Chapter 2

Preliminaries, Present Model and Method of Computations

2.1 Cohesive Energy and Lattice Vibrations

The study of the lattice vibrations is of considerable interest because several physical properties of crystal like specific heat, thermal expansion, thermal conductivity, phase transitions, and its interaction with photons, neutrons and x-rays are related to the vibrations of atoms in solids\textsuperscript{1-3}. The collective motions of atoms in solids form traveling waves called lattice vibrations which are quantized in terms of "PHONONS". In order to understand the physical properties of solids it is of interest to study the energy-wavelength relation (phonon dispersion curves) of thermal motions the atoms determined by the interatomic interactions. This chapter covers discussion on the dynamical theory and underlying physics of the lattice dynamical model used for the study of lattice dynamical properties of perovskite oxides considered in the present thesis. Besides these, a subsection is devoted for the brief discussion about the some experimental techniques, most suitable for the study of phonons.

2.1.1 Cohesive Energy

In order for a crystal to hold together, there exist attractive interactions. It is an electrostatic attraction between positive and negative charges, which is common for all solids. As the atoms come close together, their closed electron shells start to overlap, for which electrons have to be excited to higher states. The excitation to higher energy states costs energy and leads to a repulsive interaction between the atoms. The repulsive interaction dominates for short distances between atoms, while the attractive interaction dominates at large distances. The actual atomic spacing in a crystal is defined by the equilibrium where the potential energy exhibits a minimum. The cohesive energy is the energy that must be added to the crystal to separate it to neutral free atoms at rest, at infinite separation. For ionic crystals the term lattice energy is used instead; the definition is similar except that the energy is defined for relatively free ions at rest at infinite separation. The importance of cohesive energy is that it is the ground-state energy of solid, sign of which determines whether the solids will be stable or not. Its generalization to nonzero temperatures, the Helmholtz free energy, a function of volume and temperature, contains all equilibrium thermodynamic information about the solid. Depending on the
distribution of the outer electrons with respect to the ions, different binding types can occur. There are four types of interactions, which can be treated by simple models and give a good approximation to atomic distances and cohesive energies: (i) Ionic bonding (ii) van der Waals bonding (iii) Metallic bonding (iv) Covalent bonding. Crystalline solids are therefore, classified into four principal types: (a) Ionic crystals (b) van der Waals crystals (c) Metals and (d) Valency crystals.

2.2 Theoretical Formalism and Method of Computations for Lattice Vibrations

The formalism of lattice dynamics is based on the Born–Oppenheimer or adiabatic approximation. Ions are about $10^3 - 10^5$ times heavier than electrons and move much slower than the electrons. The electrons contribute an additional effective potential for the nuclear motions and the lattice vibrations are associated only with nuclear motions. However, a thorough discussion of lattice dynamics in the harmonic approximation can be found in several books and monographs on this subject, we present here a short account of the theory mainly to clarify the notations and a basis for our model. The crystal potential energy is a function of the instantaneous positions of the atoms. If $u_l^{(k)}$ is the displacement of the $k^{th}$ atom $(k = 1, 2, \ldots, n)$ in the $l^{th}$ primitive cell $(l = 1, 2, \ldots, N)$ about its equilibrium position $r_k$, for small displacement of the atoms, the crystal potential energy $\phi$ can be expanded using the Taylor expansion as follows:

$$\phi = \phi_0 + \sum_{k\alpha} \frac{\partial \phi}{\partial u_{\alpha}^{(k)}} u_{\alpha}^{(k)} + \frac{1}{2} \sum_{k\alpha} \sum_{l'\beta} \frac{\partial^2 \phi}{\partial u_{\alpha}^{(k)} \partial u_{\beta}^{(k')}} u_{\alpha}^{(k)} u_{\beta}^{(k')} + \ldots, \quad (1)$$

Where, suffices $\alpha$ and $\beta$ denote Cartesian coordinates. The cubic and higher order terms are neglected in the harmonic expansion. In the equilibrium configuration, the force on any atom must be zero. Therefore, $\frac{\partial \phi}{\partial u_{\alpha}^{(k)}} = 0$ for every $\alpha, k, l$. The tensor force constant between atoms $(lk)$ and $(l'k')$ can also be defined as:
Thus,

\[ \phi_{\alpha\beta}(l_k, l_{k'}) = \frac{\partial^2 \phi}{\partial u_{\alpha}(l_k) \partial u_{\beta}(l_{k'})} \]  

(2)

Thus,

\[ \phi = \phi_0 + \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \phi_{\alpha\beta}(l_k, l_{k'}) u_{\alpha}(l_k) u_{\beta}(l_{k'}) \]  

(3)

The equation of motion for the displacements of the \((lk)\)th atom becomes

\[ m_k \ddot{u}_{\alpha}(l_k) = - \sum_{l'k'\beta} \phi_{\alpha\beta}(l_k, l_{k'}) u_{\beta}(l_{k'}) \]  

(4)

Where \( m_k \) is the mass of the \((lk)\)th atom. The crystal periodicity suggests that the solutions of eq. (4) must be such that the displacements of atoms in different unit cells must be same apart from phase factor. The equations of motion (4) are solved by assuming wave like solutions of the type

\[ u_{\alpha}(l_k) = U_{\alpha}(k | q) \exp \left\{ i \left[ q \cdot r(l_k) - \omega(q) t \right] \right\} \]  

(5)

Here, \( U_{\alpha}(k | q) \) is the amplitude of the wave, \( q \) is the wave vector and \( \omega(q) \), the angular frequency associated with the wave. Substituting (5) in (4)

\[ m_k \omega(q) U_{\alpha}(k | q) = \sum_{k'\beta} D_{\alpha\beta}(k' | q) U_{\beta}(k' | q) \]  

(6)

Where \( r(l_k) \) is the position co-ordinate of the \((lk)\)th atom.

The dynamical matrix \( D_{\alpha\beta}(q_{kk'}) \) is given by

\[ D_{\alpha\beta}(q_{kk'}) = \sum_{l'} \phi_{\alpha\beta}(l_k, l_{k'}) \exp \left[ i \left[ q \cdot \left( r(l_{k'}) - r(l_k) \right) \right] \right] \]  

(7)

The dimension of the dynamical matrix is \( 3n \). Thus for a periodic crystal we have a set of \( 3n \) equations. The frequencies of the normal modes and eigenvectors are determined by diagonalizing the dynamical matrix:
2.2 Theoretical Formalism and Method of Computations for Lattice Vibrations

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Lattice dynamics studies of solids are usually carried out by a lattice dynamical model based on the interatomic interaction and formation of a dynamical matrix. The interatomic interactions are selected based on the type of bonding present in any solids. We describe below the brief description to calculate the different phonon properties, many time even useful to test the success of the selected interatomic potentials by comparing with available experimental data.

2.2.1 Group Theoretical Analysis

Group theoretical symmetry analysis enables a classification of phonon modes belonging to various representations enabling their direct comparisons with observed Raman and infrared scattering data. In the experiments due to the selection rules (governed by the symmetry of the system and the scattering geometry in experiments), only phonon modes belonging to certain group theoretical representations are active in typical Raman, infrared and inelastic neutron scattering experiments which enable their mode assignment. The general theoretical scheme is based on irreducible representations described in detail in refs. [3, 6]. The procedure essentially involves construction of symmetry adapted vectors, required for block diagonalizing the dynamical matrix, which yields the phonon modes belonging to a given representation.

2.2.2 Phonon Frequencies and Phonon Dispersion Relation

The solutions of eq. (8) yield the $3n$ eigenvalues of $\omega_j^2(q)$ ($j = 1, 2... 3n$). The dynamical matrix is Hermitian, therefore its eigenvalues $\omega_j^2(q)$ are real, and eigenvectors $\xi_j(q)$ are orthonormal. However, for the stability of the lattice $\omega_j^2(q)$ must be positive. The components of the eigenvectors $\xi_j(q)$ determine the pattern of displacement of the atoms in a particular mode of vibration. These yield the normal modes of vibrations characteristic of the crystal. The variation of $\omega_j^2(q)$, ($j = 1, 2... 3n$) with wave vector $q$ gives the phonon dispersion relation or phonon band structure, which is of interest to understand the physical properties of solids. Though, some of these modes are degenerate because of symmetry, in general they are distinct. The form of dispersion relation depends on the crystal structure as well as on the nature of the interatomic forces. A cyclic crystal always has three zero frequency modes at $q = 0$, which correspond to lateral translational of the crystal along three mutually perpendicular directions. These three branches are referred to as acoustic branches. The remaining ($3n -$
3) branches have finite frequencies at $q = 0$, which are labeled as optic branches. These phonons can propagate in the lattice of a single crystal as a wave and exhibit dispersion depending on their wavelength or equivalently their wave vector in the Brillouin zone.

### 2.2.3 Total and Partial Phonon Density of States and Anisotropic Thermal Expansion

From the phonon band structure $\omega_j(q)$, it is straightforward to find the corresponding density of states as it gives the information of phonons in whole Brillouin zone (BZ). In order to obtain the information about the whole phonon spectrum, Brillouin-zone scanning is necessary. Such a scanning consists in $D_{ab}\left(\frac{q}{kk}\right)$-matrix diagonalization over the three-dimensional net of wave vector

$$q = \left(\frac{a^*, b^*, c^*}{n_1, n_2, n_3}\right), \text{ at } n_1, n_2, n_3 = -N, ..., N. \text{ In total, this includes } N = (2N + 1)^3$$

points in Brillouin zone. The phonon density of states (DOS) is determined by summation over all the phonon states and is defined by

$$g(\omega) = D' \int_{BZ} \sum_j \delta(\omega - \omega_j(q)) dq = D' \int_{BZ} \sum_{jp} \delta(\omega - \omega_j(q)) dq_p$$

(9)

Where, BZ corresponds to the Brillouin zone, $D'$ is a normalization constant such that $\int g(\omega) d\omega = 1$; that is, $g(\omega)d\omega$ is the fraction of phonons which have energies within a range from $\omega$ to $\omega + d\omega$. $p$ 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. Partial atomic density of state (PDOS) shows the contribution of different atoms to phonon density of states (DOS) and therefore, it essentially helps in understanding the atomic level contribution to the total phonon DOS. It is defined as

$$g(\omega) = D' \sum_{jp} \delta(\omega - \omega_j(q)) \left| \frac{\xi_j(q)}{\sum_{jp} \xi_j(q)} \right|^2$$

(10)

For a solid at a temperature $T$, the mean number of phonons with energy $\hbar \omega_j(q)$ is given by the Bose-Einstein distribution $n_{jq}(T) = \left[ \exp\left(\frac{\hbar \omega_j(q)}{k_B T}\right) - 1 \right]^{-1}$. The mean square displacement of a single quantum mechanical harmonic oscillator,
can easily be generalized to that of a single atom in the direction $i$ as

$$
\langle u^2 \rangle = \left( \frac{\hbar}{m_\omega} \right)^2 \left( n + \frac{1}{2} \right)
$$

It can be seen from the above expression that light atoms vibrating at low frequencies exhibit large zero point motions. The off-diagonal elements can be calculated in a similar way. The thermal and zero point motion of the atoms are often described using the matrix of anisotropic temperature factors $B$. For an atom $k$, it is defined by

$$
\overline{B_{ij}}(k) = 8\pi^2 \left\langle \bar{u}_{ki} \bar{u}_{kj} \right\rangle
$$

2.2.4 Thermodynamic Functions and Specific Heat

The theory of lattice dynamics described above allows us to determine the phonon frequencies in the harmonic approximation. Anharmonic effects are relatively small at low temperature in most crystals and become more important at high temperatures. The thermodynamic properties of a crystal may be calculated in the quasiharmonic approximations. In quasiharmonic approximation the vibrations of atoms at any finite temperature are in principle, assumed to be harmonic about their mean positions appropriate to that temperature. The free energy, in three dimensional case, is a function of temperature $T$ and the volume $V$ and the equation of state is given by

$$
P = -\left( \frac{\partial F}{\partial V} \right)_T
$$

Where, $F^P(T) = \frac{K_B T}{N_t} \sum_{j p} \ln \left( 2 \sinh \left( \frac{\hbar \omega_j(q_p)}{2K_B T} \right) \right)$.

Here, $\beta_{jp} = \frac{\hbar \omega_j(q_p)}{2K_B T}$. The quantity $\hbar \omega_j(q_p)$ is the phonon energy and $\hbar = h/2\pi$ with $h$ and $\omega_j(q_p)$ as Planck constants and phonon branch at $q_p$, respectively. $K_B$ is Boltzmann's constants and $T$ is temperature. The internal energy $U$ and the entropy $S$ are given by the relations

$$
\begin{align*}
\langle u^2 \rangle &= \left( \frac{\hbar}{m_\omega} \right)^2 \left( n + \frac{1}{2} \right) \\
\overline{B_{ij}}(k) &= 8\pi^2 \left\langle \bar{u}_{ki} \bar{u}_{kj} \right\rangle
\end{align*}
$$

$$
P = -\left( \frac{\partial F}{\partial V} \right)_T
$$

$$
F^P(T) = \frac{K_B T}{N_t} \sum_{j p} \ln \left( 2 \sinh \left( \frac{\hbar \omega_j(q_p)}{2K_B T} \right) \right)
$$

$$
\begin{align*}
\langle u^2 \rangle &= \left( \frac{\hbar}{m_\omega} \right)^2 \left( n + \frac{1}{2} \right) \\
\overline{B_{ij}}(k) &= 8\pi^2 \left\langle \bar{u}_{ki} \bar{u}_{kj} \right\rangle
\end{align*}
$$
\[ U = F - T \left( \frac{\partial F}{\partial T} \right)_V = F + TS. \]  

Here, \( S(T) = \frac{1}{N_t} \sum_{jP} \beta_{jp} \coth(\beta_{jp}) - \ln(2 \sinh(\beta_{jp})) \).  

The Heat capacity is defined by \( C(T) = \frac{1}{N} \sum_{jP} \left[ \frac{\beta_{jp}}{2 \sinh(\beta_{jp})} \right]^2. \)

The relations (eq. (14), (16), and (17)) concern with the specific values per unit cell. However, the specific heat \( C_V(T) \) can also be expressed as

\[ C_V(T) = \frac{dE}{dT} = \frac{\hbar^2}{K_B T^2} \int \frac{\omega^2 \exp\left(\frac{\hbar \omega}{K_B T}\right)}{\left(\exp\left(\frac{\hbar \omega}{K_B T}\right) - 1\right)^2} g(\omega) d\omega \]

Where \( g(\omega) \) is the phonon density of states. Since the experimental measurements usually provides \( C_P \) value, which differs from \( C_V \) value at elevated temperature, the following corrections is required: \( C_P = C_V + B \beta V_m T \), where \( B \) is the bulk modulus expressed as \( B = -V(d^2V/dP)_V \), \( \beta \) is the thermal expansion coefficient and \( V_m \) is the molar volume at equilibrium.

2.2.5 Atomic Thermal Parameters and Pair Distribution Function

Atomic thermal parameters (ATP), or atomic thermal amplitudes, are determined by the expression:

\[ a_{i,\alpha\beta}(T) = \frac{1}{N_t} \sum_{jP} \frac{\hbar}{2\omega_j(q)} \coth(\beta_{jp}) e_{i\alpha}(q) e_{j\beta}(q) \]

Pair distribution function (PDF)-the probability distribution of the interatomic distances-within the quasiharmonic approximation is determined by the expression:

\[ f(R,T) = \sum_j \frac{1}{\sqrt{\pi} \sigma_j} \exp\left(-\frac{(R_j - R_j^0)^2}{\sigma_j^2}\right) \]

Here, \( R_j \) is the temperature-dependent distance between atoms \( i \) and \( j \) which is related to the static equilibrium interatomic distance \( R_{ij}^0 \) by the relation:
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\[ R_j^2(T) = R_j^2 + \sigma_j \] Where \( \sigma_j \) is the corresponding dispersion determined by the relation: \( \sigma_j = \langle u_j, u_j \rangle + \langle u_j, u_j \rangle - 2 \langle u_j, u_j \rangle \). The isotropic atomic displacement correlation is defined by the relation:

\[
\langle u^+_i u_j \rangle = \frac{1}{N} \sum_{q} \frac{\hbar}{2 \omega_j(q)} \coth(\beta_j p_j) \left( e^{i \xi_j x_j} + e^{i \eta_j y_j} + e^{i \zeta_j z_j} \right)
\]

(21)

2.2.6 Infrared and Raman intensity

It is always necessary to calculate the infrared and Raman modes at zone centre of Brillouin zone to compare with the experimental measured Raman and infrared (IR) data. Infrared intensity is proportional to the square of the oscillator strength, \( S_j = \frac{dP}{dQ_j} \), which is also associated with atomic displacements (i.e. eigen vectors) as \( S_j = \sum_i P_i S_{ij} \). Here, \( P \) is the polarization per unit cell. The corresponding contribution of the mode \( j \) to the static dielectric constant is

\[ \Delta \varepsilon = \frac{4\pi}{\lambda_j \nu_c} (\xi_j^2) \]

where \( \nu_c \) is the unit cell volume. Other important characteristics of the IR spectrum are longitudinal (LO) frequencies, which are determined using LST relation:

\[
\varepsilon(\omega) = \varepsilon^{\infty} + \frac{4\pi}{\nu_c} \sum_j \frac{(\xi_j^2)^2}{\omega_j^2 - \omega^2}
\]

(22)

The Raman scattering intensity, which is proportional to the square of the derivative \( \zeta_j = \frac{d\varepsilon^{\infty}}{dQ_j} \), is also associated with atomic displacements as \( \zeta_j = \sum_i \xi_i \varepsilon_{ji} \).

Here, \( \varepsilon_i^F = \frac{d\varepsilon^{\infty}}{dX_i} \) is the atomic derivatives of the dielectric constant.

2.2.7 Elastic Constants

The determination of the elastic constants of crystals has been of importance due to its use for the study of many properties mainly the sound velocities\(^7\)\(^8\). For any direction in a single crystal three types of sound wave may be propagated: one longitudinal and two transverse waves. These three corresponding velocities are the roots of a cubic equation called as Christoffel's equation, whose coefficients are the functions of the elastic constants and the direction cosines for the direction of propagation of the sound. In the case of a
cubic crystal there are only three independent elastic constants while for other structures the number of elastic constants is more. The elastic constant expression can be written as

\[ C_{\mu \nu} = \frac{1}{V_c} \left( V_{\mu \nu}^{\text{nn}} - \sum_j \lambda_j Q_{\mu} Q_{\nu j} \right), \] (23)

Where atomic relaxation along the normal co-ordinate is defined as

\[ Q_{j \mu} = \frac{dQ_j}{du_{\mu}} = -\frac{1}{\lambda_j} V_{j \mu} \] (24)

under \( u_\mu \) and

\[ \frac{d^2 V}{dQ_j du_{\mu}} = \sum_i V_{ij \mu} \epsilon_i. \] (25)

\[ 2.3 \text{ Interatomic Potential and Parameters Determination} \]

As it is widely accepted fact that the dominant interactions in the perovskite like compounds are ionic type, a model of rigid-ion or shell model type are the obvious choices. In the rigid ion model, the ions are treated as point charges, which are not rigid during vibrations in reality. The electric field set up by the displacements of the ions is modified by their electronic polarizability, which in turn modifies the force on them and affects the phonon frequencies. This may be described by a shell model, in which each ion is regarded as composed of a rigid or non-polarizable core and charged shell with effective charges \( X(K) \) and \( Y(K) \), respectively. In general the shell model is the extension of the rigid ion model. In the present thesis, the lattice dynamics of the perovskite oxides is carried out in the frame work of the shell model. The model is not only appropriate for the perovskite-like oxides such as high \( T_C \) superconductors and manganites because in accordance with their predominately ionicity, the interatomic interactions are represented as sums of long-range Coulomb interactions and short-range interactions but also has been quite successful in predicting the phonon properties of the perovskite oxides. In addition, it considers the ionic polarizability of the ions. In the present shell model every ion is represented by a shell coupled to a core through a harmonic force constants \( K \), and the short-range interactions between ions are represented by pair potentials of the Born-Mayor form and the total potential along with the Coulomb interactions are written as

\[ U_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + b_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) \] (26)
Where the first and second term represent the long-range Coulomb potential and Born-Mayer repulsion energies, respectively. Here, \( r_{ij} \) is the interatomic distance between atoms \( i \) and \( j \), \( Z_i \) and \( Z_j \) are the effective charges of the respective atoms, \( b_v \) and \( \rho_0 \) are the short-range potential parameters (hardness and strength, respectively) for each pair of atoms usually found by fitting to experimental data. As a first step in the present model calculation for \( \text{LaMnO}_3 \) in cubic and rhombohedral phase and \( \text{La}_0.7\text{Sr}_{0.3}\text{MnO}_3 \) in rhombohedral phase, we have transferred the O-O short-range (SR) interactions from \(^{11} \), which were successfully used for the modeling of many oxides \(^{12-14} \). The cation-anion SR potentials parameters are obtained by ensuring that the total stress and forces for the given structure vanishes. In the present study, in principle no fitting of the experimental data on phonon frequencies is done to obtain the parameters. However, it is ensured that the physically significant parameters are obtained which give nearly vanishing forces on all the atoms and right magnitude of the eigen frequencies in the harmonic approximation. For the right magnitude of the eigen frequencies guidance has been taken from the experimental \( A_{1g} \) phonon mode. The electronic polarization of the lattice is included by the shell model, in which an ion is represented by a massless shell of charge \( \gamma \) and a core of charge \( \lambda \) which are coupled by a harmonic spring constant \( K \). The free ionic polarizability is expressed by

\[
\alpha = \frac{(Y_e)^2}{K}
\]

Where \( Y \) is the dimensionless shell charges and \( e \) is the absolute value of the electron charge. To calculate the phonon properties the software LADY for lattice dynamical simulation is used \(^{15} \) which have been quite successfully used recently by us \(^{14} \). In the present case, only the oxygen ions are considered to be polarizable and the short-range interactions are restricted to only nearest neighbor shell-shell interaction.

### 2.4 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 \(^{16-19} \) 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.

2.4.1 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. 1.

![Figure 1: Scattering Geometry](image)

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 \( d^2\sigma/(d\Omega d\omega) \). 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 \( d\omega \). 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

\[
E = \hbar \omega = E_i - E_f \quad \text{and} \quad hQ = \hbar |k_i - k_f|
\]  

(28)

Here, a brief discussion on scattering of a probe is restricted to the transferred energy smaller than the photon energy \( (E << E_i) \). In this case, the momentum transfer \( hQ \) is simply connected with the scattering angle \( \theta \) by
The double-differential scattering cross section, which is expressed as

$$\frac{d^2}{d\Omega \, d\omega_f} = \left( \frac{d\sigma}{d\Omega} \right)_0 : S(Q, \omega)$$

(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 \( S(Q, \omega) \) which expresses the properties of the sample in the absence of the perturbing probe. The sophisticated form of scattering function can be given by

$$S(Q, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} \left\langle \sum_{i,j} e^{iQr_j(t)} e^{iQr_j(0)} \gamma_i \right\rangle dt$$

(31)

which describes the correlations of the scattering phases of the particles at positions \( r_j(t) \) at different times \( t \). The phase of the scattering amplitude is described by \( e^{iQr_j} \). 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, \( \gamma_n \) at different times. The dependence of the scattering phases on the term \( Qr_j \) can be used for a classification of the scattering process\(^{19} \). Thereby, the inverse of the transferred momentum \( hQ \) 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 \( Q_{\text{char}} \ll 1 \), there exists interference between the scattering amplitudes from many particles of the system. Consequently, mainly the collective behaviour 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 \( Q_{\text{char}} \gg 1 \), 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\(^{19} \) 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. (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\(^{20} \).
2.4.2 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 $(3/2)K_BT$, 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 ($= \hbar/(3m_0K_BT)^{1/2}$, 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 $\sim 10^{-13}$ 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.

2.4.2.1 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 scatterer. Hence, by measuring the energy distribution of neutrons, which are incoherently scattered through a certain angle, the frequency spectrum (phonon density of states) of scatterer 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, $G(r,t) = \text{probability of finding a particle at position } r \text{ at time } t \text{ when there is a particle at } r = 0 \text{ and } t = 0$. 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 $t = 0$. 

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2.4.2.2 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 $r = 0$.

2.4.3 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 inelastically 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 plot 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,

$$\left.\frac{\partial \alpha}{\partial Q}\right|_{Q} \neq 0 \quad (32)$$

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. Scattering intensity is proportional to the square of the induced dipole moment, i.e.,

$$I_{\text{Raman}} \propto \left(\frac{\partial \alpha}{\partial Q}\right)^2 \quad (33)$$

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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, $\nu$, or Raman shift in wave numbers ($\text{cm}^{-1}$), is calculated by,

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

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 frequency information. 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

Figure 1: Energy level diagram for Raman scattering (a) Stokes Raman scattering (b) Anti-Stokes Raman scattering.
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.

2.4.4 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:

$$I_{IR} \propto \left( \frac{\partial \mu}{\partial Q} \right)_0^2$$

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 $k$:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where, $\mu = m_1 m_2 / (m_1 + m_2)$ (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.
2.4.5 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. 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.

2.4.6 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. Furthermore, elements having too large absorption or incoherent cross sections for neutrons can be investigated.
References


