Chapter 5

Pressure dependent electrical properties of $\text{MoSe}_{2-x}\text{Te}_x (x = 0.25, 0.5, 1, 1.5, 1.75)$ single crystals

Man is ever emulating nature. In his attempts to duplicate pressures that exist in the universe, however, he falls short of the tremendous pressures that are to be found. Nearly all the minerals have high-pressure origins. Crystal minerals may come from high-pressure sources such as rising plumes or meteorite impacts. By far the major fraction of minerals in the earth is still hidden at great depth under pressure. This remains the ever encouraging factor for mankind to study the behaviour of materials at high pressure. Recent studies of different properties of several materials at very high pressure are yielding numerous surprises that present a considerable challenge to our understanding of minerals. Present chapter deals with the study of high pressure effects on electrical resistivity of $2\text{H-MoSe}_{2-x}\text{Te}_x$ single crystals.
5.1 INTRODUCTION

Gapless graphene has limitations for its applications in nano-electronics and nano-photonics which led to the finding of the 2D-materials with finite optical band gap such as BN, Transition Metal Dichalcogenides (TMDCs) and Transition Metal Oxides (TO2). Depending on the interaction of transition metal and chalcogen orbitals, TMDCs offer a wide range of 2D-layered materials which have properties of metals, superconductors, Charge Density Wave (CDW) Systems, Mott-insulators and semiconductors [1-9]. Single layer of TMDCs having stoichiometric of MX2 like MoS2, MoSe2, MoTe2, WS2 and WSe2 consists of a hexagonally arranged transition metal (M = Mo and W) sandwiched between two layers of chalcogen atoms (X = S, Se and Te). Within the layers, the metals and chalcogens form strong ionic-covalent bonds, while in bulk TMDCs, the layers are bonded by weak van-der Waals forces. TMDCs like MoS2, MoSe2, MoTe2, WS2 and WSe2 have emerged as promising materials for a range of applications. 2H-MoSe2-xTe x (x = 0.25, 0.5, 1, 1.5, 1.75) have semiconducting optical band gap in the range of 0.9 to 1.2 eV. In order to use these materials as blocks in nanoelectronics, their electronics properties should be modified. Applied pressure offers novel way of modifying the optical band gaps in terms of dc electrical resistivity measurement over a wide range. Some theoretical aspects of TMDCs show the semiconductor (S) to metal (M) transition for bilayers subjected to hydrostatic pressure [10].

High pressure science is an exciting area of research. In the past three to four decades this field has grown rapidly as a research tool and also supports the development of other new technologies. There has been a considerable interest in the study of the high pressure behavior of solids because of academic, technological and geophysical reasons [11-19]. The academic interest owes its origin to the fact that at high pressure, nature of the inter-atomic forces in matter change considerably. These changes in solids can be studied in greater detail to reveal several new features of the inter-atomic forces, which are
responsible for their diverse physical properties. In addition, the high pressure studies are also of great importance to visualize the mechanism governing the structural changes and to reveal solid state properties associated with different structure. Under extreme pressure fluid lubricants squeeze out from between meting surfaces causing high friction and wear. With lamellar solids such as TMDCs, shearing takes place more easily when loads are high. Therefore lamellar solids are well suited to extreme pressure lubrication.

The technological interest lies in the synthesis of super hard materials like diamond, cubic boron nitride and their polycrystalline sintered compacts. All these materials are strategic to a country’s economic and industrial development. Considerable interest has also been shown by the geophysicists in high-pressure studies to explore the inner mantle of the earth where most of the matter is expected to be confined under very high pressures and temperatures. Under normal conditions, solids exhibit a particular crystal structure for which the total energy is minimum. However, on application of high pressure the atomic arrangement in solid changes resulting in the change of inter-atomic distances and crystal structure. Such a structural phase transition can be noticed experimentally by observing the X-ray diffraction pattern, electrical resistivity and optical properties at different pressures. In this context, it will be of great interest to study the physical behaviour of materials under extremely high pressure. In the present work, our aims to use the resistivity measurements at different pressure to study the possibility of any phase transitions in 2H-MoSe$_2$-$x$Te$_x$ single crystals.

5.2 EXPERIMENTAL ASPECTS

5.2.1 Generation of pressure

There has been an explosive growth in high pressure research in recent years. Without question, the great interest manifested in this field stalked from the diamond synthesis announcement of the General Electric Company in 1955. When considered in detail, there
are perhaps as many high pressure devices as there are high pressure researchers, because each worker seems to develop certain aspects of the art to suit his own tastes [20-32]. When considered in broad perspective, however, there are a limited number of basic apparatus that have been developed for simultaneous use at high pressure and high temperature. They are:

- Piston-cylinder device
- Bridgman anvil device
- Belt device
- Multiple anvil device
- Supported piston apparatus

5.2.1.1 Bridgman anvils

In 1950, P. W. Bridgman [33] reported the construction of an anvil apparatus utilizing two important principles: the principle of massive support and the principle of motion by means of a compressible gasket.

![Diagram of Bridgman anvils](image)

**Figure 5.1** Principle of massive support.

The principle of massive support can be readily visualized from figure 5.1, where a broad truncated cone is depicted alongside of a right circular cylinder. The surface areas of the circular section marked (a')
and \((a)\) are equal. If the cone and the cylinder are subjected to compressive load between flat plates, it will be observed that the pressure on \((a')\) will be much greater than the pressure on \((a)\) at destructive failure of the cone and cylinder respectively. The reason for this lies in the fact that the circular tip near the apex of the cone has mechanical ties fanning out into a greater volume behind the tip than is the case in a right circular cylinder. The greater the included angle of the cone, the greater will be the pressure to which the tip can be subjected. Bridgman anvils, utilizing this principle, are shown in figure 5.2. Such anvils can be forced together until the force over area pressure existing on the two contact faces is as high as 200,000 atmospheres before failure of the carbide occurs. The maximum pressures above this limit are possible only when the carbide binding rings are surrounded by shrunk-on or interference fit steel binding rings. These provide lateral support to the carbide and absorb some of the tensile load that is fanned out from the truncated surface near the apex into the volume immediately behind.

![Figure 5.2 Gasket arrangements in Bridgman anvil apparatus.](image)

There are limitations in the Bridgman anvil device that it would be desirable to overcome for some purposes. One limitation, of course, is
the smallness of the sample. Another is the simple geometry (the sample is in fact, two dimensional). For many purposes it would be desirable to have a sample whose depth was of the same order of magnitude as its length and breadth. This would be particularly important in an apparatus design where in the specimen were to be heated internally by an electrical resistance furnace. Another limitation in this design is the fact that it is not possible to measure volume of the sample as a function of pressure. The principle of massive support was so effective in increasing the ultimate pressure obtainable in a single stage apparatus that several attempts have been made to utilize this principle in other ways in order to obtain an apparatus that was free from one or both of the afore mentioned limitations.

5.2.1.2 Gasket

Earliest experiments with Bridgman anvils were conducted by placing thin wafers of materials to be compressed between the anvil faces. As the anvils were forced together, material would extrude from between the faces until the lateral friction near the edges of the specimen was sufficient to balance the pressure towards the center of the specimen. In general, the higher the internal friction of a substance the thicker would be the resultant specimen when equilibrium between the frictional forces and the pressure would be attained. The type of experiment just described was not particularly useful. A device utilizing massive support was needed in which relative motion could be obtained and controlled. Bridgman solved this problem by surrounding a wafer like disc (now known as gasket) of the sample by a pipe stone ring as shown in figure 5.2. Pipe stone’s frictional and compressive properties are such that the ring would form a seal around the wafer-like sample preventing its extrusion from between the anvils and, at the same time, it would compress with the anvil advance allowing motion to be obtained.
The first function performed by the gasket is that of “yielding” to the thrust placed on it by a moving anvil or similarly functioning apparatus component. Yielding can occur through simple compression of the gasket material by flow or by a combination of compression and flow. The amount of yielding should be relatively large in order that the anvils might move a sufficient amount to compress the contents of the high-pressure chamber. The second function of the gasket is that of “confining” (not yielding to the thrust of) the material being compressed by the advancing anvil. The tasks of yielding and confining are, of course, contradictory and must somehow be reconciled. A third gasket function is that of “support.” Just inside the inner edge of the gasket, the surfaces of the high-pressure apparatus components are subjected to the full pressure generated within the chamber. At the outer edge of the gasket, the apparatus components are subjected to only one atmosphere pressure. Ideally, the pressure exerted by the gasket against the components of the apparatus should gradually decrease from the full chamber pressure at the inner gasket edge to one atmosphere pressure at the outer edge. When this is the case, a sharp line of demarkation between chamber pressure and atmospheric pressure is avoided and consequently there will be no line of high stress concentration. If the gasket width and pressure gradient are judiciously chosen, the apparatus components will support each other and make it possible for the highly stressed portions of the components to withstand more load than would otherwise be possible. Pressure gradient patterns can be varied by choice of gasket materials and by changing the cross-sectional profile of the gasket from the inner to the outer edge. The gasket functions of yielding, confining, and supporting enumerated above, must, in any given design, be accomplished without having the gasket absorbs an inordinate fraction of the ram thrust available for operating the device. In the belt and tetrahedral designs, the thrust absorbed by the gaskets and by the internal friction of the solid pressure transmitting medium has been kept rather low. It amounts to only 10 to 20
percent of the total applied thrust. These devices could probably be improved with respect to maximum pressure attainable and component lifetime by increasing the gasket-absorbed thrust to 50 percent of the total thrust. The additional thrust absorbed by the gaskets would be used to provide a more gradual pressure gradient from inner to outer edges of the gasket and to provide for additional component support. If yield to anvil advance were the only function to be performed by the gasket, the gasket material would, ideally, be extremely compressible and/or would flow very easily. The latter condition would be met by materials that have very low coefficients of internal friction. On the other hand, if confining the cell contents were the only function of the gasket, the gasket would ideally be composed of an extremely incompressible material that possessed great strength and a correspondingly high coefficient of internal friction. Selection of a material to meet these opposing requirements must be made from materials of intermediate compressibility and internal friction. Universal, optimum values of compressibility and internal friction probably do not exist. Optimum values of these quantities probably depend on geometrical parameters associated with each apparatus design. Some of the data collected are displayed in table 5.1 [33, 34].

Most ultrahigh-pressure gaskets in use today have coefficients of friction in the range of 0.25 to 0.50.

**Table 5.1** Coefficient of Friction of Some Materials at ~2.4 GPa.

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Oxide Powder</td>
<td>0.71</td>
</tr>
<tr>
<td>Aluminum Hydroxide Powder</td>
<td>0.39</td>
</tr>
<tr>
<td>Zinc Oxide Powder</td>
<td>0.58</td>
</tr>
<tr>
<td>Pumice Stone Powder</td>
<td>0.52</td>
</tr>
<tr>
<td>Chromic Oxide Powder</td>
<td>0.50</td>
</tr>
<tr>
<td>Pyrophyllite Powder</td>
<td>0.25</td>
</tr>
<tr>
<td>Pyrophyllite Natural Block</td>
<td>0.47</td>
</tr>
<tr>
<td>“Attasol” Clay Powder</td>
<td>0.47</td>
</tr>
<tr>
<td>Lead Dioxide Powder</td>
<td>0.46</td>
</tr>
<tr>
<td>Manganese Dioxide Powder</td>
<td>0.45</td>
</tr>
<tr>
<td>Titanium Dioxide Powder</td>
<td>0.45</td>
</tr>
<tr>
<td>Molybdenum Trioxide Powder</td>
<td>0.42</td>
</tr>
<tr>
<td>Tin Oxide Powder</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Indium Sheet</td>
<td>0.01</td>
</tr>
<tr>
<td>Boron Carbide Powder</td>
<td>0.40</td>
</tr>
<tr>
<td>“Micro-Cell” Earth Powder</td>
<td>0.37</td>
</tr>
<tr>
<td>Calcium Hydroxide Powder</td>
<td>0.27</td>
</tr>
<tr>
<td>“Permagel” Clay Powder</td>
<td>0.18</td>
</tr>
<tr>
<td>Boric Acid Powder</td>
<td>0.14</td>
</tr>
<tr>
<td>KCl Powder</td>
<td>0.12</td>
</tr>
<tr>
<td>NaCl Powder</td>
<td>0.12</td>
</tr>
<tr>
<td>Mica Sheet</td>
<td>0.07</td>
</tr>
<tr>
<td>Boron Nitride Powder</td>
<td>0.07</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>0.04</td>
</tr>
<tr>
<td>Molybdenum disulfide Powder</td>
<td>0.04</td>
</tr>
<tr>
<td>Silver Chloride Powder</td>
<td>0.03</td>
</tr>
</tbody>
</table>

In order for the gasket to confine the material within the chamber, it must inherently possess great strength or else it must transmit the expulsion force imposed upon it by the chamber contents to the anvils or other apparatus components. Apparently, thin sheets of many substances subjected to heavy loads perpendicular to the sheet develop high strengths in directions parallel to the sheet. In spite of this, the gasket may be expelled or extruded by the expulsion force. This may be due to too low coefficient of internal friction of the gasket material or to too low coefficient of sliding friction between the gasket material and the apparatus components or both. The coefficient of sliding friction can be increased by roughening the anvils, by using a gasket material with a higher coefficient of internal friction, or by interposing a thin layer of very high friction material between the gasket and the anvil. The latter procedure is used in the tetrahedral anvil device. In this instance a thin layer of rouge is applied to the surface of the pyrophyllite tetrahedron. In order for the gasket to successfully confine the chamber contents, it has been necessary to use the gasket material in relatively thin sections. This, of course, limits the relative motion of apparatus components and imposes limits on the chamber size for a given pressure. Additional relative motion was obtained in the belt design by using a sandwich gasket in which a thin sheet of steel was interposed between two sections of pyrophyllite. Appropriate geometrical considerations in the apparatus design, in this case, also
increase the relative motion of the pressure generating components. There may be more elaborate composition-type gaskets constructed of multiple layers of materials with widely differing strength and frictional properties that would perform the tasks required of the gasket more effectively than does the sandwich gasket currently used in the belt.

5.2.1.3 Pressure transmitting medium

An effective way to subject a substance to high pressure for electrical measurements in anvil devices is to enclose the substance in a gasket to which pressure is transmitted by a solid medium. Ideally, this solid pressure transmitting medium must meet the requirements enumerated below. It must:

- transmit pressure hydrostatically.
- have very low compressibility.
- have very low thermal conductivity.
- should be electrically insulator.
- be chemically inert.

These requirements must be met at both ordinary and high pressures. In some instances additional special requirements must be met as would be the case where x-ray transparency is necessary for diffraction work at high pressure. Of course, it is impossible to find a solid pressure transmitting medium wherein all these requirements are fully and simultaneously met. Consequently, a compromise must be made. At the present time, pyrophyllite, talc, and hexagonal boron nitride are being widely used as pressure transmitting materials in high-pressure work. Each of these materials has its virtues and drawbacks. None of them transmits pressure as hydrostatically as would be desirable. It seems certain that no one has up to the present time, conducted a systematic investigation to discover materials that better meet the requirements enumerated above than do the materials now commonly used. Such research would indeed be important to the
advancement of the high-pressure art. It seems reasonable that hydrostatic solids would possess low coefficients of friction as measured in Bridgman’s shear apparatus. Some semi-quantitative information on this point has been obtained, but a great deal of additional work would be desirable.

5.2.2 Pressure measurement

Pressure is directly related to the applied force $F$ and cross sectional area of piston $A$ as

$$P = \frac{F}{A} \quad (5.1)$$

In this way it seems very easy to determine the pressure generated in the piston-cylinder type high pressure devices, but in fact it is quite difficult due to the spending of a large amount of applied force in compressing the gasket and in opposing the friction between piston and cylinder. In order to determine the generated pressure with accuracy as much as possible, different techniques are available today [35]. Each of them is having their own merits and demerits according to the type of measurements to be performed. These techniques are listed below;

- Primary scale
- Thermodynamic absolute pressure scale
- Ruby scale
- X-ray gauges
- Equation of state
- Fixed pressure points (Secondary pressure scale)

The fixed pressure point scale has been replaced in many experiments now days by ruby and X-ray gauges but still it is effectively used in large anvil systems. It also serves for calibration of some other gauges. In this technique reproducible phase transitions of some materials are used for scaling the pressure. General requirements for such calibrants are as under;
- The measured effect (electrical resistance, volume etc.) should be large.
- Hysteresis of the phase transition should be small.
- Temperature effect on transition pressure should be small.

**Figure 5.3** Resistance changes associated with Bi I-II and Bi II-III transitions at 30 °C.

Above figure 5.3 shows the Bi I-II and Bi II-III transitions at 30 °C at fixed point pressure for the calibration of pressure gauge.

**Table 5.2** Recommended phase transitions for fixed pressure points.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Pressure (GPa)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_{I-II}$</td>
<td>2.55±0.006</td>
<td>Midpoint of Hysteresis</td>
</tr>
<tr>
<td>Bi$_{II-III}$</td>
<td>5.5±0.010</td>
<td>Midpoint of Hysteresis</td>
</tr>
<tr>
<td>Bi$_{III-IV}$</td>
<td>7.7±0.300</td>
<td>Change in the value of Resistance in its high pressure phase</td>
</tr>
<tr>
<td>Ba$_{I-II}$</td>
<td>5.5±0.200</td>
<td>Midpoint of Hysteresis</td>
</tr>
<tr>
<td>Tl$_{I-II}$</td>
<td>3.67±0.030</td>
<td>Midpoint of Hysteresis</td>
</tr>
<tr>
<td>Si</td>
<td>12.5±0.500</td>
<td>Confirmed by NaCl scale</td>
</tr>
<tr>
<td>ZnSe</td>
<td>13.7±0.300</td>
<td>Confirmed by NaCl scale</td>
</tr>
<tr>
<td>ZnS</td>
<td>15.0±0.500</td>
<td>Confirmed by NaCl scale</td>
</tr>
<tr>
<td>GaP</td>
<td>22.0±1.000</td>
<td>Confirmed by NaCl scale</td>
</tr>
<tr>
<td>NaCl</td>
<td>29.2±1.000</td>
<td>Confirmed by Ruby scale</td>
</tr>
</tbody>
</table>
Some widely accepted phase transitions recommended by various researchers are summarized in table 5.2. These values are widely accepted and used for calibration of several other pressure gauges.

5.3 MEASUREMENT OF PRESSURE DEPENDENT ELECTRICAL RESISTIVITY OF 2H-MoSe$_{2-x}$Te$_x$ SINGLE CRYSTALS

5.3.1 Experimental arrangement
The measurements of in-plane resistivity of 2H-MoSe$_{2-x}$Te$_x$ single crystals were performed using Bridgman anvils pressed against each other by piston cylinder type hydraulic press. A photograph of the high-pressure set-up is shown in figure 5.4. The Bridgman anvils consist of a tungsten carbide cylindrical piece, one face of which is ground in a tapered form ending with a flat anvil surface (cullet). In a typical anvil, the anvil has a diameter of 100 mm, the WC cylinder is of 25 mm diameter with the culet surface of 11.2 mm diameter and the taper angle about 10$^0$. The anvil face experiences a high pressure but the material is heavily supported to prevent a failure of the material. Thus the anvil faces can support pressures in excess of 10 GPa. Typical anvil dimensions are depicted in figure 5.5.

![Figure 5.4](image-url) Hydraulic press used to generate high pressure.
Initially a pyrophellite gasket of ~150 µm thickness is fixed on the culet of anvil with epoxy. After that the crater inside the gasket is filled by putting a disc of pressure transmitting medium (talc). The sample is directly placed on this disc and four wires are drawn above it as shown in figure 5.6. Then another such gasketed anvil is placed on it. Whole assembly is pressed in a hydraulic press to generate high pressure. Generated pressure is measured by fixed pressure point scale utilizing pressure dependent electrical resistance of bismuth.

**Figure 5.5** Typical anvil dimensions.

**Figure 5.6** Arrangement of sample and probes in the pressure dependent electrical resistivity measurement system.
Using described experimental arrangement four-probe resistivity measurements were performed on 2H-MoSe$_{2-x}$Te$_x$ single crystals grown by chemical vapor transport technique. All the measurements were performed at room temperature. Obtained results are plotted in figures 5.7-5.11.

**Figure 5.7** Pressure dependent in-plane electrical resistivity of 2H-MoSe$_{1.75}$Te$_{0.25}$ single crystals.
Figure 5.8 Pressure dependent in-plane electrical resistivity of 2H-MoSe$_{1.5}$Te$_{0.5}$ single crystals.

Figure 5.9 Pressure dependent in-plane electrical resistivity of 2H-MoSeTe single crystals.
5.3.2 Results and discussion

It is observed from figures 5.7-5.11 that in all these materials, initially at low pressure, resistivity decreases rapidly while above some value of pressure it becomes stable and starts decreasing with in a regular manner.

The resistance of all the materials is found to decrease with increase in pressure. Initially it decreases rapidly with increase in pressure but the rate of change of resistance with pressure is found to change with pressure. Exact interpretation of the behaviour of pressure dependent resistivity of these materials can be constructed by considering some simple pictures of semiconductor conduction as under.

The variation of d.c. resistivity with pressure for $2H$-MoSe$_{2-x}$Te$_x$ single crystal is shown in figures 5.7-5.11. It is seen that the d.c. resistivity
of sample shows two different regions of behaviour. In the low pressure region of 0.4–2.20 GPa, the resistivity decrease is rapid, while in the region of higher pressure, the resistivity decrease is gradual. The resistivity decrease in the low pressure region of 0.4–2.20 GPa may be attributed to the presence of the layer structure in the crystals. The inter-layer spacing changes more rapidly than the intra-layer bonds at low pressure, since the inter-layer bonds are relatively much weaker (van der Waals bond). The decrease in electrical resistivity in the low pressure region may correspond to a decrease in the inter-layer spacing [14].

The carrier mobility in the conduction band increases with pressure due to decrease in the intra-layer bonds and shift from a two-dimensional material to a more three-dimensional material in nature under high pressure. The increase of carrier mobility of the conduction band is due to the contribution of carriers from the valence band. The total density of states near the Fermi level reduces due to the shift of the conduction band maxima (CBM) and the valence band maxima (VBM) towards the Fermi level. By increasing the pressure, the contributions to the CBM from Mo-d and Se/Te-p orbital decrease, while Se/Te-d increase. The change in the resistivity as a function pressure follows the same pattern for all the materials studied here. The change in the resistance as function of pressure predicts that at still higher pressure, materials might become metallic in nature. As the concentration of selenium is decreasing in these materials, the value of resistivity is also decreasing; this may due to the fact that selenium is more semiconducting than tellurium. This leads to reduced interaction between metal and chalcogen atoms at lower pressure.

In conclusion, we report the change in the resistivity of 2H- MoSe_{2-x}Te_x as a function applied pressure. The reduction of resistivity as a function of applied hydrostatic pressure may cause due to the interlayer interactions, which eventually lifts the degeneracies of
bands and move them closer to the Fermi level. The decrease in the rate of change of resistivity with increasing pressure indicates the decrease in the compressibility of the sample under pressure. Furthermore, with increasing the pressure all the materials become more and more conducting.

### 5.4 SOME REMARKS

Research in the field of high pressure is highly dependent on the experimental techniques and every advancement in them resulted in the phenomenal expansion in the knowledge of mankind concerning to the behaviour of matter under high pressure. Up to the date generation of pressure comparable to that exists at the center of earth and to utilize it in order to determine the pressure dependent material properties is a challenge. Present work dealt with the pressure dependent in plane resistivity of grown crystals, but still certain parameters are kept unattended by us which may be studied in details in future. They are summarized below.

- In the present chapter pressure dependent in-plane resistivity of grown crystals are measured and obtained results are interpreted according to simple picture of semiconducting conduction. At the end of discussion it is concluded that the material may tend to be more metallic under the influence of hydrostatic pressure. Measurements of electrical resistivity along c-axis of crystals (and calculation of anisotropy ratio from it) may provide the experimental support to present explanation. Such measurements are possible (two probe resistivity measurements) if enough care is taken.

- Pressure dependent TEP measurements are also possible to conduct. Currently these measurements are in progress.
REFERENCES


