Chapter 2

Experimental Techniques for High Pressure Research and Measurement of Phonons

2.1 Introduction

The technology of high pressure generation and measurement is fast developing field. Generally, measurements in the high pressure studies become more complicated due to practical difficulties suffered by experimental studies. This arises from the fact that the high pressure can often be generated only in very small sample volumes with a container, which may affect the signal. However, in recent developments in the high pressure experimental techniques these problems have been sorted out effectively. The commercial and scientific importance of high pressure studies of the materials makes them very interesting and therefore it is essential to understand these experimental techniques, their technical advantages as well as limitations and their usefulness at both commercial and research level. In this chapter, we have reported brief survey of the experimental techniques recently being used for generation and measurement of high pressure to study phonon related properties of the materials.

In general high pressure measurement techniques may be divided in to two categories i.e. dynamic methods and static methods. The use of these methods for data acquisition and analysis has revealed many new and surprising results on high pressure behavior of the materials.

2.2 Challenges in Experimental Techniques

As mentioned earlier almost all experimental techniques suffers from few practical difficulties to which one should take care of to get better result of research work.

Therefore, it is noteworthy to discuss some of the challenges faced by these techniques in brief which are presented below.

- **The pressurizing medium**

High pressure x-ray diffraction studies are mostly done by coupling DAC, which can be used to study the crystal structure, compressibility, and pressure induced phase transition. Ideally, the pressure transmitting medium should remain fluid at high pressure since it has considerable effect within the sample chamber. To achieve this material as 4:1 methanol-ethanol mixture or silicon oil is used. However, at high enough pressure stress in the pressure chamber develops strong nonhydrostatic components and inhomogeneity since these materials becomes solid at high pressure. This can affect the diffraction pattern and cause difficulty to determine average pressure inside the chamber. The use of N_2, Ar or He can provide wide nearly isotropic and homogeneous pressure range but it requires complicated experimental set up.

However, the occurrence of nonhydrostatic pressure provides an opportunity to study the unexplored field of effect of nonhydrostatic pressure on structural stability of high pressure phases.

- **Coexistence of phases**

The coexistence of different phases has been one of the regular difficulties observed over range of pressure. The diffraction pattern then consists of peaks arising from each phase and therefore weighted mean of the diffraction patterns of the constituent phases reflects in the model of the diffraction pattern.

- **The Effect of the microstructure**

The diffraction patterns of powder samples are complicated by the effects of microstructure or texture. The forces in the DAC are applied uniaxially and nonspherical micro crystallites will tend to align with their long axes perpendicular to cell axes. This preferred orientation effect is relatively common in high pressure samples and can alter diffraction peak intensities substantially. The effect of other microstructural features such as planer defects can also be significant. In these cases, the avaibality of the two dimensional direction patterns can be useful in detecting the effect of microstructure and offers the possibility of correcting for it by for example simply averaging over the diffraction rings.

- **Site order in binary compounds**

The similarity in x-ray scattering powers of the chemical species in a binary compound often makes it difficult to distinguish between different occupations of the atomic sites which are compatible with a proposed structure. In these cases extended x-ray absorption fine structure spectroscopy can provide information on the degree of local ordering. The total energy calculation can also be significant value in determining the energies of different site occupation.

2.2.1 Dynamic Methods

To study the high pressure elastic behavior and vibrational properties of the material, most commonly dynamic methods used are ultrasonic techniques and shock wave techniques. These methods are discussed here in brief.

2.2.1 I Ultrasonic techniques

Both ultrasonic and static methods are used to study the high pressure elastic behavior of the single crystals, but ultrasonic has clear advantage over the static method of providing all elastic constants and their variation with pressure accurately compared to others.

In this method, an ultrasonic pulse.of frequency 10 to 20 MHz is generated by a quartz piezoelectric transducer and transmitted through test crystal. The reflected pulse from the rear surface of the crystal reaches back to the transducer, makes successive reflections, and detected each time. The actual physical measurement consists of the transit times by standard electronic instruments. For measurements of pressure effect, the small pressure induced charges in ultrasonic pulse transit time can be measured by automatic gated carrier pulse superposition equipment with a resolution of better than a part in 10^7. The experimental details concerning the ultrasonic methods have been given in [1]. Velocities of the longitudinal and transverse waves propagated in the specific crystallographic directions are functions of the second order elastic constants or their combinations Chang and Grahem [2] have used this method to study elastic properties of some metal oxides in the NaCl phase.

2.2.1 II Shock wave techniques

A shock wave is a propagating condensation wave in a medium, which carries a jump in state and flow variables such as pressure/stress, density, and entropy and particle velocity. Shock waves propagate at supersonic velocities in the material, typically at several kilometers per second, and can carry pressure jumps ranging upwards from a few Kb. Shock waves in materials can be generated in a variety of ways. Projectile impact is one of the most common and a variety of systems such as gas guns, electromagnetic rail guns, plasma guns and laser/fiber mini-fliers are designed to generate shock waves by impact. Intense irradiation of a material surface by laser, electron beam, and X-ray sources also generates shock waves propagating through the bulk of the material. Shock wave generation is often carried out using explosive based systems, which can generate pressure of 500 GPa and above. The pressure of similar magnitude is also produced if a solid accelerated by the detonation of some explosive is made to impinge on the sample. In either case the results is the introduction of a step pressure that propagates through the sample, and changes the shape as a result of the action of inertial forces derived from mechanical properties of the sample. This method produces dynamic pressures with time duration of the order of few micro seconds. The small time duration poses experimental problems requiring sophisticated instrumentation. The propagation of shock waves through solids is quite complicated which leads to involved data reduction procedures.

All methods of shock wave state generation involve the rapid deposition or generation of large amounts of energy in (usually) a relatively small area which goes on to rapidly disassemble under the effects of the high thermal pressure generated in the material. This feature of shock wave generation carries the added difficulty that the generated states are transient, with lifetimes of the order of millionths of a second (micro-second, ms), which poses severe constraints on diagnostic techniques. In a special shock wave, the sample should be maintained in a state of uniaxial strain for sufficient time for measurements to be completed. This is achieved by different loading systems, which are designed to apply loads over large plane areas of samples. Some important loading systems are described below, and shown schematically in figure 1. Recently Dharneshwar et al [3] have reviewed the experimental methods for generation of ultra high pressure using LASER driven shocks.

2.2.1 II (a) Contact Explosives

The first quantitative shock loading experiments were made possible by fabrication of high explosive lenses that produce plane shock waves over diameters up to about 0.3 meters. These plane wave generators (Figure 1) with various explosive pads produce pressure in Aluminum in the range of 10 to 40 GPa under relatively routine conditions.

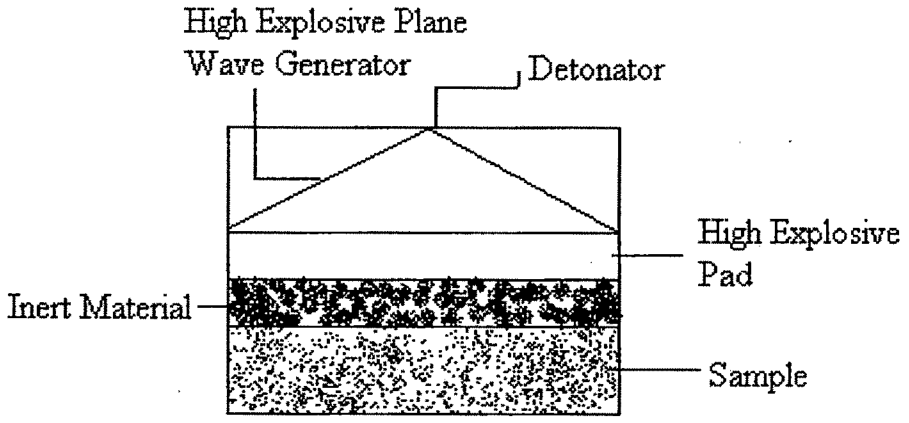

Figure 1: Direct contact high explosive

Pressure imparted to the sample depends upon the particular explosive materials and mechanical impedance of the sample. In these methods, it is difficult to vary input pressure in small increments and there is also lack of control on pressure release. These utilize flyer or projectile impact as described below.

2.2.1 II (b) Flyer Plates Techniques

Figure 2 shows the plane wave generators with explosive to accelerate flyer plates to high velocities. AA separation of the explosive from the flyer plate by a thin plastic insert or thin air space protects the flyer plates form damage.

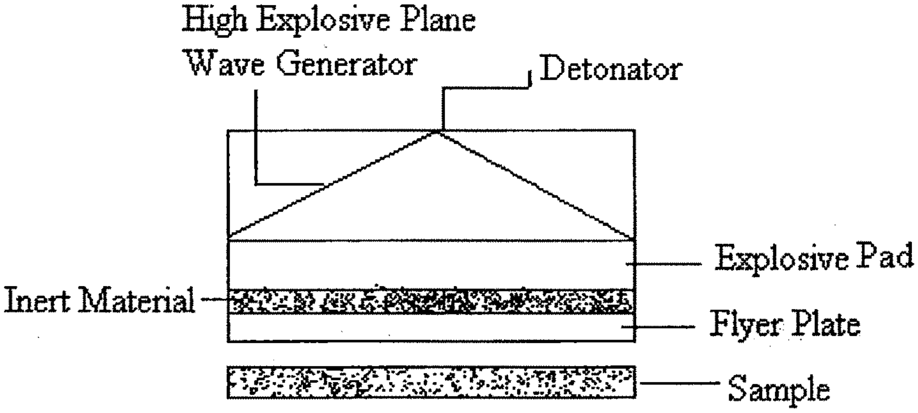

Figure 2: Explosively accelerated flyer plate

Typical impact velocities achieved by this technique range from 1 to 7 km/sec and produce 10 to 100 GPa pressure. Aluminium systems of this type have been described by Queen et al [4].

2.2.1 II (c) Projectile Impact Technique

In this method figure 3 (a), a precisely dimensioned projectile is faced with the desired impacting material. It is smoothly accelerated in vacuum through a distance of many projectile lengths and allowed to strike its target in a plane impact with precise alignment of impacting surface. Compressed gases or propellants are used to accelerate projectiles to the desired velocities. In a two stage gas gun, hot gases from gun powder detonation drive the piston, which compresses hydrogen gas in the pump tube. The high pressure hydrogen then break the rupture valve and accelerates a 20g metal impactor against a target sample of velocities up to 8 km/sec. Impact velocity is directly measured by flash x-ray method. Nearly 100 GPa pressure is produced when the impactor (Aluminium projectile) strikes Aluminium target [5].

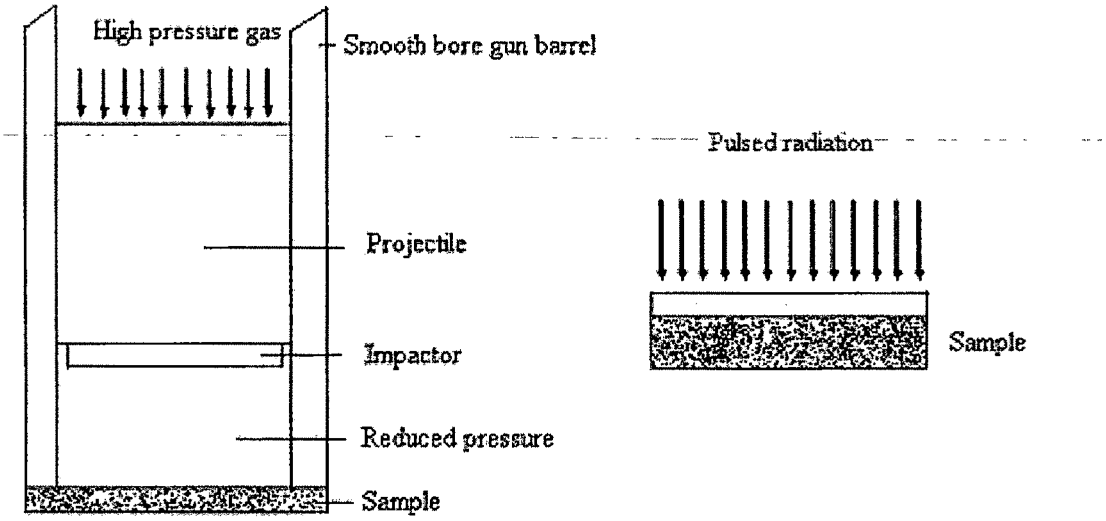

Figure 3: (a) Precisely Controlled Projectile Impact and (b) High intensity pulsed lasers or electron beams

There are several other techniques for producing very high pressure such as pulsed radiation from Laser, underground nuclear explosion, electric rail guns and magnetic compressions etc. [6]. The principle of the pulsed radiation technique is illustrated in figure 3 (b). When intense radiation pulse from lasers or electron beams are directed on a target, they are absorbed and a thin layer of the target material is ablated which drives a shock into the material producing large stresses and high temperature.

2.2.1 III Measurement Techniques

Most of our knowledge about shock induced effects is derived from measurements of shock and particle velocities produced by well controlled loading. The shock wave techniques involve measurements of shock velocities determined by detecting times of arrival of the wave at two or more wave stations at known locations. In these experiments, arrival times are to be determined with few nanoseconds to achieve suitable accuracy in the derived shock velocity. Resistivity measurements have been of limited value owing to the complications of the environment. These are serious limitations on the type of information that can be obtained by this technique. So far, attempts have been made mostly to obtain the equation of state of solids from the experimental shock wave data. For these reasons, the shock wave techniques do not enjoy the popularity of other high pressure techniques, even though shock wave technique can produce extremely high pressures. The details of this technique can be found in reference [7].

2.2.2 Static Methods

The static methods allow the measurements to be carried out under purely hydrostatic conditions. Sufficient time to attain thermodynamic equilibrium under isothermal conditions is available for static measurement. Hence, the conditions assumed in the theoretical calculations are experimentally achieved in these methods. With the recent refinements in the diamond anavil cell technique the range of pressure in static experiments has been increased up to 550 GPa.

2.2.2 I Piston Cylinder Method

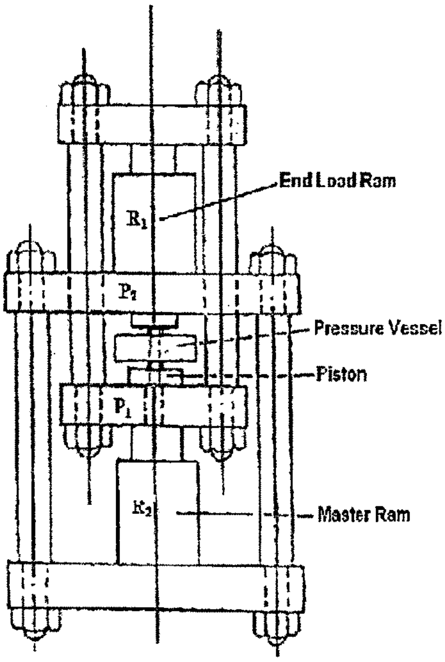

Figure 4: Piston cylinder method.

Bridgmann [8-9] used a piston cylinder apparatus for compressibility measurement, which is one of the useful devices for this purpose. The apparatus consists of tungsten carbide laterally supported by axial load. The sample is placed in the cylindrical chamber and pressure is applied on it with the help of tungsten carbide piston. Generally, to generate pressure of few thousand atmosphere single stage pump is sufficient. A pressure multiplying device known as an intensifier can be used to produce high pressure. P.C intensifier consists of two hydraulic rams figure 4. The ram at the top R1 carries the platen P1. The pressure vessel is clamped between the platen P1 and P2. The ram R1 is operated such that the tungsten carbide supports the entire load.

The sample in the pressure vessel is pressurized by forcing a tungsten carbide piston in to the pressure vessel. At the same time ram, R2 provides the necessary load. Sufficient care must be taken while designing high pressure equipment by adjusting the field strength of the vessel material according to stress on the inner surface of the vessel when limiting pressure is reached. To achieve this non viscous fluid can be used as a transmitting medium for the pressure up to 3 GPa, while sample can be enclosed in a thin sheet of some soft material such as indium which can act like pseudo liquid to create approximately hydrostatic pressure when applied pressure exceeds 10 GPa [10].

2.2.2 II Diamond Anvil Cell Technique (DAC)

In order to examine material behavior at high pressure it is necessary to generate high pressure states in the material. The most flexible tool in this area is the diamond anvil cell, which is very widely used, in academic research because of the comprehensive range of diagnostics, which have been developed for it. The development of diamond anvil cell technology has resulted in tremendous gains in knowledge of the physical world through scientific investigation of the behavior of matter under a wide range of pressures. In earth and planetary sciences, laboratory experiments utilizing high pressure and temperature offer the only means to examine directly the conditions of deep planetary interiors. Fundamental questions about phase transformations, crystal structure, and the nature of atomic bonding can be answered using high-pressure techniques. Finally, the use of high pressure to synthesize new materials, to study the behavior of existing materials and to tune material physical properties provides tremendous potential for advances in applied materials research.

Diamond, in addition to being recognized as the hardest and least compressible material, has the important property of being transparent to most of the spectrum of electromagnetic radiation, including γ-ray, X-ray, portions of ultraviolet, visible, and most of the infrared region. The DAC is based upon the opposed-diamond configuration, in which a sample is placed between the polished culets of two diamonds and is contained on the sides by a metal gasket. In this configuration, very little force is required to create extremely high pressures in the sample chamber, and, because of the transparency of diamond, the sample may be examined in situ (while at elevated pressure) by optical microscope, spectroscope (Raman, Infrared, Brillouin), and diffraction techniques. For fabricating DAC the cut, color, clarity and carat are four most important characteristics.

Color in diamond is due to the absorption band in the visible range, arising as a consequence of the characteristics impurities (aluminium, nitrogen etc.). Nearly colorless, light brown or light yellow diamonds are acceptable from the point of view of strength. However for the spectroscopic experiments in the visible region optically transparent diamond is essential. The clarity of the diamond is important for its use in optical spectroscopy. An important feature that is crucial for achieving ultrahigh pressure is the shape of the diamond anvil. A perfectly circular culet (for pressure up to 60 GPa) or a beveled culet (for ultrahigh pressure) is the most reliable requirement. Trench fabrication in the conical surface, close to the culet, is expected to arrest the gasket material flow and hence to enhance the pressure sustaining capability of the diamond anvils (DAs).

It is observed that under loading, the pressure increase sharply from the culet center, where it maximizes. Above a certain pressure limit, a part of the applied load is used up in deforming DAs. The simulation work indicates that under uniaxial stress, a mechanical instability sets in at 550 GPa [11, 12]. Under loading, once the deformation is initiated, the anvil in the central part starts cupping. Further increase in the load increases the cupped area as well as the stress around the remaining part of culet, which is an annulus. When this annular area becomes small and is around the edge only the DA fails due to chipping. The introduction of a bevel in the DA is an important landmark in the enhancing the pressure sustaining capability of diamond anvils, since bevels postpone the cupping of the DA.

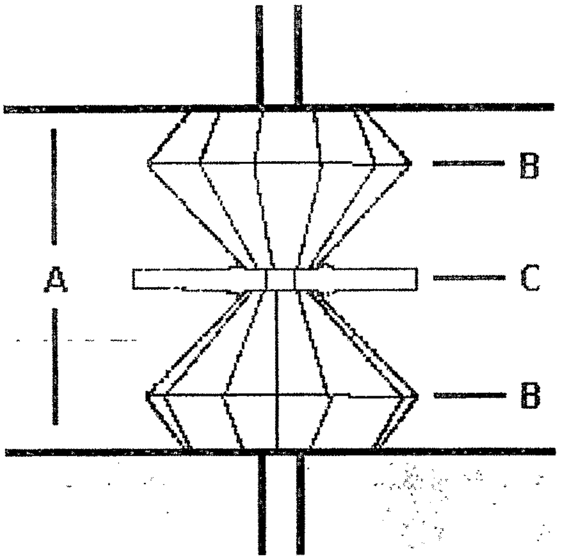

Figure 5: Opposed diamond anvil configuration with a metal gasket for sample confinement in a pressure medium. A) Diamond supports B) Diamond anvils C) Inconel gasket

The diamond anvils are skillfully cut from natural, gem quality stones to have 16 pavilion facets, a 70% table, and a working surface (culet). The anvils are cut to correct crystallographic orientation [table and culet parallel to the (100) diamond plane] and care is taken to insure parallelism of the table and culet. The culet of the diamond anvil is typically 0.6 mm in diameter. This size insures that pressures of up to 20 GPa (GPa = 10 Kbar = 10,000 bar = 9,870 atm) can be achieved (depending upon the choice of DAC). To perform studies to higher pressures, diamonds cut with smaller, beveled culets are recommended. The selection of diamond type and culet size should be based upon the experimental techniques, which are to be employed, and the maximum pressure to be achieved.

The basic principle of DAC is depicted in Figure 5. Here a metal gasket is compressed between the culets of the DAs. The gasket has a central hole that is filled with a pressure transmitting medium, the sample to be investigated, and the pressure calibrant, such as ruby chip. Since the area of culet is very small, a modest load of 10^4 N is sufficient to generate a pressure in excess of 100 GPa. For achieving success in DAC experiment, the gasket hole must be centered accurately with respect to the culet center. Use of gasketing material is also important to avoid compressive yielding.

The introduction of gasket into the DAC is very important development in the history of the DAC. The gasket reduces the magnitude of pressure gradients and confines the sample, pressure calibrant, and pressure transmitting medium. Gasket also provides an additional support to the DAs, thereby enhancing their pressure sustaining capability. Generally, hardened stainless steel is used as gasket. The gasket is required to before indented before hole drilling. This reduces the deformation of the hole during compression. After preindentation, a hole is drilled in the center of the gasket. The preindentated gasket with a central hole is then mounted on to the piston diamond. Single crystal or powdered samples are loaded in the gasket hole. Six major type of DAC are:

1. NBS Cell
2. Mao Bell Cell
3. Hubber Syassen Holzapfel Cell
4. Basset Takahashi stook Cell
5. Le Toullec Pinceaux Loubeyre Cell
6. Merril Basset Cell

2.2.2 III Pressure Scale and Pressure Calibration

It is not possible to calculate the pressure directly by measuring the applied load. It is so because the distribution of the load over the anvil is unknown. In the lower range, pressure can be measured by a free piston gauge and then with secondary gauges such as the Resistivity gauges [13, 14]. By using a quasi free piston, method pressure can be measured up to 7.7 GPa. Those materials that undergo phase transition in this range can be used as pressure calibrant. All measurement of static pressure above 7.7 GPa depend on the equation of state of materials. Once it is known using x-ray measurement, volume can be found and hence pressure.

Using Brillouin scattering, the sound velocity U, can be measured and using the equation measurement of pressure can be attempted [15].

$$P_2 - P_1 = \int_1^2 \left(\frac{\gamma_S}{U_S} \right) dP \qquad (1)$$

A rapid and convenient method of pressure measurement uses ruby fluorescence shift. Piermarini et al [16] tied the ruby scale to the variation of the V/V_0 of NaCl via the Dekker EOS [17] and showed that it is linear up to 19 GPa. Reduction of the intensity of ruby fluorescence at high pressure is the major problem with this technique. At 100 GPa, the intensities of R-lines decrease so much that they become comparable tot that of an R_3 line. It can be noted that above 100 GPa the R_3 line and R_1 and R_2 combined have similar intensities.

2.3 Measurement of Phonons

The thermal diffuse scattering of x-rays by the atomic vibration of a crystal and the coherent, inelastic scattering of thermal neutrons by one phonon processes permit the determination of the frequencies of individual normal modes of the perfect crystal. Similarly experiments involving the absorption or scattering of light by crystals containing impurity of atoms or defects can provide the frequencies of various types of exceptional vibrational modes induced by these impurities and defects. The frequencies of exceptional, impurity induced normal modes of crystal can also be observed in the phonon side bands to the absorption or emission spectra associated with electronic transition at impurity centers in crystal.

Spectroscopy is an analytical technique arising from the interaction of a species with electromagnetic radiation. The electromagnetic radiation absorbed, emitted or scattered by the molecule is analyzed. Typically, a beam of radiation from a source such as a laser is passed through a sample, and the radiation exiting the sample is measured. For example, in vibrational absorption spectroscopy, by varying the frequency of the radiation, a spectrum can be produced, showing the intensity of the exiting radiation for each frequency. This spectrum will show which frequencies of radiation have been absorbed by the molecule to raise it to higher vibrational energy states. Each molecule will have its own characteristic spectrum, making spectroscopy indispensable in analytical chemistry.

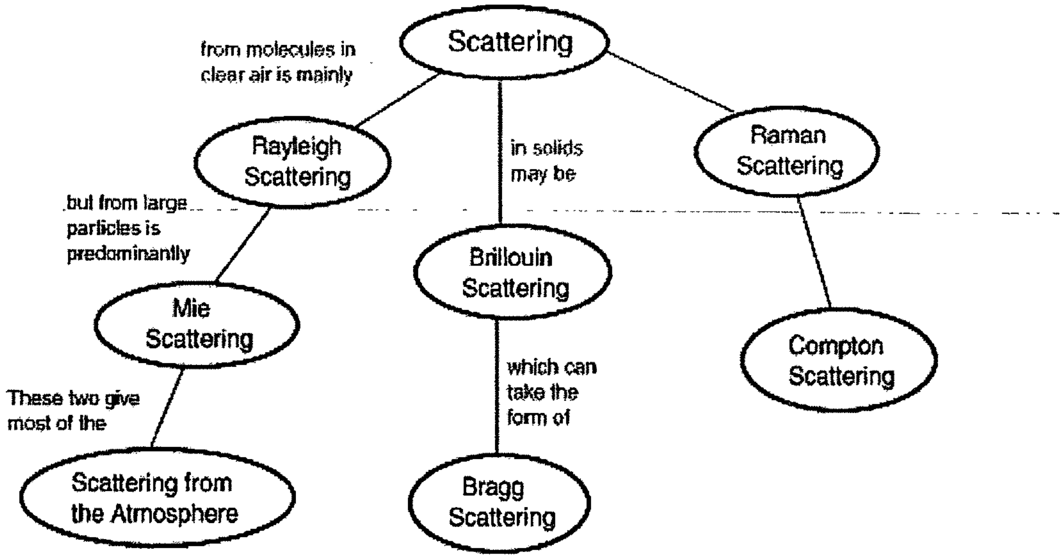

Figure 7: Schematic diagram of types of scattering

Consider a light wave as a stream of photons each with energy hν. When each photon collides with a molecule, many things may happen. However, we briefly discuss below three main measurement techniques being widely used to study the phonon dynamics at high pressure.

2.3.1 Raman Scattering

The Raman Effect is an inelastic scattering of light by elementary excitations of matter. When a photon interacts with a medium, it can be scattered in one of the three ways: a) it can be elastically scattered and thus retain its incident energy (Rayleigh scattering), this scattering is responsible for the blue color of the sky; it increases with the fourth power of the frequency and is more effective at short wavelengths. b) It is also possible for the incident photons to interact with the molecules in such a way that energy is either gained or lost so that the scattered photons are shifted in frequency i.e. photon can be inelastically scattered by quasi-particle excitations of the medium, thereby either giving energy to the medium (Stokes scattering) or, c) removing energy from it (anti-Stokes scattering). Such inelastic scattering is called Raman scattering.

Thus, the Raman Effect involves a coupling between incident photons and the quasi-particle excitations such as phonons (lattice vibrations), magnons and electronic single particle or collective excitations within a sample, which results in the emission of light from the sample which is shifted in frequency from the incident "excitation" light. The phenomenon was discovered in 1928 by Sir Chandrasekhera-Venkata Raman who was awarded the 1930 Nobel Prize in physics for this discovery and for his systematic exploration of the phenomenon.

In the Raman, scattering a photon is scattered inelastically by crystal with creation or annihilation of a phonon or magnon. The process is identical to the inelastic scattering of x-rays and similar to the inelastic scattering of neutron by a crystal. The selection rules for the first order Raman effect are

$$\omega = \omega' \pm \Omega \; ; \qquad \mathrm{k} = \mathrm{k}' \pm \mathbf{K} \tag{2}$$

Where ω, k refer to the incident photon; k' refer to scattered photon and Ω, **K** refer to the phonon created or destroyed in the scattering event. In the second order Raman Effect, two phonon are involved in the inelastic scattering of the photon.

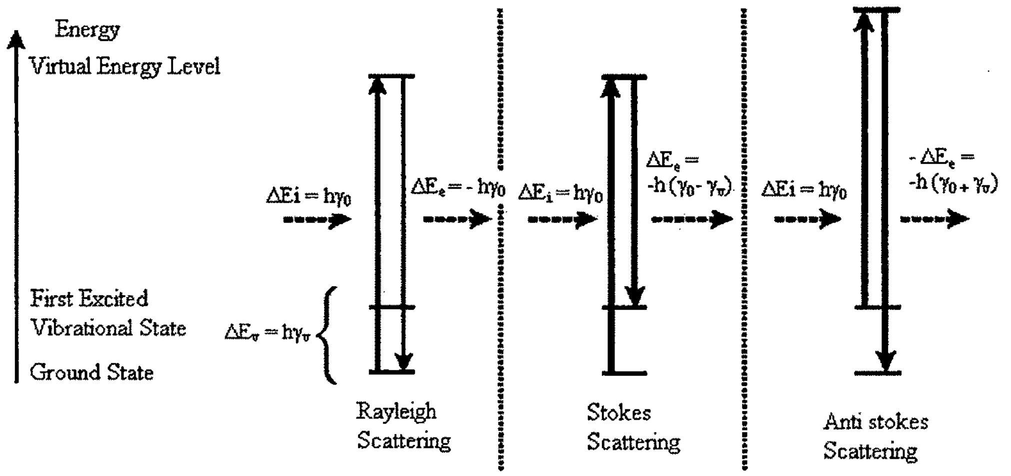

Figure 8: Schematic representation of energy level in Raman scattering

Raman spectroscopy is an excellent probe to investigate the low energy elementary excitations in materials as well as to characterize their structural, electronic, vibrational, and magnetic properties. It is interesting to elucidate the physics governing the mechanisms driving the properties of new materials like carbon nanotubes, silicon nanowires, etc. Raman spectroscopy is also used in combustion diagnostics. Being a completely non-intrusive technique, it permits the detection of the major species and temperature distribution inside combustors and in flames without any perturbation of the (mainly fluid dynamic and reactive) processes examined. Stimulated Raman transitions are also widely used for manipulating a trapped ion's energy levels, and thus basis qubit states, in ion trap quantum computing. Raman spectroscopy has found some application in remote monitoring for pollutants. For example, the scattering produced by a laser beam directed on the plume from an industrial smokestack can be used to monitor the effluent for levels of molecules, which will produce recognizable Raman lines.

In Raman scattering, an intense monochromatic light source (laser) can give scattered light, which includes one or more "sidebands" that are offset by rotational and/or vibrational energy differences. This is potentially very useful for remote sensing, since the sideband frequencies contain information about the scattering medium, which could be useful for identification. Current projects envision Raman scattering as a tool for identification of mineral forms on Mars. Such remote sensing could become a major tool in planetary exploration. As far as the pressure effect on phonon dynamics is concerned, it can be observed by the peaks shift and appearance and disappearance of the peaks.

2.3.2 Brillouin Scattering

Scattering of light from acoustic modes is called Brillouin scattering. 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 one of interaction of light photons with acoustic or vibrational quanta (phonons). Two examples will provide some context for this phenomenon. From a quantum point of view, Brillouin scattering is considered to consist of interaction of light photons with acoustic or vibratinal quanta (phonons).

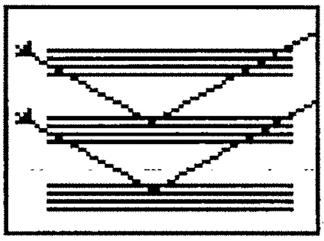

Figure 9: Bragg type Brillouin scattering from standing wave acoustic modes

When acoustic standing waves are produced in a solid, they create a periodic condition which can scatter light waves according to the Bragg law. In addition to its application to x-ray diffraction, the Bragg law applies to some cases of light scattering from acoustic standing wave modes in a solid. This is an example of Brillouin scattering. It is used in acousto-optic modulators. Benedek, et al., reported the production of sidebands from the interaction of a helium-neon laser with water. This can be considered to be Brillouin scattering. The first theoretical study of the the light scattering by thermal phonons was done by Mandelstam in 1918 (*see Fabelinskii, 1968; Landau et al, 1984*), however, the correspondent paper was published only in 1926 (*Mandelstam, 1926*). L. Brillouin predicted independently light scattering from thermally excited acoustic waves (*Brillouin, 1922*). Later Gross (1930) gave the experimental confirmation of such a prediction in liquids and crystals.

The principles of the Brillion scattering can be explained briefly as follows:

2.3.2 I Elasto-optical scattering mechanism

In the case of a transparent solid, most of the scattered light emanates from the refracted beam in a region well away from the surface, and the kinematic conditions relating wave vector and frequency shift of the light pertain to bulk acoustic wave scattering (Fabelinskii, 1968; Hayes, W. and R. Loudon, 1978; Grimsditch, 2001). The scattering in this case is mediated by the *elasto-optic scattering mechanism*, in which dynamic fluctuations in the strain field bring about fluctuations in the dielectric constant, and these in turn translate into fluctuations in the refractive index. These fluctuating optical inhomogeneities result in inelastic scattering of the light as it passes through the solid.

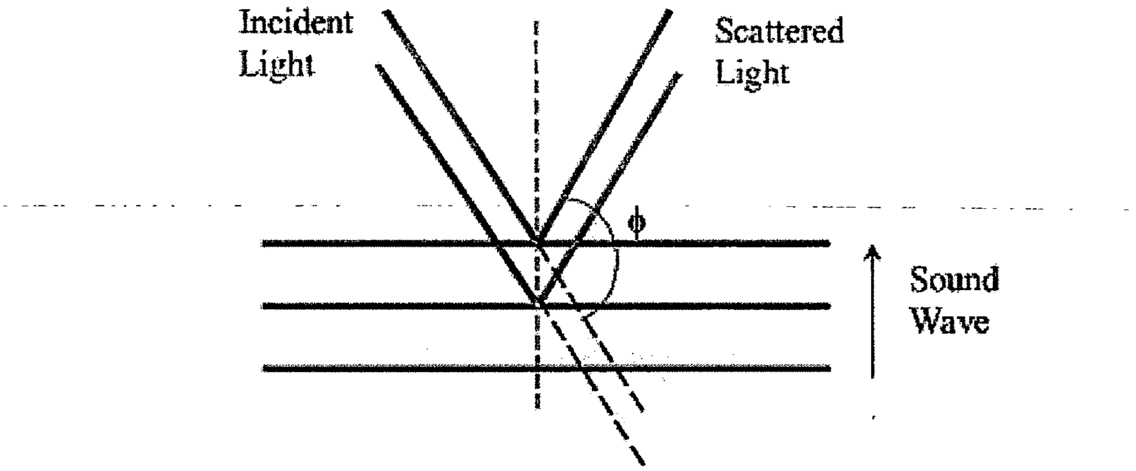

Figure 10: Schematic representation of Interaction of the sound waves with light.

The phonons present inside a solid move in thermal equilibrium with very small amplitudes creating fluctuations in the dielectric constant, which is viewed as a moving diffraction grating by an incident light wave. Therefore, Brillouin scattering can be explained by the two concepts of Bragg's reflection and Doppler shift:

- SBS can be viewed as a Bragg's reflection of the incident wave by the diffraction grating created by thermal phonons. According to the Braggs law, the grating spacing d can be expressed in terms of Braggs angle ($\varphi/2$)and wavelength of the laser light inside solid $\lambda = \lambda o / n$, λ_o where λ_o is the laser wavelength in vacuum, and n is the index of refraction in the solid.

$$2d \sin(\varphi/2) = \lambda o / n \qquad (3)$$

- The moving grating scatters the incident light with a Doppler effect, giving scattered photons with shifted frequencies Δf. Brillouin spectrum gives frequency shift (Δf) of the thermal phonon, and its wavelength (d space) can be determined from the experiment geometry (see expression above). Then the velocity of the phonon V_l has a form

$$V_l = \lambda_o \Delta f \,/\, (2\, n \sin \varphi/2) \qquad (4)$$

For back scattering configuration, $\varphi = \pi$, this equation yields

$$V_l = \lambda_o \Delta f \,/\, (2\, n) \qquad (5)$$

2.3.2 II Ripple Mechanism

Unlike the elasto-optic effect, this mechanism does not occur in the bulk but at the surface of the specimen *(Mutti et al, 1995; Comins, 2001, Beghi, 2003).* The phonons present at the surface of the sample move in thermal equilibrium with very small amplitudes creating corrugation of the surface, which can diffract incident light.

The moving corrugating surface scatters the incident light with a Doppler effect, giving scattered photons with shifted frequencies. For backscattering from surface acoustic phonons, the phase velocity (V_{SAW}) of surface acoustic wave can be written as

$$V_{SAW} = \lambda_o \Delta f \,/\, (2 \sin \theta) \qquad (6)$$

Where, θ is the angle between the incident laser beam and the normal to the surface.

Surface Brillouin Scattering (SBS) is a non-contact measurement technique that exploits light scattering to probe the properties of surface acoustic waves (SAWs), either at the surface of homogeneous solids or in thin supported layers. The near-surface elastic properties of solids often differ markedly from those of the underlying bulk material. They are a sensitive indicator of residual stress, annealing and other near-surface physical conditions. SBS is widely used in the characterization of thin (sub-micron) supported layers, whose elastic properties can differ from those of the corresponding bulk material. It can alternatively be exploited to measure other properties, like the layer thicknesses or mass density, or the presence of interfacial layers. The systems that have been studied to date are many and diverse, and include inorganic materials like silicon and silicides, a variety of carbonaceous materials like diamond, CVD diamond and diamond-like films, various types of hard coatings like carbides and nitrides, Langmuir-Blodgett films, and various types of multilayer. SBS can probe acoustic waves of frequencies up to 100 GHz and characterize films of thickness as thin as a few tens of nanometers.

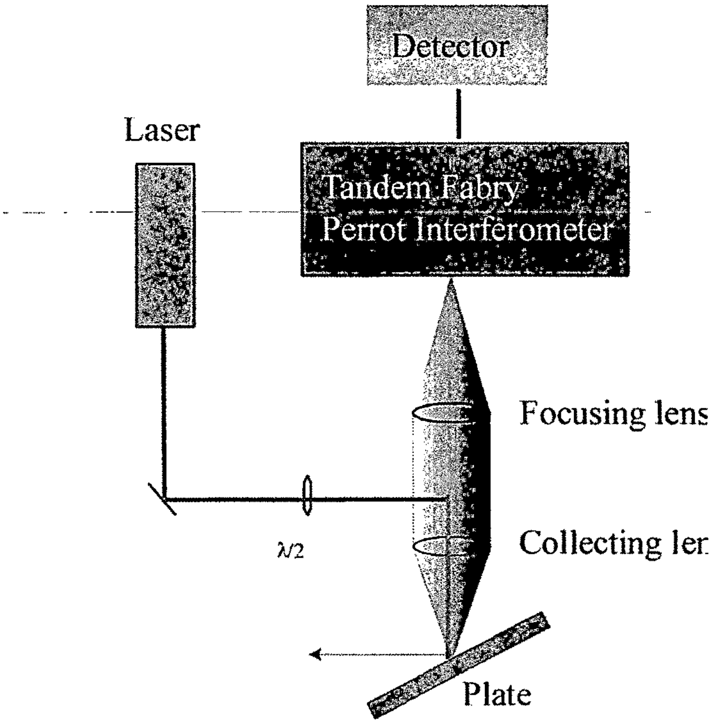

Figure 11: Sketch of the Brillouin spectrometer.

In almost Brillouin experiments, the Fabry-Perrot interferometer has been instrument of choice (Grimsditch,—2001). However, conventional Fabry Perot interferometers do not achieve the contrast needed to resolve the weak Brillouin doublets. Sandercock first showed that the contrast can be significantly improved by multipassing (Sandercock, 1970). The usefulness of coupling two synchronized Fabry-Perot, thus avoiding the overlapping of different orders of interference, was also recognized (Sandercock, 1982).

For intense beams (e.g. laser light) traveling in a medium, the variations in the electric field of the beam itself may produce acoustic vibrations in the medium via electrostriction. The beam may undergo Brillouin scattering from these vibrations, usually in opposite direction to the incoming beam, a phenomenon known as **Stimulated Brillouin Scattering** (SBS). For liquids and gases, typical frequency shifts are of the order of 1–10 GHz (wavelength shifts of ~1–10 pm for visible light). Stimulated Brillouin scattering is one effect by which optical phase conjugation can take place. This phenomenon was first described by Leon Brillouin (1889-1969).

2.3.3 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) KBT, where KB is the Boltzmann constant. Corresponding to room temperature (T ~ 300 K) this energy is ~ 0.04 eV. Such neutrons represent an excellent probe for two reasons: (i) the de Broglie wavelength of such neutrons (= h/(3m0KBT)1/2, where m0 is the mass of neutron) is of the same order as the interatomic distance in crystals (~ 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 x 10^5 cm/sec. The time that these neutrons take to cover the distance 3 Å is ≈ 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.

2.3.3 I 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.

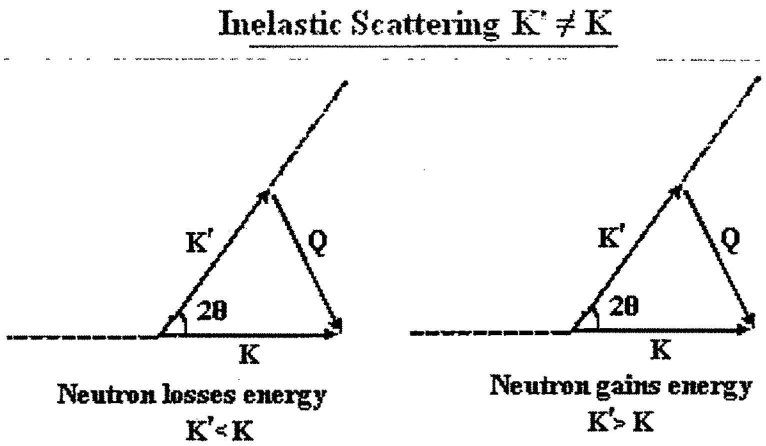

Figure 12 (a): Schematic diagram for inelastic neutron scattering.

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 $t = 0$.

2.3.3 II 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.

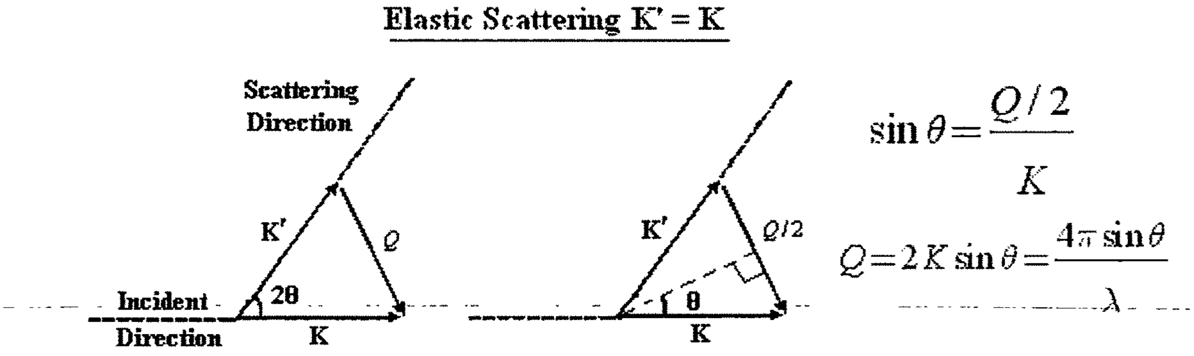

Figure 12 (b): Schematic diagram for inelastic neutron scattering

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.

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