CHAPTER 2

Lattice Dynamics of Solids: Theory and Experiments
Chapter-2

Lattice Dynamics of Solids: Theory and Experiments

2.1 A Short History of Matter and Lattice Dynamics

Since, early antiquary, mankind has been fascinated with the behavior of matter. Questions such as what it is made of, why unsupported objects drop to the ground, why various materials have different properties and other, more difficult topics have been the subject of considerable human endeavor for many thousands of years and will probably remain so for many hundreds of years more. As time has passed, several theories have been proposed and developed to explain matter’s characteristics and behavior of these theories, some have proved to be highly accurate and some have proved to fallacy. It was not until the seventeenth century, in what many refer to as the scientific revolutions that science was born in the term which would evolve into what we recognized today. It is also from this period that the firm scientist arose. Many of the ideas which were commonly accepted before the seventeenth centaury and had originated with Greek scholars such as Aristotle, underwent rigorous scientific testing and were found to be highly inaccurate or completely unfounded. This led to the development of what many refer to now as scientific method and also to the beginning of physics. Galileo and then Newton are said to mark the beginning of this age where such rigorous testing and investigations of materials and their properties would become the standard practice until this day. Both of these two scientists were interested in the ways matter interested and set out to test and understand the classical theories of
Greeks, which led both of them to propose new theories about matter’s interactions and properties.

After these two notable figures the birth of thermodynamics is said to have begun with German scientist Otto Von Guericke, who, like Newton and Galileo, wished to test the Greek theories. In particular, Guericke wanted to test Aristotle’s belief that “Nature abhors a vacuum.” In 1650 Guericke designed and built the first vacuum pump which was to prove useful to early experimental developments. After this several physicist (such as R. Hook and R. Boyle) improved and used the vacuum pump design to analyze the characteristic of gas and propose simple theories regarding their behavior. This led to the eventual developments of the ideal gas laws. These simple experiments more led Bernoulli [1] to suggest the conservations of energy and beginning of the kinetic theory. While other theories were to be developed and proposed over the coming century the kinetic theory was to have a leading influence and gain eventual acceptance. This period also suggested the beginning of the creation and application of electronic circuits. Historically, the 1800’s saw the kinetic theory being adopted and accepted by the scientific establishment as a whole and the fundamental laws of thermodynamics were suggested and developed. It was during this period that Boltzmann developed the famous equation which bears his name to this day and beginnings of the statistical physics appeared. The theory of thermodynamics and solid state physics grew and in 1907, Einstein [2] applied the new developing field of quantum mechanics to explain the specific heat of an object by suggesting that particles acted as simple harmonic oscillators in solids. This was to be followed by the famous Debye [3] model in 1912 for specific heat capacity where the first concept of a phonon (that is a quantum of lattice vibration) was introduced. As quantum mechanics...
took form, Einstein and Bose proposed for “Bosons” and consequently phonons, the Bose-Einstein distribution as an improvement to the now familiar and accepted Boltzmann function. The latter half of the twentieth century saw the field of electronics reaching maturity and development of theories of lattice dynamics based upon quantum and statistical physics occurring simultaneously. The study of lattice dynamics is the study of vibrations in crystal [4]. When one considers harmonic vibrations (that is when the expansion of the crystal potential is truncated at the second order term) one can explain and understand many physical properties, such as phonon modes, specific heat. Anharmonic forces are needed to explain other physical properties, such as thermal conductivity, piezoelectricity, ferroelectric phase transitions and melting. By combining the theory of lattice dynamics with electronic structure information, one can explain properties such as superconductivity and John-Teller effect.

The study of solids at the microscopic level basically involves a detailed investigation of the crystal structure and the dynamics of atoms. Many low temperature equilibrium properties such as chemical properties material hardness, shapes of crystals, Bragg scattering of X-ray, electron and neutron beams, electronic structure and electrical properties etc. of solids especially metals are determined to a large extend by the behavior of the conduction electrons. These properties can be explained in terms of models based on the static approximation such as Drude-Sommerfield model which assumes that the atoms are fixed at their equilibrium positions. On the other hand, macroscopic properties of solids such as phase transition, thermal expansion, specific heat, thermal conductivity, melting, displacive ferroelectric phase transition, piezoelectricity and transmission of sound that are not dominated by a large
electronic contribution depends essentially on the dynamics of atoms around their equilibrium positions [5-9]. The collective motion of atoms in crystalline solids form travelling waves (called lattice vibrations). These vibrations which are called normal modes are essentially non-interacting and harmonic in nature at low temperature (typically below the Debye temperature) and are also called normal modes. The quanta of these normal modes are called “phonons”. Phonons are bosons and are characterized by their energy, wave-vector and polarization vector. The polarization vector is a measure of the relative atomic vibrations.

Vibrational spectroscopy [10] which exploits the interaction of radiation with lattice vibrations, either through a scattering process, specifically in the case of electromagnetic radiation or through an absorption process can be effectively used for the study of dynamic processes in solids. In the scattering processes (such as Raman scattering), the changes in the energy and wave-vector of the scattered beam with respect to the incident beam gives information about the energies and wave-vector of the phonons involved in the scattering process. In the case of absorption spectroscopy (such as infrared (IR) absorption), the incoming beam of radiation is absorbed at vibrational frequencies as a resonance process resulting in the creation of phonons. Analysis of this resonance energy provides direct information about the energies of the phonons. However, Raman and IR studies provide information of only selected (optically active) long wavelength phonons corresponding to the zone-center of the Brillouin zone. On the other hand, inelastic neutron and X-ray scattering can measure phonons with wave vectors spanning the entire Brillouin zone and hence can be effectively utilized for studying phonon dispersion relations (i.e., phonon energy as a function of wave-vector) and density of states (the frequency distribution of phonons).
Further, in the case of X-ray inelastic scattering, the atomic scattering factor fall to zero at increasing values of the scatter vector ($Q$) which implies that this technique works better at lower values of $Q$, in contrast to neutron inelastic scattering methods, which work better at higher values of $Q$. Thus, while inelastic neutron scattering is widely used for the study of a large number of materials, inelastic X-ray scattering is particularly important in the study of the dynamics of liquids and glasses.

Direct measurement of material properties at high pressures and temperatures are often beyond the range of achievable experimental limits. In such cases, accurate models for prediction of material properties theoretically, come to the rescue. The challenge faced by these models in predicting thermodynamic properties depends on their precision to explain a variety of microscopic and macroscopic dynamical properties. This includes an understanding of the crystal structure, equation of states, phonon dispersion relations and density of states. The data obtained from neutron scattering and Raman or infra-red data are used to test and validate these models of interatomic potentials, which in turn could be used to predict thermodynamic properties at extreme conditions.

### 2.2 Theory and Formalism of Lattice Dynamics

The theory of lattice dynamics can be explained best by the Born and Karman formalism [11] which assumes the atoms as point masses, with no internal structure and attempts to analyze the dynamics of atoms, given the concept of the crystal potential function $\phi$ which describes the binding of atoms. In reality, however, the atoms consist of nuclei and electrons and on the face of it; dynamics involves nuclear motions while binding involves electrons. Hence, it is essential to consider the Born-
Oppenheimer or adiabatic approximation in order to make the motions of the nuclei independent of the motions of the electrons and thus approximate.

The approximation is usually valid for insulators, semiconductors and metals. But, it is unjustified in the case of hydrogen bonds where there is more than one potential energy minimum available for the atom. Further, this approximation also fails in circumstances where the dynamics of the electrons are directly involved such as the resistance due to scattering of electrons by phonons and superconductivity. The brief description of adiabatic approximation is presented in chapter 3. However, the entire description of the formal theory of lattice dynamics can be found in literature [5-9]. A summary of the mathematical formalism for a perfect crystal in the harmonic approximation is presented here. Harmonic and quasi-harmonic approximations are alternative lattice dynamics strategies, which differ in the choice of the reference structure. In the case of harmonic lattice dynamics, the structure is at the minimum of the potential energy (mechanical equilibrium) at 0 k in the absence of zero-point motions, whereas for quasi-harmonic lattice dynamics, the average structure is at the minimum of the free energy (thermodynamic equilibrium). In the harmonic approximation, the dynamics of atoms $u\left(\begin{array}{c}l \\ k \end{array}\right)$ about their equilibrium positions $r\left(\begin{array}{c}l \\ k \end{array}\right)$ (where, l denotes the $l^{th}$ unit cell ($l=1, 2, 3...N$) and k is the $k^{th}$ type of atom ($k=1, 2, ...n$) within the unit cell) can be entirely specified by the Taylor series expansion of the crystal potential energy $\phi$ up to the second derivative given by

$$\phi = \phi^{(0)} + \phi^{(1)} + \phi^{(2)} \tag{2.1}$$
Where

\[
\phi^{(0)} = \phi \left( r \left( \frac{l}{k} \right) \right)
\]

\[
\phi^{(1)} = \sum_{lk\alpha} \frac{\partial \phi}{\partial u_{\alpha}} \left( \frac{l}{k} \right) u_{\alpha} \left( \frac{l}{k} \right) = \sum_{lk\alpha} \phi_{\alpha} \left( \frac{l}{k} \right) u_{\alpha} \left( \frac{l}{k} \right)
\]

\[
\phi^{(2)} = \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \frac{\partial^2 \phi}{\partial u_{\alpha} \left( \frac{l}{k} \right) \partial u_{\beta} \left( \frac{l}{k} \right)} u_{\alpha} \left( \frac{l}{k} \right) u_{\beta} \left( \frac{l'}{k'} \right) = \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \phi_{\alpha\beta} \left( \frac{l'k'}{kk'} \right) u_{\alpha} \left( \frac{l}{k} \right) u_{\beta} \left( \frac{l'}{k'} \right)
\]

Where the suffixes \( \alpha \) and \( \beta \) denotes cartesian coordinates.

In the equilibrium configuration, the force on every atom must vanish. This leads to the result

\[
\phi_{\alpha} \left( \frac{l}{k} \right) = 0 \quad \text{for every } \alpha, l, k
\]

Hence, \( \phi^{(1)} = 0 \)

Thus, in the harmonic approximation

\[
\phi = \phi^{(0)} + \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \phi_{\alpha\beta} \left( \frac{l'k'}{kk'} \right) u_{\alpha} \left( \frac{l}{k} \right) u_{\beta} \left( \frac{l'}{k'} \right)
\]

(2.2)

Accordingly, the equation of motion of the \((lk)\)th atom becomes

\[
m_k \ddot{u}_{\alpha} \left( \frac{l}{k} \right) = \sum_{l'k'\beta} \phi_{\alpha\beta} \left( \frac{l'k'}{kk'} \right) u_{\beta} \left( \frac{l'}{k'} \right)
\]

(2.3)
From eq. (2.3), it is clear that $\phi_{\alpha\beta}\left( \mathbf{ll'}_{kk} \right)$ is the negative of the force exerted on atom $\left( \mathbf{l}_{k} \right)$ in the $\alpha$ direction due to unit displacement of the atom $\left( \mathbf{l'}_{k'} \right)$ in the $\beta$ direction, with all the other atoms being fixed in their equilibrium positions. The quantity $-\phi_{\alpha\beta}$ is referred to as the force constant and usually expressed in unit of dyne.cm$^{-1}$. These forces constant satisfy the symmetry condition $\phi_{\alpha\beta} = \phi_{\beta\alpha}$.

The periodicity of the crystal implies that the solutions of equation (2.3) must be such that the displacement of atoms in different unit cells must be same apart from phase factor. The equations of motion (2.3) are solved by assuming wave like solutions of the type

$$u_{\alpha}\left( \mathbf{l}_{k} \right) = U_{\alpha}(k|q)\exp\left\{ i\left( q.r\left( \mathbf{l}_{k} \right) - \omega(q)t \right) \right\}$$

(2.4)

Here $U_{\alpha}(k|q)$ is the wave amplitude, $q$ is the wave-vector and $\omega(q)$ is the angular frequency associated with the wave.

Substitution of eq. (2.4) in eq. (2.3) leads to the following 3n simultaneous equations

$$m_{k}\omega^{2}(q)U_{\alpha}(k|q) = \sum_{k'} D_{\alpha\beta}\left( q_{kk'} \right)U_{\beta}(k'|q)$$

(2.5)

here, the components of the dynamical matrix $D_{\alpha\beta}\left( q_{kk'} \right)$ is given by

$$D_{\alpha\beta}\left( q_{kk'} \right) = \sum_{l} \phi_{\alpha\beta}\left( ll'_{kk} \right)\exp\left\{ i\left( q.r\left( \mathbf{l'}_{k} \right) - r\left( \mathbf{l}_{k} \right) \right) \right\}$$

(2.6)
The $3n$ coupled equations of motion are thus obtained. The frequencies of the normal
types and eigenvectors are determined by diagonalizing the dynamical matrix through
a solution of the secular equation

$$
m_k \omega_j^2(q) \delta_{kk} \delta_{\alpha\beta} - D_{\alpha\beta} \left( \frac{q}{kk} \right) = 0 \quad (2.7)
$$

The fact that the dynamical matrix is Hermitian which implies that the $3n$ eigenvalues

$$
\omega_j(q), \quad (j=1,2,...,3n)
$$

are real, so that $\omega_j(q)$ is either real or purely imaginary. The
imaginary value would imply a motion of the lattice which erupts exponentially either
in the past or future. Therefore, the microscopic condition for the stability of the lattice
is that each $\omega_j(q)$ be either positive or zero. Thus, the frequencies $\omega_j(q)$ are real and
its eigenvectors may be chosen as orthonormal.

The displacement of the atoms in one of these normal modes, labeled by

$$(qj)$$

corresponds to a wave like displacement of atoms and are given by

$$
U_{\alpha} \left( k \left| \frac{q}{j} \right. \right) = P \left( \frac{q}{j} \right) \xi_{\alpha} (k|qj) \exp \left\{ i \left( q \cdot \left( \frac{l}{k} \right) \right) \right\} \quad (2.8)
$$

Where, $P \left( \frac{q}{j} \right)$ is the normal coordinate and $\xi_{\alpha} (k|qj)$ is the normalized eigen
vector of the normal mode $(qj)$, where $j$ runs from 1 to $3n$ and is used to distinguish
between the $3n$ normal modes at $q$. The components of the eigenvectors $\xi_{\alpha} (k|qj)$
determine the pattern of displacement of the atoms in a particular mode of vibration.

There are $3n$ curves $\omega = \omega_j(q), \quad (j=1, 2...3n)$ corresponding to every direction in $q$-

space. The alteration in phonon frequency as a function of $q$-space is termed
dispersion, and each set of vibrational modes related by dispersion is a branch. The
index $j$, which distinguishes the various frequencies corresponding to the propagation vector, characterizes various branches of the dispersion relation. The allowed values of $\tilde{q}$ that can be sustained by the lattice are determined by periodic boundary conditions. These conditions can be applied in such a manner that all the distinct possible values of $\tilde{q}$ can be obtained by considering only one primitive cell of the reciprocal lattice, i.e. the first Brillouin zone.

The plane-wave lattice vibrations in the long wavelength ($q \to 0$) are of two types. The first type of lattice vibration is such that the displacements of neighboring ions are identical which is consistent with the propagation of a sound wave through the lattice; hence these modes are called acoustic branches. Elastic constants are related to the slopes of the acoustic branches at $(q \to 0)$. The second kind of lattice vibration corresponds to the displacement of oppositely charged neighboring ions in opposite directions and their magnitudes are such that the centre of mass remains stationary. Such modes can be excited by electromagnetic fields and are called optic branches. The optical vibration frequencies approach finite limits while the acoustic frequencies tend to zero as the wave vector $\tilde{q}$ approaches zero. For any crystal containing $n$ atoms in its primitive cell, there are three acoustic branches corresponding to the lateral translation of the crystal along three mutually perpendicular directions while the remaining $3n-3$ branches are optic branches.

The displacement corresponding to the acoustical as well as optical lattice vibrations can be further resolved into three components, one parallel to the wave vector $q$ (longitudinal motion) and the other two being mutually perpendicular to the wave vector $q$ (transverse motion). Further, in the case of optical vibrations, the frequencies of the longitudinal optic (LO) modes are higher than the transverse optic
(TO) modes. This can be attributed to the fact that the optical vibrations give rise to a slowly varying polarization density \( P \) due to the displacement of the point ions in the crystals. This polarization gives rise to a macroscopic field \( E \) which is related by

\[
E = -4\pi q \cdot (q \cdot P)
\]  

(2.9)

This shows that the macroscopic field \( E \) is parallel to \( q \). The energy density associated with \( E \) and \( P \) is \( -P \cdot E \). In case of TO modes, since \( P \) is perpendicular to \( q \) and \( E \) is parallel to \( q \), the contribution from this interaction energy is zero. On the other hand, in the case of LO modes, since both \( P \) and \( E \) are parallel to \( \vec{q} \), the interaction energy term provides an additional restoring force which raises the frequency of the LO mode over that of the TO mode. This is the reason behind the optical splitting between the LO and TO phonon modes.

In addition, according to the macroscopic theory of cubic diatomic crystals, the optical frequencies at the zone-centre (\( \Gamma \)-point of BZ) are connected with the dielectric properties, through the Lyddane, Sachs and Teller (LST) [12]

\[
\frac{\omega_{LO}^2(\Gamma)}{\omega_{TO}^2(\Gamma)} = \frac{\varepsilon_0}{\varepsilon_\infty}
\]  

(2.10)

Here \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the static and high frequency dielectric constants, respectively. \( \varepsilon_\infty \) implies a frequency which is much higher than the vibrational frequencies. The ions in the lattice on account of their inertia may not respond to an electric field of such a high frequency. Thus, only electrons respond to such fields and hence the LST relation signifies the necessity of including the electronic polarization effects in any rigorous theory of lattice dynamics.

[23]
The phonon density of states is defined by the equation

\[ g(\omega) = C \int_{BZ} \sum_j \delta(\omega - \omega_j(q)) dq = C \sum_{jp} \delta(\omega - \omega_j(q)) dq_p \tag{2.11} \]

Where, \( C \) is normalization constant such that \( \int g(\omega)d\omega = 1; \) that is \( g(\omega)d\omega \) is the ratio of the number of eigenstates in the frequency interval \( (\omega, \omega + d\omega) \) to the total number of eigenstates; \( p \) is the mesh index characterizing \( q \) in the discretized irreducible Brillouin zone and \( dq_p \) provides the weighting factor corresponding to the volume of \( p^{th} \) mesh in q-space.

The eigenvalue problem can be simplified by the application of group theoretical methods at various high symmetry points and directions in the Brillouin zone. The characterization of the combinations of symmetry operations of point group that can be preserved or lost in a single deformation of a structure constitutes the group theoretical representation. These symmetry operations lead to irreducible representations which can then be diagonalized to give the eigenvalues corresponding to the respective representations. This classification of phonon modes facilitates direct comparison with single-crystal Raman, infrared and neutron data. The modes of types A and B are non-degenerate, E is doubly degenerate, and T (or F) is triply degenerate. Further, in case of the A modes, the rotational symmetry operations are preserved while the B modes represent the loss of some of the rotational symmetry operation. In addition, the key to the labels of all these modes are the subscripts g and u (from the German gerade and ungerade for even and odd parity, respectively) which indicate that the centre of symmetry is either preserved (symmetric) or non-preserved (anti-symmetric) with respect to inversion. According to the rule of mutual exclusion, for
crystals with a centre of inversion, infrared bands are never Raman active and vice versa. In general, a symmetric vibration is more intense in the Raman spectrum and weaker in the infrared, while strong infrared bands are generally associated with asymmetric modes of low Raman intensity.

2.3 Thermodynamic Properties

The theory of lattice dynamics described in previous section allows us to determine the phonon frequencies in the harmonic approximation which assumes completely free propagation of non-interacting phonons. However, elastic and inelastic collisions give rise to anharmonicity in the crystal which limit the lifetime of phonons. Anharmonic effects become more important at high temperatures. This change at high temperatures affects physical properties of the crystal. The harmonic approximation fails to explain the phenomena such as thermal conductivity, thermal expansion, multi-phonon process and many other [5-8]. These properties can be accounted to some extent by considering the quasi-harmonic approximation in which the temperature dependence of the force constants and phonon frequencies is only due to the effects of thermal expansion. In the quasi-harmonic approximation, the thermodynamic properties of a crystal are based on the averages of energies associated with the 3nN vibrations corresponding to the number of degrees of freedom of the n atomic constituents in the N unit cells of the crystal.

The thermodynamic properties, namely the free energy, the specific heat and the entropy are obtained from the partition function Z defined as,

\[
Z = Tr \left\{ \exp \left( \frac{-H}{k \beta T} \right) \right\}
\]  

(2.12)
The evaluation of this trace in terms of the eigen energies of the Hamiltonian (H) yields

\[ Z = \exp \left( -\frac{\phi(V)}{k_B T} \right) \prod_{q} \frac{\exp \left( \frac{-\hbar \omega_j(q)}{k_B T} \right)}{1 - \exp \left( \frac{-\hbar \omega_j(q)}{k_B T} \right)} \]  

(2.13)

All the thermodynamic properties of the crystal derived from the partition function involve summations over the phonon frequencies in the entire Brillouin zone and can be expressed as averages over the phonon density of states. The Helmholtz free energy \( F \) and entropy \( S \) are given by,

\[ F = -k_B T \ln z = \phi(V) + \int \left\{ \frac{1}{2} \hbar \omega + k_B T \ln \left[ 1 - \exp \left( \frac{-\hbar \omega}{k_B T} \right) \right] \right\} g(\omega) d\omega \]  

(2.14)

And

\[ S = -\frac{dF}{dT} = k_B \int \left\{ \ln \left[ 1 - \exp \left( \frac{-\hbar \omega}{k_B T} \right) \right] + \frac{\left( -\frac{\hbar \omega}{k_B T} \right)}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \right\} g(\omega) d\omega \]  

(2.15)

The energy \( E \) of the crystal with volume \( V \) is

\[ E = F - T \frac{dF}{dT} = \phi(V) + E_{\text{vib}} \]  

(2.16)

Where \( \phi(V) \) is the static lattice energy and \( E_{\text{vib}} \) is the vibrational energy at temperature \( T \).

\[ E_{\text{vib}} = \int \left\{ n(\omega) + \frac{1}{2} \right\} \hbar \omega g(\omega) d\omega \]  

(2.17)

Where \( n(\omega) \) is the population factor given by Bose-Eistein relation
\[ n(\omega) = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \]  \hspace{1cm} (2.18)

The specific heat \( C_v(T) \) is given by

\[
C_v(T) = \frac{dE}{dT} = k_B \int \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1\right)^2} g(\omega) d(\omega) \hspace{1cm} (2.19)
\]

The calculated phonon density of states can be used to compute the specific heat. While lattice dynamical calculations yield \( C_v \), the specific heat at constant volume; experimental heat capacity data correspond to \( C_p \), the specific heat at constant pressure. Thus, comparison of the calculations with the experimental data necessitates the evaluation of the difference \( C_p - C_v \) which is given by

\[
C_p(T) - C_v(T) = \left[\alpha_v(T)\right]^2 B V T \hspace{1cm} (2.20)
\]

Where \( \alpha_v \) the volume thermal expansion coefficient and \( B \) is the bulk modulus defined as

\[
B = -V \frac{dP}{dV}
\]

The volume thermal expansion coefficient in the quasi-harmonic approximation is given by

\[
\alpha_v = \frac{1}{B V} \sum_i \Gamma_i C_{v_i}(T) \hspace{1cm} (2.21)
\]
Where $\Gamma_i$ is the mode Grüneisen parameter of the phonons in state $I (=q_j$, which refers to the $j^{th}$ phonon mode at wave vector $q$) which is given by

$$\Gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \tag{2.22}$$

The procedure for the calculation of thermal expansion is applicable when explicit anharmonicity of phonons is not very significant, and thermal expansion arises mainly from the implicit anharmonicity, i.e., the change of phonon frequencies with volume.

### 2.4 Lattice Dynamical Models

The biggest problem in any lattice-dynamical problem is the evaluation of the dynamical matrix and hence led to the development of several lattice dynamical models [13]. These lattice dynamical models are broadly classified into three categories: (1) phenomenological models, (ii) semimicroscopic models and (iii) microscopic models. In this section, the emphasis will be laid on the phenomenological models since they are easily adaptable and hence have preserved interest among worker in this field.

**Rigid Ion Model**

In the Rigid Ion Model (RIM) developed by Kellermann [14-15], the ions are regarded as rigid (or under formable) and unpolarizable point ions. They are prevented from collapsing under their mutual Coulomb attraction by the presence of short-range overlap repulsion operative generally, between the nearest neighbors. It is observed that when neighboring ions overlap during vibrations, the electronic configuration is distorted which produces an additional polarization. However, RIM assumes the electrons to be rigidly bound to the nucleus which prevents it from taking into account the electronic polarization. This defect leads to unity value $\varepsilon_e$ in the LST relation...
discussed earlier for all the ion crystals, while its experimental value lies between 2 and 3. This leads sometimes to poor agreement between the phonon dispersion curves achieved from RIM and experimental data. This inadequacy can be taken into account by assigning electronic polarizability to the ions. This polarization mechanism is employed in the shell model described below.

**Shell Model**

The shell model (SM) [16] postulates the ions to be composed of a central massive core, consisting of the nucleus and the tightly bound electrons, coupled by harmonic springs, to an outer mass less spherical shell made of valence (or loosely bound) electrons. The shell retains its charge but can move with respect to its core, which gives rise to the mechanism of electronic polarization. The effective charges of the core and shell are $X(k)$ and $Y(k)$, respectively, while the force constant of the harmonic spring is $K(k)$. The dynamical matrices are calculated between the pairs, core-core, core-shell, shell-core and shell-shell, denoted $D^{cc}$, $D^{cs}$, $D^{ss}$ respectively. The equations involving the displacement vectors associated with the core ($U$) and polarization ($W$) are given by

$$m \omega^2 U = D^{cc} U + D^{cs} W \quad (2.23)$$

$$0 = D^{sc} U + D^{ss} W \quad (2.24)$$

Eliminating $W$, we get

$$m \omega^2 U = \left[ D^{cc} - D^{cs} \left( D^{ss} \right)^{-1} D^{sc} \right] U \quad (2.25)$$

And the dynamical matrix is given by

$$D = D^{cc} - D^{cs} \left( D^{ss} \right)^{-1} D^{sc} \quad (2.26)$$
For the sake of simplicity, the short-range forces between atoms are included only between the shells. The interactions among the atomic constituents of the lattice are described by employing a two-body inter-atomic potential function consisting of Coulomb, short range interactions of the Born-Mayer type and van der Waals interaction and is given by

\[
V(r) = \left\{ \frac{e^2}{4\pi\varepsilon_o} \right\} \left\{ \frac{Z(k)Z(k')}{r} \right\} + a\exp \left\{ \frac{-br}{R(k)+R(k')} \right\} - \frac{C}{r^6} \quad (2.27)
\]

Where \( r \) is the separation between the atoms of a type \( k \) and \( k' \), \( Z(k) \) and \( R(k) \) are effective charge and radius parameter of the atom type \( k \), \( \frac{1}{(4\pi\varepsilon_o)} = 9x10^9 \) Nm\(^2\)/Coul\(^2\), \( a = 1822 \) eV, \( b = 12.364 \). The last term in equation (2.27) which is the van der Waals term is applied only between certain atomic pairs.

The potential parameters are varied in such a way that they give an equilibrium structure at the minimum of the potential energy equivalent to the experimentally obtained lattice constants with the respective atomic positions in the unit cell. The optimized parameters in addition should satisfy the condition of dynamical equilibrium which requires that all the calculated phonon frequencies be real at all the wave-vectors in the Brillouin zone. Further, the parameters of potentials should also reproduce various other available experimental data, namely elastic constants, optical phonon frequencies or the range of phonon spectrum, etc. The crystal structures at high pressures are obtained by minimization of the free energy with respect to the lattice parameters and the atomic positions. The vibrational as well as thermodynamic
properties have then been successfully calculated by using the equilibrium structure thus obtained.

2.5 Experimental Techniques: Measurement of Phonons

Experimental studies of lattice vibrations include use of techniques like Raman spectroscopy, infrared absorption, inelastic neutron scattering, inelastic X-ray scattering, etc. Unlike Raman and infrared studies, which probe only the long wavelength excitations in one-phonon scattering, inelastic neutron and X-ray scattering can directly probe the phonons in the entire Brillouin zone. The most powerful technique currently used for studying lattice vibrations is inelastic neutron scattering. While inelastic neutron scattering is widely used for such measurements, inelastic X-ray scattering has also been used [17-20] at intense synchrotron sources for the study of phonons in a few materials. Despite the wealth of information which has been obtained from this technique, it does have some limitations such as the need for expensive equipment, a relatively low resolution, and the fact some materials cannot be investigated because they have a low scattering cross section or high absorption cross section for neutrons. Infrared absorption and Raman and Brillouin light scattering provide complimentary techniques for investigating lattice vibrations. These methods have higher resolution than neutron scattering but first order phonon processes are limited to the center of Brillouin zone by momentum conservation. Second order processes are not subject to this restriction but it is usually quite difficult to unfold the combined density of phonon states. These techniques are also limited by rigorous selection rules.
2.5.1 General Theory of Scattering

Scattering experiments, for instance, are very important for studies in material science and condensed matter physics, since they allow a unique insight into the arrangement of the atoms through the observation of the electron distributions and their fluctuations in space and time. A general scattering experiment is shown schematically in Fig.2.1. This schematic arrangement is valid for all probes such as neutrons, electron beams, and electromagnetic radiation. The incident beam of well defined wave vector $k_i$, energy $E_i$ and polarization unit vector $e_i$ is scattered into the solid-angle element $d\Omega$ under the scattering angle $2\theta$. The scattered beam is completely defined by the new wavevector $k_f$, the energy $E_f$ and the polarization unit vector $e_f$. The scattered intensity is described by the double-differential cross section $d^2\sigma/(d\Omega d\omega_f)$. It is given by the removal rate of particles out of the incident beam as the result of being scattered into a solid angle $d\Omega$ with a frequency range of $d\omega_f$. The scattered beam is usually distributed over a range of energies $E_f$. There can be beam contributions that have been scattered elastically with no change of energy and other contributions that have changed energy due to inelastic scattering. Therefore, the scattering process contains information on energy and momentum transfers by

$$E = \hbar \omega = E_i - E_f \quad \text{And} \quad \hbar \mathbf{Q} = \hbar \left( \mathbf{k}_i - \mathbf{k}_f \right)$$  \hspace{1cm} (2.28)

Here, a brief discussion on scattering of a probe is restricted to the transferred energy smaller than the photon energy ($E \ll E_i$). In this case, the momentum transfer $\hbar \mathbf{Q}$ is simply connected with the scattering angle $\theta$ by
\[ h\mathbf{Q} \equiv 2h k_j \sin \theta \]  
\text{(2.29)}

the double-differential scattering cross section, which is expressed as [19],

\[ \frac{d^2}{d\Omega \, d\omega_f} = \left( \frac{d\sigma}{d\Omega} \right)_0 \cdot S(\mathbf{Q}, \omega) \]  
\text{(2.30)}

This involves two contributions: (1) the coupling of the beam to the scattering system characterized by the intrinsic cross section \( \left( \frac{d\sigma}{d\Omega} \right)_0 \) and (2) the scattering function \( S(\mathbf{Q}, \omega) \) which expresses the properties of the sample in the absence of the perturbing probe.

The sophisticated form of scattering function can be given by

\[ S(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} \left\langle \sum_{j} e^{-i\mathbf{Q} \cdot \mathbf{r}_j(t)} e^{i\mathbf{Q} \cdot \mathbf{r}_j(0)} \gamma_i \right\rangle dt \]  
\text{(2.31)}

which describes the correlations of the scattering phases of the particles at positions \( \mathbf{r}_j(t) \) at different times \( t \). The phase of the scattering amplitude is described by \( e^{i\mathbf{Q} \cdot \mathbf{r}_j} \). In classical limit, it represents essentially the Fourier transform in time of the density correlation function and gives information on the particle fluctuations in the scattering system in the same state, \( \gamma_i \), at different times. The dependence of the scattering phases on the term \( \mathbf{Q} \cdot \mathbf{r}_j \) can be used for a classification of the scattering process [20]. Thereby, the inverse of the transferred momentum \( h\mathbf{Q} \) has to be compared with a characteristic length \( \zeta_{\text{char}} \) of the scattering system describing the spatial inhomogeneity. This can be an interparticle distance or a screening length. For \( \frac{\zeta_{\text{char}}}{Q} \ll 1 \), there exists interference between the scattering amplitudes from many particles of the system. Consequently, mainly the collective behavior of the particles will be detectable. Therefore, collective motions of the scattering system like phonons, magnons or plasmons can be observed.
if, in addition, the transferred energy is in the characteristic frequency range of these motions.

For $Q_{\text{char}} >> 1$, the interference of the scattering amplitudes is negligible and the scattering contributions of different particles are independent. Therefore, single-particle properties are observed, like, for example, Compton scattering [20] in the case of photon interaction with an electron system, if the photon energy is large compared with the binding energy of the electron. In the intermediate ranges $Q_{\text{char}} \approx 1$, both collective and single-particle properties are visible. The scattering function (eq. (2.31)) is often transformed to representations that are more suitable to describe important physical properties of a particular system. The discussion on the general scattering theory by a probe is based on the review of Burkel [21].

2.5.2 Neutron Scattering

Neutron scattering in solids is of considerable interest to solid state and reactor physicists and slow neutron scattering by solids has developed into a powerful tool for investigating details of lattice vibrations. The average energy of neutrons that have reached thermal equilibrium with the atoms of any moderating material at temperature $T$ is nearly $(3/2) K_B T$, where $K_B$ is the Boltzmann constant. Corresponding to room temperature ($T \sim 300$ K) this energy is $\sim 0.04$ eV. Such neutrons represent an excellent probe for two reasons: (i) the de Broglie wavelength of such neutrons ($= h/(3 m_0 K_B T)^{1/2}$, where $m_0$ is the mass of neutron) is of the same order as the interatomic distance in crystals ($\sim 10^{-8}$ cm) so that, like X-rays, they can be used for diffraction studies, and (ii) the energy of such neutrons being of the same order as the thermal energy of the atoms in a solid, on collision the relative change in energy of the neutron can be large.
and readily measured. A study of the energy of scattered neutrons thus provides a
direct method of studying lattice dynamics.

Thermal neutrons have velocities of the order of $3 \times 10^5$ cm/sec. The time that
these neutrons take to cover the distance 3 Å is $\approx 10^{-13}$ sec, which is of the same order
as the characteristic time of atomic vibrations. Hence, they can notice the atomic
motions in their passage through a crystal and provide a method for studying a lattice
dynamics. If the nuclei have zero spin and no isotope, the scattering of neutron waves
interfere with the scattering from others. The interference part of the scattering is
called coherent scattering and both elastic and inelastic scattering can give rise to it. If
the nuclei composing the lattice have a spin or exist in more than one isotopic state,
because of their random distribution, the different nuclei scatter independently and part
of both elastic and inelastic scattering is incoherent.

2.5.2.1 Inelastic Neutron Scattering

Scattering of a neutron, which involves a change in its initial energy as a result
of emission, or absorption of one or more phonons is called inelastic scattering.
However, it is only the one-phonon scattering which gives us information about the
frequency distribution function and the dispersion relation. Inelastic coherent scattering
leads directly to the information of phonon dispersion relations, while a study of
inelastic incoherent scattering determines directly the frequency distribution function
of the scattered. Hence, by measuring the energy distribution of neutrons, which are
incoherently scattered through a certain angle, the frequency spectrum (phonon density
of states) of scattered can be determined. The intensity of inelastic coherent neutron
scattering is proportional to the space and time Fourier Transforms of the time-
dependent pair correlation function, $G(r,t) =$ probability of finding a particle at position
‘r’ at time ‘t’ when there is a particle at \( r = 0 \) and \( t = 0 \). For inelastic incoherent scattering, the intensity is proportional to the space and time Fourier Transforms of the self-correlation function, \( G_s(r,t) \) i.e. the probability of finding a particle at position ‘r’ at time ‘t’ when the same particle was at \( r = 0 \) at \( t = 0 \).

2.5.2.2 Elastic Neutron Scattering

By elastic scattering are implied those scattering processes, such as Bragg reflections, in which neutron energy remains unaltered. Elastic coherent scattering studies lead to information about the structure of the crystal, including information about the magnetic state of the crystal. Elastic incoherent scattering does not give any direct useful information, though its temperature variation gives information about the validity of any model for the frequency distribution function. The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, \( G(r) \) i.e. the probability of finding a particle at position ‘r’ if there is simultaneously a particle at \( r = 0 \).

2.5.3 Raman Scattering

Raman spectroscopy is one of the most powerful, versatile and fascinating tools for the investigation of matter. It is the measurement of the wavelength and intensity of in elastically scattered light from molecules. It is possible for the incident photons to interact with the molecules in such a way that the energy is either gained or lost so that the scattered photons are shifted in frequency. Such inelastic scattering is called Raman scattering. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A lot of intensity of scattered light versus energy difference is a Raman
spectrum. Raman scattering occurs due to the change in polarizability during the molecular vibrations. The change is described by the polarizability derivative \( \frac{\partial \alpha}{\partial Q} \), where \( Q \) is the normal coordinate of the vibration. The selection rule for a Raman-active vibration emphasizes that there be a change in polarizability during the vibration and it is given as,

\[
\frac{\partial \alpha}{\partial Q} \neq 0
\]  \hspace{1cm} (2.32)

For polarizable molecules, the incident photon energy can excite vibrational modes of the molecules, yielding scattered photons, which are diminished in energy by the amount of the vibrational transition energies. From group theory, it is straightforward to show that if a molecule has a center of symmetry, vibrations, which are Raman active, will be silent in the infrared, and vice versa.

\[
I_{\text{Raman}} \propto \left( \frac{\partial \alpha}{\partial Q} \right)_0^2
\]  \hspace{1cm} (2.33)

Scattering intensity is proportional to the square of the induced dipole moment i.e. to a good approximation Raman scattering occurs from zero-wavevector phonons. However, to the extent that the phonon wavevector differs from zero, phonon selection rules will deviate from the zero-wavevector rules and will depend on the angle between the direction of propagation of the incident and scattered light. For "optical phonons," which have zero dispersion at the zone center, any direction dependence in the Raman shift is quite small. On the other hand, for the "acoustic phonons," which have a linear dispersion near the zone center, the angular dependence of the Raman shift is more pronounced.
A spectral analysis of the scattered light under these circumstances reveals spectral satellite lines below the Rayleigh scattering peak at the incident frequency. Such lines are called "Stokes lines". If there is significant excitation of vibrational excited states of the scattering molecules, then it is also possible to observe scattering at frequencies above the incident frequency as the vibrational energy is added to the incident photon energy. These lines, generally weaker, are called “anti-Stokes lines”.

Numerically, the energy difference between the initial and final vibrational levels, $\bar{\nu}$, or Raman shift in wave numbers (cm$^{-1}$), is calculated by,

$$\bar{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}$$

in which $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. The Stokes and anti-Stokes spectra contain the same

![Energy level diagram for Raman scattering](image)

**Figure 2.2:** Energy level diagram for Raman scattering: (a) Stokes Raman scattering (b) Anti-Stokes Raman scattering.

The ratio of anti-Stokes to Stokes intensity at any vibrational frequency is a measure of temperature. The energy of a vibrational mode depends on
molecular structure and environment. Atomic mass, bond order, molecular substituents, molecular geometry, and hydrogen bonding all affect the vibrational force constant, which, in turn dictates the vibrational energy. Vibrational Raman spectroscopy is an extraordinarily versatile probe into a wide range of phenomena ranging across disciplines from physical biochemistry to materials science.

2.5.4 Infrared Scattering

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra. For a molecule to absorb infrared radiation (IR), the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The intensity of an infrared absorption band $I_{IR}$ depends on the change of the dipole moment $\mu$ during this vibration:

$$I_{IR} \propto \left( \frac{\partial \mu}{\partial Q} \right)^2$$  \hspace{1cm} (2.35)

The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule, the radiation will be absorbed, causing a change in the amplitude of molecular vibration. The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations with two main categories of stretching and bending. For simple systems, the atoms can be considered as point masses, linked by a 'spring' having a force constant $k$ and following Hooke's Law. Using this simple approximation, the equation shown below can be utilized to
approximate the characteristic stretching frequency (in cm$^{-1}$) of two atoms of masses $m_1$ and $m_2$, linked by a bond with a force constant $k$:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$  \hspace{1cm} (2.36)

Where, $\mu = m_1m_2 / (m_1+m_2)$ (termed the “reduced mass”), and $c$ is the velocity of light.

In order to be IR active, vibration must cause a change in the dipole moment of the molecule. In general, the larger the dipole change, the stronger is the intensity of the band in an IR spectrum. One selection rule that influences the intensity of infrared absorptions is that a change in dipole moment should occur for a vibration to absorb infrared energy. Molecular asymmetry is a requirement for the excitation by infrared radiation and fully symmetric molecules do not display absorbance in this region unless asymmetric stretching or bending transitions are possible.

### 2.5.5 Brillouin Scattering

Raman scattering from low-energy acoustic phonons is known as Brillouin Scattering. Brillouin scattering is a powerful and promising probe to study the surface and bulk acoustic phonons as well as magnetic excitations in opaque solids and the elasticity of materials at extreme conditions [22]. Brillouin light scattering is generally referred to as inelastic scattering of an incident optical wave field by thermally excited elastic waves in a sample. From a strictly classical point of view, the compression of the medium will change the index of refraction and therefore lead to some reflection or scattering at any point where the index changes. From a quantum point of view, the process can be considered as interaction of light photons with acoustic or vibrational quanta (phonons). Brillouin spectroscopy is an experimental method of performing such velocity measurements on small samples of high-pressure phases. The Brillouin
spectrum of light scattered from thermal phonons contains, in its shift, the phase
velocity of sound and, in its line width, the acoustic absorption. Brillouin scattering
manifests as extra phonons, at low energy. The essential difference between Raman
and Brillouin scattering is the sensitivity of the "Brillouin shift" to the relative angle of
scattering. Brillouin scattering is a nondestructive light scattering technique, which
allows for extracting all necessary information from exceptionally small samples. The
properties obtained by Brillouin techniques include, but are not limited to, a full set of
single crystal elastic moduli, aggregate bulk and shear moduli, and density as a
function of pressure. Due to the requirements of such small samples, Brillouin
scattering experiments can be readily combined with the Diamond Anvil Cell (DAC)
or high-temperature cells to obtain high-pressure and/or high-temperature data.

2.5.6 X-ray Scattering

X-rays are tools with a very wide field of application. Traditionally,
experimental determination of lattice dynamics is the domain of inelastic neutron
scattering, but the restrictions on sample size imposed by the technique relegated the
achievable information to low or at most moderate pressures (~10 GPa).
Characterizing the effect of pressure on the propagation of elastic wave is instead
singularly important of understanding elasticity, mechanical stability of solids, material
strength, inter-atomic interactions, and phase transition mechanism. The elastic
properties and the sound wave anisotropy of hexagonal metals at high pressure are
experimentally investigated by Inelastic X-ray Scattering (IXS). This technique allows
the collection of the phonon dispersion curve and is particularly well suited for extreme
conditions. X-rays, originally a tool for structural investigations and imaging purposes,
are nowadays successfully applied in many ways in an enormously broad field:
materials science, biology and medicine among others. Another advantage is the accessible range in energy and momentum transfer, particularly advantageous in the study of noncrystalline matter [23]. Furthermore, elements having too large absorption or incoherent cross sections for neutrons can be investigated.
### References


