

4.1.4. *The indirect gap*

The electrical energy gap of about 0.3 eV in MoS₂ has been assigned (Wilson and Yoffe 1969) to an indirect gap between a lower filled band arising from metal d_{z²} levels and that same conduction band as is involved in the direct optical absorption (i.e. peaks A and B). Electrical measurements under pressure have been made on MoS₂ crystals with the current flowing parallel to the *c* axis. The resistance fell with both increasing temperature and pressure, but there is no information on the variation of the carrier mobility in this direction with either pressure or temperature, so that an analysis similar to the above but in terms of the indirect energy gap cannot be given at present.

4.2. *Tungsten Diselenide: Pressure Coefficients and the Interlayer Interaction*

The second excitonic doublet, labelled A' and B', is well resolved at liquid nitrogen temperature in the absorption spectrum of WSe₂ (fig. 1) from the usual peaks of the stronger doublet AB. The energy splittings are similar, with 0.47 eV for AB and 0.41 eV for A'B'.

Under pressure, peaks A and B move to higher energy, with B moving somewhat faster than A, as was the case for MoS₂. Peaks A' and B' however, both move in the opposite direction, to lower energies. The pressure coefficients suggest that the two doublets should superpose, appearing as a single doublet for pressures of order 100 kilobars. The data are not sufficiently accurate to permit a definite conclusion regarding the variation with pressure of the A'B' energy splitting; the AB splitting is initially greater and increases further with pressure. Any simultaneous superposition of AA' and BB' therefore represents only a tentative possibility.

The above result is clearly of significance in connection with band structure calculations for layer crystals, since the deformation potentials of the two doublets AB and A'B' must be of opposite sign. The hypothesis (Bromley 1971) that the origin of the energy splittings AA' and BB' lies in the interlayer interaction is supported by the work of Consadori and Frindt (1970). These authors thinned crystals of WSe₂ down to only two or three molecular layers, and found that the energy of peak A increased from 1.71 eV to 1.87 eV. Unfortunately the weaker A' peak rapidly merged with B, and it was not possible to observe the likely reduction in energy of this peak on thinning. The AB splitting was however observed to be reduced for very thin specimens of WSe₂ by some 8%. In this connection we may recall that the AB splitting is less in 3R-MoS₂ than in the 2H polytype; probably the 3R material is more closely comparable to a 'single layer' crystal without interlayer interactions. The effect of thinning a 2H crystal would then be expected to lead to modification of the 2H spectrum towards that of the 3R material, namely by a reduction in the AB splitting.

4.3. Niobium Disulphide

There are no sharp features in the interband absorption spectrum of NbS₂ at energies corresponding to the allowed direct bandgap of MoS₂, since the high density of free carriers—one per Nb atom—screens out the AB excitons which might otherwise appear. With the small range of hydrostatic pressure available (0–6 kilobars) no observable change in the spectrum around 2.3 eV was found at 80°K. The basic similarity in the band structures of NbS₂ and MoS₂ has received support from intercalation studies (Acrivos, Liang, Wilson and Yoffe 1971).

The 'free carrier' region of the spectrum, below about 1.3 eV, is found to be temperature independent to within a few per cent between liquid helium and room temperatures. A similar result for NbSe₂ was found by Bachmann, Kirsch and Geballe (1971). Transmission measurements in this region are somewhat unsatisfactory because they do not distinguish between the increase in reflectivity of the metal and the intraband absorption. However qualitative measurements up to 60 kilobars, using a van Valkenburg opposed diamond anvil apparatus, established a decrease under pressure in the slope of the reflectivity versus wavelength. This may be due partly to an increase in the plasma frequency under pressure, and partly to an enhancement in the free carrier lifetime due to a decrease in lattice scattering.

An effect of particular interest is the striking increase under pressure of the superconducting transition temperature for the related compound NbSe₂, which is reported elsewhere (Jérome, Grant and Yoffe 1971).

4.4. Zirconium and Hafnium Chalcogenides

The octahedrally bonded layer crystals of Group 4 (Zr, Hf) have properties distinct from the trigonal Group 6 (Mo, W) materials. The optical spectra (figs. 1 and 2, after Wilson and Yoffe 1969) are quite different. In addition the Group 4 materials are insulators, whereas the Group 6 materials are semiconductors having a narrow filled band derived mainly from the metal d_z^2 orbitals.

The distinction is reinforced in the measurements of the pressure coefficients of the first peak X in the optical absorption spectra of ZrS₂, HfS₂ and HfSe₂, shown in table 2. The coefficients are all negative, in contrast to the positive values obtained for the spin-orbit split peaks of Group 6 materials such as MoS₂. The difference between the small negative coefficient in the case of ZrS₂, and the much larger negative coefficients for HfS₂ and HfSe₂ is unexpected, in view of the close similarity in the general shape of the optical absorption spectra. Preliminary band structure calculations for these materials (Murray 1971, private communication) indicate that the bands involved in this series of compounds are similar.

Recent electric-field-modulated transmission measurements have been made on HfS₂ and HfSe₂ in the sandwich configuration (Bordas 1971).