Chapter 4

Investigation of electrical properties of $\text{WSe}_2, \text{W}_{0.9}\text{Se}_2$ and $\text{MoSe}_2$ single crystals
4.1 INVESTIGATION OF ELECTRICAL RESISTIVITY

4.1.1 Introduction

Investigation of electrical resistivity is one of the vital characteristics of semiconductor materials. The investigation of resistivity is necessary not only for realistic purposes but also for the explanation of a range of physical phenomena. Electrical resistivity is a vital experimental tool to find out the structural defects plus internal purity of crystalline solids. The transformations which occur in physical and chemical character of a material could be explained by its resistivity data [1].

4.1.2 Causes of Resistance

In pure metallic materials, when voltage is applied across a metal, the electrons drift from one end of the conductor to the other. Near room temperatures, the thermal movement of ions is the elementary source of scattering of electrons, and is thus the prime cause of metal resistance. Imperfections of lattice also contribute into resistance, although their contribution in pure metals is negligible. Longer conductors have more scattering events in each electron's path [1].

In semiconductors, the Fermi level lies within the band gap, approximately half-way between the conduction band minimum and valence band maximum for intrinsic semiconductors. Subsequently at zero Kelvin, there are no free conduction electrons and the resistance is infinite. However, the resistance decreases as the charge carrier density in the conduction band increases. In extrinsic semiconductors, a dopant atom increases the majority charge carrier concentration by donating electrons to the conduction band or accepting holes in the valence band. For both types of donor or acceptor atoms, increasing dopant density leads to a reduction in the resistance. At very high temperatures the contribution of thermally generated carriers will dominate the contribution from dopant atoms and the resistance will decrease exponentially with temperature [1].
4.1.3 Resistivity

Electrical resistivity (also known as specific electrical resistance or volume resistivity) quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. Resistivity is commonly represented by the Greek letter ρ (rho). The SI unit of electrical resistivity is the ohm meter (Ω m) although other units like ohm centimeter (Ω cm) are also in use. Electrical resistivity can be expressed by the following equation [1].

$$\rho = \frac{R A}{L}$$  \hspace{1cm} (4.1)

Where, \( \rho \) = Resistivity

\( R \) = Resistance of the conductor

\( L \) = Length of the conductor

\( A \) = Cross sectional area of the conductor

4.1.4 Temperature Dependence of Resistivity

Intrinsic semiconductors become better conductors with the increase in temperature. With help of thermal energy, electrons jumps from valance band to conduction band, where they flow freely and leave behind holes in the valence band. The electrical resistivity of a typical intrinsic semiconductor decreases exponentially with rise in temperature. For semiconductors, temperature dependence of the resistivity can be expressed by the following expression [2].

$$\rho = \rho_0 \exp \left( -\frac{E_a}{kT} \right)$$  \hspace{1cm} (4.2)

Where, \( \rho \) = Resistivity of the material

\( \rho_0 \) = Resistivity at room temperature

\( k \) = Boltzmann constant

\( E_a \) = Activation energy
**4.1.5 Experimental Procedure**

In the present research work variation of resistivity with temperature of the sample of WSe$_2$, W$_{0.9}$Se$_2$, and MoSe$_2$ were investigated. A traditional two probe measurement system was utilized for the measurement of variation in resistivity with the temperature. The resistivity along the c axis (perpendicular to basal plane) and perpendicular to c axis (parallel to basal plane) can be measured by the two probe method. To measure the resistivity of a material under investigation a furnace was employed. The sample of a material under investigation was inserted in to the furnace using sample holder. The experimental set up of resistivity measurement system is shown in fig.4.1.

To increase the temperature of the furnace a dc voltage supply was utilized. Temperature of the furnace is assorted in the range of 310K to 673K. To measure the resistance of the sample two probes is connected to multimeter. Resistances of the sample at various temperatures were carried out. Readings were taken in the interval of every 5k. For stable reading slow and steady increase of temperature was assured during the experiment. For slow and stable increase in the temperature a dc voltage supplier is kept at a very low voltage throughout the experiment. It will take nearly 8 to 9 hr for one set of reading. To measure the resistivity from the resistance following mathematical expression was utilized [3].

\[
\rho = R \frac{A}{t}
\]  

(4.3)

Where, \(\rho\) = Resistivity of the specimen

\(R\) = Resistance of the specimen

\(A\) = Area of the specimen

\(t\) = Thickness of the specimen
4.1.6 Results and Discussion

Resistivity along the c axis (perpendicular to the Basel plane) and perpendicular to the c axis (parallel to the Basel plane) were carried out using two probe methods. Investigation of anisotropy was also carried out for the sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals.

4.1.7 Investigation of Resistivity along C Axis

(Perpendicular to the Basel Plane)

In present investigation it was found that resistivity and resistance of sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ crystal were decreases exponentially with temperature. As temperature increases electron in the covalent bond start to vibrate with higher amplitude. At specific temperature they become free from the covalent bonds. This electron collides with some more electrons and makes them free as well. This phenomenon increases with the increase in the temperature. As a result resistivity of all three samples exponentially decreases with temperature. This is
the typical behavior of the semiconducting material. Variation in resistance and resistivity found in present investigation are shown in the fig.4.2 to fig 4.9.

**Fig. 4.2** Variation of resistance (along c axis) with temperature of the WSe$_2$ single crystal

**Fig. 4.3** Variation of resistance (along c axis) with temperature of the W$_{0.9}$Se$_2$ single crystal
**Fig. 4.4** Variation of resistance (along c axis) with temperature of the MoSe$_2$ single crystal.

**Fig. 4.5** Comparison of variation of resistance (along c axis) with temperature of the WSe$_2$, W$_{0.9}$Se$_2$, and MoSe$_2$ single crystals.
Fig. 4.6 Variation of resistivity (along c axis) with temperature of the WSe$_2$ single crystal

Fig. 4.7 Variation of resistivity (along c axis) with temperature of the W$_{0.9}$Se$_2$ single crystal
Fig. 4.8 Variation of resistivity (along c axis) with temperature of the MoSe$_2$ single crystal

Fig. 4.9 Comparison of variation of resistivity (along c axis) with temperature of the WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals
As discussed earlier resistivity of the semiconductor can be represented by the following equation [3].

\[
\therefore \rho = \rho_0 \exp \left( -\frac{E_a}{KT} \right)
\]

\[
\therefore \log \left( \frac{\rho}{\rho_0} \right) = -\frac{E_a}{KT}
\]

\[
\therefore \log \rho = -\frac{E_a}{KT} + \log \rho_0
\]

\[
\therefore \log \rho = -\frac{E_a}{K1000} \left( \frac{1000}{T} \right) + \log \rho_0
\] (4.4)

From the above equation it is certain that plot of \( \log(\rho) \) versus \( 1000 / T \) must be a straight line and its slope can be represented by the following equation.

\[
\therefore \text{slop} = \frac{E_a}{K1000}
\]

\[
\therefore E_a = \text{slop} \times K_B \times 1000
\] (4.5)

Where, \( K_B = \) Boltzmann constant \( (8.602 \times 10^{-5} \text{ eV/K}) \).

Using equation 4.5 microscopic parameter ‘activation energy (Ea)’ can be carried out. Activation energy (Ea) of the semiconducting material varies with temperature. Hence Ea has been calculated in all possible temperature ranges. Variation of \( \log(\rho_{\|}) \) versus \( 1000/T \) is illustrated in the fig. 4.10 to fig 4.13. Evaluated data of activation energy are denoted in the table 4.1. Close look into result reveal that activation energy decreases with the temperature. The reason for that is the number of free electron increases with increase in temperature. These electrons take part in current conduction. Hence activation energy decreases with the increase in temperature.
Fig. 4.10 Variation of log\(\rho_{\parallel}\) versus 1000/T(K\(^{-1}\)) of WSe\(_2\) single crystal

Fig. 4.11 Variation of log\(\rho_{\parallel}\) versus 1000/T(K\(^{-1}\)) of W\(_{0.9}\)Se\(_2\) single crystal
Fig. 4.12 Variation of log\(\rho_{\parallel}\) versus 1000/T(K\(^{-1}\)) of MoSe\(_2\) single crystal

Fig. 4.13 Comparison of variation of log\(\rho_{\parallel}\) versus 1000/T(K\(^{-1}\)) of the WSe\(_2\), W\(_{0.9}\)Se\(_2\) and MoSe\(_2\) single crystals
4.1.8 Investigation of Resistivity Perpendicular to C Axis

(Parallel to the Basel Plane)

In present investigation resistivity perpendicular to c axis was analyzed for the sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$, single crystal. A variation in resistivity and resistance is demonstrated in fig.4.14 to fig.4.21. It was established from the mentioned plots that resistivity exponentially decreases with the temperature for all the samples under investigation. A similar sort of a characteristic curve is found for resistivity perpendicular to c axis is well. This is an additional proof of semiconducting nature of the all the samples under investigation. Again activation energy has been evaluated using slopes of the plots of log$\rho$ versus 1000/T. All the resulting value of activation energy has been indicated in the table 4.2. Similar sort of findings was reported by deshpande et.al. [2] in their research work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity type</th>
<th>Temp. range (K)</th>
<th>Slop</th>
<th>Activation energy (Ea) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>W$_{0.9}$Se$_2$</td>
<td>$\rho$ (Ω · m)</td>
<td>543-448</td>
<td>0.674</td>
<td>0.134</td>
</tr>
<tr>
<td></td>
<td></td>
<td>433-373</td>
<td>1.155</td>
<td>0.229</td>
</tr>
<tr>
<td></td>
<td></td>
<td>358-323</td>
<td>1.452</td>
<td>0.288</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>$\rho$ (Ω · m)</td>
<td>628-493</td>
<td>1.319</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
<td></td>
<td>483-418</td>
<td>2.168</td>
<td>0.430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>408-378</td>
<td>4.11</td>
<td>0.816</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>$\rho$ (Ω · m)</td>
<td>608-528</td>
<td>0.735</td>
<td>0.146</td>
</tr>
<tr>
<td></td>
<td></td>
<td>453-388</td>
<td>0.893</td>
<td>0.177</td>
</tr>
<tr>
<td></td>
<td></td>
<td>378-312</td>
<td>0.518</td>
<td>0.103</td>
</tr>
</tbody>
</table>

Table 4.1 Data of activation energy found in resistivity experiments
Close glance of the resistivity plot indicate noticeable difference among the value of resistivity parallel and perpendicular to c axis. Resistivity in the parallel to c axis was found to be reasonably high then that of the perpendicular to c axis. This is the typical behavior of material having layered structure. Due to layered structure of the crystals resistivity in the parallel to c axis is found higher then that of the perpendicular to c axis.

Value of activation energy found in the direction parallel to c axis is slightly higher then that of the perpendicular to c axis. As a consequence of the layered structure a quantity of energy gap exist for the current conduction in the direction parallel to c axis. Due to this reason value of activation energy found bit higher in the direction parallel to c axis then that of the perpendicular to c axis.

Fig.4.5, 4.9, 4.17 and 4.21 demonstrate comparison of resistance and resistivity of, \( W_{0.9}Se_2 \), \( WSe_2 \) and \( MoSe_2 \) single crystals. The mentioned plots reveal that resistivity of the \( MoSe_2 \) crystal is highest among three samples and resistivity of \( W_{0.9}Se_2 \) is found to be lowest. This fact is reflected in the value of activation energy of the respective samples. Activation energy of \( MoSe_2 \) crystal found to be highest and activation energy of \( W_{0.9}Se_2 \) crystal found to be lowest.

**Table 4.2** Data of activation energy evaluated in the resistivity experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity type</th>
<th>Temp. range (K)</th>
<th>SLOP</th>
<th>Activation energy (Ea) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W_{0.9}Se_2 )</td>
<td>( \rho_{\perp} (\Omega \cdot m) )</td>
<td>623-428</td>
<td>0.253</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td></td>
<td>478-418</td>
<td>0.692</td>
<td>0.137</td>
</tr>
<tr>
<td></td>
<td></td>
<td>378-328</td>
<td>0.805</td>
<td>0.159</td>
</tr>
<tr>
<td>( MoSe_2 )</td>
<td>( \rho_{\perp} (\Omega \cdot m) )</td>
<td>663-573</td>
<td>1.367</td>
<td>0.271</td>
</tr>
<tr>
<td></td>
<td></td>
<td>563-498</td>
<td>1.468</td>
<td>0.291</td>
</tr>
<tr>
<td></td>
<td></td>
<td>413-368</td>
<td>1.726</td>
<td>0.342</td>
</tr>
<tr>
<td>( WSe_2 )</td>
<td>( \rho_{\perp} (\Omega \cdot m) )</td>
<td>598-508</td>
<td>0.221</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td></td>
<td>488-368</td>
<td>0.830</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353-312</td>
<td>1.351</td>
<td>0.268</td>
</tr>
</tbody>
</table>
Fig. 4.14 Variation of resistance (perpendicular to c axis) with temperature of the \( \text{WSe}_2 \) single crystal

Fig. 4.15 Variation of resistance (perpendicular to c axis) with temperature of the \( \text{W}_{0.9}\text{Se}_2 \) single crystal
**Fig. 4.16** Variation of resistance (perpendicular to c axis) with temperature of the MoSe\(_2\) single crystal

**Fig. 4.17** Comparison of variation of resistance (perpendicular c axis) with temperature of the WSe\(_2\), W\(_{0.9}\)Se\(_2\) and MoSe\(_2\) single crystals
Fig. 4.18 Variation of resistivity (perpendicular to c axis) with temperature of the WSe$_2$ single crystal

Fig. 4.19 Variation of resistivity (perpendicular to c axis) with temperature of the W$_{0.9}$Se$_2$ single crystal
Fig. 4.20 Variation of resistivity (perpendicular to c axis) with temperature of the MoSe$_2$ single crystal

Fig. 4.21 Comparison of variation of resistivity (perpendicular c axis) with temperature of the WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals
Fig. 4.22 Variation of $\log\rho_\perp$ versus $1000/T(K^{-1})$ of WSe$_2$ single crystal

Fig. 4.23 Variation of $\log\rho_\perp$ versus $1000/T(K^{-1})$ of W$_{0.9}$Se$_2$ single crystal
Fig. 4.24 Variation of $\log \rho_\perp$ versus $1000/T(K^{-1})$ of MoSe$_2$ single crystal

Fig. 4.25 Comparison of variation of $\log \rho_\perp$ versus $1000/T(K^{-1})$ of the WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals
4.1.9 Investigation of Anisotropy

Anisotropy ratio has been carried out in the temperature range 310K - 673K using following mathematical expression.

\[
\text{Anisotropy} (\gamma) = \frac{\rho_\parallel}{\rho_\perp}
\]  

Investigation of Fig.4.26 to Fig.4.29 shows that anisotropy ratio decreases with temperature. It has been found that at very high temperature the anisotropy ratio move towards unity. As soon as temperature increase number of free electron in crystal configuration increases. This leads to decrease in energy band gap formed due to layered structure of the crystal. As a result as temperature increases energy gap due to layered structure decreases and at very high temperature it become almost negligible. Similar sort of phenomenon was also observed by unadkat et.al. [4] in their research work.

![Graph of Anisotropy vs Temperature for WSe₂](image)

**Fig. 4.26** Variation in anisotropy with temperature of WSe₂ single crystal
Fig 4.27 Variation in anisotropy with temperature of W$_{0.9}$Se$_2$ single crystal

Fig. 4.28 Variation in anisotropy with temperature of MoSe$_2$ single crystal
Fig. 4.29 Comparison of variation in anisotropy with temperature of $\text{WSe}_2$, $\text{W}_{0.9}\text{Se}_2$ and $\text{MoSe}_2$ single crystal
4.2 INVESTIGATION OF THERMOELECTRIC POWER MEASUREMENT (TEP)

4.2.1 Introduction

Thermo electric power measurement is very important measurement of TMDCs materials. Important parameters like type of semiconductor and Fermi energy level were directly found out from the TEP experiment. Fundamental concept of Seebeck effect has been utilized in the TEP experiment. If a temperature gradient were applied between two ends of the junction of a semiconductor then a potential difference develop across the junction. The voltage developed across the junction is directly proportional to temperature gradient. Same concept has been utilize in our experiment is well. Hot probe method was utilized for the measurement of thermo electric power [5].

4.2.2 Hot Probe Method

![Circuit diagram of TEP experiment](image)

**Fig. 4.30** Circuit diagram of TEP experiment
The DVT grown sample of MoSe$_2$, WSe$_2$ and W$_{0.9}$Se$_2$ single crystals have been utilized in the TEP experiment. The experiment was carried out in the temperature range 310K to 473K. Circuit diagram of the experiment was displayed in the fig. 4.30. Temperature of the hot end is gradually increased with help of low power heater and temperature of the cold end was kept at a constant value. Due to temperature gradient a voltage was develops across two end of sample [5].

Now if a sample comprises N type conductivity then electron will drift toward cold end. Because of that hot end become positively charge while cold end become negatively charged. Correspondingly if a material comprises P type conductivity then hot end became negatively charged and cold end became positively charged. In the TEP experimental set up, positive terminal of a voltmeter was connected with cold end and negative terminal was connected with hot end. Such type of voltmeter connection indicates positive voltage for P type semiconductor and negative voltage for N type semiconductor [5].

![Experimental set up of TEP experiment](image)

Fig. 4.31 Experimental set up of TEP experiment
The sample holder containing two low power heaters is shown in fig.4.31. Sample under investigation was inserted between hot end and cold end of heater. The temperature \( T \) of the heater A is calculated by thermocouple (TC1) and the temperature gradient \( \Delta T \) between A and B is calculated by differential thermocouple (TC2). K type thermocouples are utilized in the TEP experiment. The sample under examination is inserted directly on the heaters, and is held there by two pick up probes, which made of brass. These probes additionally measure the Setback voltage developed across the two ends of the sample. If the temperature difference \( \Delta T \) between the two ends of a material is small, then the thermo electric power \( (S) \) of a material is conventionally defined by the following equation [6].

\[
S = -\frac{\Delta V}{\Delta T}
\]  

(4.7)

When any isolated conducting sample is subject to a temperature gradient, a voltage is generated within arrangement of material. For the investigation of temperature dependent thermoelectric power ‘S’ of a semiconductor, the expression given by goldsmith.et.al.[6] has been utilized. The expression of thermoelectric power ‘S’ is given by following equation,

\[
S = \pm \frac{K}{e} \left[ A + \frac{E_{Fv}}{KT} \right]
\]  

(4.8)

Where \( K \) represent Boltzmann constant, \( e \) is the electronic charge, \( A \) is the constant carried out by the dominant scattering process and \( E_{Fv} \) is the separation of the Fermi level from the top of the valance band [6]. The value of thermo electric power ‘S’ is positive for P type of semiconductor and negative for N type of semiconductor. The assessment of constant \( A \) is calculated by following equation [6].
Where, ‘s’ indicate the scattering parameter. Scattering parameter was also carried out for all the samples under investigation and is listed in table 4.3.

4.2.3 Results and Discussion

For a minute temperature range, $E_{Fv}$, is the reasonably constant and therefore from equation (4.8) if the thermoelectric power (TEP) is plotted with the inverse of temperature, a straight line is predictable from where we can establish Fermi energy $E_{Fv}$ and a constant $A$ from the slope and intercept correspondingly [6].

A figure 4.32 to 4.35 demonstrates the deviation of TEP with an inverse of temperature for WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals. It is clear from the graph that as temperature gradient increase thermoelectric power also increases. This phenomenon occurs by reason of as temperature increases number of free electron increases in the crystal arrangement. As a result accumulation of charge carrier increases at a cold end of a semiconductor. This phenomenon results in increase of thermoelectric power with the temperature. All the samples under investigation demonstrate positive thermo voltage. This information confirms that DVT grown, WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals are P type semiconductors.

The values of $E_{Fv}$ and $A$ was carried out using slope and intercept found from each plot. Several set of observations were taken during the experiments of each type of sample. Evaluated value of ‘Fermi energy’ and scattering parameter are listed in Table 4.3. Similar sort of findings was also reported by deshpande et.al.[2] and patel et.al.[7] in their research work.
Fig. 4.32 Variation in thermo electric power with the reciprocal of the temperature for WSe$_2$ single crystal.

Fig. 4.33 Variation in thermo electric power with the reciprocal of the temperature for MoSe$_2$ single crystal.
Fig. 4.34 Variation in thermo electric power with the reciprocal of the temperature for $W_{0.9}Se_2$ single crystal

\[ y = -0.0003788x + 0.0015120 \]

Fig. 4.35 Comparison of variation in thermo electric power with the reciprocal of the temperature for MoSe$_2$, WSe$_2$ and $W_{0.9}Se_2$ single crystals
### Table 4.3 Fermi energy and scattering parameter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Semiconductor type</th>
<th>Fermi Energy (E_f) eV</th>
<th>Constant A</th>
<th>Scattering parameter S=$\frac{5}{2}$-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>P</td>
<td>0.293</td>
<td>0.014</td>
<td>2.485</td>
</tr>
<tr>
<td>W$_{0.9}$Se$_2$</td>
<td>P</td>
<td>0.378</td>
<td>0.017</td>
<td>2.482</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>P</td>
<td>0.279</td>
<td>0.015</td>
<td>2.484</td>
</tr>
</tbody>
</table>
4.3 INVESTIGATION OF HALL PARAMETER

Hall Effect measurement was carried out for the sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystal to investigate the type of semiconductor, mobility and carrier concentration. Hall Effect measurement system “LAKESHORE” model 7504 was utilized for the measurement of hall parameter. The experiments were carried out at Department of Physics, S.P.University, Vallabhidhyanagar.

4.3.1 Experimental Setup and Procedure

Fig. 4.36 Schematic set up for Hall parameter measurement system “LAKESHORE” model 7504
The Lake Shore 7504 Series Hall Effect / Electronic Transport Measurement System shown in Fig. 4.36 is designed to measure electronic properties of electrically conductive materials. The system consists of advanced, integrated hardware and software. The 7504 series system is easy to operate using the Lake Shore Hall Measurement System Software. The Hall System Software is in charge of system instrumentation controls throughout an experiment and establishes sample resistance, resistivity, Hall coefficient, Hall mobility and charge carrier concentration. Furthermore it maintains the magnetic field throughout the experiments [8].

The system includes electromagnet which can create a magnetic field of maximum 10 KG, with 4 inch air gap among the two pole pieces. The essential current is being supplied through the magnetic power supply LS 689 with voltage limits of 0 to ± 32V. The Model 450 is a tremendously precise full featured gauss meter that covers a broad variety of magnetic fields. The instrument offers a straightforward use of front panel programming and a vacuum fluorescent alphanumeric display. This alphanumeric format permits the message based front panel procedure. Almost all the experimental procedures can be achieved and observed by the front panel keypad and message display [8].

The crystals having large size and flat surface were normally selected for investigating their electrical behavior through this method. The basic requirements of the experimental procedure are as follow [8]:

- The contacts should be adequately small enough as compare to that of the sample exterior area.
- All the contacts of the sample holder should be ohmic.
- The sample should not contain any steps or discontinuities.
- The sample should be thin enough as compare to its surface area.
- The sample should be even so that its surface and contacts lie in the identical plane.
- The functional field should be small enough so that breakdown does not take place.
The investigational arrangement for this method is shown in figure 4.36. The sample under investigation is set aside in a recognized magnetic field created by an electromagnet. Experiment was carried out for the sample of, WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystal. Only those samples were used in the experiment which matches the above mention conditions. Before the actual experiment of Hall Effect ohmic nature of all the pair of contact were assured. After the verification of ohmic contact experiment was carried out at the room temperature. Magnetic field up to ±3KG was applied during the each experiment. Data found in the experiment were stored in the commuter system. Results and findings of the experiment were shown in table 4.4 and table 4.5.

The computerized system makes 32 diverse resistance measurements for every measurement point in a Hall Effect assessment. Hall resistance measurement for +ve magnetic field, zero field resistance measurement, resistivity measurements for +ve magnetic field, Hall resistance measurements for -ve magnetic field, and resistivity measurements for -ve magnetic field were accomplished by the system [9]. In the present examination the experiments has been conducted with a magnetic field of ±3KG. Some of the essential formulas which are utilized to calculate hall parameter are discussed briefly in the following section.

With the help of thickness ‘$t$’ of the sample and by measurements of voltage and current with a polarity turnaround across the contacts, the hall coefficient can be carried out using following formula,

$$R_{HC} = \frac{t[V_{31,42}^+(+B) - V_{31,42}^-(+B) + V_{31,42}^-(+B) - V_{31,42}^+(+B)]}{B[I_{31}^+(+B) - I_{31}^-(+B) + I_{31}^-(+B) - I_{31}^+(+B)]}$$  \hspace{1cm} (4.10)
Where, \( V_{31,42} \) indicate a voltage measured across terminals 4 and 2, when a positive current flows in to a terminal 3 and out of terminal 1. \( I_{31} \) denotes +ve forward current measured between contact 3 and 1. The other terminology can be understood in a same manner.

The Hall mobility \( (\mu_H) \) and carrier concentration \( (\eta) \) can be calculated using the following formula [9].

\[
\mu_H = \frac{|R_{Hav}|}{\rho_{av}}
\]  
(4.11)

\[
\eta = \frac{1}{R_H \cdot e}
\]  
(4.12)

### 4.3.2 Results and Discussion

Ohmic nature of all the contacts is necessary for the accurate measurement of hall parameter. Measurement of voltage and current has been carried out between contacts \( R_{12,12} \), \( R_{23,23} \), \( R_{34,34} \) and \( R_{41,41} \) before each experiment of hall effect. Voltage current relations found out in each experiment were displayed in fig. 4.37 to fig. 4.48. It is observed from the figures that there is a liner ohmic relation exists between each pair of contacts. Fig. 4.37 to fig. 4.48 confirms ohmic relation between voltage and current for the sample of \( \text{WSe}_2 \), \( \text{W}_{0.9}\text{Se}_2 \) and \( \text{MoSe}_2 \) single crystals. Medium size, flat, discontinuity free and step free sample were selected for the experiments.
Fig. 4.37 V-I Characteristic of contact $R_{12,12}$ for WSe$_2$ single crystal

Fig. 4.38 V-I Characteristic of contact $R_{23,23}$ for WSe$_2$ single crystal
Fig. 4.39 V - I Characteristic of contact $R_{34,34}$ for WSe$_2$ single crystal

Fig. 4.40 V - I Characteristic of contact $R_{41,41}$ for WSe$_2$ single crystal
Fig. 4.41 V-I Characteristic of contact $R_{12,12}$ for $W_{0.9}Se_2$ single crystal

Fig. 4.42 V-I Characteristic of $R_{23,23}$ contact for $W_{0.9}Se_2$ single crystal
Fig. 4.43 V-I Characteristic of $R_{34,34}$ contact for $W_{0.9}Se_2$ single crystal

Fig. 4.44 V-I Characteristic of contact $R_{41,41}$ for $W_{0.9}Se_2$ single crystal
Fig. 4.45 V-I Characteristic of contact $R_{12,12}$ for MoSe$_2$ single crystal

Fig. 4.46 V-I Characteristic of contact $R_{23,23}$ for MoSe$_2$ single crystal
Fig. 4.47 V-I Characteristic of contact $R_{34,34}$ for MoSe$_2$ single crystal

Fig. 4.48 V-I Characteristic of contact $R_{41,41}$ for MoSe$_2$ single crystal
After the conformation of ohmic nature of the all the contacts actual experiment was carried out at a room temperature. The magnetic field was assorted up to 3KG during all three experiments. The hall parameters carrier concentration ($N_C$), hall coefficient ($R_H$), hall mobility ($\mu_H$) and resistivity ($\rho$) were carried out for all the samples under investigation with the Hall Effect experiment. Values of all these parameter found from the experiment were displayed in the table 4.4. Values of hall coefficients were found to be positive for the sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals. Positive value of hall coefficient confirms that all the sample are P type semi conductors and comprise holes as a majority charge carriers. Positive thermo electric voltage found in TEP experiment indicates same results. A Hall experiment reconfirms the result found in TEP experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity $\rho$ (Ω * cm)</th>
<th>Conductivity $\sigma$ (mho cm$^{-1}$)</th>
<th>Hall coefficient $R_H$ (cm$^3$/C)</th>
<th>Carrier density $N_C$ (1/cm$^3$)</th>
<th>Hall mobility $\mu_H$ (cm$^2$/V*S)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSe$_2$</td>
<td>0.863</td>
<td>1.158</td>
<td>9.709 X 10$^3$</td>
<td>6.429 X 10$^{14}$</td>
<td>1.561X 10$^6$</td>
<td>P</td>
</tr>
<tr>
<td>W$_{0.9}$Se$_2$</td>
<td>8.369</td>
<td>0.119</td>
<td>2.164 X 10$^5$</td>
<td>2.884X 10$^{13}$</td>
<td>1.785X 10$^6$</td>
<td>P</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>0.963</td>
<td>1.038</td>
<td>7.526 X 10$^3$</td>
<td>8.33 X 10$^{14}$</td>
<td>1.452 X 10$^5$</td>
<td>P</td>
</tr>
</tbody>
</table>

The carrier consecration of the crystal depends on the Fermi energy level. Fermi energy remains almost constant in the small temperature range. Thus the equation 4.8 can be rewritten as [10].

$$S = \frac{K}{e} \left[ A + \ln \left( \frac{N_A}{p} \right) \right]$$  (4.13)
The effective density of states $N_A$ can be expressed by the following mathematical formula [10].

$$p = N_A \exp \left(-\frac{E_f}{K T}\right) \quad (4.14)$$

Using the value of carrier concentration from table 4.4 and Fermi energy from table 4.3 the effective density of states were carried for the sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals. Evaluated value of density of states where displayed in the table 4.5.

The relation between effective density of states $N_A$ and effective hole mass $m_h$ can be expressed by the following equation,

$$N_A = 2 \left(\frac{2\pi m_h^* k T}{h^3}\right)^{\frac{1}{2}} \quad (4.15)$$

Using the equation 4.15 effective ‘hole mass’ has been carried out for the sample of, WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystals. Effective hole mass was found to be in the range of $10^{-31}$ kg. The data found are quite comparable with ideal hole mass value. The ratio of effective hole mass and ideal hole mass ($m_h^*/m_h$) was also carried out for the sample of, WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$. Same sort of conclusions were also reported by deshpande et.al.[2] and patel et.al.[7] in their research work.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Fermi Energy $E_f$ (eV)</th>
<th>Carrier density $N_C$ (1/m$^3$)</th>
<th>Effective density of states $N_A$ (1/m$^3$)</th>
<th>Effective mass $m^*$ (Kg)</th>
<th>$(m^* / m_h)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>0.293</td>
<td>8.33 X 10$^{20}$</td>
<td>4.886 X 10$^{25}$</td>
<td>9.314 X 10$^{-31}$</td>
<td>1.02</td>
</tr>
<tr>
<td>W$_{0.5}$Se$_2$</td>
<td>0.378</td>
<td>2.884X 10$^{19}$</td>
<td>4.073 X 10$^{25}$</td>
<td>8.260 X 10$^{-31}$</td>
<td>0.91</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>0.279</td>
<td>6.429X 10$^{20}$</td>
<td>2.242 X 10$^{25}$</td>
<td>5.571 X 10$^{-31}$</td>
<td>0.61</td>
</tr>
</tbody>
</table>
4.4 CONCLUSIONS

1. Exponential decline in resistivity of sample of WSe$_2$, W$_{0.9}$Se$_2$ and MoSe$_2$ single crystal specify that all three samples are semiconductor.

2. High value of resistivity in the direction parallel to c axis specifies that all three samples acquire layered structures.

3. Present investigation shows that MoSe$_2$ single crystal hold highest resistivity and W$_{0.9}$Se$_2$ single crystal has lowest resistivity among the three samples.

4. Activation energy of MoSe$_2$ single crystal was found to be highest while W$_{0.9}$Se$_2$ single crystal acquires lowest value of activation energy among the three samples.

5. Anisotropy ratio and energy gap due to layered structure decrease with temperature.

6. Positive value of seebeck coefficient indicates that all the samples are P type semiconductor.

7. Fermi energy and scattering parameter was evaluated for all the samples under investigation.

8. Positive value of hall coefficient confirms that all the sample under investigation are P type semiconductor and have holes as majority charge carrier.

9. Effective density of states and effective mass were found out for all the samples under investigation.
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