

## § 3. RESULTS

Optical transmission spectra for 2H-MoS<sub>2</sub> and 2H-WSe<sub>2</sub> are given in fig. 1 after Wilson and Yoffe (1969). The upper right insert shows in detail the A and B exciton peaks in the 2H and 3R polytypes of MoS<sub>2</sub>, measured at 77°K. The metallic layer crystal NbS<sub>2</sub> is included in fig. 1, with the three spectra displaced vertically for clarity, but having a common absorption coefficient of about  $5 \times 10^5 \text{ cm}^{-1}$  in the region of the C peak in MoS<sub>2</sub>.

Table 2. The hydrostatic pressure coefficient of the first peak in the optical absorption spectra of some zirconium and hafnium chalcogenides

Material : Peak	Energy (ev)	$(\partial E/\partial p)_T \times 10^{-6} \text{ ev/bar}$	$T^\circ\text{K}$
ZrS <sub>2</sub> X	2.78	-0.5 ± 0.4	80
X	2.78	Not measurable, no peak	293
HfS <sub>2</sub> X	2.88	-7.0 ± 0.4	80
X	2.85 (shoulder)	-10.5 ± 1.0	293
HfSe <sub>2</sub> X	2.26	-9.6 ± 0.4	80
X	2.26	-12.5 ± 0.6	293

Table 3. The room-temperature compressibility values (Flack 1970) for some layer crystals parallel to, and perpendicular to, the crystallographic *c* axis.

Material	$\beta_{\parallel} \times 10^{-7}/\text{bar}$	$\beta_{\perp} \times 10^{-7}/\text{bar}$	<i>P</i> range kilobars
2H-MoS <sub>2</sub>	17 ± 2	3.3 ± 1.0	0-12
NbSe <sub>2</sub>	11 ± 1	1.5 ± 0.3	0-48
HfS <sub>2</sub>	19 ± 1	2.8 ± 0.5	0-35

The hydrostatic pressure coefficients which have been measured for MoS<sub>2</sub> and WSe<sub>2</sub> are presented in table 1. The possible error associated with each measurement varies according to the strength and sharpness of the particular feature (with the exception of the C peak in 2H-MoS<sub>2</sub>, which was mentioned in the previous section).

The optical transmission spectra for the sulphide and selenide of Hf and Zr are shown in fig. 2. The pressure coefficients of the feature X for each material (except ZrSe<sub>2</sub>, for which sufficiently large crystals were not available) are presented in table 2.

The room-temperature compressibility values of Flack (1970) for three-layer materials parallel to, and perpendicular to the crystallographic *c* axis are given in table 3. These measurements were made with an

opposed diamond anvil high pressure x-ray apparatus. Powdered samples mixed with powdered NaCl as the pressure marker were placed in a molybdenum gasket to produce quasi-hydrostatic conditions.

#### § 4. DISCUSSION

It will be convenient to discuss the results for the different layer materials separately, dealing first with the semiconductors MoS<sub>2</sub> and WSe<sub>2</sub>, then the metal NbS<sub>2</sub>, and then the insulators HfS<sub>2</sub>/Se<sub>2</sub> and ZrS<sub>2</sub>.

##### 4.1. Molybdenum Disulphide

###### 4.1.1. Pressure coefficients in 2H and 3R polytypes of MoS<sub>2</sub>

The pressure coefficients of exciton peaks A and B for 2H-MoS<sub>2</sub> bear interesting comparison with those for the 3R polytype; the (2H) coefficients are at least 50% larger in each case. This result was anticipated by Connell (1967), who found low values for the pressure coefficients of the A and B peaks in 3R-MoSe<sub>2</sub> and WS<sub>2</sub>, similar to those reported here for 3R-MoS<sub>2</sub>. This paper, however, reports the first measurements on different polytypes of the same compound.

It has been usual to suppose that the energy levels in layer crystals are adequately described in terms of the electronic interactions within a single layer, although it had been observed that the energy separation of the A and B peaks in (3R) was only about three-quarters of the separation in 2H-MoS<sub>2</sub> (fig. 1, inset). It is now apparent that interlayer interactions are important in determining not only the energy splitting of the band extrema but also the deformation potentials of the energy levels in the layer crystals under consideration.

The pressure coefficient of the B peak is always slightly larger than that of the A peak, in both 2H- and 3R-MoS<sub>2</sub>, and at both liquid nitrogen and room temperatures. Band structure calculations (Bromley, Murray and Yoffe 1971) have shown that the AB energy splitting can be influenced by sulphur-sulphur interactions between adjacent layers of crystal across the van der Waals gap, and it is of interest to note that this splitting increases under pressure for both polytypes of MoS<sub>2</sub>.

The pressure coefficient of the C peak in MoS<sub>2</sub> is much smaller than those of the exciton peaks A and B. The C peak has been assigned by Bromley (1971) to a density of states effect at the symmetry point Q, and calculations of the deformation potential for this transition would help to confirm this assignment.

###### 4.1.2. Temperature variation of the pressure coefficients

The temperature variation of the pressure coefficients in 2H-MoS<sub>2</sub> observed previously in this laboratory (Connell *et al.* 1969) was explained at that time in terms of a reduction in the exciton binding energy due to screening of the electron-hole interaction by carriers promoted across the narrow indirect bandgap present in this material.