Chapter II

High Pressure Resistivity
“Basics and Measurement Technique”
CHAPTER-2
HIGH PRESSURE RESISTIVITY: “BASICS AND MEASUREMENT TECHNIQUE”

2.1 INTRODUCTION

Of all the physical variables, pressure spans the largest range of over 60 orders of magnitude in the universe, from the non-equilibrium “pressure” of hydrogen gas in intergalactic space \(10^{-31}\) atm to the pressure at the centre of neutron star \(10^{28}\) atm. In classical thermodynamics, pressure couples the volume of a system to its free energy. The relative stability of a phase is a predictive goal of material science and is determined by the minima of free energy surface. Therefore, pressure is a powerful tool for probing material properties that depend strongly on volume. However, the high-pressure study in solid state physics has been kept untouched until the Bridgman era (from 1910 to 1950). Percy W. Bridgman (who got the noble prize in 1946 for his contribution towards high-pressure work) was the first person to study materials under pressure [1]. His most important contribution was the invention of special seal and use of sintered Tungsten Carbide in place of hardened stainless steel. Harry George Drickamer (1918-2002) started the study of materials under pressure using UV-Vis spectroscopy and Mössabauer spectroscopy [2].

**Hydrostatic Pressure**

Pressure is defined as force per unit area. However, when we apply force on a body, we generate stress (also defined as force per unit area). Under certain special conditions, we call the stress as ‘hydrostatic pressure’ [3]. When an external force (load) is applied on a solid body, the state of stress in the solid body is expressed by the stress tensor. Stress is a physical quantity that expresses the internal forces that neighbouring particles of a continuous material exert on each other. Stress inside a body may arise by various mechanisms such as reaction to external forces applied to the bulk material or to its surface (like contact forces, external pressure or friction). Quantitatively the stress is expressed by the Cauchy traction vector \(T\) defined as the traction force \(F\) between adjacent parts of the material across an imaginary separating surface \(S\) divided by the area of \(S\). In a fluid at rest the force is perpendicular to the surface.
and is the familiar pressure. In a solid or in a flow of viscous liquid, the force $F$ may not be perpendicular to $S$, hence the stress across the surface must be regarded a vector quantity not a scalar. Moreover, the direction and magnitude generally depend on the orientation of $S$. Thus the stress state of the material be described by a tensor called the Cauchy’s stress tensor which is a linear function that relates the normal vector $n$ of surface $S$ to the stress $T$ across $S$. With respect to any chosen coordinate system, the Cauchy stress tensor can be represented as a symmetric matrix of $3 \times 3$ real numbers. Even within a homogeneous body, the stress tensor may vary from place to place and may change over time, therefore the stress within a material is in general a time varying tensor field. In general the stress $T$ that a particle $P$ (assumed) applies on another particle $Q$ (assumed) across a surface $S$ can have any direction relative to $S$. The vector $T$ may be regarded as the sum of two components, the normal stress perpendicular to the surface and the shear stress that is parallel to the surface. If the normal unit vector $n$ of the surface is assumed fixed, the normal component can be expressed by a single number the dot product $T.n$. This number will be positive if $P$ is pulling on $Q$ (tensile stress) and negative if $P$ is pushing against $Q$ (Compressive stress), The shear component is then the vector $T-(T.n)n$. In some situations the stress within a body may adequately be described by a single number or by a single vector (a number and a direction), three such simple stress situations that are often encountered are uniaxial normal stress, the simple shear stress and isotropic normal stress.

Fig. 2.1 shows a common situation with a simple stress pattern when a straight rod with uniform material and cross section is subjected to tension by opposite forces of magnitude $F$ along its axis. If the system is in equilibrium and not changing with time (the weight of the rod can be neglected) then through each transverse section of the bar the top must pull on the bottom part with the same force $F$, therefore the stress throughout the bar across any horizontal surface can be described by $\sigma = F/A$, where $A$ is the area of cross section. With the assumption that the stress is evenly distributed over the entire cross section. In practise depending on how the bar is attached at the ends and how it was manufactured, this assumption may not be valid then the value $\sigma = F/A$ will be only the average stress.
Fig. 2.1: (a) Idealized stress in a straight bar with uniform cross-section. (b) The ratio $\sigma = F/A$ may be only an average stress. The stress may be unevenly distributed over the cross section (m–m), especially near the attachment points (n–n).

Another simple type of stress occurs when the material body is under equal & isotropic compression or tension. In these situations the stress across any imaginary internal surface turns out to be equal in magnitude and always directed perpendicularly to the surface independent of the surface’s orientation, this type of stress may be called isotropic normal stress or isotropic stress. If it is compressive it is called hydrostatic pressure. The representation of this type of stress on a cube is shown in Fig. 2.2.

Fig. 2.2: Isotropic tensile stress. Top left: Each face of a cube of homogeneous material is pulled by a force with magnitude $F$, applied evenly over the entire face whose area is $A$. The force across any section of $S$ of the cube must balance the forces applied below the section. In the three sections shown, the forces are $F$ (top right), $F\sqrt{2}$ (bottom left), and $F\sqrt{3}/2$ (bottom right); and the area of $S$ is $A$, $A\sqrt{2}$ and $A\sqrt{3}/2$, respectively. So the stress across $S$ is $F/A$ in all three cases.
Often mechanical bodies experience more than one type of stress at the same time (combined stress) whose magnitude is maximum for surfaces perpendicular to a certain direction \( d \) and zero across surfaces parallel to \( d \). Biaxial stress can be viewed as the sum of two normal or shear stresses. For triaxial stress, the magnitude is nonzero across every surface element. Fig. 2.3 shows the components of stress in three dimensions.

![Fig.2.3: Components of stress in three dimensions](image)

Combined stresses cannot be described by a single vector. The material is not stressed in the same way throughout the volume of the body, the stress across any imaginary surface will depend on the orientation of that surface in a non-trivial way. However Cauchy observed that the stress vector \( T \) across a surface will always be a linear function of the surface’s normal vector \( n \) of the unit length vector perpendicular to it, i.e. \( T = \sigma(n) \) where the function \( \sigma \) satisfies:

\[
\sigma(\alpha u + \beta v) = \alpha \sigma(u) + \beta \sigma(v)
\]

for any vector \( u \) and \( v \) and for any real number \( \alpha \) and \( \beta \) the function \( \sigma \) now called the Cauchy stress tensor completely describes the stress state of a uniform body. The stress tensor can be represented in any chosen coordinate system by a 3x3 matrix of real numbers.

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix}
\]

[2.1]
consequently the stress vector $T = \sigma(n)$ across a surface with normal vector $n$ with coordinates $n_1,n_2,n_3$ could be represented as

$$
\begin{bmatrix}
T_1 \\
T_2 \\
T_3 
\end{bmatrix} =
\begin{bmatrix}
\sigma_{11} & \sigma_{21} & \sigma_{31} \\
\sigma_{12} & \sigma_{22} & \sigma_{32} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix}
\begin{bmatrix}
n_1 \\
n_2 \\
n_3
\end{bmatrix}
$$

[2.2]

The linear relation between $T$ and $n$ follows from the fundamental laws of conservation of linear momentum and static equilibrium of forces and is therefore mathematically exact for any material and any stress situation. The principle of conservation of angular momentum implies that the stress tensor is symmetric, that is $\sigma_{12} = \sigma_{21}, \sigma_{13} = \sigma_{31},$ and $\sigma_{23} = \sigma_{32}$. Therefore, the stress state of the medium at any point and instant can be specified by only six independent parameters:

$$
\sigma_{ij} = S_{ij} + P\delta_{ij}
$$

[2.3]

Where the elements $\sigma_{22}, \sigma_{33}$ are called the orthogonal normal stresses (relative to chosen coordinate system) and $T_{21}, T_{31}, T_{12}, T_{32}, T_{13}, T_{23}$ are called orthogonal shear stresses. When we consider a stress tensor $\sigma_{ij}$ on body, the stressed body tends to change both its volume and its shape, The stress tensor that tends to change the volume of the body is called mean hydrostatic tensor or volumetric stress tensor and that tends to distort the body is called stress deviator tensor. Thus total stress tensor can be expressed as the sum of both the components namely the hydrostatic tensor and the deviatoric stress tensor [4-6] expressed as

$$
P = 1/3\sigma_{KK} = 1/3(\sigma_{11}+\sigma_{22}+\sigma_{33})
$$

[2.5]

and $S_{ij}$ is the deviatoric stress tensor, the product $P\delta_{ij}$ is known as hydrostatic stress tensor, can be represented as follows:
Where \( \sigma_m = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \)

and

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix}
= 
\begin{bmatrix}
\sigma_m & 0 & 0 \\
0 & \sigma_m & 0 \\
0 & 0 & \sigma_m
\end{bmatrix}
+ 
\begin{bmatrix}
S_{11} & S_{12} & S_{13} \\
S_{21} & S_{22} & S_{23} \\
S_{31} & S_{32} & S_{33}
\end{bmatrix}
\]

\[ \text{[2.6]} \]

2.1.1 Units of Pressure

One atmospheric pressure is defined as the pressure exerted by 76 mm column of Hg. The SI unit of pressure Pascal (Pa), defined as 1 Pa = 1 N/m\(^2\), is a very small unit compared to atmospheric pressure. Relation between various units of pressure is given as 1 bar = 10\(^5\) Pa = 10\(^6\) dynes/cm\(^2\) (1 atmosphere = 1.01325 bar). MPa (10\(^6\) Pa) and GPa (10\(^9\)). Conversion relations are 1 MPa = 10 bar, 1 GPa =10 Kbar and 1 TPa = 10 Mbar (mega bar).

2.2 High Pressure Generation Devices

P.W. Bridgman (1882-1962), the father of high pressure research, introduced most of the fundamental concepts, built and tested the basic types of apparatus that are being used now. For his effort he was awarded the Nobel Prize for Physics in 1946. Since the beginnings of high pressure techniques many different pressure devices have been developed. In order of their development, basic devices are (1) piston-cylinder (2) Bridgman anvil or opposed anvil (3) the belt and (4) multiple anvils. The origin of the piston-cylinder apparatus are lost in antiquity, but some important adaptations of it for high pressure high temperature use are still present. Opposed anvil devices are the invention of Percy W. Bridgman and widely known as Bridgman anvil devices. The belt and multiple-anvil presses were devised by H. Tracy hall.

All the static high pressure generating devices can be basically divided into two categories-

a) Piston Cylinder
b) Opposed Anvils
a) **Piston Cylinder Devices**

The simplest possible piston cylinder apparatus consist of two opposed pistons compressing the sample in a single walled cylinder. Pistons are generally constructed of cemented tungsten carbide. Pressure capabilities of this device can be changed by providing external support to both, the piston and the cylinder. The cylinders are generally of multiring design. By using a suitable pressure transmitting fluid (silicon oil, methanol-ethanol mixture) hydrostatic pressure up to ~8GPa can be achieved. These are used for high pressure electrical resistivity, optical studies and compressibility of fluids.

b) **Opposed Anvil Devices**

The opposed anvil devices work on the principle of massive support. The principle is a laboratory analogue of the tapered foundation design. The taper reduces the large working stresses quickly to tolerable levels. By applying high enough load on the larger area (loading face) of the anvil, a large stress is generated at the smaller area (working face). The Opposed Anvil devices are used to generate pressure up to 25GPa. Apart from using for material synthesis, they can also be used for a variety of measurements such as electrical resistivity, X-Ray diffraction etc. The Diamond anvil cell also comes under this category, through which one can achieve very high pressure and can be used for electrical resistivity, thermoelectric power X-ray diffraction, optical studies, Laser Raman, Mössbauer spectroscopy.

A gasket is used firstly to house the sample and the pressure transmitter, and secondly to convert the stress into hydrostatic pressure in the sample region. Generally for Electrical Resistivity measurements with WC pyrophyllite (hydrous aluminium silicate) is used as the gasket material and steatite (hydrous magnesium silicate), MgO, AgCl, Talc is used as pressure transmitting medium for generating quasi-hydrostatic pressure.

The basic high pressure apparatus have been instrumented in numerous ways to study a great variety of phenomena. Considerable ingenuity has been used by many researchers for high – pressure measurements like Differential Thermal Analysis (DTA) [7], Mössabauer effect[8], Diffusion [9], Manganin
gauge pressure measurements [10], Time of flight[11], Optical measurements [12], X-ray Diffraction [13], Cryogenic Techniques [14], Nuclear Magnetic Resonance and Electron Spin Resonance [15], Thermal Conductivity [16]. The work of Jayraman, Eremets Dunstan and Spain are good references for various high pressure devices, theories and applications [17-20].

To generate quasi hydrostatic pressure opposed anvil devices are mostly used, the basic design of anvil is shown in fig. 2.4.

![Fig. 2.4: Shape of Gasket after Compression](image)

Designing of opposed anvil device depends on the following factors:

(a) **The Property of Material Used**

The material of the anvil should sustain the pressure to be generated therefore should be very hard material. Depending on the size, price, strength, transparency to radiation and other physical properties, various materials such as steel, tungsten carbide, Sapphire, Cubic Zirconia and diamond have been used in high pressure anvils. In high pressure apparatus the maximum pressure is limited by the plastic flow strength of these materials and maximum pressure is determined by the compressive strength of the anvils to withstand the tension. Most popular anvil materials used are following:

(i) **Diamond**: As the hardest material diamond is ideal for high pressure generation. The highest thermal conductivity and transparency over wide electromagnetic spectrum range spanning IR, VIS, UV and X-ray range also makes it ideal for high pressure spectroscopic experiments. Cryogenic related research and to observe directly a phase transformation...
taking place at high pressure using a microscope. Due to its various advantages diamond anvil cell (DAC) is the most extensively used device, where pressure can be achieved in laboratory up to 560 GPa [21].

(ii) **Tungsten Carbide:** Extreme hardness of tungsten carbide with hexagonal structure makes it useful in manufacturer of cutting tools, abrasives and bearings, as a cheaper and more heat – resistant alternative to diamond. The tungsten carbide opposed anvil type apparatus consists of two anvils made up of “ cemented carbide” or tungsten carbide with 6 % Co. Tungsten carbide is a brittle material with a high compressive strength[20].These are used for electrical resistivity measurements under high pressure.

(iii) **Sapphire:** Sapphire has desirable optical properties to transmit wavelength from 150 to 6000 nm because the strength of sapphire when thinned is useful at wavelength close to their transmission limits.

(b) **Massive Support Factor (MSF)**

The opposed anvil technique is based on the principle of massive support. In case of gasketed anvil an expression for maximum pressure generated under massive support is derived in terms of the geometric parameters, the strength of the anvil material and the gasket properties. In particular for a given maximum pressure it is possible to calculate the taper angle, the taper height and the gasket thickness (equation 2.8) from the derived expression. Fig. 2.5 illustrates the massive support factor of anvil.

![Fig. 2.5: Illustrating the Massive support factor](image-url)
The general expression for maximum pressure generated at the center of the gasket is

\[ P(0, 0) = S \left( \frac{b}{a} \right)^2 (GA) \]  \[2.8\]

Where \((GA) = \frac{1}{2} a^2 B \left[ \exp(Ba) - Ba^{-1} \right]^{-1} \)

\(P(0, 0)\) is pressure at center of anvil, \(S\) is compressive strength of the anvil and \(2a\) is the diameter of working face of anvil while \(b\) is overall diameter of anvil, \((GA)\) is the interaction term between the anvil and gasket known as gasket amplification factor which approaches unity for a very thin gasket. Thus maximum pressure generated at the center is just the product of the compressive strength of the anvil and the ratio of the squares of the overall and working face diameter. Hence by reducing the anvils working face diameter, pressure can be increased. However the pressure between the anvils is not uniform and maximal pressure at the center of anvil may be much higher than the mean pressure over the anvil. Bridgman introduced a gasket into the cell Fig.2.6 so that material squeezed between the anvils is not extruded completely even at the highest pressures. The high pressure volume, the part of the gasket with the sample and high pressure medium is supported by the gasket made of plastic or compressible material [22].

Fig.2.6:(a) Schematic representation of a contact of a spherical indenter with a plane base (b) The pressure distribution corresponded to the contact shown in fig. (a)
(c) **Tapering Angle**

The yielding or the failure of the anvil is function of tapering angle. Generated pressure is much greater when the anvils are made in the form of truncated cone because the loaded area is supported by the surrounding material [Fig.2.5], this support is greater when the angle of the cone is larger, the limiting case of massive support is realized in hardness measurements when the compressed volume of a material is supported by a half space of the material [23]. The expression for the massive support factor of anvil can be given as

$$MSF = (a + Z_b \cot \alpha / a)^2$$

Where $Z_b$ = tapered height, $\alpha$ = tapering angle

Fig.2.7 is indicates that while the yielding load increases with decreasing tapering angle, it is independent of the length of straight portion for a given load.

![Fig.2.7: Illustration of the effect of tapering angle](image-url)
(d) Gasket

The use of gasket for the containment of a hydrostatic medium as well as of the sample was first demonstrated by Van Valkenburg in 1965. A gasket is a mechanical seal that fills the space between two objects generally to prevent leakage between two objects while under compression. In general metallic half-hardened stainless steel with thickness 0.25 to 0.20 mm are popular for high pressure measurements. A hole (200 µm in diameter) is drilled at the center of the indentation made by the anvil face to provide the room for the sample.

The performance of a high pressure device with gasket is largely affected by the nature of the gasket material and its geometry, therefore considerable attention has been given to the behaviour and properties of the gasket under various stress conditions. For electrical resistivity measurements pyrophilite gasket is used. Pyrophilite is kind of aluminium silicate mineral (Al₂SiO₃) with small compressibility, low strength and good thermal and electrical insulation enhancing its uses as gasket material. In general the gasket performs four functions:

1. It yields at a sufficiently low load to allow the compression of the contents of high pressure chamber [Deformation in gasket is quite commonly seen during high pressure experimentation].
2. It confines the material being compressed.
3. It provides stress distributions such that stress gradients are reduced to acceptable values, the inner edge of the gasket is subjected to the full pressure generated in the chamber while the outer edge is at atmospheric pressure.
4. It provides electrical insulation to the sample [24].

Thickness of the gasket

Apart from the gasket material, the geometric dimensions of the gasket particularly the gasket thickness influence the gasket performance. An attempt is made to understand this behavior from the theory of elastic and plastic deformation. The gasket yields and gives a quasi-hydrostatic environment to the sample. Considering pyrophilite to be homogeneous, isotropic non-porous and
plastic subjected to a compressive load parallel to its axis one can calculate the load \((L)\) essentially concentrating in the hydrostatic region as:

\[
L = \pi P_h \left[ a^2 - \frac{ah}{\mu_c} \right] \ln \left( \frac{K}{\mu_c} \right)
\] \[2.9\]

Here symbols represent the following parameters:

- \(L\) = load exerted on anvil
- \(P_h\) = Pressure generated on the gasket of thickness \(h\)
- \(a\) = radius of working face diameter of anvil
- \(\mu_c\) = Combined coefficient of friction between gasket and anvil
- \(K\) = ratio of axial stress and yielding stress of material.

**Fig.2.8:** Change in pressure distribution within the gasket with increasing thickness of gasket.

**Fig.2.9:** Schematic representation of the distribution of pressure at different places within the gasket.
Fig. 2.8 shows the distribution of pressure at different values of initial gasket thickness. All gaskets with an initial thickness $h_i$ will reduce to $h_c$ (critical thickness $h_c$ is the thickness of gasket on which the plastic flow region reaches near the centre). It was found that for a given load, the final gasket thickness (optimum thickness required for the measurement) is a function of initial gasket thickness ($h_i$) that is $h_f = h_i$ for $h_i < h_c$ and $h_f = h_c$ for $h_i \geq h_c$. Thickness of the gasket is reduced by rubbing it on an Emery paper piece with the index finger in such a manner that ‘8’ shape is maintained Whole time of rubbing [17]. Fig.2.9 is showing the change in pressure distribution within the gasket with increasing thickness of gasket.

**Quasi Hydrostaticity**

For converting stress into hydrostatic pressure we transmit the external load to the body via a fluid medium. But when the pressure transmitting medium is not a fluid, then there will be some finite deviatoric stress components and the state of the body would be quasi hydrostatic. Generally steatite (hydrous component magnesium oxide), silver chloride AgCl, talc or petroleum jelly is used as the pressure transmitting medium for generating quasi hydrostatic pressure and reducing the pressure gradient [25]. Others are 4:1 Methanol ethanol mixture for room temperature and Ar, He, $H_2$, for low temperature measurements.

### 2.3 Measurement of Pressure

There are two categories of Pressure Measurements:

1. **Primary Method**
2. **Secondary Method**

#### 1. Primary method

Primary methods are based on fundamental equation relating pressure to other physical quantities whose measurements would determine the pressure.

i) The fundamental equation relating Pressure ($P$) to the force ($F$)

$$ P = \frac{F}{A} $$

By knowing load and area we can determine Pressure
ii) The thermo dynamical formula.

\[ P = - \left( \frac{\delta H}{\delta V} \right) T \]

Where \( H \) is Helmholtz function \( H = U - TS \), \( V \) is volume & \( T \) is absolute temperature of the system. Determinations of these quantities would evaluate pressure.

2. **Secondary method**

   It is based on the systematic variation of any physical property of a material with pressure. Generally two techniques were used:

   (a) Ruby fluorescence method.  
   (b) Fixed point method.

**a) Ruby fluorescence Method**

Forman [26] first showed that the R lines of Cr\(^{3+}\) doped Al\(_2\)O\(_3\) (ruby lines) shift linearly with hydrostatic pressure in the range of 1-22 Kbar and that the R lines broaden if the ruby experiences non-hydrostatic stresses. Further work by Barnett, Block and Piermarini [27] has made the ruby fluorescence technique a very rapid and convenient method for the measurement of pressure. A small chip (~5-10\(\mu\)m) of ruby introduced in the pressure chamber is excited by a suitable laser (Ar-ion, He-Cd or He-Ne). The fluorescence spectrum detected with an optical spectrometer, contains two well-defined peaks (R1-6928A) & (R2-6992A) which shift to higher wavelengths with increasing pressure. Ruby fluorescence technique is valid up to 200 kbar. The shift of the ruby fluorescence lines has been calibrated against standard substances to construct a pressure scale.

**b) Fixed Point Method**

Several materials undergo phase transitions under pressure accompanied with well marked changes in their physical properties such as electrical resistivity, volume, specific heat, *etc.* These transition points can be used as fix points for pressure calibration. In general pressure generated at room temperature are calibrated against the well known phase transition of bismuth, Mangnin *etc.*
Phase transition of Bi is shown in Fig.2.9. The resistance jumps across the phase transitions corresponding to 25Kbar, 27 Kbar and 77 Kbar.

![Fig.2.9: Phase Transition of Bismuth](image)

### 2.4 Effect of High Pressure on Electrical Resistivity

Pressure like temperature is an important thermodynamic variable. Application of pressure is the cleanest way to decrease the interatomic distances in solids, resulting changes in bond lengths, bond angle and even the nature of the bonding. The effect of pressure on materials can broadly be classified into two categories. One is the lattice compression and the other electronic structure change. However these two categories are not totally independent. The decrease in interatomic distance or increase in the density leading to changes in the phonon spectra, increase in the free energy (G) and the associated phase transitions stabilizing compact structures characterised by significant changes in the physical properties come under “lattice effects”. As the atoms are brought closer by the application of pressure, the lattice becomes stiffer and more incompressible as the atoms have to overcome stronger repulsive potentials. As the lattice becomes stiffer under high pressure, the Debye temperature $\theta_D$, defined as the temperature above which all the modes of lattice vibrations are excited, also increases leading to changes in the phonon spectra. As a result, significant changes in the bulk properties, such as, transport properties and
specific heat are expected. The free energy of a solid is given by the expression: 
\[ G = E - TS + PV \]
Here, \( E \) is the internal energy, \( T \) is the temperature and \( S \) entropy. A minimum \( G \) stabilizes a crystal structure at ambient conditions. But the free energy of solid increases with pressure, and at higher pressure, the minimum free energy criterion for the parent structure may not be satisfied. In this case, the system may undergo phase transition to a new structure which satisfies the minimum free energy criterion.

Although pressure has its strong impact on many properties of material, we will focus here on the Electrical resistivity of materials under high pressure. Before trying to understand the particular sample behaviour we here present a general concept about the electrical resistivity of material and its measurement technique at ambient conditions as well as at high pressure.

No property of solids varies as widely as their ability to conduct electric current. Copper, a good conductor, has a resistivity of \( \rho = 1.7 \times 10^{-8} \, \Omega \cdot \text{m} \) at room temperature, whereas for quartz a good insulator, \( \rho = 7.5 \times 10^{17} \, \Omega \cdot \text{m} \), more than 25 order of magnitude. If in a constant electric field \( E \) there are \( n \) electrons of charge \( q = -e \) per unit volume, the electric current density can be represented as

\[
J = nqv = ne^2\tau E/m \quad [\text{v} = -eE\tau/m]
\]

This is ohm’s law. Time \( \tau \) describes the relaxation time depending on magnitude of electric field. The electrical conductivity \( \sigma \) defined by \( j = \sigma E \) is related to \( \tau \) as

\[
\sigma = ne^2\tau/m
\]

The electrical resistivity \( \rho \) is defined as the reciprocal of the conductivity, so that

\[
\rho = m/ ne^2\tau \quad [2.11]
\]

The electrical resistivity of most metals is dominated at room temperature (300 K) by collisions of conduction electrons with lattice phonons and at liquid helium temperature (4K) by collisions with impurity atoms and mechanical imperfections in the lattice. The rate of these collisions is often independent to a
good approximation, so that if the electric field were switched off the momentum distribution would relax back to its ground state with the net relaxation time

$$1/\tau = 1/\tau_L + 1/\tau_i \quad [2.12]$$

Where $\tau_L$ and $\tau_i$ are the collision times for scattering by phonons and by imperfections respectively. The net resistivity is given by

$$\rho = \rho_L + \rho_i \quad [2.13]$$

Where $\rho_L$ is the resistivity caused by thermal phonons and $\rho_i$ is the resistivity caused by scattering of the electron waves by static defects that disturb the periodicity of the lattice. Often $\rho_L$ is independent of the number of defects when their concentration is small, and often $\rho_i$ is independent of temperature. This empirical observation expresses the Matthiessen’s rule, which is convenient in analyzing the experimental data. The residual resistivity $\rho_i(0)$ is the extrapolated resistivity at 0K because $\rho_L$ vanishes as $T \rightarrow 0$. The lattice resistivity at $\rho_L = \rho - \rho_i(0)$ is the same for different specimens of metal, even through $\rho_i(0)$ may itself vary widely. The resistivity ratio of a specimen is usually defined as the ratio of its resistivity at room temperature to its residual resistivity.

### 2.4.1 Effect of temperature on Resistivity of materials

Variation in resistivity with temperature depends only on the relaxation time. With increase in temperature, the collisions between free electrons and ions become more frequent. As a result of this relaxation time decreases and hence the resistivity increases. Thus, resistivity of a metallic conductor increases with increase in temperature and vice versa.

### 2.4.2 Effect of Pressure on Resistivity of materials

The electrical resistivity of metal can be written in terms of collision time as

$$\rho = m/ ne^2 \tau \quad [2.14]$$

where $n$ = number of free electrons per unit volume, $e$ = electronic charge, $m$ = mass of electron. In the above expression $m$ and $e$ are insensitive to pressure where $n$ increase with pressure. The number of free electrons remain unchanged,
but the volume $V$ decreases with pressure leading to increase in $n = N/V$. As the lattice becomes stiffer at high pressure, the Debye temperature $\theta_D$ also increases leading to changes in phonon spectra. Hence in general resistivity of a material should decrease with pressure.

2.5 Measurement of Electrical Resistivity

Many conventional methods for measuring resistivity are unsatisfactory for semiconductors because metal-semiconductors contacts are usually rectifying in nature. Also there is generally minority carrier injection by one of the current carrying contacts. The excess concentration of minority carriers affects the potential of other contacts thus modulates the resistance of materials. The two probe method is the simplest way to perform resistance measurements [Fig. 2.10(a)] in two-lead technique there is an error in the resistance measurement due to addition of lead resistance in the measurement. Four-lead measurement eliminates the effect of lead resistance in the measurement [Hall 1967]. In four-lead method [Fig. 2.10(b)] ideally no current will pass through the voltage leads, as the internal resistance of the voltmeter would be very high. Therefore the measured voltage is effectively due to the sample. For two lead method,

$$V = V_{AC} + V_{AB} + V_{BD} = I R_L + I R_S + I R_L,$$

Where $R_L$ is lead resistance and $R_S$ is sample resistance. For $R_S < 2R_L$, the measurement of $R_S$ by two probe technique has no meaning. But it can be used in the case $R_S >> 2R_L$ with an error $2R_L/R_S$ assuming the internal resistance of the voltmeter is infinitely large.

![Two and Four Probe Method Diagram](Image)
In the situation when, $R_S < 2R_L$, one has to use the four probe technique to eliminate the error induced in the measurement by the lead resistance. Thus, the four probe method yields $V = V_{AC} + V_{AB} + V_{BD}$. Since no current pass through the loop ABDC as internal resistance of voltmeter is infinitely large we have $V_{AC} \approx 0$ and $V_{BD} \approx 0$. Then, $V = V_{AB}$. Thus one can measure low resistance to a good accuracy except for the error due to leakage current through voltmeter.

In above discussion we have described general four probe method to determine the resistivity of samples at ambient conditions, but when we do the same measurements with four probe method under high pressure the conditions are quite different. In next section the technique for the measurement of electrical resistivity under high pressure is described.

### 2.6. High Pressure Electrical Resistivity Technique

The measurement of high pressure electrical resistivity under high pressure can be done in two steps:

(a) Loading of sample in High Pressure Cell [28,29]

(b) Measurement of resistivity using Compression Testing Machine.

The arrangement of the system is shown in Fig.2.11

![Fig.2.11: High Pressure Electrical Resistivity set up showing Compression testing machine (CTM), Current source and Voltmeter.](image)
2.6.1 Loading of Sample in High Pressure Cell

The schematic diagram of Loading of high pressure cell is shown in Fig. 2.12. The main parts of sample assembly are Tungsten Carbide Anvil cell, Gasket, pressure transmitting medium, sample and connecting wires. The arrangement of Cu wires for four probe method on sample is also shown in Fig.2.12.

All the parameters of sample assembly for high pressure measurement are discussed as follows using the exact dimensions of our laboratory set up.

(i) The high pressure cell is made up of tungsten carbide (WC) with 6% Co doping as binder using opposed anvil arrangement, the anvil size is 1 cm while the working face diameter is 25 mm, and tapering angle is $12^0$, tapering height is 30 mm.
Fig. 2.14 Tungsten Carbide Anvill Cell

(ii) Pyrophilite gasket (2mm, 3mm hole) and heat treated at 600°C for four hour to remove the porosity of material. Thickness of the gasket optimized at 0.25 mm (1/10 part of the diameter of hole of gasket).

(iii) Magnesium Oxide (MgO) powder as steatite was used as quasi hydrostatic pressure transmitting medium it is well established that MgO can be used as pressure transmitting medium in the electrical resistivity measurements up to 10 GPa and 1300K.

(iv) The sample taken during the experiment should be of very small size. As we know that P = F/A and to obtain high pressure we can apply load on smaller area, The sample having nearly 1 mm diameter is placed at the center of gasket hole.

(v) Iron oxide (Fe₂O₃) powder with epoxy was used as tight binder on gasket and connecting wires.
(vi) Connecting probes of Cu-- SWG 44/48, insulation of probes was removed
using Emery paper by rubbing it in both directions to maintain the
homogeneity in thickness (cross-sectional area of wire).

Fig. 2.16 Assembly of sample and connecting wires on anvil

The arrangement of Cu wires for four probe method on sample is also
shown in Fig.2.12.

Fig. 2.17: Loading of sample in High Pressure Cell

2.6.2 Measurement of Resistivity using CTM:
The necessary components for the measurement are:

(i) AIMIL 3000KN Compression Testing Machine (CTM) with needle valve.
(ii) Keithley current source (model no.263)
(iii) Digital multimeter (model no.199)

(iv) Electrometer (model no.614)

Detailed description of following components are as follows:

(i) **Compression Testing Machine:** Compression testing machine consists of a loading unit, a motorized pumping unit and digital processing unit.

(a) **Load Frame Unit:** It consists of steel cross head and machined steel base with solid plates connecting the base and the cross head. The hydraulic jack is fixed on the base. The upper platen has a self aligning action and is attached to a block protruding from the cross head. The lower platen rests on the jack ram and is positioned centrally with the help of cantering pin. Loading is accomplished by the upward movement of the lower platen. Diameter of the platen decides the maximum load delivered. The system with maximum load of 3000 KN (300 ton) has platen with diameter 30 cm.

(b) **Motorizing Pumping Unit:** A two speed motorized pumping unit, driven by AC electric motor, for lifting the lower platen of digital compression testing machine at a faster rate under no load condition, is housed in a cabinet. A power supply is fixed with the pumping unit to supply 220/230 V AC power supply. Oil is pushed inside the load frame unit with pressure using motorized pumping unit. The lower platen is pushed upward under oil pressure.

(c) **Digital Processing Unit:** A digital load indicator has a digital display of load in KN. The sensor is incorporated in the motor unit sense the oil pressure (in psi) which is converted in KN through electronics of DPU.
Fig. 2.18: (a) Total set up of high pressure electrical resistivity measurement unit, with CTM, current source, voltmeter. The component of CTM are also shown. (b) Enlarged view of the sample assembly placed in between platens of CTM.

(d) **Calibration of High Pressure Cell:** The high-pressure cell was calibrated against the well known solid phase transition in Tellurium, Bismuth and Thallium (typical error base in the pressure measurement is 4.2%). For pressure lower than 2 GPa, cell is calibrated by studying the pressure dependence of the electrical resistivity of a standard mangnin.
wire to avoid the effect of variation of sizes with pressure on the values of the resistivity at ambient temperature and pressure.

Fig. 2.19: Actual Phase diagram of Bismuth, with respect to which the load of CTM Calibrated.

2.7 Summary

This chapter gives us a detail and brief understanding about the electrical resistivity and its measurement under high pressure. After having a look we can say that how the measurement technique as well as measurement conditions are important to find the accurate behaviour of sample. The whole measurement of Electrical resistivity comprised many steps and each step has its own beauty and importance. Size of Anvil, Thickness of Gasket, Steatite medium, Probe wires, Sample size, Measuring units as well as the purity of sample are the factors for accurate study. Along with these factors controlling the motor speed is also important.
REFERENCES


