \frac{\theta_E}{\theta_C}$ (4.5.16)

This cannot be satisfied for the situation noted above.

Therefore we do not consider \dot{Q}_β . In this event, the relaxation time ~~this~~ τ_{sp} is given by the process calculated above and we have

$$\frac{1}{\tau_{sp}(f)} = \frac{\dot{Q}_{\alpha\beta}(f)}{\Delta T} \left(\frac{1}{C_{Lo}} + \frac{1}{C_{La}} + \frac{1}{C_s} \right), \quad (4.5.17)$$

where C_{Lo} and C_{La} are given by (4.4.20a) and (4.4.20b) respectively.

Further the spin specific heat can be easily calculated using the dispersion relation for the acoustic branch (4.2.31a) thus

$$C_s = \frac{dE_s}{dT}$$

and

$$E_s = T \sum_{\underline{k}} \frac{E_{\underline{k}}^{\alpha}}{(e^{E_{\underline{k}}^{\alpha}/k_B T} - 1)} \quad (4.5.18)$$

After a simple calculation we obtain for a b,c.c. crystal

$$C_s = \frac{Nk_B}{18 \cdot 69} \left(\frac{T}{\theta_C} \right)^{3/2} \quad (4.5.19)$$

Arguing similar to the antiferromagnetic case, we get for the relaxation frequency,

$$\gamma_{sp}^{-1}(f) = \frac{\hbar}{Mk_B^2} \frac{3.11 S_A S_B (S_A^2 + 3S_B^2)}{\pi^3 \cdot |S_A - S_B|^2} \frac{\theta_E}{\theta_C} (e_J)^2 \left(\frac{\theta_E}{\theta_C} - r \right)^3 \frac{e^{-\theta_E/T}}{T^{7/2}} \quad (4.5.20)$$

4.6 DISCUSSION

In the foregoing sections, we have given magnon-optical phonon interaction processes in antiferro- and ferrimagnetic crystals. For the calculation of the relaxation frequencies we confined our attention only to those processes which are likely to conserve energy. For both types of systems, the important terms involved the splitting of an optical phonon into two magnons. Other interaction terms are not expected to be important for $\theta_E > \theta_C$. For this reason, we select those system which have low θ_C values. It is apparent that

the optical magnon modes will be excited in the low temperature region say 10 to 30°K, for crystals having low θ_C . In order to estimate the results of theoretical calculation we select the following systems as typical examples:

Antiferromagnetic case: MnF₂

This is an ideal antiferro magnetic system consisting of two interpenetrating body centered tetragonal lattice of magnetic ions. Based on some earlier work (Upadhyaya and Sinha)¹⁰⁷, the following values of the relevant parameters are chosen

$$s = \frac{5}{2}; \quad (e_J) = 10^{-8} \text{ dynes/cm}, \quad \theta_E = 200^\circ\text{K},$$

$$\theta_C = 3^\circ\text{K}, \quad T_N = 67^\circ\text{K}$$

With these values, the variation of $\frac{1}{\gamma_{sp}(af)}$ with temperature in the interval 10°K to 30°K is given in Table-I and Fig.2.

The value of $\frac{1}{\gamma_{sp}(af)}$ at 10°K turns out to be $1.337 \times 10^6 \text{ Sec}^{-1}$. The corresponding value of $\frac{1}{\gamma_{sp}}$ involving acoustic phonons is 10^8 Sec^{-1} as estimated earlier. This shows that interaction with acoustical phonons dominates at 10°K. However, as temperature increases, the role of optical phonons become quite appreciable. Thus at 30°K

$$\frac{1}{\gamma_{sp}} \sim 2.818 \times 10^9 \text{ Sec}^{-1}$$

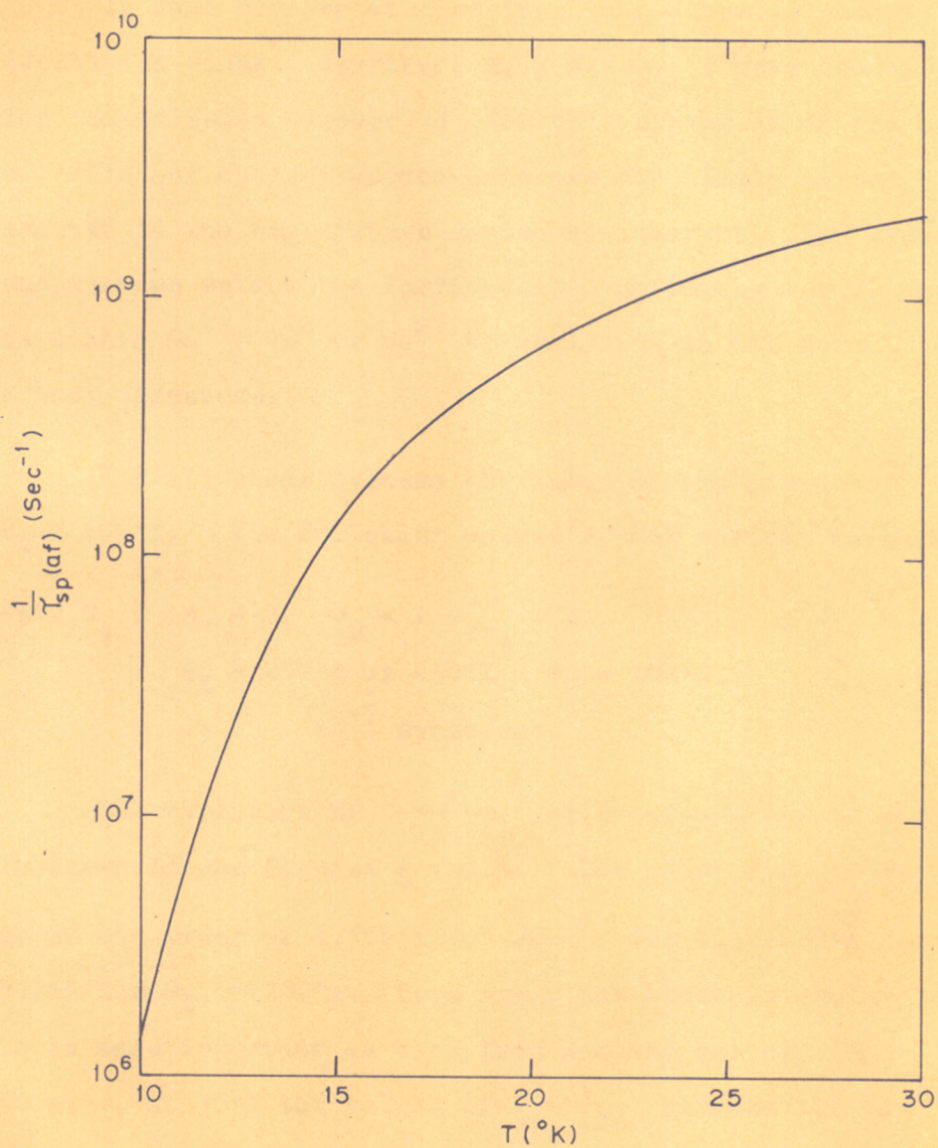


FIG. 2. MAGNON-OPTICAL PHONON RELAXATION FREQUENCY OF MnF_2 VERSUS TEMPERATURE WITH $\theta_E = 200^{\circ}\text{K}$.

Ferrimagnetic case

In some earlier studies involving acoustic phonons (Joshi and Sinha)¹⁰⁸, ferrites ($\epsilon, g \text{ MnFe}_2\text{O}_4$) were chosen for comparison. However, θ_C for this system is of the order of 783°K and optical magnon modes are not likely to be excited in the temperature region of interest. For present purposes we select the ferrimagnetic chromates ACr_2O_4 where A is either Mn^{2+} , Fe^{2+} or Co^{2+} crystalising in the normal spinel structure.

For all these systems the value of the parameter $\theta_C \leq 100^\circ\text{K}$. The following values of the various parameters were taken.

$$\begin{aligned} \text{FeCr}_2\text{O}_4 : S_A &= 2, S_B = 2 S_{\text{Cr}_3}^{3+} = 3. \\ \theta_E &= 200^\circ\text{K or } 250^\circ\text{K}, \theta_C = 100^\circ\text{K}, \\ (e_J) &= 10^{-7} \text{ dynes/sec.} \end{aligned}$$

The variation of $\frac{1}{\gamma_{sp}(f)}$ with temperature is shown in ~~Table II~~ and figures 3 and 4. The value for $\frac{1}{\gamma_{sp}(f)}$ at 10°K is of the order of $1.564 \times 10^4 \text{ sec}^{-1}$ for $\theta_E \sim 250^\circ\text{K}$ and $7.215 \times 10^5 \text{ sec}^{-1}$ for $\theta_E \sim 200^\circ\text{K}$. Here again the acoustic phonons seem to be more important as seen from earlier calculation. However, at 30°K the values of $\frac{1}{\gamma_{sp}(f)}$ reaches 10^9 sec^{-1} .

The above calculations show that optical phonon-magnon interaction processes are quite important at temperature above 10°K. Below this, the acoustic phonon scattering processes dominates.

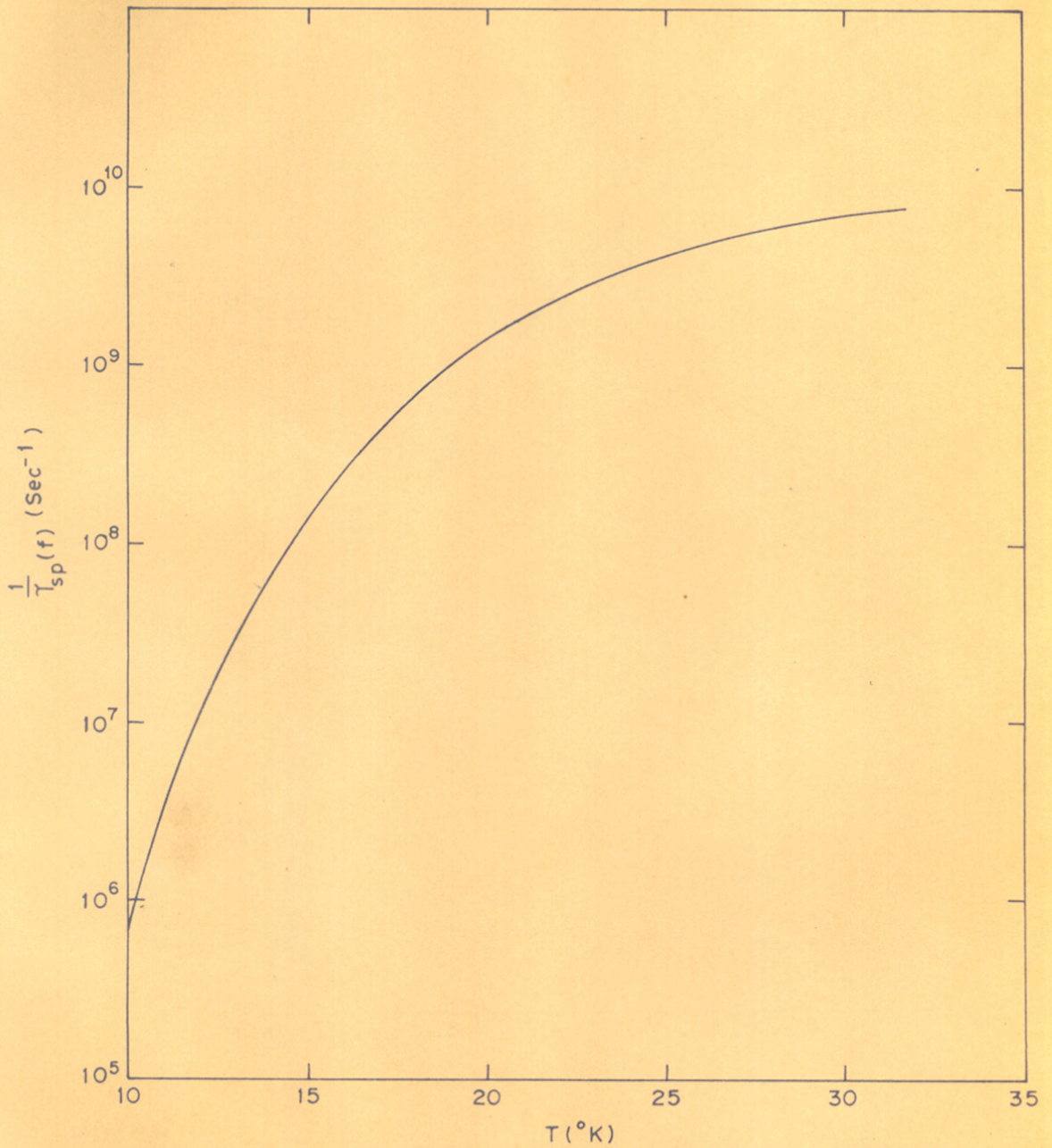


FIG. 3. MAGNON-OPTICAL PHONON RELAXATION FREQUENCY OF FeCr_2O_4 VERSUS TEMPERATURE WITH $\theta_E = 200^\circ \text{K}$.

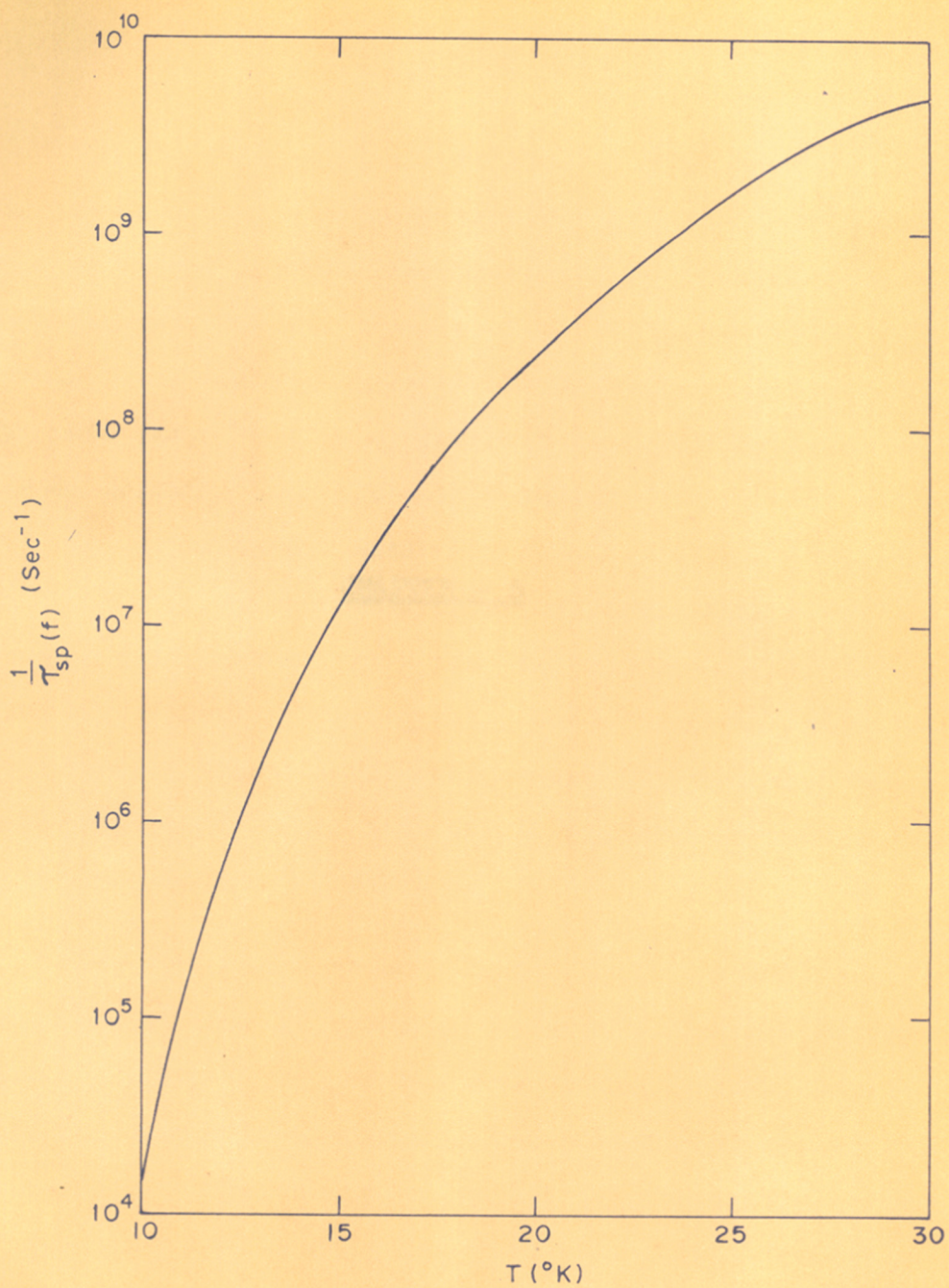


FIG. 4. MAGNON - OPTICAL PHONON RELAXATION FREQUENCY OF FeCr_2O_4 VERSUS TEMPERATURE WITH $\theta_E = 250^\circ \text{K}$.

CHAPTER - 5

CONCLUDING REMARKS

In the first part of the thesis, a microscopic theory for the ferroelectric phase transformation in perovskite type structure has been formulated. It has been recently realized that lattice dynamics may play an essential role in the ferroelectric phase transformation (i.e. in BaTiO_3). The main point in this approach is that the structure should become unstable with respect to certain vibrational modes at some temperature. According to this approach, the region where $\underline{k} = 0$, is responsible for the ferroelectric phase and the region where $|\underline{k}| = \pi/a$ is responsible for the antiferroelectric phase, \underline{k} being the propagation vector of transverse lattice vibrational modes. The frequency of this particular mode (i.e. soft-mode) is temperature dependent being of the form $w_T^2 \propto (T - T_c)$.

However, the idea of relating lattice dynamics and phase transitions in perovskites suffers from two drawbacks. Firstly, below T_c , w_T^2 is negative which, in turn, implies that the system is unstable in the harmonic approximation. Also, it is not possible to predict the transition. These ad hoc aspects are done away ~~with~~^{by} taking into account vibronic interactions_{for such systems}. Also, the following remarks can be made regarding the present work.

1. It resolves the difficulty concerning the ionic character of the system because the treatment automatically takes into account the covalency effect.

2. The importance ^{of TiO_6} ~~Ti-O~~ octahedron structure is invariably connected with the occurrence of ferroelectricity in $BaTiO_3$ and related structures. Matthias proposed the hypothesis that all substances are ferroelectric which have an atom or ion with a closed shell surrounded by oxygen octahedron in the manner of the structure of $BaTiO_3$, provided the dimension of the octahedron approximated ^{to} a definite size. Similar conclusions were derived by Smolenskii and Kozhevnikova. Thus substances $LiTaO_3$, $NaTiO_3$, $KTaO_3$, $RbTaO_3$, $LiNbO_3$, $NaNbO_3$, $KNbO_3$, $LaFeO_3$, $PbZrO_3$, MoO_3 , and WO_3 , conform to ferroelectricity with Curie points ranging from a few degrees absolute to nearly $1000^\circ K$. Thus the oxygen octahedron structure seems to be a necessary element for producing ferroelectricity in perovskite structures. The present work gives a quantum mechanical justification of the above propositions.

3. The present theory of ferroelectric phase transformations may be extended to explore the phase transformations in solids as a result of instability of certain vibrational modes arising from vibronic interactions.

In the second part of the thesis a microscopic formulation of the optical phonon-magnon interaction in antiferro- and ferrimagnetic systems has been presented following earlier work of the acoustic phonon-magnon interaction. Also, a study of the relaxation times associated with the flow of energy from the spin systems to lattice or vice-versa is considered. The study reveals interesting

points, namely, the optical phonon-magnon relaxation processes are dominated by acoustic phonon-magnon processes at very low temperature $\leq 10^{\circ}\text{K}$ but with the increase of temperature optical phonon ^{Contribution.} combination becomes quite appreciable. Further, such a study can be utilized to explore some properties of magnets - dielectrics.

In our calculations, we have assumed, as is customary, that there is no dispersion of the optical mode i.e. $\hbar\omega_{q_0}$ is constant. Thus, we have disregarded a few interaction processes which ~~did~~ ^{might} fulfill the condition of energy conservation. Perhaps, the dispersion relation

$$\omega_{q_0}^2 = \omega_0^2 + \beta q_0^2$$

where the coefficient β may have plus or minus sign, may make the other processes plausible.

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