

CHAPTER - 1

Existing information on WSe₂ single Crystals

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1.1 INTRODUCTION

Most of the transition metals of group IV to group VIII form compounds with sulphur, selenium and tellurium having the composition MX_2 . Where M is one of the metals and X is a chalcogen. These layered transition metal dichalcogenides (TMDC) have aroused a remarkable degree of interest in recent years which has been reviewed by various authors (1-3). This interest stems essentially from the quasi-two dimensional nature of these compounds. Recently these TMDC compounds have been used for constructing photoelectrochemical (PEC) solar cells (4), used as solid lubricants (5-12), as optical windows and semiconducting material for fabricating conducting devices.

Among the TMDC crystals which have been used for the fabrication of PEC solar cells, the maximum efficiency has been obtained with tungsten diselenide liquid junction solar cells. Author has therefore been focussed firstly on its growth, characterization and then later on its use in the fabrication of PEC solar cells.

A brief survey of the existing information on WSe_2 finds its place in the following sections.

1.2. SYNTHESIS :

Usually, the material of interest is not known to occur naturally and so has to be synthesised in the laboratory.

Several reports exist on the preparative conditions of these compounds. Silverman (13) used high pressure upto 70 K bar and temperature upto 2400°C and got the hexagonal form of WSe₂. Wildervanck (14), Al. Hilli and Evans (15) and Hicks (16) reported the preparation of the polycrystalline powder of WSe₂ by the direct reaction of the elements in the stoichiometric ratio.

In Wildervanck's experiment only bromine and iodine were used as transporting agents. With bromine transport took place T_H (high zone) = 800-850°C, T_L (low zone) = 750°C and with iodine the gradient was $T_H = 1055^\circ \longrightarrow T_L = 890^\circ\text{C}$. The grown samples were formed as thin small crystals having the hexagonal 2H-MoS₂ type lattice. Al. Hilli and Evans (15) have grown WSe₂ with and without bromine as transporter, transport was from $T_H = 850^\circ\text{C} \longrightarrow T_L = 700^\circ\text{C}$ with 2.7 mg Br₂cm⁻³ in four days. The grown material consisted of thin bulked crystals with no obvious surface features and crystals grown without Br₂ were platelets with hexagonal growth features. In **both** cases the lattice parameters were similar to those published by Glemser etal (17).

Brixner (18) used iodine transport to grow the crystals of WSe_2 . Kershaw et al (19) used a modification of Brixner's procedure to produce large homogenous melt formed crystals.

The information on preparation and growth conditions are given in Table.1.1.

1.3. STRUCTURE

Tungsten diselenide belongs to the general family of group VI, MX_2 type layer materials. It consists of a stacking of hexagonally packed planes in the sequence shown in Fig. 1.1, 6:3 coordination results, that around the metal atoms being either trigonalprismatic or octahedral (Fig.1.2).

The arrangement of such units in a single layer brings about hexagonal symmetry (Fig.1.3). The stacking sequences of these basic units determine the polytype and is either 2H-polytype or 3R-polytype (Fig.1.3 and 1.4). There are two molecules per unit cell in the 2H form (Fig.1.5(a)) and 3 molecules per unit cell in the 3R form (Fig.1.5(b)). In the 2H form the space group is D_{6h}^4 (or $P6/mmc$) with anions centered at $\pm (1/3, 2/3, 4)$, $\pm (2/3, 1/3, 1/2)$ and the cations at $\pm (1/3, 2/3, 4)$, positions. In the 3R form the space group is $C_{3v}^5(R_{3m})$ with anions centered at $(0,0,0)$, $(0,0,1/2)$ and cations at

(0,0,5/12). Figure 1.6 shows these structures. The lattice parameters and relevant structure data are given in Table 1.2.

1.4 APPROACH TOWARDS THE BAND MODEL:

The general features of the band structures of WSe_2 are similar to molybdenum dichalcogenides. It consists of a valence band made up of chalcogen s and p orbitals, above which is a broad antibonding or conduction band made up of metal s and p orbitals and in between a non-bonding band made mostly of metal d-character. If the metal atoms is in trigonal prismatic coordination, a narrow d_{z^2} band is lowest in energy. The energy difference between the valence band and low lying d_{z^2} band as well as electron occupancy will determine the optical and electrical properties of the TMDC. The d_{z^2} band is full for WSe_2 and the material exhibits diamagnetism and semiconducting behaviour. Wilson and Yoffe (24) assigned this d_{z^2} band in the gap between the valence band and fermilevel, E_f . Huisman et al (25) placed it at the top of the valence band. McMenamin and Spicer (26) and William and Sphepherd (27) from their photoemission studies concluded that this band is some where in between these two positions, the top of the band falling above the top of the valence band, with bottom at or slightly below the top of the valence band as

shown in Fig. 1.7.

Recently electron loss spectroscopic measurements have also been made to study the electronic state of tungsten dichalcogenides. Wood and Prendry (28) suggested the application of the layer method for the calculation of the band structure. Whereas Bromley and Co-workers (29,30) calculated the band structure in a two-dimensional approximation on the basis of a semiempirical tight bonding method. Mattheiss (31) used an augmented plane wave (APW) calculation for the band structure of a C_7 (MoS_2) type of layered TMDC. Apart from their quantitative aspects, the results of this method provide useful information about the correct band ordering and effect of hybridization between states and different atomic symmetry properties.

1.5 PHYSICAL AND CHEMICAL PROPERTIES :

Some of the physical properties of tungsten diselenide are given in Table 1.3. There is disagreement in the literature with regard to the numerical values of some of the properties, which may be due to the different methods by which the WSe_2 have been prepared.

The tungsten diselenide has been found to be stable in dilute non-oxidizing acids at room temperature but dissolve on heating.

1.6 ELECTRICAL PROPERTIES :

WSe₂ is found to be a diamagnetic semiconductor. Its electrical properties have been studied in detail by various workers (16,18,33-36). Table 1.4 records its electrical data e.g. carrier type, resistivity, Hall Co-efficient, carrier concentration, Hall mobility and Seebeck coefficient. Also band gaps for this material are given in Table 1.5.

1.7. OPTICAL PROPERTIES :

The study of optical properties of solids gives a good deal of information on the electronic properties and band structures of both metals and semiconductors. Willson and Yoffe (43) interpreted the optical spectra of TMDC having trigonal prismatic coordination based on the interband transition. Liang (44.) studied the reflectivity spectra of 2H-WSe₂ grown by bromine transport at 77K whereas Beal et al (45) measured the transmission spectra of iodine grown crystals. In these measurements the light was kept incident normal to the layer plane. Liang (46) therefore made further reflectance measurements on 2H-WSe₂ parallel to the crystal C-axis at liquid nitrogen temperature and room temperature. The observed peaks in the specimens were attributed to interband transitions.

The optical spectra of WSe_2 has also been studied in the 1.5 to 3.2 eV range by wavelength and temperature modulated photovoltaic effects from 4.1 to 300K (47). The resulting spectra was interpreted with the help of the known band structure of the isomorphous compound MoS_2 .

1.8 CONCLUSION :

Synthesis, Crystal Structure and band models of WSe_2 have been described. Physical, Chemical, electrical and optical properties of this compound have been reviewed. Some important uses of this compound have also been mentioned in the introduction.

TABLE 1.1
COMPOUND PREPARATION AND CRYSTAL GROWTH
TECHNIQUES FOR WSe₂

Preparation procedure	
(a) Reaction of elements at 900-1000°C for one week (Jellinek, 1971) at 600-700°C, 24th, then at 1000-1050°C for one week in 100mm x 22.5mm tube (Al. Hilli and Evans, 1972)	Br ₂ transport (Jellinek, 1971) T _H =800-850°C T _L =750°C in three weeks
(at) 600-700°C for 10-15 h then secondfiring at 1000-1200°C for 10-15 h	T _H =1055°, T _L =890°C in 2.5 to 3 weeks; The yield in these cases in 2H-WSe ₂
at 550°C, 30 min mixing and second heating at 1000°C (Hicks, 1964)	Br ₂ transport T _H =800°C T _L = 700°C, 2.7 mg/cm ³ , L _{in} 4 days.
at 650°C for 4 days, then re-firing at 800°C for 4 days (Brixner, 1962). In all cases the	190mm x 22.5mm tube Also transport without halogen (Al. Hilli and Evans, 1972)
(b) U.H. pressure high temperature technique, gives 2H-WSe ₂ with 70K bar, and 2400°C (Silverman, 1967)	Conditions reported by (Brixner, 1962 and Kershaw, etal, 1967) are also valid for crystal growth of WSe ₂ .

TABLE - 1.2
DATA OF STRUCTURE AND LATTICE PARAMETERS

Crystal structure and polymorphism	Trigonal prismatic layer structure, 2H.
Space group and stacking sequence	2H: $P6_3/mmc$ BaB AbA
X-ray density $g.ml^{-1}$	9.0 (Brixner, 1962)
Mole per unit cell (Z)	2 (Brixner, 1962)
Unit cell volume, A^3	120.7 (Brixner, 1962)
Lattice parameters in A°	
a = 0.3286 c = 2x0.6488	(Wilder Vanck and Jellinek, 1964)
a = 0.3282 ± 0.0004 c = 2 x 0.6488	(Al.Hilli and Evans, 1972)
a = 0.3286 c = 2 x 0.6492	(Mentzen and Sienko, 1976)
a = 0.3285 ± 0.0001 c = 2 x 0.6488	(Champion, 1965)
a = 0.3285 b = 2 x 0.6489	(Kalikhman, etal, 1972)

TABLE - 1.3
PHYSICAL PROPERTIES OF WSe₂

Luster	Highly shining
Colour	Grey black
Mol. Wt (g)	344.77
m.p (°C)	800°C (d)
Magnetism	Diamagnetic
Density (g.cm ⁻³)	9.35 (Brixner, 1962)
Heat of formation K.Cal. mol ⁻¹	-45 ± 15 (Mills, 1974)
Entropy	21.5 ± 3 (Mills, 1974)

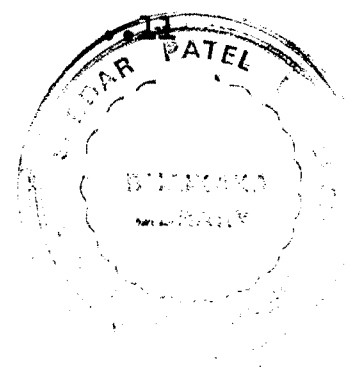


TABLE - 1.4

ELECTRICAL PROPERTIES (DATA) FOR WSe₂

Parameter	Type	Value	Authors
Resistivity ρ (Ω cm)	p	0.5 (300K) 15 (77K)	(Brixner, 1962)
	p	0.57 (100°C) 0.780 (600°C)	(Hicks, 1964)
	p	$\approx 10^3$ (300K)	(Revolinsky and Beersten, 1964)
	n	$\approx 1.23-1.33$ (300K)	(FivoZ and Mooser, 1967)
Hall Coefficient R_H ($\text{cm}^2 \text{cb}^{-1}$)	p	78 (25°C)	(Hicks, 1964)
	n	100 (300K)	(FivoZ and Mooser, 1967)
Carrier concentration n (cm^{-3})	p	8.0×10^{16} (25°C)	(Hicks, 1964)
	n	5.0×10^{16} (300K)	(FivoZ and Mooser, 1967)
Hall mobility ($\text{cm}^2 \text{V}^{-1} \text{Sec}^{-1}$)	p	99	(Hicks, 1964)
	p	236	(Span, etal, 1983)
	n	100	(FivoZ and Mooser 1967)
Seebeck Coefficient S ($\text{V}^\circ \text{C}^{-1}$)	p	+990 (300K)	(Brixner, 1962)
	p	+560 (100°C)	(Hicks, 1964)
	p	+527 (600°C)	(Hicks, 1964)
Activation energy (ev)	p	0.09	(Wani, 1979)

TABLE- 1.5

DATA OF BAND GAPS OF WSe₂

Nature of transition	Conductivity type	E _g (ev)	Authors
Direct	n	1.57	(Gobrecht, etal,1978)
Indirect	-	1.60	(Gold Berg.etal,1975)
-	n	1.35	(F.R. Fan,etal,1980)
Indirect	n	1.16	(Kautek and Gerischer, 1980)
Direct	n	1.78	(Baglio, etal, 1982)
Indirect	p	1.2	(Kautek and Gerischer, 1979).

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CAPTIONS OF FIGURES

- Fig. 1.1 Sandwich of X-M-X sheets,
Fig. 1.2 (a) Trigonal prismatic unit.
Fig. 1.2 (b) Octahedral unit.
Fig. 1.3 (a) Stacking of trigonal prismatic units.
Fig. 1.3 (b) Stacking of octahedral units.
Fig. 1.4 (a) Plane view of stacking in 2H-polytype.
Fig. 1.4 (b) Plane view of stacking in 3R-polytype.
Fig. 1.5 (a) 2H-unit cell
Fig. 1.5 (b) 3R-unit cell
Fig. 1.6 (a) Layer structure in 2H-poly type.
Fig. 1.6 (b) Layer structure in 3R-polytype.
Fig. 1.7 Band structure of trigonal prismatic dichalcogenide.

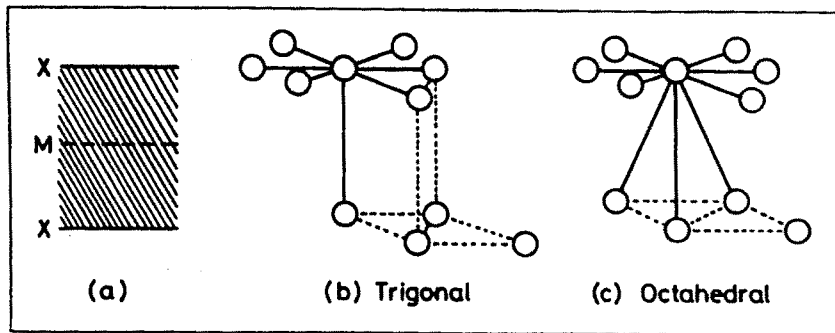


FIG.1.1

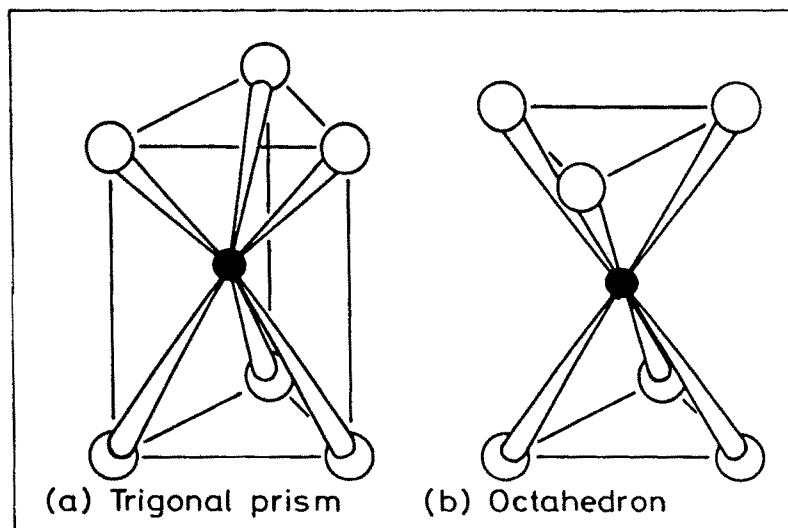


FIG.1.2

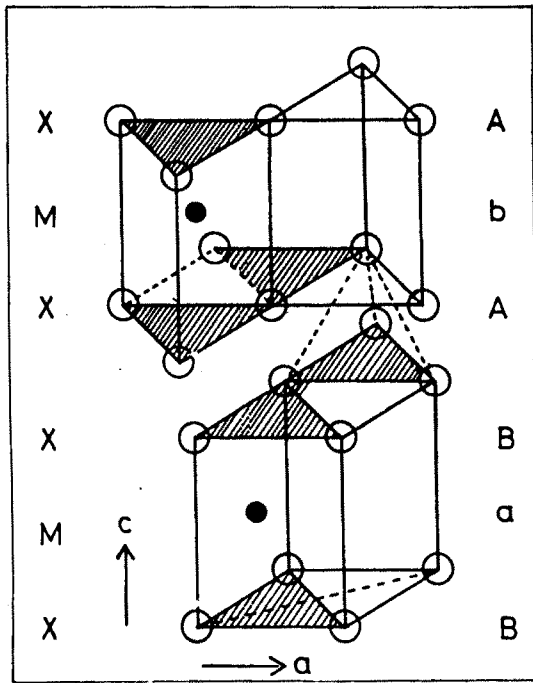


FIG. 1.3(a)

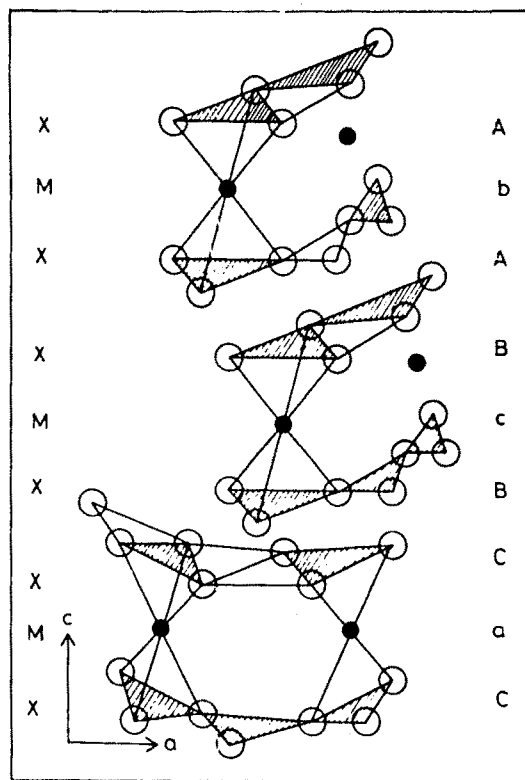


FIG. 1.3(b)

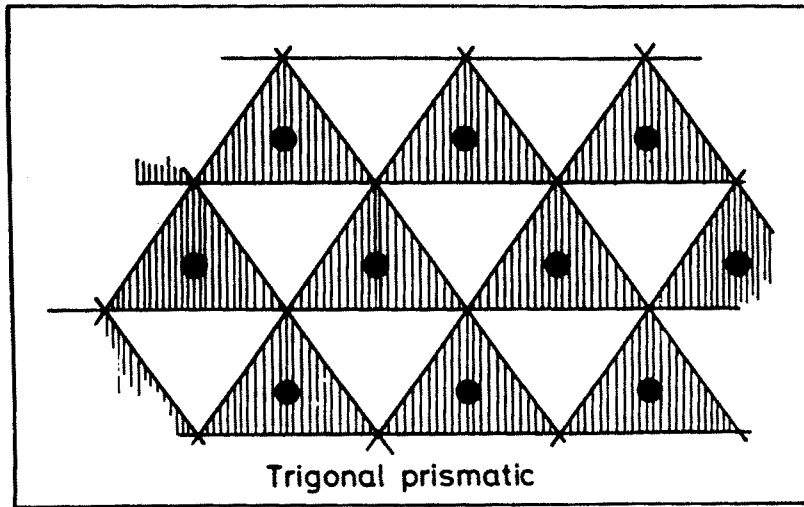


FIG.1.4(a)

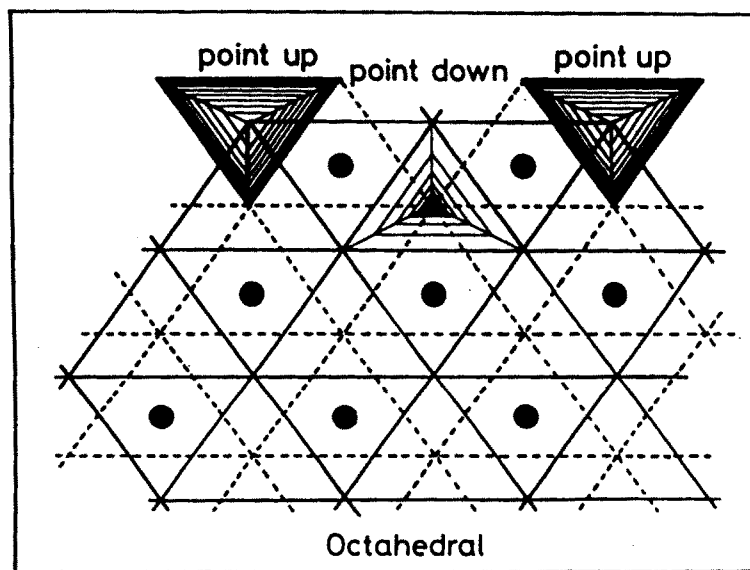


FIG 1.4 (b)

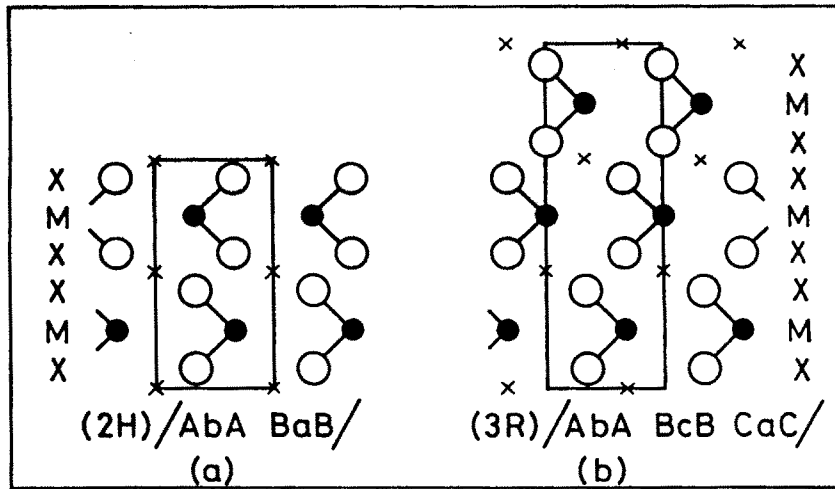


FIG.1.5

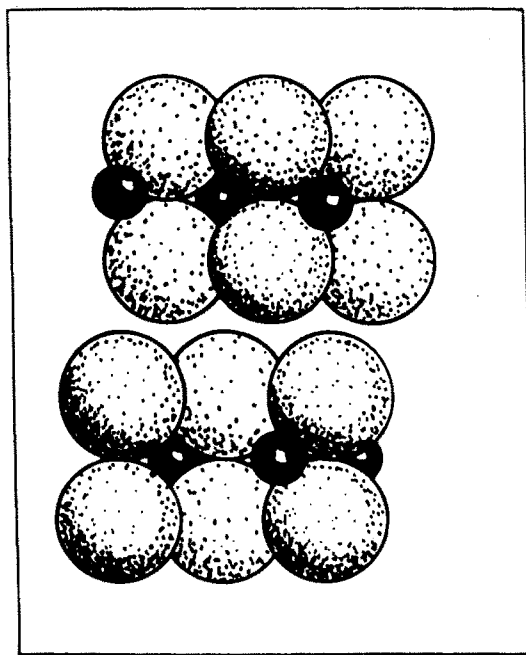


FIG.1.6(a)

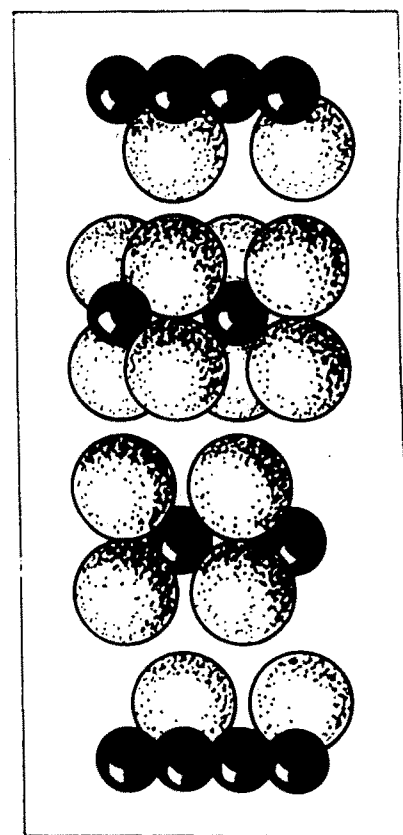


FIG.1.6(b)

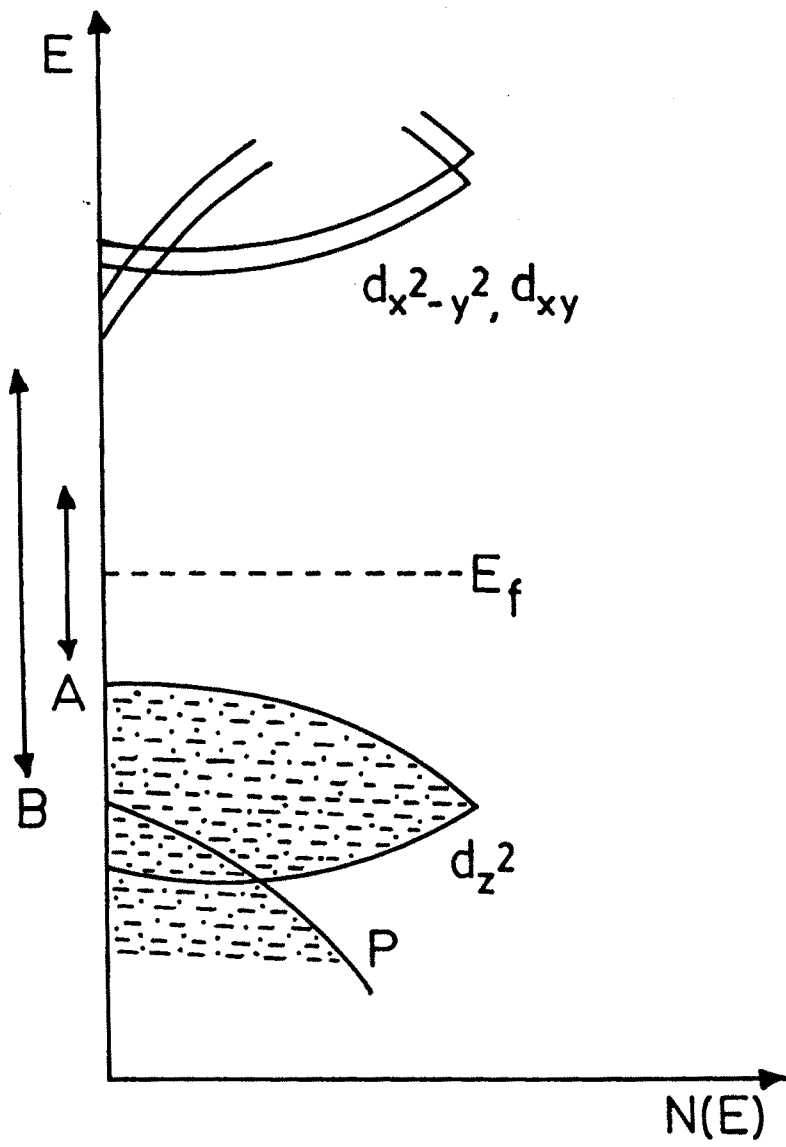


FIG.1.7