High pressure effect on MoS_2 and $MoSe_2$ single crystals grown by CVT method

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Abstract. Single crystals of MoS_2 and $MoSe_2$ were grown by chemical vapour transport method using iodine as a transporting agent and characterized by optical microscopy, energy dispersive analysis (EDAX), X-ray powder diffraction (XRD) and Hall mobility at room temperature. The variation of electrical resistance under pressure was monitored in a Bridgman anvil set-up up to 6·5 GPa to identify occurrence of any structural transition. MoS_2 and $MoSe_2$ do not undergo any structural transitions under pressure.

Keywords. Single crystals; chemical vapour transport technique; high pressure.

1. Introduction

The transition metal dichalcogenides (TMDC) have layered structure and attracted many researchers due to their interesting properties like superconductivity, charge density waves, intercalation compound formation etc. Most of the TMDC compounds studied can be considered structurally as strongly bonded two-dimensional X–M–X (M = metal, X = chalcogen) layers loosely coupled to one another by relatively weak Van der Waals type forces (Dartigeas *et al* 1997). In MoS_2 and $MoSe_2$, the metal atom has trigonal prismatic coordination within the sandwich layer and a number of stacking polytypes are possible depending upon the way in which the sandwich layers are stacked one upon the other (Zvyagin and Soboleva 1967). Molybdenum dichalcogenides as *p* or *n*-type semiconductors have been extensively studied (Wilson and Yoffe 1969; Huisman *et al* 1971; Title and Shafer 1972, 1973; Yoffe 1973, 1974; Conan and Goureaux 1975; Grant *et al* 1975; Frey *et al* 1998). In earlier measurements of MoS_2 and $MoSe_2$, it was observed that electrical resistivity decreases with pressure, while Hall mobility is relatively pressure independent. Measurements in a Drickamer anvil set up to 38 GPa on MoS_2, showed a 500 fold decrease in R up to 15 GPa and a saturation thereafter. The pressure and temperature dependence of the conductivity in natural MoS_2 has also been measured by Grant (1970) using a tetrahedral anvil apparatus up to 5 GPa.

In this paper we report room temperature resistance measurements as a function of pressure on MoS_2 and $MoSe_2$ single crystals. In each case the resistance decreases under pressure due to an increase in the carrier concentration.

2. Experimental

Single crystals of MoS_2 and $MoSe_2$ have been grown by chemical vapour transport technique using iodine as a transporting agent. Pure elements (99·95%) of molybdenum, sulphur and selenium (make: Aldrich, USA) in stoichiometric proportions and narrow capillary with I_2 (2 mg/cc) of ampoule volume were sealed in an evacuated quartz ampoule for the crystal growth. The growth parameters are given in table 1.

The crystals under magnification revealed hexagonal spirals on the growing face as shown in figure 1. The chemical composition of the crystals grown was confirmed by carrying out energy dispersive analysis by X-ray (EDAX) as shown in table 2. The lattice parameters obtained by X-ray diffraction are listed in table 3.

The electrical resistance of the crystals along the basal plane was determined by van der Pauw method. Hall measurements were carried out to determine Hall coefficient, mobility and carrier concentration. The results of measurements are listed in table 4.

The room temperature measurements of resistances for these crystals, as a function of pressure were taken up to 6·5 GPa. Pressure was generated with a Bridgman type tungsten carbide opposed anvil apparatus with *in situ* bismuth pressure calibration. The crystals were contained in a pyrophillite gasket with talc as pressure transmitting medium (Bridgman 1941). A two-probe technique was used to evaluate the resistances of MoS_2 and $MoSe_2$ crystals. The resistance variation with pressure was determined.

3. Results and discussion

The chemical vapour transport technique has been used to grow single crystals of MoS_2 and $MoSe_2$ because it

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Table 1. Growth parameters of MoS_2 and $MoSe_2$ single crystals grown using iodine vapour transport technique.

	Initial material		Ampoule dimension		Temperature distribution			Physical characteristics of crystals		
Crystal	Weight (g)	Transporting agent	Length (mm)	Inner diameter (mm)	Hot zone (K)	Cold zone (K)	Growth time (h)	Plate area (mm²)	Thickness (mm)	Colour
MoS_2	10	I_2	250	22	1130	1073	336	6	0·020	Grey black
$MoSe_2$	10	I_2	250	22	1183	1123	284	8	0·015	Grey black

Table 2. Weight % of elements taken for growth and obtained from EDAX analysis.

Crystal	Element	Weight % of elements taken	from EDAX
MoS_2	Mo	59·94	62·19
	S	40·06	37·81
$MoSe_2$	Mo	37·80	38·00
	Se	62·20	62·00

yields large single crystals with relative ease. The presence of hexagonal spirals on the growing face of the grown crystals suggests that growth involves a screw dislocation mechanism. The EDAX studies confirmed that MoS_2 and $MoSe_2$ single crystals are stoichiometrically perfect. The XRD analysis confirms that MoS_2 and $MoSe_2$ possess hexagonal crystal structure. From the sign of the Hall coefficient it is clear that both crystals are *p*-type in nature.

The variation of resistance with pressure for MoS_2 and $MoSe_2$ are shown in figure 2. In both the cases it is seen that the resistance for each crystal decreases gradually with pressure up to 6·5 GPa. No phase transition is found in both these crystals up to 6·5 GPa. However, the samples became more conducting in nature at higher pressures. This decrease of resistance is probably attributed to the charge carriers of valence band contributing to the conduction band carriers.

In MoS_2 and $MoSe_2$ the valence band is an energy band derived from sulphur to selenium, $3p$ and $4p$ orbitals, respectively. These bands are separated by nearly 1·75 eV and 1·4 eV energy as shown in figure 3. The separation of band decreases and the charge carriers of the sulphur $3p$ orbitals from valence band increases as the pressure increases on these crystals, which explains the decrease of resistance with increase in pressure as seen in MoS_2 and $MoSe_2$. In addition the electronegativity of sulphur is more than selenium and so the band overlap in MoS_2 is expected to be smaller or non-existent. The decrease of resistance of the chalcogenide compounds with pressure is in line with the behaviour of most of the metals and semimetals.
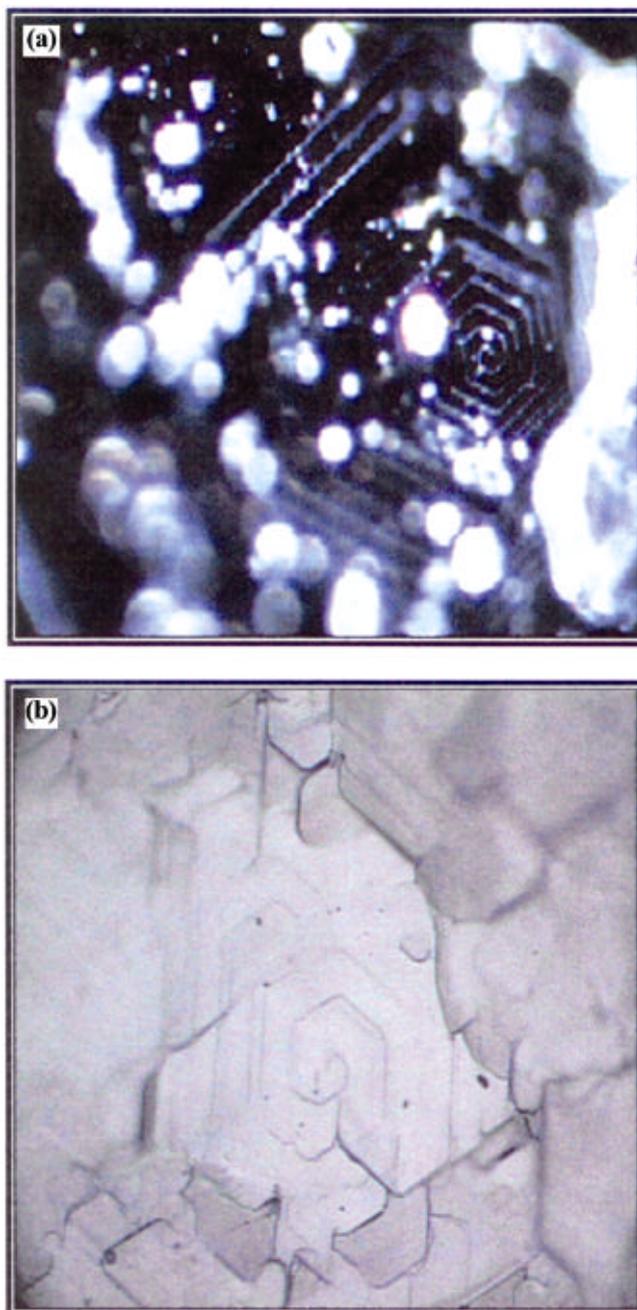
Figure 1. Microstructure of (**a**) MoS_2 and (**b**) $MoSe_2$ single crystals.

Table 3. Lattice parameters of MoS_2 and $MoSe_2$ single crystals obtained using X-ray diffraction (XRD) analysis.

Crystal	Standard value		Calculated value (in present work)	
	$a = b$ (Å)	c (Å)	$a = b$ (Å)	c (Å)
MoS_2 (Traill 1963)	3·160	18·330	3·110 ± 0·0405	18·89 ± 0·6840
$MoSe_2$ (Cech *et al* 1973)	3·287	12·925	3·157 ± 0·0098	12·926 ± 0·1958

Table 4. Results obtained from resistivity, Hall effect and optical absorption measurements for the single crystals of MoS_2 and $MoSe_2$.

Crystals	MoS_2	$MoSe_2$
Resistivity (Ω cm)	829·54	0·9096
Hall coefficient (cm^3/coul.)	1910000	1655·05
Hall mobility (cm^2/V·s)	92335·7	1819·53
Carrier concentration (cm^{-3})	$3·4 \times 10^{12}$	$3·8 \times 10^{15}$

4. Conclusions

(I) The single crystals of MoS_2 and $MoSe_2$ were grown using chemical vapour transport technique.

(II) The presence of hexagonal spirals on the growing face of the grown crystals suggests that growth involves a screw dislocation mechanism.

(III) The EDAX studies confirmed that MoS_2 and $MoSe_2$ single crystals are stoichiometrically perfect.
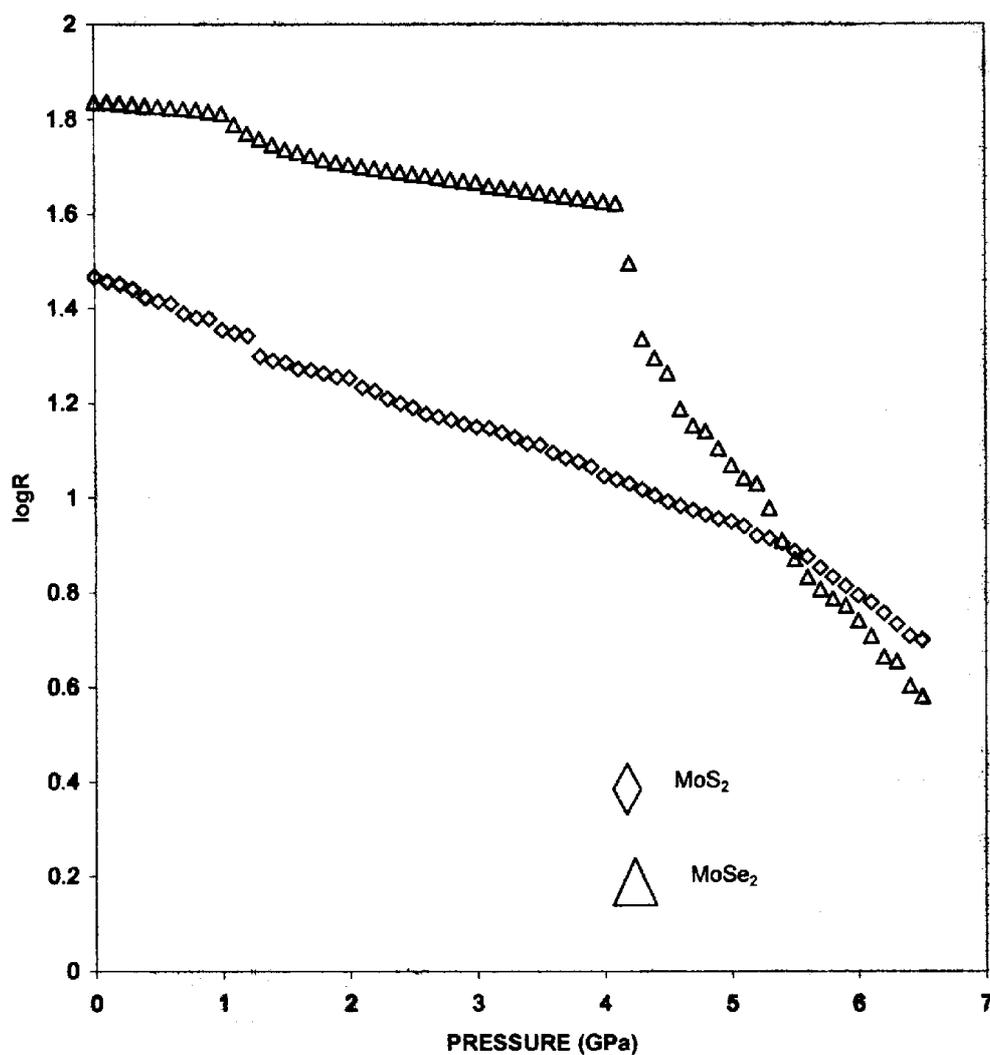
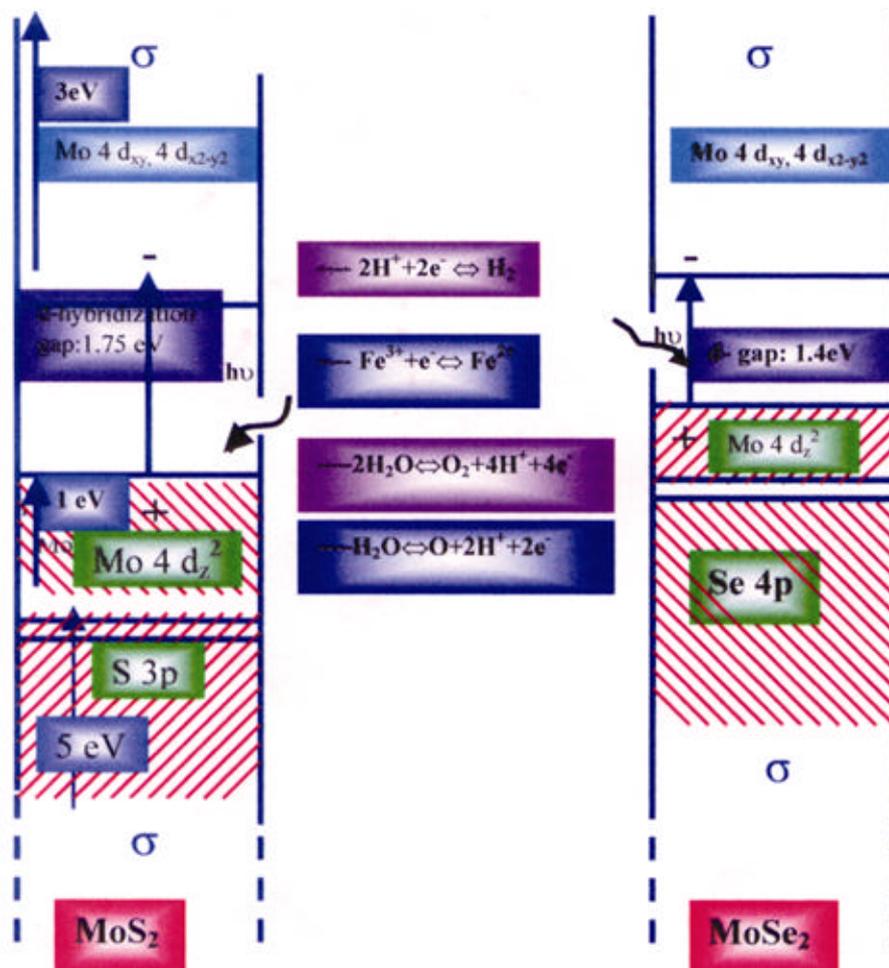**Figure 2.** The variation of resistance with pressure for MoS_2 and $MoSe_2$ single crystals.

Figure 3. Energy schemes and approximate relative energetic positions of MoS_2 and $MoSe_2$ single crystals.

(IV) The XRD analysis confirms that MoS_2 and $MoSe_2$ possess hexagonal crystal structure.

(V) From the sign of the Hall coefficient it is clear that both crystals are *p*-type in nature.

(VI) The electrical resistance decreases with pressure and is in line with the behaviour of most of the metals and semimetals.

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