

In the case of MoSe<sub>2</sub>, Evans and Hazelwood (1971) have observed the transition to intrinsic conduction at 700 K, with an activation energy corresponding to a bandgap of 1.1 eV. Their specimens were n-type with a carrier concentration  $1.3 \times 10^{17} \text{ cm}^{-3}$  at 290 K and a resistivity of 0.5  $\Omega\text{cm}$ , values similar to those in table 1.

Additional information concerning the intrinsic bandgap is available from the photoemission work of Shepherd *et al* (1974) on MoSe<sub>2</sub> and Nb<sub>0.05</sub>Mo<sub>0.95</sub>Se<sub>2</sub>. Structure is observed which is attributed to the  $d_{z^2}$  band and the neighbouring p bands, and this structure shifts by 0.8 eV in the Nb doped MoSe<sub>2</sub>. This data may be interpreted in terms of the swing in the Fermi level from a position close to the conduction band in n-type MoSe<sub>2</sub> to the valence band edge in the Nb (acceptor) doped material. The intrinsic bandgap would then be 0.93 eV, since  $E_F$  will lie 0.13 eV below the conduction band in n-type MoSe<sub>2</sub> if  $n = 1.6 \times 10^{17}$  and  $N_c = 3 \times 10^{19} \text{ cm}^{-3}$ .

This hypothesis leaves unexplained the energy interval of about 0.5 eV in Nb doped MoSe<sub>2</sub> between  $E_F$  (whose position is determined independently by the sharp d band threshold for Ni) and the onset of emission from the  $d_{z^2}$  band. Shepherd *et al* (1974) suggest that  $E_F$  is pinned by the Nb acceptor states at 0.5 eV above the  $d_{z^2}$  band, but this seems unlikely in view of the much shallower acceptor energy ( $\sim 0.09$  eV) reported for Nb-doped WSe<sub>2</sub> (see Kalikhman and Umanskii 1973). In either case, the intrinsic bandgap would be about 1 eV, with the impurity activation energy which dominates the conductivity about 0.1 eV. The small pressure coefficient of the impurity activation energy (table 1) implies that pressure in excess of 100 kbar would be required fully to ionize the donor population.

The transition from extrinsic to intrinsic conduction in MoTe<sub>2</sub> has been observed by Revolinsky and Beerntsen (1964) and by Lepetit (1965), with a bandgap of 0.9 to 1.0 eV at high temperatures in each case. Lepetit studied both n- and p-type samples and found impurity concentrations around  $10^{19} \text{ cm}^{-3}$  with compensation  $K \sim 0.8$  in each case. The donor and acceptor activation energies were 12 and 55 meV respectively. The material studied by Revolinsky and Beerntsen (1964) had a different impurity activation energy (97 meV at room temperature), and had a much higher resistivity ( $\sim 1000 \Omega\text{cm}$  at 300 K) than that studied by Lepetit ( $\sim 0.3 \Omega\text{cm}$  at 300 K) and by the present authors ( $\sim 0.1 \Omega\text{cm}$  at 300 K).

In the MoTe<sub>2</sub> studied in this work,  $R_H$  (and hence the carrier concentration) was observed to saturate at the highest pressures used (figure 1), whereas  $\rho$  continued to decrease. This suggests that the impurity levels are wholly ionized at high pressure, and the small change in  $R_H$  implies rather shallow donors which are substantially ionized even at atmospheric pressure and room temperature. With  $n = 6 \times 10^{18} \text{ cm}^{-3}$  at 1 bar and 300 K (table 1) and  $(N_D - N_A) = 1.1 \times 10^{19} \text{ cm}^{-3}$  (from the high pressure value of  $R_H$ ), the approximate expression (1) given earlier no longer holds. The donor ionization energy is given by

$$\epsilon_d = kT \ln \left( \frac{(N_D - N_A - n)(N_c - n)}{2n(N_A + n)} \right) \quad (4)$$

and therefore depends on the compensation  $K = N_A/N_D$ . The range of positive values for  $\epsilon_d$  varies from 12.8 meV when  $K = 0$ , to zero when  $K = 0.27$ , and would therefore appear to be consistent with the donor ionization energy of 12 meV given by Lepetit (1964), although with a lower value of  $K$ . There must no doubt be a spread in the energies of so high a density of donor levels; the quoted energy would represent an appropriate average value.

In the case of shallow 'hydrogenic' impurities such as As or Al in Si, the ionization

energy is given by  $E_{\text{HM}}^*/K^2$  where  $E_{\text{H}} = 13.6$  eV,  $m^*$  is the effective mass of the associated energy band extremum and  $K$  is the dielectric constant. The pressure dependence of such impurities is of order  $10^{-8}$  eV bar $^{-1}$  (Holland and Paul 1962), and has been interpreted in terms of the pressure dependence of  $m^*$  and  $K$ . The magnitude and pressure dependence of  $\epsilon_{\text{d}}$  in the semiconducting layer crystals of interest here (table 1) suggests that these are not hydrogenic levels, but are levels whose energy will not depend predominantly upon the nearest energy band extremum (Paul 1968). No simple calculation of the value expected for  $\epsilon_{\text{d}}$  or its pressure dependence is therefore possible. The values of the carrier mobility measured on our samples (table 1) indicate that both lattice scattering and ionized impurity scattering are significant (see Fivaz and Mooser 1967). High pressure measurements on much purer samples would be valuable, since these effects might then be separated.

In conclusion, there is now overwhelming evidence from transport and photoemission measurements supported by band structure calculations, that the minimum bandgap in the layer semiconductors MoS<sub>2</sub>, MoSe<sub>2</sub> and MoTe<sub>2</sub> is 1 eV or more. The conductivity in these materials remains extrinsic until well above room temperature. The high concentration and compensation of the impurity levels suggests the presence of native defects, but the species are unidentified. Optical absorption measurements on thick crystals, or photoemission studies on both n- and p-type samples should allow a more accurate determination to be made of the indirect bandgap. Recent measurements by Beal (1974) show weak absorption at energies well below the exciton peaks (A, B) in both MoS<sub>2</sub> and MoSe<sub>2</sub>. This weak absorption begins around 1.3 eV in MoS<sub>2</sub> and 1.2 eV in MoSe<sub>2</sub>. It remains to be established whether the initial state involved in the strong exciton absorption in these materials is in the occupied  $d_{z^2}$  band or in the partly overlapping p bands.

We thank STL for the use of high pressure facilities, and the SRC and St. John's College, Cambridge for financial support to AJG. We are grateful to W Y Liang, A R Beal, R S Tittle, W Paul, M J Powell, P M Williams and F R Shepherd for stimulating discussions. Crystals of As-doped MoS<sub>2</sub> were kindly supplied by IBM Research.

## References

- Beal A R 1974 *University of Cambridge* unpublished work  
 Drickamer H G 1970 *Rev. Sci. Instrum.* **41** 1667-8  
 Evans B L and Hazelwood R A 1971 *Phys. Stat. Solidi*, a**24** 181-92  
 Evans B L and Young P A 1965 *Proc. R. Soc.* A**284** 402-22  
 Fivaz R and Mooser E 1967 *Phys. Rev.* **163** 743-55  
 Frindt R F and Yoffe A D 1963 *Proc. R. Soc.* A**273** 69-83  
 Grant A J 1970 *PhD Thesis* University of Cambridge  
 Holland and Paul 1962  
 Huisman R, de Jonge R, Haas C and Jellinek F 1971 *J. Solid St. Chem.* **3** 56-66  
 Kalikhman V L and Umanskii Ya S 1973 *Sov. Phys. Uspekhi* **15** 728-41  
 Kasowski R V 1973 *Phys. Rev. Lett.* **30** 1175-8  
 Lagrenaudie J 1954 *J. Phys., Paris* **15** 299-300  
 Lepetit A 1965 *J. Phys., Paris* **26** 175-9  
 McMenamin J C and Spicer W E 1972 *Phys. Rev. Lett.* **29** 1501-4  
 Mansfield R and Salaam S A 1953 *Proc. Phys. Soc.* B**66** 377-85  
 Mattheiss L F 1973 *Phys. Rev.* B**8** 3719-40  
 —1973 *Phys. Rev. Lett.* **30** 784-7  
 Minomura S and Drickamer H G 1963 *J. Appl. Phys.* **34** 3043-8