CHAPTER 1

GENERAL INTRODUCTION

The study of materials with layered structure having interesting anisotropic behavior has attracted ever increasing attention. As a result considerable progress has been made in the past few years. The structural features and their physical and chemical consequences singularize layered structures sufficiently attractive to make them a fascinating subject of research in todays context. This is all the more true since they are met in insulators and semiconductors as well as in normal and superconducting metals. Easy cleavage and glide along the layer planes have permitted highly interesting and esthetically pleasing electron microscopic studies of the dislocation networks in layered structures. Because the cleavage faces of layered crystals do not contain broken bonds, photoemission spectra yield a nearly undistorted picture of their electron density of states. Layered materials have thus become model substances for testing and exploring photoemission method. The anisotropy of the selection rules governing optical transition in layered semiconductors often permits absorption measurement well beyond the fundamental absorption edge. The most important property of layered compound is that the weak interlayer bonding permits intercalation by which process it is possible to introduce various metal atoms, ions, organic and inorganic molecules and salt like species between the layers to form stoichiometric and non-stoichiometric compounds. Depending on the intercalate species, quite unusual and dramatic changes in the physical properties of the

host can occur and this exciting possibility stimulated a lot of research interest in the present decade.

The large family of layered materials includes silicates (mica, clays), organic compounds, inorganic compounds and the rapidly growing group of intercalation compounds. Among them transition metal dichalcogenides and post transition metal chalcogenides received considerable amount of attention due to the great diversity in their physical properties. Transition metal dichalcogenides with their solid solutions and intercalation compounds themselves make a large family of compounds while post transition metal layered ternary or quaternary chalcogenides are a flourishing new class of compound.

Since the early 60's a group of materials called the Transition Metal Dichalcogenides (TCh_2) have received a rapidly growing interest [1-2]. Of the sixty compounds of this family, about two-third assume layer structure. These TCh_2 compounds (Ch = S, Se, Te) constitute structurally and chemically a well-defined family. The layers in this structure comprise metal atoms sandwiched between the chalcogen sheets (Figure 1.1). The bonding within the layer is strong, whereas between the layers it is weak and is of van der Waal type. Similar to other layer type compounds (e.g., graphite, clay minerals) TCh_2 can be intercalated (i.e., insertion in between the layers) by a variety of foreign atoms, ions or neutral molecules to form new compounds. The preparation and properties of transition metal dichalcogenides of group IVB, VB and VIB metals and their intercalated products have been extensively studied. Several reviews have appeared in the literature consisting of crystallographic, physical and chemical properties of layered transition metal dichalcogenides [1-6] and their intercalation compounds [7-10]. These compounds find interesting practical applications though their full potential is yet to be explored. Some examples are (i) battery cathode materials in rechargeable secondary cells e.g. Li_xTiS_2 [11], (ii) selective oxidation and reduction reagents similar to CrO_3-graphite [12], (iii) high temperature - high pressure solid lubricants e.g. MoS_2, WS_2 [13], (iv) superconducting quantum interferometer device (SQUID) detector [1], used as ultra-
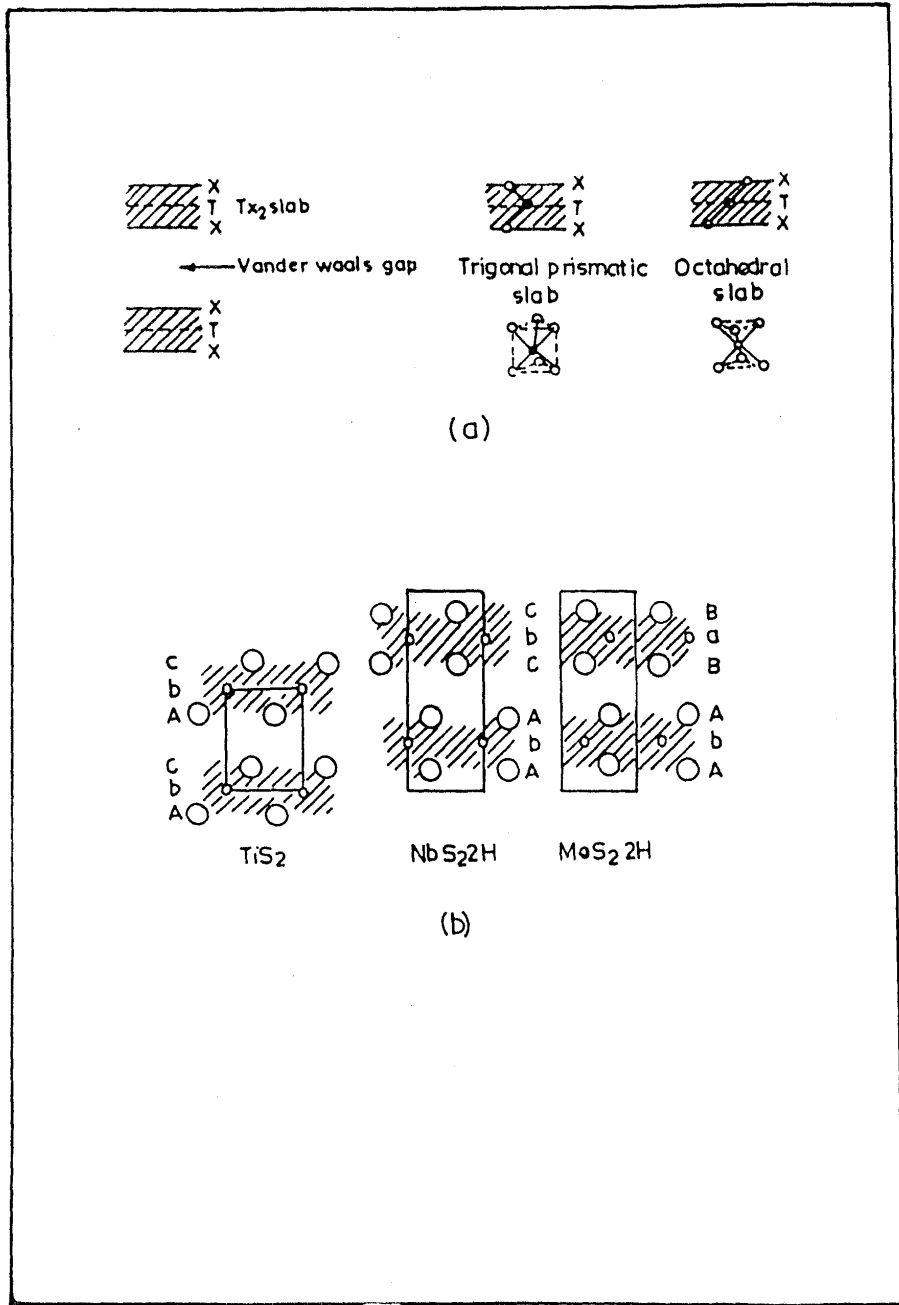
Figure 1.1.   a) Basic feature for a representation of layer dichalcogenides

b) TiS_2, 2H NbS_2 and MoS_2 structure types

sensitive magnetometer detectors and (v) anode and cathode materials in photoelectrochemical cells for solar energy conversion e.g. MoS_2, $MoSe_2$, WS_2 and WSe_2 [14].

In addition to the layered transition metal dichalcogenides wide interest has recently been paid on AB_2X_4 type of compounds where A, B and X are the group IIB, IIIB metals and chalcogen (S,Se) respectively [15-19]. These compounds show promising properties for developing photodetectors, switches, photovoltaic devices, nonlinear optical devices etc. [20-21]. In this regard studies have been mostly focussed on compounds with $ZnIn_2S_4$ IIIa layer type structure [22-26]. The layered structure also facilitates the process of intercalation allowing thereby a convenient method to change the structure and properties of the host AB_2X_4 crystal [27-29].

In this chapter the literature survey is mainly confined to layered chalcogenides of group VIB and AB_2X_4 compounds with MoS_2 and $ZnIn_2S_4$ IIIa type structure respectively.

Group VIB transition metal dichalcogenide

Group VI layered transition metal dichalcogenides mainly comprise of MoS_2, $MoSe_2$, $MoTe_2$, WS_2, WSe_2 and WTe_2. Among them $MoTe_2$ and WTe_2 do not have the same structure as the other chalcogenides of this group although they are layered. MoS_2 is the most important compound and the structure and properties of other compounds e.g. $MoSe_2$, WSe_2 and WS_2 are very much similar to those of MoS_2. The detailed preparative methods for molybdenum and tungsten dichalcogenides have been reported by several authors [3-5,30-36]. Thin films of molybdenum and tungsten dichalcogenides also were prepared by various ways and studied by different authors [37-47]. The present discussion will be focussed primarily on molybdenum dichalcogenides which are analogous to isostructural tungsten dichalcogenides.
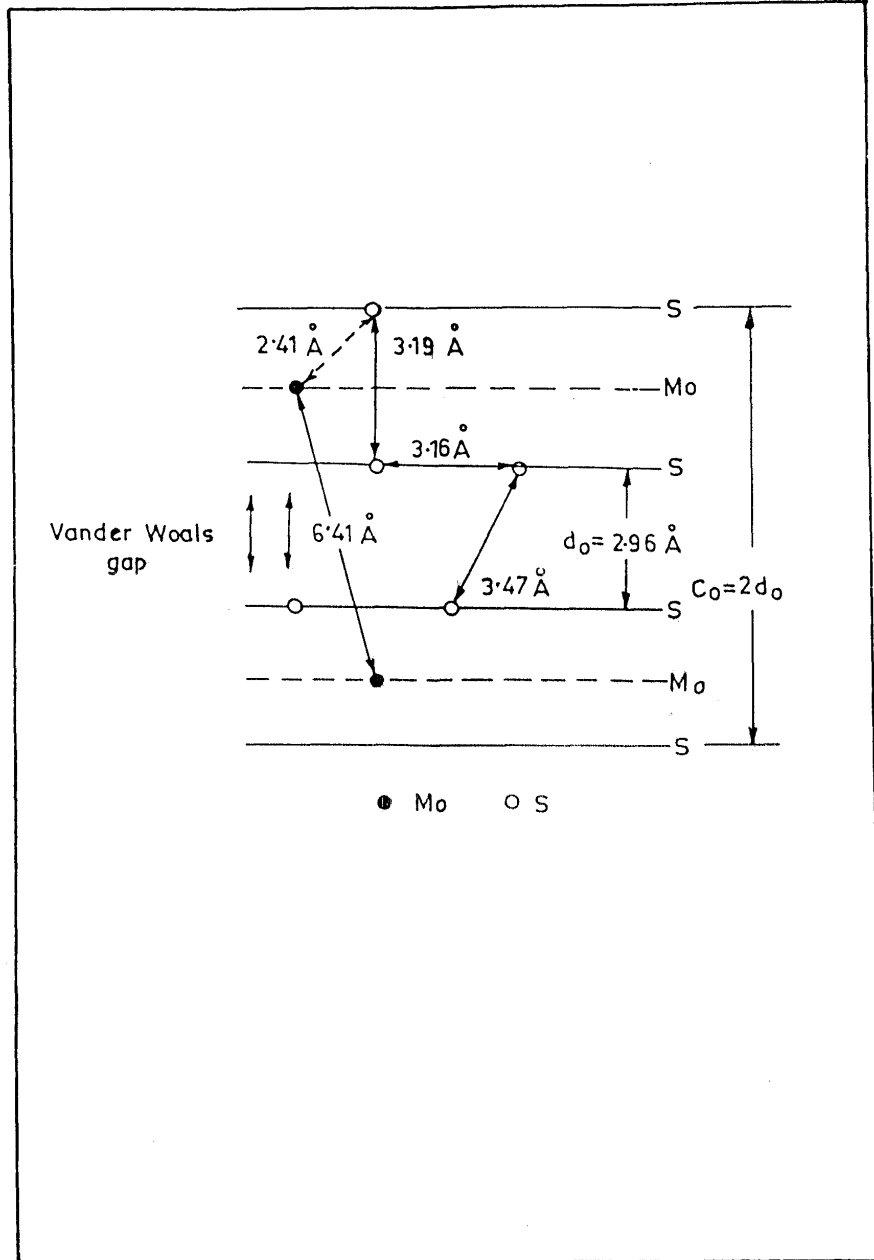
Figure 1.2.   Structure of MoS₂

Rhombohedral MoS_2 also consists of sheets of Mo^{+2} and S^{-2} and the packing within a sheet is identical with that of hexagonal form. Also, each Mo^{+2} sheet is sandwiched between two S^{-2} sheets and each S^{-2} sheet lies between one S^{-2} and one Mo^{+2} sheet. However, the stacking sequence is ABA, BCB, CAC, ABA, etc. The unit cell comprises the longer sequence ABA, BCB, CAC and hence has a correspondingly larger c value of 18.37 Å [48].

Band Model of Molybdenum Dichalcogenide

The band model of MoS_2 has received considerable attention from several workers. The main features of the band structure are a valence band based primarily on chalcogen s- and p-bonding orbital; above this band a broad antibonding band made up of s and p orbitals of transition metal; and in between, a nonbonding band, based on its d and p orbitals. The d_{z2} band is filled and the Fermi level in the gap lies between d_{z2} and d / p bands. Wilson and Yoffe [1] proposed a rigid band model based on optical data. They assigned the exciton peaks in the optical absorption spectrum of MoS_2 to transitions from top of the valence band to d / p bands, both initial and final states showing spin orbit splitting. This band model is shown in Figure 1.3. Huisman et al. [53] proposed another band model in which the order of d states was similar to that of Wilson and Yoffe, but had larger spacing between nonbonding d bands. This large spacing causes the d_{z2} band to be completely overlapped by p valence band while the upper d band overlaps the conduction band as shown in Figure 1.3. This model does not include any hybridization of d bands. Huisman and coworkers assigned the exciton peaks to transitions from d_{z2} band to spin orbit d_{x2-y2}/d_{xy} bands. Neither of the models was completely successful in explaining all the electrical properties. A simple band model for MoS_2, based on photoemission studies was proposed by McMenamin and Spicer [54] (Figure 1.3). The bands (Figure 1.3 dashed) above the Fermi level E_F have been estimated from the optical data. Unfortunately, this model could not account for the origin of A and B exciton peaks observed in MoS_2. The large forbidden gap suggests that assignment by Huisman