CHAPTER 4

GROWTH, CHARACTERIZATION AND STUDIES OF VARIOUS PROPERTIES OF PVT GROWN WSe$_{2-x}$ CRYSTALS
CONTENTS

4.1 Introduction

4.2 Experimental

4.2.1(a) Compound preparation
4.2.1(b) Crystal growth
4.2.2 Structural characterisation
4.2.2(a) Electron diffraction
4.2.2(b) Lattice parameters
4.2.2(c) Particle size determination
4.2.2(d) Estimation of growth and deformation fault, probabilities in WSe₂ and WSe₁.₉
4.2.3 Energy dispersive analysis of X-rays (EDAX)
4.2.4 High temperature (303-423 K) resistivity perpendicular to c-axis (ρ⊥)
4.2.5 High temperature resistivity parallel to c-axis (ρ∥)
4.2.6 Anisotropy
4.2.7 Hall effect measurements at room temperature
4.2.8 Thermoelectric power measurements
4.2.9 Microstructures

4.3 Discussion

4.4 Conclusions

References
4.1 INTRODUCTION

Currently binary compounds and solid solutions of $A^V B^{VI}$ and $A^{IV} B^{VI}$ semiconducting systems are widely used as thermoelectric materials for thermoelectric coolers and generators [1]. In the search for new, more efficient thermoelectric and photoelectrochemical materials for application at room and intermediate temperature region (300 - 500 K) little attention has been given to the binary tungsten dichalcogenides which are representative of the transition metal dichalcogenide (TMDC) compounds. The object of the present work is to investigate the transport properties of these TMDC compounds.

The Seebeck coefficient and electrical resistivity of semiconductor depend upon the carrier density. At a given temperature, the thermoelectric power factor and the photoelectrochemical conversion efficiency of a PEC solar cell reach their maximum values at an optimum carrier concentration which can be achieved by deviation of the composition from stoichiometry or by suitable doping. To evaluate the potential of a material for thermoelectric applications the compositional and temperature dependence of the transport properties have to be studied.

The compositional dependence of the electrophysical properties of tungsten dichalcogenides [2,3] has been studied previously at room temperature. However, the effect of non-stoichiometry on the transport behaviour of $WX_2$ ($X = S, Se$) has not been investigated systematically. It was found that single crystals of off stoichiometric $WX_2$ are formed as a bye-product through the
process of preparing WX₂ crystals with layered structure by chemical vapour transport (CVT) method [4-7].

The published data on the homogeneity range in WSe₂ are contradictory. From the lattice parameter measurements Hicks [4] showed that the homogeneity range for the compound WSe₂ must be extremely narrow i.e. it lies between the values y = -0.01 and + 0.01. Whereas, Bolgar et al. (8) and Viksman et al. [9] while studying the thermodynamic properties of tungsten diselenide in broad temperature range found that the region of homogeneity of WSe₂ extends from WSe₁.₈₇ to WSe₂.₀. In view of this contradictory data, binary compound of WX₂ (X = S, Se) both stoichiometric and off-stoichiometric have been prepared from high purity elements using a vapour transport method. Appropriate amounts of pure elements have been added to obtain WX₂ and WX₁.₉ compounds in the form of single crystals. In order to remove the slightest risk of contamination of the single crystals by the transporting agent, they have been grown by the Physical Vapour Transport (PVT) technique where no chemical transporting agent is used.

In this chapter are presented the results on growth, characterisation and temperature dependence (300 -423 K) of Seebeck coefficient and electrical resistivity of WSe₂ and its off-stoichiometric compound WSe₁.₉ together with room temperature Hall concentration and mobility data.

4.2 EXPERIMENTAL:

4.2.1.(a) Compound Preparation

The powder compounds were prepared from the elements having
the following purities (\%) W - 99.99 and Se - 99.999. Appropriate amounts of the powdered elements were introduced into a thoroughly cleaned (Chapter 3) quartz ampoule (2.2 cm inner diameter, 24 cm length) in stoichiometric proportions. A total charge of nearly 10 gm was used in each experiment. The ampoule containing the source material was evacuated to a pressure of $10^{-5}$ torr. Then the ampoule containing the charge was stirred well for nearly 1 hour to ensure the proper mixing of the powdered elements. The homogeneous mixture was properly distributed along the length of the ampoule and it was placed into the furnace. The temperature of the furnace was increased slowly to avoid any explosion, which might occur due to strongly exothermic reaction between the elements. The ampoule was then maintained at a required temperature, for sufficient time (Table 4.1) to allow complete reaction. Single phase polycrystalline material with the exact hexagonal structure (as verified by X-ray powder diffraction) was obtained.

4.2.1.(b) **Crystal Growth**

For crystal growth, the specially prepared polycrystalline powder (charge) of $\text{WSe}_2 \text{ and } \text{WSe}_{1.9} \text{ in the manner described above was placed into the quartz ampoule (having same dimensions as those used for charge preparation). The ampoule containing the charge was connected to the vacuum system for creating an inside pressure lower than } 10^{-5} \text{ torr so that the vapour pressure developed at high temperature within the ampoule does not lead to its blasting. When the desired pressure inside the ampoule was achieved, it was sealed off. The ampoule was then inserted into the two zone horizontal furnace. The furnace temperature in both the zones was increased slowly as }$
Table 4.1

Growth conditions used for the synthesis of single crystals of WSe$_2$ and WSe$_{1.9}$ grown using Physical Vapour Transport Technique

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dimension of the ampoule</th>
<th>Temperature at which the charge was prepared ($^\circ$C)</th>
<th>Time for which the ampoule was kept for charge preparation (days)</th>
<th>Temperature range ($T_1$ - $T_2$) in which the ampoule was kept in the furnace for growth of single crystals ($^\circ$C)</th>
<th>Rate at which the temperature was increased from room temperature to the temperature range ($T_1$ - $T_2$) in $^\circ$C/hr</th>
<th>Time for which the ampoule was kept in the temperature range ($T_1$ - $T_2$) (hours)</th>
<th>Rate at which the ampoule was brought down to room temperature in $^\circ$C/hr</th>
<th>Crystal size in (mm$^3$)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>2.2</td>
<td>750</td>
<td>3</td>
<td>950-930</td>
<td>50</td>
<td>240</td>
<td>20</td>
<td>16 x 16 x 0.25</td>
<td>Black opaque</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>2.2</td>
<td>750</td>
<td>3</td>
<td>950-930</td>
<td>50</td>
<td>240</td>
<td>20</td>
<td>20 x 10 x 0.20</td>
<td>Black opaque</td>
</tr>
</tbody>
</table>
was done for the charge preparation to the required final temperature for growth. The exact growth conditions for grown crystals of WSe\textsubscript{2} and WSe\textsubscript{1.9} are summarised in Table 4.1. After the required period of growth in both cases, the furnace was allowed to cool down slowly to room temperature. The ampoule containing the crystals was opened and crystals having maximum size as reported in Table 4.1 were carefully removed. Typical crystals of WSe\textsubscript{2} and WSe\textsubscript{1.9} having different dimensions are shown in Figure 4.1.

4.2 2 STRUCTURAL CHARACTERISATION:

4.2.2. (a) Electron Diffraction

Thin sections suitable for taking the electron diffraction pattern were prepared by cleaving WSe\textsubscript{2} and WSe\textsubscript{1.9} crystals by cello-tape and washing in chloroform several times to remove all impurities due to the cello-tape. When the specimen prepared in the above manner is observed with the electron beam, normal to the (001) layers (planar view), the electron diffraction pattern (DP) obtained is of the form shown in Figure 4.2. This diffraction pattern is representative of all such patterns taken on WSe\textsubscript{2} and its off stoichiometric compound and confirms clearly the single crystalline nature of the grown samples. All the spots in Figure 4.2 have been indexed. The value of ‘a’ obtained from this pattern are in good agreement with the values obtained from the X-ray diffraction patterns described below.

4.2.2. (b) Lattice Parameters

For X-ray diffraction, the samples were ground at room temperature (25°C) and were passed through a 106 mesh sieve. The x-ray diffractograms
Some typical crystals of (a) $\text{WSe}_2$ and (b) $\text{WSe}_{1.9}$ grown using PVT (No transporting agent) technique
Fig. 4.2 Electron diffraction pattern from WSe$_2$ single crystal.
(XRD) of these compounds were recorded on Philips PW 1710 Diffractometer using CuKα radiation. The scan rate used to obtain X-ray pattern for cell constant determination was 3.010 2θ/min. Figure 4.3 shows the X-ray diffractograms of WSe$_2$ and WSe$_{1.9}$ compounds obtained by powdering the single crystals synthesised during their growth by PVT methods. It is interesting to note that the diffractograms of WSe$_2$ and its off-stoichiometric compound exhibit good resemblance within themselves suggesting thereby that off-stoichiometry does not lead to a change in the crystal structure of WSe$_2$. It is evident from the diffractograms that for both the specimen, 002 reflections are of maximum intensity, indicating thereby a strong preferred orientation along the c-axis. The intensity of all other reflections is relatively weaker as compared to this reflection.

The interplanar distance ‘d’ corresponding to different hkl planes were calculated from the respective diffractograms and are recorded in Table 4.2. The lattice parameters for WSe$_2$ and WSe$_{1.9}$ are presented in Table 4.3. It is found that there is no significant variation in the values of lattice parameters a and c, but this change is, however, sufficient to lead to a change in the density of the stoichiometric material, as shown below.

The density ‘ρ’ of the grown crystals was calculated by the formula

$$\rho = \frac{\sum A}{VN} \quad (4.1)$$
### Table 4.2

Indexing of Diffraction Pattern for WSe$_2$ and WSe$_{1.9}$
grown by PVT technique

<table>
<thead>
<tr>
<th>hkl</th>
<th>WSe$_2$</th>
<th>WSe$_{1.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d$ (Å)</td>
<td>Peak intensity counts (s$^{-1}$)</td>
</tr>
<tr>
<td>002</td>
<td>6.5187</td>
<td>17530</td>
</tr>
<tr>
<td>004</td>
<td>3.2600</td>
<td>83</td>
</tr>
<tr>
<td>100</td>
<td>2.8490</td>
<td>11</td>
</tr>
<tr>
<td>101</td>
<td>2.7726</td>
<td>36</td>
</tr>
<tr>
<td>102</td>
<td>2.6122</td>
<td>74</td>
</tr>
<tr>
<td>103</td>
<td>2.3822</td>
<td>123</td>
</tr>
</tbody>
</table>
Table 4.3
Lattice parameters, unit cell volumes, X-ray densities for WSe$_2$ and WSe$_{1.9}$ grown by PVT technique

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>Unit cell volume ($\text{Å}^3$)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>3.240 ± 0.025</td>
<td>12.427 ± 0.005</td>
<td>1.918</td>
<td>112.973</td>
<td>10.046</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>3.226 ± 0.006</td>
<td>12.419 ± 0.005</td>
<td>1.925</td>
<td>111.927</td>
<td>9.906</td>
</tr>
</tbody>
</table>
Fig. 4.3(a) X-ray diffractogram from WSe$_2$ grown using PVT technique.
Fig. 4.3(b) X-ray diffractrogram from WSe$_{1.9}$ grown using PVT technique.
where $\sum A$ is the total weight of the atoms in the unit cell = $M \cdot Z$.

$M$ is the molecular weight and $Z$ is the number of molecules/unit cell,

$N$ is the Avagadro number and $V$ is the volume of the unit cell.

For a hexagonal unit cell, $V$ is given by

$$V = \frac{\sqrt{3}}{2} \frac{a^2 c (A^3)}{12} = 0.866 \frac{a^2 c A^3}{3} \quad (4.2)$$

4.2.2.(c) *Particle Size Determination* :

In order to obtain an idea about the grain size distribution in WSe$_2$ and WSe$_{1.9}$, the particle size for each sample was calculated using Scherrer’s formula [10] given as

$$t = \frac{k \lambda}{B_2 \theta \cos \theta_0} \quad (4.3)$$

where ‘$t$’ is the crystallite thickness as measured perpendicular to the reflecting plane; $k$ is Scherrer’s constant whose value is chosen as 0.9 assuming the particles to be spherical; $\lambda$ is the wavelength of the X-ray radiation; $B_2 \theta$ is the width at half the maximum intensity measured in radians and $\theta_0$ is the Bragg angle.

Table 4.4 records the crystallite size for WSe$_2$ and its off-stoichiometric compound WSe$_{1.9}$ as measured perpendicular to various planes of reflections. As the thickness measured to different planes is more or less the same, there exists an isotropy towards the crystallite size.
Table 4.4

Particle size (Å) distribution in WSe$_2$ and WSe$_{1.9}$
grown by PVT technique

<table>
<thead>
<tr>
<th>hkl</th>
<th>WSe$_2$</th>
<th>WSe$_{1.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>712</td>
<td>834</td>
</tr>
<tr>
<td>101</td>
<td>562</td>
<td>724</td>
</tr>
<tr>
<td>102</td>
<td>541</td>
<td>712</td>
</tr>
<tr>
<td>103</td>
<td>527</td>
<td>617</td>
</tr>
</tbody>
</table>
4.2.2.(d) **Estimation of Growth and Deformation Fault, Probabilities in WSe$_2$ and WSe$_{1.9}$ :**

The structure of tungsten dichalcogenide (WX$_2$) consists of planes of hexagonally close packed chalcogen atoms (X) inter-linked with planes of metal atoms (W) (also on hexagonal sites) to give a stacking sequence $A_B B_A$ $A_B B_A$ $A_B B_A$ ..... where " $A_B$ " is hexagonal X - W - X layer with 'X' atoms in 'A' positions and 'W' atoms in 'B' positions, " $B_A$ " is a layer with 'X' atoms in 'B' positions and 'W' atoms in 'A' positions. Stacking faults may arise from various types of dissociated or undissociated basal dislocations an example of which would be $A_B B_A A_C C_A$ ..... 

Warren [11] has shown that in the case of hexagonal close packed metals, it is possible to make a realistic estimation of the growth fault probability ' $\alpha$ ' and the deformation fault probability ' $\beta$ ' by measuring the half width of X-ray diffraction lines. Reflections for which $h - k = 3n$, where 'n' is an integer, are independent of stacking faults whereas reflections for which $h-k = 3n \pm 1$ and $l \neq 0$ depend upon the faults in the crystal structure. An estimation of the deformation and growth fault probability can be obtained from the following formula for (hkl) values with 'l' even

$$ (3\alpha + 3\beta) = \frac{B_{2\theta} \times \pi^2 \times c^2}{360 \times 1 \times d^2 \times \tan \theta} \quad (4.4) $$

where $B_{2\theta}$ is the full width at half the maximum intensity expressed in degrees.
c = 2 \, d_{002}

'I' is the Miller index in the (hkl) plane for which the estimation of \( \alpha \) and \( \beta \) is being made, 'd' is the interplanar spacing for (hkl) reflection in question, \( \theta \) is the Bragg angle corresponding to this (hkl) plane.

The formula for (hkl) values with 'l' odd is given as

\[
(3 \, \alpha + \beta) = \frac{B_{2\theta} \times \pi^2 \times c^2}{360 \times 1 \times d^2 \times \tan \theta}
\]  \hspace{1cm} (4.5)

From equations (4.4) and (4.5), it is clear that by measuring the half width \( B_{2\theta} \) for reflections with both even and odd values of 'l' it is possible to calculate the stacking fault probabilities \( \alpha \) and \( \beta \). In calculating the half width of the reflections, instrumental broadening is neglected. For the estimation of \( \alpha \) and \( \beta \) in WSe\(_2\) and WSe\(_{1.9}\) the following X-ray reflections (101), (102), (103) and (104) were used. The measurements are presented in tabular form in Table 4.5.

4.2.3 ENERGY DISPERSIVE ANALYSIS OF X-RAYS (EDAX):

Compositions of the single crystals of WSe\(_2\) and WSe\(_{1.9}\) grown using physical vapour transport technique were determined by means of an energy dispersive X-ray analyser attached to a scanning electron microscope (Chapter 2). Energy dispersive (EDAX) spectra taken from representative samples of WSe\(_2\) and WSe\(_{1.9}\) are shown in Figure 4.4. The quantitative elemental data obtained from an analysis of these photographs is summarised in Table 4.6.
Table 4.5

Estimation of stacking fault probability in WSe$_2$ and WSe$_{1.9}$
grown by PVT technique

<table>
<thead>
<tr>
<th>Reflection hkl</th>
<th>WSe$_2$</th>
<th></th>
<th></th>
<th>WSe$_{1.9}$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3$\alpha$ + 3$\beta$</td>
<td>3$\alpha$ + $\beta$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>3$\alpha$ + 3$\beta$</td>
<td>3$\alpha$ + $\beta$</td>
</tr>
<tr>
<td>102 even</td>
<td>0.237</td>
<td>0.047</td>
<td>0.032</td>
<td>0.378</td>
<td>0.082</td>
<td>0.044</td>
</tr>
<tr>
<td>104</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>101 odd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>0.173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6

Chemical composition (wt %) of grown WSe$_2$ and WSe$_{1.9}$ single crystals by EDAX analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>wt% of elements from EDAX</th>
<th>wt% of elements taken for growth experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>Se</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>53.87</td>
<td>46.13</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>55.07</td>
<td>44.93</td>
</tr>
</tbody>
</table>
Fig. 4.4  EDAX Spectra from representative samples of (a) WSe$_2$ and (b) WSe$_{1.9}$
A careful study of the data in this table reveals the following:

(i) Weight percentage of elements from EDAX analysis in both WSe$_2$ and WSe$_{1.9}$ closely agree with the weight percentage of elements taken for the growth of these compounds in the single crystal form.

(ii) EDAX analysis does not show the presence of any impurities in the grown samples of WSe$_2$ and WSe$_{1.9}$.

The presence of deliberately introduced off-stoichiometry in grown samples of WSe$_2$ will have a marked influence on their physical properties. The effect of this off-stoichiometry on electronic properties as observed in the transport property measurements will be described in the following sections of the thesis.

4.2.4 HIGH TEMPERATURE (303-423 K) RESISTIVITY PERPENDICULAR TO c-AXIS ($\rho_\perp$):

Using the high temperature four-probe resistivity set up (Scientific Equipment, Roorkee, India) described in Chapter 2, the resistivity of WSe$_2$ and WSe$_{1.9}$ crystals was investigated in the temperature range 303-423 K. The values of resistivities were obtained from the average number of crystals of both varieties at an interval of 10 K starting from 303 K. The values of resistivities of both varieties determined at 303 K, 383 K and 423 K are presented in Table 4.7. A graphical variation of $\log \rho_\perp$ versus 1000/T for both the cases is represented in Figure 4.5.

A study of the data in the figure reveals the following facts:
Table 4.7

Resistivities ($\rho_\perp$) at 303, 383 and 423 K, activation energies and pre-exponential factors for different samples of WSe$_2$ and WSe$_{1.9}$ single crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_\perp$ (Ω cm)</th>
<th>Activation energies in meV</th>
<th>Pre-exponential factor $\rho_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>3.286</td>
<td>2.985</td>
<td>1.957</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>1.638</td>
<td>1.392</td>
<td>1.090</td>
</tr>
</tbody>
</table>
Fig. 4.5 Variation of inplane resistivity $\rho_\perp$ with reciprocal of temperature from 303 to 423K for WSe$_2$ and WSe$_{1.9}$ single crystal
(a) The values of resistivity at each temperature in the entire temperature range is always more for stoichiometric compound WSe$_2$ as compared to the off-stoichiometric compound WSe$_{1.9}$

(b) In both the samples, the resistivity decreases with increase in temperature.

(c) Both samples show two distinct regions of resistivity variation with temperature. The first region extends from 303 to 383 K and the other from 383 to 423 K. In both regions, the decrease in resistivity with temperature is linear.

The slopes of the linear portions in fig. 4.5 provide values of thermal activation energy of conduction $E$ in the expression.

$$\rho = \rho_0 \exp \left( \frac{+ E}{kT} \right)$$

(4.6)

where $\rho_0$ is the pre-exponential factor and $k$ is the Boltzman constant.

All the values of activation energies and pre-exponential factors for both the samples are represented in Table 4.7. Although it is difficult to derive any inference about the dependence of activation energy on the exact stoichiometric composition of WSe$_{2-x}$ crystals, one thing is absolutely clear that in both the cases the activation energy increases and pre-exponential factor decreases with rise in temperature.

4.2.5 HIGH TEMPERATURE RESISTIVITY PARALLEL TO $c$-AXIS ($\rho_\parallel$) :

In view of the large number of interesting applications of WSe$_2$ (Chapter 1), several studies have been made on the transport properties of this
compound. However, most of these studies are confined to the investigations on the in-plane electrical resistivity. Since WSe\textsubscript{2} has a layered structure and exhibits anisotropy, the interlayer interaction cannot be neglected in a discussion of the electronic properties. Recently, c-axis conduction of the acceptor type layered compounds of graphite intercalation compounds which show a considerable anisotropic behaviour has received considerable attention [12-14]. A number of experimental studies have been made on the temperature dependence of the c-axis resistivity of these compounds. However such studies are comparatively less in WSe\textsubscript{2} and to the best of author's knowledge, the effect of off-stoichiometry on the temperature dependence of c-axis resistivity has never been reported in the literature. Hence, author has made an attempt to investigate the temperature dependence of c-axis resistivity in WSe\textsubscript{2} and off-stoichiometric WSe\textsubscript{1.9} single crystals grown by the physical vapour transport method (Chapter 3).

For resistivity measurements an ordinary two-probe contacting system with the zinc-based pressure contacts [15] as described in Chapter 2, was employed. The resistivity for different samples of both WSe\textsubscript{2} and WSe\textsubscript{1.9} was determined at an interval of 10 K in the temperature range 313-873 K. It may be mentioned here that for c-axis resistivity measurements same samples (which were used for resistivity measurements \perp to c-axis) were used.

The c-axis resistivity data obtained from the above measurements has been used in the Arrhenius plot of log $\rho_\parallel$ versus 1000/T in Figure 4.6. This figure clearly shows the overall temperature dependence of $\rho_\parallel$ for WSe\textsubscript{2} and
Fig. 4.6 Variation of c-axis resistivity ($\xi_{||}$) with reciprocal of temperature from 313 to 873 K for WSe$_2$ and WSe$_{1.9}$ single crystals.
WSe$_{1.9}$. It can be noticed that for both representative samples of WSe$_2$ and WSe$_{1.9}$ there is a decrease in resistivity with increase in temperature. Further it is observed that upon making tungsten diselenide off-stoichiometric there is a decrease in resistivity at all temperatures. The values of resistivity at 313 K, 473 K, 673 K and 873 K are reported in Table 4.8. A careful study of figs. 4.5 and 4.6 show that in comparison to the resistivity along the basal plane the resistivity is considerably high in a direction normal to the basal plane.

The data in Figure 4.6 indicates three linear regions in the temperature ranges 313 - 473 K, 473 - 673 K and 673 - 873 K. The slopes of these linear portions enable us to determine the values of activation energies in these temperature ranges for WSe$_2$ and WSe$_{1.9}$. The values thus obtained are given in Table 4.8. The change in activation energy values in the three ranges is noticeable for both the specimens.

4.2.6 ANISOTROPY:

An interesting question particularly relevant to the family of layered materials is the anisotropy of their transport properties. Mechanically, single crystals of layered materials, behave perfectly 2-dimensionally. It is extremely difficult to handle the crystals because planes slide easily along the X-X (where X = S, Se) layers held together by the very weak van der Waals bond. Intuitively and inquisitively enough; one might also expect similar anisotropies in the electrical properties i.e. the conductivities or mobilities.

The measurements of resistivities along the basal plane $\rho_\perp$ and normal to the basal plane, $\rho_\parallel$ probed in the temperature range 313 to 423 K
Table 4.8

Resistivities ($\rho_\parallel$) at 313, 473, 673 and 873 K and activation energies in different temperature ranges for WSe$_2$ and WSe$_{1.9}$ single crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_\parallel$ ((\Omega) cm)</th>
<th>Activation energies in meV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature range</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>473 K</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>29032</td>
<td>24749</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>21097</td>
<td>20501</td>
</tr>
</tbody>
</table>
and described above can easily be used to determine the anisotropy ratio $\rho_{||}/\rho_{\perp}$ for the representative samples of WSe$_2$ and WSe$_{1.9}$. The results of these calculations are furnished in Table 4.9.

One important derivative which emerges from the data is that anisotropy ratio increases with increase in temperature. This trend is maintained by both the samples of WSe$_2$ and WSe$_{1.9}$. In order to visualise the exact nature of variation of anisotropy ratio with temperature, graphs of $\log \rho_{||}/\rho_{\perp}$ versus $1000/T$ have been plotted and are demarcated in Figure 4.7.

It is seen from both the graphs that this variation of anisotropy ratio indeed follows an exponential relation represented by

$$(\rho_{||}/\rho_{\perp}) = A \cdot e^{-\left(\Delta E/kT\right)}$$

where $\rho_{||}$ and $\rho_{\perp}$ are resistivities - parallel and perpendicular to the crystallographic c-axis, respectively, $\Delta E$ is the activation energy with which the conductivity parallel to c-axis differs from that in the layers and is of the order of 10-800 meV. The pre-exponential factor $A$ is of the order of $m_{||}/m_{\perp}$ where $m_{||}$ and $m_{\perp}$ in the present case are the hole effective masses parallel and perpendicular to the c-axis respectively, $k$ is the Boltzmann constant and $T$ is the temperature. The values of activation energies obtained from the linear portions of the graphs in the different temperature intervals are reported in Table 4.10.

The pre-exponential factor $A$ of the above equation was computed for both WSe$_2$ and WSe$_{1.9}$ crystals. Its value was found to be quite large and
Table 4.9 Anisotropy $\xi = \frac{\rho_{||}}{\rho_{\perp}}$ data for WSe$_2$ and WSe$_{1.9}$ single crystals upto 423 K.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$\frac{1}{T} \times 10^3$ K$^{-1}$</th>
<th>WSe$_2$</th>
<th>WSe$_{1.9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_{</td>
<td></td>
<td>}$ $\Omega$ cm</td>
</tr>
<tr>
<td>313</td>
<td>3.1949</td>
<td>29032</td>
<td>3.224</td>
</tr>
<tr>
<td>403</td>
<td>2.4814</td>
<td>26641</td>
<td>2.450</td>
</tr>
<tr>
<td>413</td>
<td>2.4213</td>
<td>26343</td>
<td>2.196</td>
</tr>
<tr>
<td>423</td>
<td>2.3641</td>
<td>26209</td>
<td>1.957</td>
</tr>
</tbody>
</table>
Table 4.10

Activation energies ( ΔE) obtained from the variation of anisotropy ratio with reciprocal of temperature in different temperature ranges for WSe$_2$ and WSe$_{1.9}$ single crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energies in meV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature range</td>
</tr>
<tr>
<td></td>
<td>313-383 K</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>2.38</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Fig. 4.7 Variation of anisotropy ratio \( \frac{g_u}{g_L} \) with reciprocal of temperature for WSe\(_2\) and WSe\(_{1.9}\), single crystal.
also temperature dependent. Figure 4.8 shows the variation of $A$ with temperature for WSe$_2$ and WSe$_{1.9}$ crystals.

**4.2.7 HALL EFFECT MEASUREMENTS AT ROOM TEMPERATURE:**

Hall measurements provide a sensitive method for detecting the presence of impurity atoms in a crystal. A number of investigators [Table 1.11 Chapter 1] have carried out Hall effect measurements on WSe$_2$. However, there appears to be no such work on off-stoichiometric (WSe$_{1.9}$) single crystals. Author has therefore used a modification of the van der Pauw technique described in Chapter 2 to evaluate the type, mobility and carrier concentration of WSe$_2$ and WSe$_{1.9}$ single crystals. Hall mobility of the samples was determined by measuring the change in resistance ($\Delta R$) when a magnetic field was applied perpendicular to the sample. Hall mobility $\mu_H$ is given by the relation.

$$\mu_H = \frac{t}{B} \left( \frac{\Delta R}{\rho} \right)$$  \hspace{1cm} (4.7)

where $t$ is the thickness of the crystal, $B$ is the intensity of the magnetic field, $\Delta R$ is the change in resistance due to the magnetic field and $\rho$ is the resistivity along the plane of the sample.

The resistivity $\rho$ of the samples was determined by using the formula

$$\rho = \frac{\pi d (R_1 + R_2) f(R_1 / R_2)}{2 \frac{1}{1+n2}}$$ \hspace{1cm} (4.8)

as described in Chapter 2.
Fig. 4.8 Variation of pre exponential factor ‘A’ with temperature for WSe$_2$ and WSe$_{1.9}$ single crystal.
The range of magnetic field used here varied from 0.25 to 10.35 k Gauss. Knowing the values of $t$, $B$, $\Delta R$, and $\rho$, the mobility of carriers was calculated using equation (4.7).

The Hall coefficient and carrier concentration were also calculated as:

$$R_H = \frac{\mu_H \rho}{q} \quad (4.9)$$

and

$$\rho = \frac{1}{R_H} \quad (4.10)$$

All the results obtained from Hall effect measurements and the resistivity $\rho$ of the representative samples are given in Table 4.11. A careful study of the data presented in this table indicates the following.

(a) The positive values of Hall coefficient clearly point out that both $\text{WSe}_2$ and $\text{WSe}_{1.9}$ are p-type and majority carriers in them are holes.

(b) Room temperature resistivity decreases when tungsten diselenide is made selenium deficient. This supports the inference drawn from the resistivity measurements carried out in different temperature ranges.

(c) The mobility decreases and carrier concentration of the charge carriers increases upon making them selenium deficient.

### 4.2.8 THERMOELECTRIC POWER MEASUREMENTS :

An electrical potential (voltage) is generated within any isolated conducting material that is subjected to a temperature gradient. This is called...
Table 4.11

Resistivity $\rho$, Hall coefficient $R_H$, mobility $\mu$, carrier concentration $p$ at room temperature for WSe$_2$ and WSe$_{1.9}$ single crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Resistivity $\rho$ Ω cm</th>
<th>Hall coefficient $R_H$ cm$^3$ C$^{-1}$</th>
<th>Mobility $\mu$ cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>Carrier Concentration $p$ cm$^{-3}$</th>
<th>Type of crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>0.514</td>
<td>212.6</td>
<td>413.63</td>
<td>0.98 x 10$^{17}$</td>
<td>p</td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>0.203</td>
<td>300.8</td>
<td>148.2</td>
<td>8.4 x 10$^{17}$</td>
<td>p</td>
</tr>
</tbody>
</table>
absolute Seebeck effect, ASE. The absolute Seebeck coefficient,

$$\text{ASC} = \left[ \frac{d}{dT} \text{ASE} \right]$$

is defined as the instantaneous rate of change of the ASE with respect to temperature at a given temperature.

The least complicated example of the way in which this phenomenon is used is to form a thermocouple composed of two dissimilar conductors or thermoelements by electrically joining one set of their ends.

The complimentary effect to Seebeck effect is the Peltier effect, which is the reversible change in the heat content at an interface between dissimilar conductors that results from the flow of current across it. Application of the Peltier effect include thermoelectric devices for refrigeration and power generation.

The possibility of using thermoelectric phenomena in the generation of electricity was considered as early as in 1885 by Rayleigh who first calculated the efficiency of a thermoelectric generator. Following the five-fold increase in the price of coal in 1974, a closer look, was taken at the possibility of large-scale production of electricity by thermoelectric effect. Moreover, concern over the depletion of the ozone layer in 1980s and a general public interest in environmentally friendly energy sources have been accompanied by a renewed interest in thermoelectric generation as a potential source of large-scale electrical power using waste heat. Therefore from the view point of future energy problems, it is important to study the thermoelectric conversion of materials because the conversion of thermal energy into electrical energy meets the need when the
available temperature difference is comparatively small. Thermoelectric devices are reliable, operate unattended in hostile environments and are environmentally friendly. In this context, in the recent years there has been a renewed interest in searching for novel materials that may be used for efficient, environmentally sound cooling and power generation purposes.

Established thermoelectric materials used in power generation can be divided into three categories [16] depending on their temperature range of application. Bismuth telluride and its alloys work around room temperature and have a maximum operating temperature of about 500 K. In the intermediate temperature range (600 - 900 K), PbTe based alloys and TAGS (Te - Ag - Ge-Sb) are the most efficient materials. At the highest temperature (1000-1300 K) Si-Ge alloys are used in power generation devices mainly for space applications.

Looking to the tremendous potential of thermoelectric power generation, several countries have taken up research on new materials exhibiting high thermoelectric efficiencies [17].

The conversion efficiency of thermal energy into electrical energy of a material is characterised by its thermoelectric figure of merit $Z$, which is defined by the following equation.

$$Z = \frac{S^2 \sigma}{\lambda}$$

(4.11)

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\lambda$ is the thermal conductivity of the thermoelectric material.

This parameter $Z$ is of central importance in any program to optimise the thermoelectric properties. The Seebeck coefficient and electrical conductivity
depend strongly on the Fermi level [18-20] which in turn depends upon the
carrier concentration, the carrier effective mass and the temperature. In
theoretical formulations it is convenient to express the thermoelectric transport
coefficients in terms of the Fermi energy $E_F$ (conventionally measured) from
the band edges). Since the thermal conductivity depends weakly on the carrier
concentration ($n$) the general effect of an increase or change in carrier
concentration would manifest itself in the figure-of-merit, through the power
factor, $S^2 \sigma$.

In general the Seebeck coefficient [21] for a non-degenerate
semiconductor using classical statistics can be expressed as

$$ S = m \frac{k}{e} \left[ \frac{5}{2} + s - \xi \right] $$

(4.12)

where signs $m$ refer to the contributions from electrons and holes, respectively.

$\xi = \frac{E_F}{kT}$ is the reduced Fermi energy, $k$ is the Boltzmann constant, $T$ the
absolute temperature, $s$ refers to the scattering parameter, ‘$s$’ assumes
different values depending upon the scattering mechanism [Table 4.12]. Equation
(4.12) can also be expressed [23] in the form

$$ S = m \frac{k}{e} \left[ A - \xi \right] $$

(4.13)

where the constant $A$ is related to the scattering parameter ‘$s$’ by the relation

$$ A = \frac{5}{2} + s $$

(4.14)

The electrical conductivity for a non-degenerate semiconductor is
given by
Table 4.12

Values of Scattering parameter ‘s’ for different scattering mechanism

<table>
<thead>
<tr>
<th>Scattering Mechanism</th>
<th>Values of scattering parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionised impurities / defects</td>
<td>+ 1.5</td>
<td>[17]</td>
</tr>
<tr>
<td>Acoustic phonons</td>
<td>- 0.5</td>
<td>[17]</td>
</tr>
<tr>
<td>Optical phonons</td>
<td>- 1.5</td>
<td>[22]</td>
</tr>
</tbody>
</table>
\[ \sigma = n \ e \ \mu_c \]  \hspace{1cm} (4.15) \\

where \( \mu_c \) is the carrier mobility and \( n \) is the carrier concentration, which is related to the reduced Fermi energy by the equation.

\[ n = 2 \left( \frac{2\pi m^* kT}{\hbar^2} \right)^{3/2} \exp \xi \]  \hspace{1cm} (4.16) \\

The thermal conductivity is written as a sum of the lattice and the electronic components i.e. \( \lambda = \lambda_L + \lambda_e \). Evidently \( \xi \) affects the thermal conductivity only through the electronic contribution \( \lambda_e \).

In addition

\[ \lambda_e = L_0 \ (k/e)^2 \ \sigma \ T \]  \hspace{1cm} (4.17) \\

where the dimensionless quantity \( L_0 \) is referred to as the Lorentz factor.

The use of classical statistics in describing the behaviour of the charge carriers is justified only for non-degenerate semiconductors where the carrier concentration is low. For a degenerate \([24]\) semiconductor, when the carrier concentration is high (> \( 10^{18} \text{ cm}^{-3} \)), Fermi Dirac statistics must be employed. The expressions for the Seebeck coefficient and the Lorentz factor then take the form \([18,21]\).

\[ S = m \ k/e \left( \delta - \xi \right) \]  \hspace{1cm} (4.18) \\

where

\[ \delta = \frac{(s + 5/2) F_{S+3/2}(\xi)}{(s + 3/2) F_{S+1/2}(\xi)} \]  \hspace{1cm} (4.19)
and

\[ L_0 = \frac{(s + 7/2) F_{s+5/2}(\xi)}{(s + 3/2) F_{s+3/2}(\xi)} - \delta^2 \] (4.20)

where \( F \) \( \xi \) are the Fermi-Dirac integrals. The Fermi-Dirac integral \([17]\) is given by the expression

\[ F_s(\xi) = \int \frac{\varepsilon^s}{\exp(\xi - \varepsilon) + 1} \, d\varepsilon^* \] (4.21)

Ohsugi et al. \([25]\) have proposed a novel calculating procedure for \( F_s(\xi) \) with an arbitrary real index \( s \).

The carrier concentration is related to \( \xi \) and the effective mass \( m^* \) by the following relation \([26,27]\).

\[ n = \frac{4\pi}{h^3} (2m^* kT)^{3/2} \, F_{1/2}(\xi) \] (4.22)

Thus \( m^* \) can be calculated by determining \( F_{1/2}(\xi) \) from equation (4.21) and substituting the value in equation (4.22).

The electrical conductivity is given by

\[ \sigma = \sigma_0 \varepsilon \] (4.23)

where

\[ \sigma_0 = 2 (2\pi m^* kT / h^2)^{3/2} e \mu_c \] (4.24)
According to [28] the performance of a thermoelectric material is characterised by three important coefficients - electric, thermal and thermoelectric. It is seen from the expression for $Z$ (equation 4.11) that a high ratio of electrical to thermal conductivity as well as large thermoelectric power are needed in selecting materials for both thermoelectric generation and refrigeration.

One of the important issues relative to the development of thermoelectric materials at any temperature is identifying mechanisms which might give high thermopower ($S$) at the temperature of interest. In most materials [29] at temperatures far from a phase transition, the electrical conductivity $\sigma$ and thermopower are related to the electron density of states near the Fermi energy $g(E_F)$. The conductivity is proportional to $g(E_F)$ while $S$ is proportional to $\frac{1}{g} \left( \frac{dg}{dE} \right)$ at $E_F$. An exact variation of $\sigma$, $S$ and $S^2\sigma$ with carrier concentration is shown in Fig. 4.9. It is seen that as $n$ (or $g$) is increased $\sigma$ typically increases while $S$ decreases. At a given temperature, the power factor reaches its maximum value at an optimum carrier concentration which can be achieved by suitable doping or by changing the deviation of the composition from stoichiometry. It is therefore possible to achieve optimisation of the thermoelectric properties through doping / intercalation or by a change in chemical composition of the material to tune
Fig. 4.9 Dependence of $S$, $\sigma$, and $S^2\sigma$ on the concentration of free carriers.
the number of carriers. In this scheme high mobility carriers are especially desirable so that $\sigma$ can be large without also having a large carrier density.

In a search for potentially high performance thermoelectric materials a critical literature survey was undertaken. As a result, author came across lamellar (quasi-three dimensional) semiconducting transition metal dichalcogenides which appear very promising. Some of the earlier works [4, 30] on thermoelectric properties measurements and Hall effect measurements of these compounds is given in Tables 4.13 and 4.14. It is seen from the data presented in these tables, that among the transition metal dichalcogenides $TX_2$ (with $T = W, Mo, Te$ and $X = Se, Te$), $WSe_2$ possesses excellent properties as a thermoelectric material around room temperature. Its figure of merit is comparable to the best known thermoelectric materials. Efforts should therefore be made to synthesise $WSe_2$ by altering its stoichiometry or growth conditions and a thorough investigation of its thermoelectric properties around room temperature should be made. This should give us an efficient thermoelectric material to work in the temperature range around room temperature.

It is also well known [31] that thermoelectric power provides an independent method for determining the carrier sign density and position of Fermi levels in semiconductors. The thermoelectric effect offers a distinctive advantage over other methods because the measured thermoelectric voltage is directly related to the carrier concentration which makes the thermoelectric measurements simpler even for low mobility materials [32]. Thermoelectric
<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck coefficient S $\mu$ V/deg</th>
<th>$\rho$ $\Omega$ cm</th>
<th>Thermal conductivity $K$ $\text{W cm}^{-1}\text{C}^{-1}$</th>
<th>Thermo-electric power factor $S^2/\rho$ $\text{W cm}^{-1}\text{deg}^{-2}$</th>
<th>Figure of merit $Z$ $\text{K}^{-1}$</th>
<th>Seebeck coefficient S $\mu$ V/deg</th>
<th>$\rho$ $\Omega$ cm</th>
<th>Thermo-electric power factor $S^2/\rho$ $\text{W cm}^{-1}\text{deg}^{-2}$</th>
<th>Seebeck coefficient S $\mu$ V/deg</th>
<th>$\rho$ $\Omega$ cm</th>
<th>Thermo-electric power factor $S^2/\rho$ $\text{W cm}^{-1}\text{deg}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>990</td>
<td>0.5</td>
<td>0.017</td>
<td>1.96 x 10$^{-6}$</td>
<td>1.15 x 10$^{-4}$</td>
<td>560</td>
<td>0.57</td>
<td>5.5 x 10$^{-7}$</td>
<td>527</td>
<td>0.78</td>
<td>3.56 x 10$^{-7}$</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>-900</td>
<td>3.44</td>
<td>0.023</td>
<td>2.35 x 10$^{-7}$</td>
<td>1.02 x 10$^{-5}$</td>
<td>20</td>
<td>20.00</td>
<td>4.05 x 10$^{-8}$</td>
<td>190</td>
<td>1.0</td>
<td>3.6 x 10$^{-8}$</td>
</tr>
<tr>
<td>MoTe$_2$</td>
<td>-780</td>
<td>8.5</td>
<td>0.020</td>
<td>7.16 x 10$^{-8}$</td>
<td>3.58 x 10$^{-6}$</td>
<td>25</td>
<td>25.0</td>
<td>5.18 x 10$^{-9}$</td>
<td>-104</td>
<td>0.1</td>
<td>1.1 x 10$^{-7}$</td>
</tr>
<tr>
<td>TaSe$_2$</td>
<td>-13</td>
<td>0.0004</td>
<td>0.017</td>
<td>4.23 x 10$^{-7}$</td>
<td>2.48 x 10$^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaTe$_2$</td>
<td>-14</td>
<td>0.00036</td>
<td>0.014</td>
<td>5.44 x 10$^{-7}$</td>
<td>3.89 x 10$^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WTe$_2$</td>
<td>-57</td>
<td>0.00287</td>
<td>0.016</td>
<td>1.13 x 10$^{-6}$</td>
<td>7.08 x 10$^{-5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.14

Hall effect measurements of certain TX₂ compounds at room temperature (T = Mo, W, X = Se, Te) [Ref. 4]

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ρ (Ω cm)</th>
<th>Hall coefficient RH (cm² /coul.)</th>
<th>Carrier Concentration p (cm⁻³)</th>
<th>Mobility μ (cm² V⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe₂</td>
<td>0.78</td>
<td>78</td>
<td>8.0 x 10¹⁶</td>
<td>99</td>
</tr>
<tr>
<td>MoSe₂</td>
<td>7.6</td>
<td>-100</td>
<td>5.6 x 10¹⁶</td>
<td>15</td>
</tr>
<tr>
<td>MoTe₂</td>
<td>7.0</td>
<td>-85</td>
<td>7.3 x 10¹⁶</td>
<td>12</td>
</tr>
</tbody>
</table>
measurements are therefore, frequently employed in the study of semiconductors because of the information they can provide about effective density of states, effective mass of the carriers and the scattering mechanism.

Looking to the importance of WSe$_2$ as a thermoelectric material outlined above, author has carried out a detailed study on the thermoelectric properties of WSe$_2$ and its off-stoichiometric compound (WSe$_{1.9}$) in the temperature range (308-433 K) and the results thus obtained are presented in this section.

The thermoelectric power measurements were carried out with the help of "Difference Temperature Controller" developed by Scientific Solutions, Mumbai. The details of this set up have already been provided in Chapter. 2. Several experimental measurements were made on each sample. A good reproducibility was obtained and experimental data for TEP were always within the error bars i.e. ~ 5%.

The values of thermoelectric power $S$ for representative samples of WSe$_2$ and WSe$_{1.9}$ were determined at different temperatures using the above set up. The variation of $S$ with temperature in the temperature range 308-433 K is very clearly depicted in Figure 4.10 for both the samples.

A study of the data presented in this figure brings about the following revelations:

(a) In both the samples of WSe$_2$ and its off-stoichiometric compound WSe$_{1.9}$ the sign of thermoelectric power (TEP) is positive and remains positive over the entire temperature range.
Fig. 4.10 Thermoelectric power 'S' versus 'T' for WSe$_2$ and WSe$_{1.9}$, single crystal
(b) The absolute value of thermoelectric power is more in WSe$_2$ crystals as compared to WSe$_{1.9}$. This trend is maintained at all temperatures.

(c) In both the cases, the values of ‘S’ increase steadily with an increase in temperature, confirming thereby the typical semiconducting behaviour of the different samples of WSe$_2$ and WSe$_{1.9}$. TEP increases from $668 \ \mu \text{V K}^{-1}$ at 308 K to $715 \ \mu \text{V K}^{-1}$ at 433 K for WSe$_2$ and from $463 \ \mu \text{V K}^{-1}$ at 308 K to $510 \ \mu \text{V K}^{-1}$ at 433 K for WSe$_{1.9}$. This increasing trend of TEP with increasing temperature resembles that reported by Hicks [4] for WSe$_2$ in the similar temperature range.

According to Hicks [4] and Rahman and Ashraf [33] a simple relationship can be obtained for a p-type non-degenerate semiconductor which directly relates the Seebeck coefficient to the carrier concentration ‘p’, which in turn is determined from the Hall effect measurements.

\[
S = \frac{k}{e} \left[ A + \ln \left( \frac{2(2\pi m k T)^{3/2}}{p h^3} \right) \right] \tag{4.26}
\]

In this expression, $k$ is the Boltzmann constant, $e$ is the electronic charge, $A$ is the scattering coefficient whose value depends upon the scattering mechanism, $h$ is the Planck’s constant, $m$ is the effective mass of the charge carriers and $T$ is the temperature.

It is well known [34] that in a p-type non-degenerate semiconductor model the carriers are scattered in three different ways (i) by ionised impurities (or defects), (ii) by acoustic phonons or (iii) by optical phonons. For scattering by ionised impurities or defects, the mobility of charge carriers increases with
increasing temperature. The mobility $\mu$ shows a $T^s$ dependence with $s = 1.5$. If acoustic or optical phonons dominate the scattering mechanism then the mobility of charge carriers decreases with increasing temperature and $\mu$ shows a $T^{-s}$ dependence with $s = 0.5$ for acoustic phonons and $s = 1.5$ for optical phonons [Table 4.12].

The mobility measurements [35] on p-type WSe$_2$ samples carried out in the temperature range [308-450 K] show an increase in mobility with increase in temperature. This indicates that scattering of holes in WSe$_2$ is regulated by defect concentration in these crystals and the scattering parameter $s$ assumes the values 1.5. Using this value of $s$ in equation (4.14) we get the value of $A$ as 4.

Using this value of $A$, the value of $p$ form the Hall effect measurements [Table 4.11] and the value of $S$ from the TEP measurements, the effective mass of charge carriers i.e. holes in WSe$_2$ and WSe$_{1.9}$ can be easily determined with the help of equation [4.26]. The values thus obtained are listed in Table 4.15.

Further equations (4.12) and (4.13) suggest that if TEP is plotted against the reciprocal of temperature ($T^{-1}$) a straight line should result. From the slope of this line, the value of fermi energy $E_F$ [36] can be determined.

Figure 4.31 shows the variation of TEP with an inverse of temperature for WSe$_2$ and WSe$_{1.9}$ single crystals. The values of $E_F$ obtained from the slopes of the plots are represented in Table 4.15.

In the absence of reliable measurements on thermal conductivity
Table 4.15

Values of Fermi energy $E_F$, Effective mass, Theromoelectric Power factor and Figure of merit for WSe$_2$ and WSe$_{1.9}$ single crystals at room temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Fermi Energy $E_F$ (meV)</th>
<th>Effective mass $m_\text{h}^*$</th>
<th>$S$ ($\mu$V K$^{-1}$)</th>
<th>$\sigma$ ($\Omega \text{ cm}$)$^{-1}$</th>
<th>Thermoelectric power factor $S^2 \sigma$ ($\mu$W cm$^{-1}$ K$^{-2}$)</th>
<th>Figure of merit $Z$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>50.44 0.295 $m_e$</td>
<td>668</td>
<td>1.945</td>
<td>0.87 x 10$^{-6}$</td>
<td>0.51 x 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>WSe$_{1.9}$</td>
<td>49.88 0.253 $m_e$</td>
<td>463</td>
<td>4.926</td>
<td>1.06 x 10$^{-6}$</td>
<td>0.62 x 10$^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>
the thermoelectric properties of a semiconducting material are decided by its
thermoelectric power factor $S^2 \sigma$. Taking the values of $S$ and $\sigma$ at room
temperature for WSe$_2$ and WSe$_{1.9}$, $S^2 \sigma$ has been determined for them and
the values thus obtained are represented in Table 4.15. However, taking the
value of thermal conductivity for WSe$_2$ from the literature [Table 4.13], the
figure of merit for WSe$_2$ and WSe$_{1.9}$ have also been estimated and are given
in Table 4.15.

Further, looking to the importance of tungsten diselenide as a
thermoelectric material, the variation of thermoelectric power factor $S^2 \sigma$ with
temperature has been studied in the small temperature range [313 - 423 K]
around room temperature. For this purpose, the values of thermoelectric
power 'S' have been taken from the data used for Figure 4.11 and the resistivity
$\rho_\perp$ from the data for fig. 4.5. Figure 4.12 shows the variation of $S^2 \sigma$ with
temperature for WSe$_2$. In order to see the effect of off-stoichiometry on the
performance of WSe$_2$ as a thermoelectric material, similar data has been
evaluated for WSe$_{1.9}$. The variation of $S^2 \sigma$ with temperature for WSe$_{1.9}$
is also shown in Figure 4.12. A study of this figure and Table 4.16 reveals the
following points.

(a) In both the cases the thermoelectric power factor increases steadily
with increase in temperature.

(b) In the temperature range 313 to 393 K the value of power factor is
more for off-stoichiometric WSe$_{1.9}$ crystal as compared to the
stoichiometric WSe$_2$. 
Fig. 4.11 Variation of thermoelectric power ‘S’ with an inverse of temperature for WSe$_2$ and WSe$_{1.9}$ single crystal
Fig. 4.12 Variation of Thermoelectric Power Factor $S^2\sigma$ with temperature $T$ in WSe$_2$ and WSe$_{1.9}$ single crystal
(c) As the temperature exceeds 393 K, the value of power factor in WSe$_2$ becomes more and remains larger than WSe$_{1.9}$ with further increase in temperature.

4.2.9 MICROSTRUCTURES:

The Numann principle states that the symmetry of a physical property of a crystal includes its point group symmetry. Thus the morphology of the surface of a crystal near equilibrium condition reflects the symmetry of the latter. Consequently, characteristic features on crystal surfaces, the distribution of steps around e.g. a screw dislocation, exhibit the symmetry of the surface. The as grown surfaces of the crystals grown in the laboratory or those which occur in nature offer some features which signify how they grow under different conditions. Morphology of as grown surfaces of the bulk single crystals consists of variety of structures whose study lead us to derive the condition and mechanism of growth.

A study of microstructures on the (a, b) basal planes of the grown crystals of WSe$_2$ and WSe$_{1.9}$ has been made with the help of Axiotech Reflected Light Microscope described in Chapter 2. The features most common to both the crystals have been presented below.

**Features showing layer growth:**

A typical photograph showing the presence of growth layers on an otherwise homogeneously flat surface of WSe$_2$ is shown in Figure 4.13. One is inclined to conjecture that layer mechanism is operative during crystal growth. In support of this we have Figures. 4.14, 4.15 and 4.16. Figure 4.14 shows the
Fig. 4.13 Micrograph showing the presence of growth layers on the flat surface of a WSe$_2$ single crystal
Fig. 4.14 Micrograph showing the initiation of growth layers from the edge of a $\text{WSe}_2$ single crystal
Fig. 4.15 Growth layers initiating from impurities on a WSe$_{1.9}$ single crystal.
4.16 Micrograph showing the presence of thin and thick layers on the surface of a WSe$_{1.9}$ single crystal
initiation of the growth layers from the edge of the crystal resulting into a flat surface along with growth layers. Figure 4.15 depicts the growth layers initiating from impurities on the crystal surface while in fig. 4.16 one can clearly see the presence of thin and thick layers on the grown surface of a WSe$_{1.9}$ single crystal. Figure 4.17 shows the surface of a WSe$_2$ crystal showing perfectly flat surface with practically no features upon it.

According to Strickland - Constable [37], in order that a crystal face may grow flat it is necessary that a crystal grows by spreading of layers of constant thickness across the face. Existence of a flat region on a crystal surface is therefore corroborative of layer spreading and piling. All the microstructures presented in Figures 4.13 and 4.17 clearly suggest that layer growth mechanism is operative in the growth of WSe$_2$ and WSe$_{1.9}$ crystals.

**Growth Spirals**:

Figure 4.18 shows the surface of a WSe$_{1.9}$ single crystal where a polygonal spiral having a slightly distorted hexagonal shape originating from a single point can be clearly viewed. Spirals shown in Figures 4.19(a) and 4.19(b) are single spirals starting from single screw dislocations in a hexagonal shape in accordance with the symmetry of the face. The clockwise and anticlockwise nature of the spirals in Figures 4.19(a) and (b) respectively show that they are originating from screw dislocations of opposite sign. Examples of three clockwise hexagonal spirals consisting of two turns in WSe$_2$ and two clockwise hexagonal spirals consisting of five turns in WSe$_{1.9}$ are provided in Figures 4.20 and 4.21. It is generally observed that when two or more
Fig. 4.17  Perfectly flat surface with almost no other features on single crystal of WSe$_2$
Fig. 4.18

Polygonal spiral having a slightly distorted hexagonal shape on WSe$_{1.9}$
Micrographs showing the presence of two polygonal clockwise and anticlockwise spirals of perfect hexagonal shape starting from single screw dislocation on the surface of a WSe$_2$ single crystal
Fig. 4.20 Micrograph showing three clockwise hexagonal spirals consisting of two spiral furns on the surface of a WSe$_2$ single crystals.
Fig. 4.21 Micrograph showing two clockwise hexagonal spirals consisting of five spiral turns on the surface of a WSe$_{1.9}$ single crystal.
screw dislocations of the same sign are situated very close to each other a group of non-interacting spirals of the same number as that of screw dislocation points are generated [38].

**Evidence of layer and spirals growth on the same face:**

An example showing simultaneous existence of layer growth and spirals on the same face of a WSe$_2$ single crystal which is representative of both crystals is shown in Figure 4.22. Here one can clearly notice along with a hexagonal spiral the presence of growth layers in the upper region of the micrograph.

### 4.3 DISCUSSION:

The photographs of different crystals in fig. 4.1 clearly portray that it is possible to grow single crystals of WSe$_2$-$x$ ($x = 0$ and 0.1) having fairly large size by the PVT technique. It is also seen that the resulting dimensions of the crystals bear no systematic relationship with the stoichiometry, but instead they depend on the crystallisation conditions. The electron diffraction photograph shown in Figure 4.2 confirms the single crystallinity of the grown crystals.

The observations on lattice parameters on WSe$_2$ presented in Table 4.3 are nearly in agreement with those obtained by earlier investigators (Chapter 1). The values of lattice parameters for WSe$_{1.9}$ have been reported for the first time. It is found that although there is no significant variation in the values of lattice parameters $a$ and $c$ in WSe$_{2-x}$, the density ($\rho$) in the case of pure WSe$_2$ is more than the off-stoichiometric crystals i.e. WSe$_{1.9}$. The decrease in $\rho$ can be attributed to the formation of defects introduced due to off-stoichiometry.
Fig. 4.22 Micrograph showing simultaneous existence of hexagonal spiral and growth layer on the same face of a WSe$_2$ single crystal.
The stacking fault probability \((\alpha)\) or \((\beta)\) is the fraction of the layers undergoing stacking faults in a given crystal and hence one fault is expected to be found in \(1/\alpha\) or \(1/\beta\) layers. The values of \(\alpha\) and \(\beta\) obtained for WSe\(_2\) in Table 4.5 indicate that there is 1 growth fault per 12 layers and 1 deformation fault per 23 layers. Similarly the values of \(\alpha\) and \(\beta\) for WSe\(_{1.9}\) thus indicate that there is 1 growth fault per 12 layers and 1 deformation fault per 23 layers. The values of \(\alpha\) and \(\beta\) for WSe\(_2\) and WSe\(_{1.9}\) thus clearly suggest that a high density of defects are introduced into the samples due to off-stoichiometry. This increase of stacking faults due to off-stoichiometry supports the decrease in density in the off-stoichiometric crystals of WSe\(_2\).

The EDAX analysis of the grown crystals point out that in both stoichiometric and off-stoichiometric single crystals of WSe\(_2\) the weight percentage of elements obtained from EDAX analysis agrees with the weight percentage of elements taken for their synthesis in the form of single crystals. Thus it is possible to prepare off-stoichiometric single crystals of WSe\(_2\) by a PVT method.

The electrical resistivity \((\rho_\perp)\) measurements in the temperature range (303-423 K) exhibit a semiconductor like behaviour. The decrease in resistivity with increasing temperature and Arrhenius plots of resistivity show a thermally activated behaviour which can be described by different temperature regimes with distinct activation energies. The low values of activation energies characterise an extrinsic conductivity. There is an increase in the value of the activation energy when the temperature range of resistivity measurements is
extended from 303-383 K to 383-423 K. However, the values of activation energy are quite low as compared to the band gaps of these materials (Chapter 6).

We have observed that in both WSe$_2$ and WSe$_{1.9}$ crystals $\rho_{||}$ is much larger than the in plane resistivity $\rho_{\perp}$, thus making these crystals highly anisotropic. These results suggest that virtually all $\pi$-electrons are directionally localised i.e. they can move along the basal planes but are unable to diffuse across the stack of layers along the c-axis. These $\pi$-electrons may transfer to the neighbouring WSe$_2$ layers through various kinds of conduction processes [39,40].

(i) conduction path (conducting channel) caused by structural imperfections,

(ii) impurity and phonon assisted hopping,

(iii) thermal activation hopping, and

(iv) small polaron effect.

Recently Sugihara’s group [41,42] has proposed models to explain their results on c-axis conduction in layered graphite intercalation compounds [GICs]. According to them the overlapping of a wave function of carrier over adjacent layers in the layered compounds is crucial to the c-axis conduction. Depending on the degree of overlapping the following two models have been proposed:

A two dimensional (2D) band model and a three dimensional (3D) band model.
In a 2D model there is no overlapping of the wavefunctions over nearest neighbour layers of the layered compound. Carriers are localised in each layer along the basal plane. In this model c-axis conduction can occur through a hopping of carriers between layers stacked along the c-axis through a conduction-channel (conduction path) Hamiltonian. Alternately, the wave function of carriers are not localised in layer along the basal plane (a 3D band model) leading to a band-like conduction along the c-axis.

Agarwal et al's [43,44] group explained the c-axis conduction by supposing the presence of stacking faults in layered compounds they studied. Existence of such faults led to a localisation of electron states which could provide possibility of conduction perpendicular to the layers.

The resistivity anisotropy observed in samples of WSe\(_2\) was explained by Agarwal et al. [44] and Kautek [45] in terms of stacking disorder. They suggested that frequently observed stacking faults in crystals of TX\(_2\) (where T is the transition metal and X is chalcogen) were responsible for the observed strong anisotropic carrier scattering. In fact, a model for scattering of stacking faults was proposed by Fivaz and Schmid [46]. According to this model, even though the scattering power of stacking faults is weak their random formation is highly probable in layer structures and pronounced effects on charge transport may be expected since translational invariance is systematically destroyed in one direction. Real crystals should then be viewed as structures with a one-dimensional disorder.

The description of transport properties in layered semiconductors
can be given by introducing a “mobility edge $\Delta E$” for the scattering across the layers [46]. The expression for anisotropy then becomes

$$\frac{\rho_{||}}{\rho_{\perp}} = \frac{m_{||}}{m_{\perp}} \exp \left( \frac{\Delta E}{kT} \right) = \frac{\mu_{\perp}}{\mu_{||}} \exp \left( \frac{\Delta E}{kT} \right)$$

The observed anisotropy can thus be accounted for by the assumption of a mobility edge for the vertical mobility. At high enough temperatures, conductivity across the layer is not a hopping process but a bound process. Only at very low temperatures does the carrier transport occur as a hopping process between localised states.

It can be noticed from the observations reported in fig. 4.8 that the pre-exponential factor $A$ is quite large and temperature dependent. The large value of $A$ can be attributed to the presence of strong anisotropic scattering mechanism caused by the presence of stacking faults [15]. The presence of stacking faults in WSe$_2$-$\chi$ crystals has been shown by weak beam transmission electron microscopy of the samples by Singh [47].

In the case of thin doped n-type InSe layered crystals the pre-exponential factor was found to depend on the carrier concentration [48] and its room temperature value was explained assuming the existence of two dimensional electrical sub bands associated with planar faults.

In essence, we see that the c-axis conduction and the pre-exponential factor which expresses the anisotropic effective mass ratio $m_{||} / m_{\perp}$ have so far been explained in terms of the existence of stacking faults. However, recently crystals of WSe$_2$ have been extensively studied by scanning tunneling
microscope STM [49-52] and in no case the investigators have found the stacking faults, indicating an improved crystal quality under the growth conditions used for the growth of these crystals. Therefore one has to look for an alternate explanation for the small c-axis conduction, large basal plane conduction and an anisotropic effective mass ratio \( m_\parallel / m_\perp \) frequently observed in such compounds.

As discussed in chapter 1, band structure calculations made by Wison and Yoffe [53], Bromley et al. [54], Coehoorn et al. [55] and Mattheiss [56] on WSe\(_2\) and related materials place the valence band maximum (VBM) at the centre (i.e.) \( \Gamma \) of the BZ. Since at \( \Gamma \), the top of the valence band is mainly composed of \( W 5d_2^2 \) and \( \text{Se}4pz \) out of plane orbitals, considerable band dispersion is found not only along the layers but also perpendicular to them, resulting in a fairly isotropic effective mass ratio (i.e. \( m_\parallel / m_\perp \)) \( \sim 1.0 \) for holes. One therefore can not explain the anisotropic effective mass ratio on the basis of band structure calculations made by these investigators.

Recently, Straub et al. [57] and Finteis et al. [58] have shown that the valence band maximum (VBM) is located at the edge of the BZ (K) rather than at its centre (\( \Gamma \)). According to them VBM is found as much as 170 meV higher in energy than the top most state at \( \Gamma \). While the top most occupied states at \( \Gamma \) consist of hybridised \( \text{Se}4pz \) and \( W 5d_2^2 \) out of plane orbitals, the states at K(H) are almost exclusively derived from \( W 5d_{xy} \) in plane orbitals leading to a very weak dispersion perpendicular to WSe\(_2\) sheets. From their LDA calculations authors [58] find an appreciable band mass
anisotropy \( \frac{m_{||}}{m_{\perp}} \sim 4 \). This explains the anisotropic effective mass ratio observed in the present work.

Through this finding one can also explain the observed transport anisotropy, the major part, however, can still be attributed to carrier scattering. The two dimensional band dispersion [58] near the VBM induces an anisotropy also in the scattering rate. With the VBM at K and negligible dispersion along KH, thermally excited holes will only exist in a narrow energy "valley" centred along this line. From the topological shape of the valley it is obvious that the carriers are much more likely to be scattered along the valley axis than perpendicular to it. This results in an enhanced dissipation of current along the c-axis as compared to in plane directions.

This explanation given by Finteis et al. [58] explains the large resistivity along the c-axis and low resistivity of the WSe\(_2\)-\(_x\) samples along the basal planes.

However in view of the controversy [59] regarding the exact band structure calculations on WSe\(_2\) the other plausible way by which we can explain the c-axis conduction is by means of a qualitative explanation within the framework of a 2D-model with hopping conduction mechanism [42]. Accordingly, the carriers mainly diffuse along each layer of the layered compound along the basal plane and occasionally make transitions to the nearest neighbours along the c-axis through hopping.

The increased conduction along the c-axis in WSe\(_{1.9}\) crystals as compared to WSe\(_2\) can be due to the defects formed by structural changes
induced due to deliberate off-stoichiometry in the tungsten diselenide samples.

The sign of TEP in the semiconducting material depends on whether the majority carriers are electrons or holes. Positive thermoelectric power indicates p-type conduction and negative indicates n-type [60]. The fact that TEP in WSe$_2$ and WSe$_{1.9}$ is positive clearly indicates that these crystals are p-type semiconductors. Further in both cases there is no change in the sign of TEP with an increase in temperature. This suggests that the materials WSe$_2$ and WSe$_{1.9}$ do not change their semiconducting nature in the entire temperature range studied. The p-type nature of the samples supports the conclusions drawn from the Hall effect measurements.

The effective mass of the carriers (i.e. holes) has been estimated from the TEP measurements assuming impurity/defect scattering. It is seen that the magnitude of the hole effective mass in WSe$_2$ agrees with the value recently obtained by Klein et al. [7]. The slight decrease of hole effective mass in WSe$_{1.9}$ can be attributed to the off-stoichiometric nature of these samples. The decrease of effective mass in the off-stoichiometric WSe$_2$ crystals is in line with the decrease in the value of Seebeck coefficient in WSe$_{1.9}$ [61].

According to Zoaeter et al. [36], the values of $E_F$ in Table 4.15 represent the distance of the fermi level from the top of the valence band. A decrease in the value of $E_F$ in off-stoichiometric WSe$_{1.9}$ crystal suggests that due to off-stoichiometry in WSe$_2$ the fermi level gets closer to the valence band making it more p-type as compared to WSe$_2$. 
The variation of TEP with temperature clearly suggests the dominance of defects scattering in WSe₂ and WSe₁.₉ single crystals in the temperature range 313-423 K. The presence of defects in these crystals is shown by the scattering fault probability calculations made in the earlier section. Moreover the electron microscope studies of WSe₂ [62] and WSe₂-ₓ [47] carried out in our laboratory, elegantly showed the presence of stacking faults and basal dislocations in them.

A careful look at the data in Tables 4.5 and 4.16 shows that (i) the figure of merit for WSe₂ crystals is nearly of the same order of magnitude as that reported in the literature [Table 4.13] and (ii) upto 393 K off-stoichiometry increases the value of thermoelectric power factor in WSe₂ and thus improves its value as a thermoelectric material.

The increase in power factor with increase in temperature upto 393 K and the fact that at each temperature in the temperature range 313-393 K the power factor of WSe₁.₉ is greater than the stoichiometric WSe₂ lead us to believe that we must devote our concentration on off-stoichiometric WSe₁.₉ for obtaining efficient thermoelectric materials to work in the temperature range around room temperature. However, the increase in S²α above 393 K in WSe₂ suggests that while working with tungsten diselenide we must carefully arrange the value of x in WSe₂-ₓ and look for an optimum temperature to obtain the maximum value of thermoelectric powerfactor. This will help us to obtain the maximum usefulness of WSe₂ as an efficient thermoelectric material.

The study of microstructures on the as grown surfaces of WSe₂
Table 4.16 Thermoelectric power factor for WSe$_2$ and WSe$_{1.9}$ single crystals

<table>
<thead>
<tr>
<th>K Temp.</th>
<th>WSe$_2$</th>
<th></th>
<th></th>
<th>WSe$_{1.9}$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S$ (μV K$^{-1}$)</td>
<td>$S^2$ (μV K$^{-1}$)$^2$</td>
<td>$\sigma$ (Ω cm)$^{-1}$</td>
<td>$S^2 \sigma$ (μW cm$^{-1}$ K$^{-2}$)</td>
<td>$S$ (μV K$^{-1}$)</td>
<td>$S^2$ (μV K$^{-1}$)$^2$</td>
</tr>
<tr>
<td>303</td>
<td>669</td>
<td>447561</td>
<td>0.304</td>
<td>1.39 x 10$^5$</td>
<td>465</td>
<td>216225</td>
</tr>
<tr>
<td>313</td>
<td>673</td>
<td>452929</td>
<td>0.310</td>
<td>1.42 x 10$^5$</td>
<td>469</td>
<td>219961</td>
</tr>
<tr>
<td>323</td>
<td>677</td>
<td>458329</td>
<td>0.314</td>
<td>1.45 x 10$^5$</td>
<td>472</td>
<td>222784</td>
</tr>
<tr>
<td>333</td>
<td>681</td>
<td>463761</td>
<td>0.317</td>
<td>1.49 x 10$^5$</td>
<td>476</td>
<td>226576</td>
</tr>
<tr>
<td>343</td>
<td>685</td>
<td>469225</td>
<td>0.322</td>
<td>1.53 x 10$^5$</td>
<td>480</td>
<td>230400</td>
</tr>
<tr>
<td>353</td>
<td>688</td>
<td>473344</td>
<td>0.327</td>
<td>1.56 x 10$^5$</td>
<td>484</td>
<td>234256</td>
</tr>
<tr>
<td>363</td>
<td>692</td>
<td>478864</td>
<td>0.330</td>
<td>1.59 x 10$^5$</td>
<td>487</td>
<td>237169</td>
</tr>
<tr>
<td>373</td>
<td>696</td>
<td>484416</td>
<td>0.335</td>
<td>1.62 x 10$^5$</td>
<td>491</td>
<td>241081</td>
</tr>
<tr>
<td>383</td>
<td>700</td>
<td>490000</td>
<td>0.362</td>
<td>1.77 x 10$^5$</td>
<td>495</td>
<td>245025</td>
</tr>
<tr>
<td>393</td>
<td>703</td>
<td>494209</td>
<td>0.408</td>
<td>2.02 x 10$^5$</td>
<td>498</td>
<td>248004</td>
</tr>
<tr>
<td>403</td>
<td>707</td>
<td>499849</td>
<td>0.455</td>
<td>2.27 x 10$^5$</td>
<td>502</td>
<td>252004</td>
</tr>
<tr>
<td>413</td>
<td>711</td>
<td>505521</td>
<td>0.511</td>
<td>2.58 x 10$^5$</td>
<td>506</td>
<td>256036</td>
</tr>
</tbody>
</table>
and WSe\textsubscript{1.9} crystals has clearly pointed out that in both of them layer growth is indeed operative. In the initial stages of growth, when supersaturation is very high, spontaneous nucleation takes place on the surface of the crystal. On the nuclei thus formed, growth proceeds either two dimensionally or by coalesced crystals formed without the help of screw dislocations.

In both WSe\textsubscript{2} and WSe\textsubscript{1.9} single crystals along with layer growth mechanism growth on steps provided by the presence of screw dislocations also takes place. Growth layers starting freely from screw dislocations present on the crystal surfaces give rise to the formation of spiral patterns observed during the study of microstructures, described in the text. It may be mentioned here that on the basis of microstructures it is not possible to distinguish between WSe\textsubscript{2} and its off-stoichiometric compound WSe\textsubscript{1.9}.

4.4 CONCLUSIONS:

1. Single crystals of WSe\textsubscript{2} and its off-stoichiometric compound WSe\textsubscript{1.9} have been grown successfully by using a physical vapour transport technique. Single crystal nature of the grown crystals has been confirmed from electron diffraction.

2. Growth conditions, growth mechanism and lattice parameters of the grown crystals have been determined.

3. EDAX analysis of the crystals reveals that the weight percentage of elements obtained from this analysis agree with the weight percentage of elements taken for their synthesis and it is possible to prepare off-stoichiometric compounds of WSe\textsubscript{2} in the single crystal form.
4. A realistic estimation of stacking faults in WSe$_2$ and WSe$_{1.9}$ indicates that a high density of stacking faults are introduced when the samples are synthesised in off-stoichiometric form. This increase in stacking faults due to off-stoichiometry supports the decrease in density in WSe$_{1.9}$.

5. High temperature resistivity curves confirm the semiconducting nature of both the samples of WSe$_2$ and WSe$_{1.9}$.

6. Conductivity along the basal plane in both the cases is more than that along the direction normal to the basal plane.

7. D.C. electrical resistivity anisotropy has been measured for the first time in WSe$_{2-x}$ semiconducting crystals having interesting applications. The enhanced resistivity along the c-axis and anisotropic effective mass ratio obtained during this investigation have been explained on the basis of band theory.

8. The positive values of Seebeck coefficient and the Hall coefficient indicates that both WSe$_2$ and WSe$_{1.9}$ semiconductors are p-type in nature and majority charge carriers in them are holes.

9. Values of effective mass for WSe$_2$ and WSe$_{1.9}$ estimated from the TEP measurements agree with the value reported in the literature. It is seen that off-stoichiometry leads to a reduction in the values of effective mass and Seebeck coefficient.

10. Around room temperature, the overall power factors in WSe$_{1.9}$ is higher than WSe$_2$. It should therefore work as a superior thermoelectric
material in TEP based services. However, for an optimum performance the value of x in WSe$_2$-x and the temperature should be carefully selected.

11. Observation of microstructures clearly indicate that growth by layer mechanism and growth at steps provided by screw dislocations are operative in the growth of WSe$_2$-x single crystals.
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