

MoS₂[18], is explained by a half-filled X_2 bands, since NbS₂ is crystallographically similar to MoS₂. No separation of bonding and antibonding states occurs in X_2 since the band is essentially equivalent to the ground state in 2-D metallic hydrogen. A separation in X_3 , however, may occur, but is probably too small to be observed. Finally, an inspection of the band structure of GaS[19], in which the sulphur atoms occupy similar crystallographic positions, suggests that the sulphur 3s subshells form a narrow valence band that lies below the other valence bands in X_1 .

3.2 Comparison with optical data

More comprehensive optical measurements have been made by Wilson on MoS₂ and the related transition metal dichalcogenides [11(b)]. A weak absorption was observed at room temperature at about 0.25 eV, showing that the direct transition between the non-bonding bands is forbidden and that the curvature of one band at $k=0$ is not related to the other through the $k.p$ perturbation. In addition, the existence of a weak shoulder at the bottom of the fundamental absorption edge in NbS₂, in which band X_2 is half empty, suggests that an indirect Burstein transition is involved, and the minimum gap between bands X_2 and X_3 is not at the Γ -point.

The optical spectra of the different stacking polytypes of MoS₂ are basically the same. The majority of transitions occur in pairs that are characteristic of a spin-orbit split valence band, although the magnitude of the splitting differs in 2H- and 3R- material as shown by the inset in Fig. 4. Group theoretic arguments, however, suggest that spin-orbit split bands can occur only along the ΓZ axis of the rhombohedral Brillouin zone corresponding to point group C_{3v} [20], and therefore the majority of transitions in 3R-MoS₂ occur on this axis, at critical points required by the symmetry of the zone. These are situated at Γ and Z , but, as already emphasized, the band structure is largely determined by a single layer, so that as a first approximation, we suggest that the

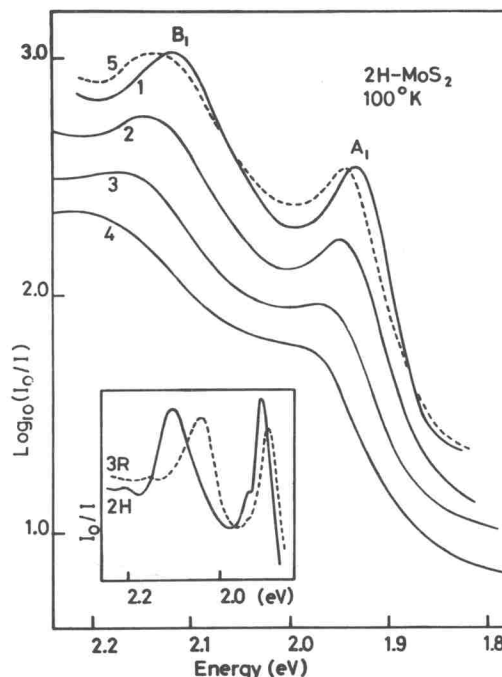


Fig. 4. Some experimental absorption spectra for 2H-MoS₂ at 100°K and at different pressures. Curves numbered in the order in which the data were taken: (1) 0.5 kbars (2) 15.8 kbars; (3) 30.0 kbars; (4) 45.0 kbars; (5) 3.0 kbars. Intermediate and higher pressure curves were consistent with those shown. The curves have been shifted vertically for clarity from the zero pressure absorption curve. The inset shows the absorption spectra in the region of the fundamental absorption edge of 2H-MoS₂ and 3R-MoS₂.

transitions in 2H-MoS₂ occur at the analogous critical points Γ and A , in the hexagonal Brillouin zone corresponding to point group D_{6h} .

If the exciton series are now associated with the direct gap at Γ between the spin-orbit split valence band in X_1 and the conduction band in X_3 , the remaining absorption peaks in the whole family of materials may be consistently assigned to transitions allowed by the model [11(a), 21]. Furthermore, the widths of bands X_2 and X_3 , the splitting of the valence band edge in X_1 , and the widths of the forbidden energy gaps, all shown in Fig. 3, are determined with an accuracy of a few tenths of an eV.

However, the work function of the material has not been measured, but it is possible to assign absolute energies to the system, by the examination of the relevant valence states in the sulphur atom and the hybridised molybdenum atom. In this approximation the work function is 8 eV, although an error of the order of an eV must be expected.

The rest of the paper describes an experimental investigation of the band model. The approach taken is to measure the effect of pressure on the exciton series and to relate the results to shifts in the various band edges.

4. EFFECT OF PRESSURE ON EXCITON FORMATION

4.1 Introduction

Measurements on the shape and position of the A_1 and B_1 peaks have been made at both room and liquid nitrogen temperatures. The main features in both cases are the shift of the peak positions to higher energies and a considerable weakening and eventual disappearance of the peaks themselves at the highest pressures. However, with the reduction of pressure, the peaks reappear and return to their zero pressure positions. Figure 4 summarizes these statements for a typical run at 100°K. Intermediate and higher pressure curves were consistent with those shown, but have been omitted for clarity. The second order exciton was not observed at pressures above 5 kbars, nor after the reduction of pressure, although the resolution of the system was better than 0.005 eV in this spectral range. It will also be noticed that the absorption coefficient at the minimum the A_1 and B_1 peaks has increased on returning to zero pressure. Similar effects were observed previously by Evans and Young[4] when MoS_2 crystals were subjected to mechanical working. We suggest, therefore, that changes in the dislocation density occur during the initial application of pressure to the cell, owing to very high, though localized, stress concentrations that temporarily exist around non-uniformities in the surface of the ZnS crystal. The reversible region is reached when

plastic flow has produced intimate contact throughout the cell.

4.2 Pressure coefficient of the A_1 -peak

The shift of the A_1 -peak is shown at both room and liquid nitrogen temperatures in Fig. 5. In both cases a linear change occurs at

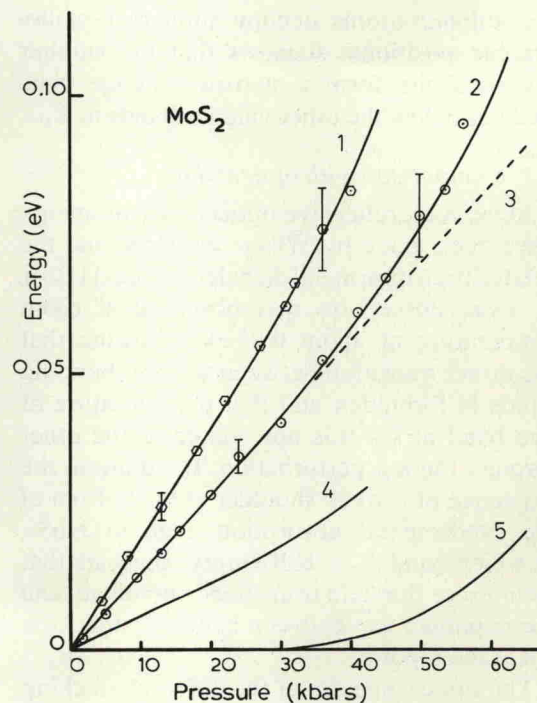


Fig. 5. The effect of pressure on the A_1 -peak at 300° (1) and 100°K (2). Curve (3) indicates the relative shift of the band edges in X_1 and X_3 at the Γ -point, so that curves (4) and (5) represent the change in binding energy of the exciton with increase in pressure at 300° and 100°K respectively.

lower pressures, but at higher energies, the shift becomes non-linear. The error in positioning the exciton peak increases at these higher pressures, but is insufficient to explain the deviation from linear behaviour.

Apart from these similarities in shape, a most striking difference in pressure coefficient exists for the two temperatures. The values obtained in the linear regions are