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LETTER TO THE EDITOR

The electrical properties and the magnitude of the indirect gap in the semiconducting transition metal dichalcogenide layer crystals

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Abstract. Room-temperature electrical resistivity and Hall effect measurements as a function of pressure are reported on p-type MoS_2 and on n-type MoS_2, $MoSe_2$ and $MoTe_2$. In each case, the resistivity decreases under pressure, due to an increase in the carrier concentration. The Hall mobility is relatively pressure-independent. The data are consistent with the predominance of extrinsic conduction in these semiconductors until well above room temperature. The impurity activation energy and its pressure dependence are given, together with estimates of the intrinsic indirect bandgap obtained from high temperature conductivity measurements, photoemission studies and band structure calculations.

Considerable literature exists on the electrical properties of the semiconducting transition metal dichalcogenide layer crystals MX_2, where M is Mo or W and X is S, Se or Te. Much of this work has been reviewed by Wilson and Yoffe (1969), who originally proposed a minimum bandgap of 0·2 to 0·3 eV between the filled d_{z^2} band formed from the metal d_{z^2} orbitals and the d/p conduction band. An alternative model is that proposed by Huisman *et al* (1971), in which the minimum bandgap is considerably greater (1·3 eV in MoS_2), and in which the occupied d_{z^2} band is completely overlapped by the chalcogen p valence bands. The electron paramagnetic resonance studies of Title and Shafer (1972, 1973) on Nb and As acceptors in MoS_2 established the d_{z^2} character of the uppermost filled band extremum, thus confirming the ordering of the bands as proposed by Wilson and Yoffe (1969). However, there is now considerable evidence that the minimum indirect bandgap in these semiconductors is greater than 0·3 eV, (Yoffe 1973, 1974) and that the electrical conductivity in these materials is extrinsic at 300 K.

The value of the conductivity at 300 K varies widely from sample to sample, probably due to varying impurity concentrations (Kalikhman and Umanskii 1973). At high temperatures, usually above 400–600 K, intrinsic conduction has been observed with an activation energy corresponding to a bandgap of 1·4 eV (Lagrenaudie 1954) to 1·7 eV (Evans and Young 1965) in MoS_2, 1·1 eV (Evans and Hazelwood 1971) in $MoSe_2$, and 0·9 eV (Revolinsky and Beerntsen 1964) to 1·0 eV (Lepetit 1965) in $MoTe_2$. Photoemission studies (Williams and Shepherd 1973, Shepherd and Williams 1974, Wertheim *et al* 1973, McMenamin and Spicer 1972, Williams 1973, Murray and Williams 1974) indicate that the d_{z^2} band maximum lies in the order of 1 eV below the Fermi level, so that carrier concentrations in the range 10^{16} to $10^{19}\ \mathrm{cm}^{-3}$ as observed in these materials must be attributed to the presence of donor or acceptor levels.

In addition, recent band structure calculations (Wood and Pendry 1973, Kasowski 1973, Mattheiss 1973) support a value of 1 eV or greater for the indirect bandgap in MoS_2. Weak optical absorption has been observed at 1·5 eV in MoS_2 films by Frindt and Yoffe (1963) and at the same energy in single crystals by Evans and Young (1965), which may be attributed to the indirect gap.

In this paper we report room-temperature resistivity and Hall effect measurements as a function of pressure on p-type MoS_2 and on n-type MoS_2, $MoSe_2$ and $MoTe_2$. In each case the resistivity decreases under pressure, due to an increase in the carrier concentration. The Hall mobility is relatively pressure-independent. The data are consistent with the predominance of extrinsic conduction in these semiconductors until well above room temperature. The impurity activation energy and its pressure dependence are given, together with estimates of the intrinsic indirect bandgap obtained from high temperature conductivity measurements, photoemission studies and band-structure calculations.

The experimental work was carried out mainly at the Standard Telecommunication Laboratories, where two types of high pressure equipment were used. In the hydrostatic pressure apparatus (Pitt and Gunn 1970) resistivity and Hall effect measurements were made at room temperature, and the pressure could be cycled in the range 0–15 kbar. In the Bridgman opposed anvil apparatus (Pitt 1968), the sample was encapsulated in an epoxy ring and resistivity and Hall measurements were made for increasing pressure only. Shear stresses were present below about 30 kbar, but the pressure was quasihydrostatic at higher pressures up to 90 kbar.

Natural crystals of n-type MoS_2 were used and the other samples were grown by vapour phase transport. The crystal dimensions were typically two or three mm square and a few hundredths mm thick. Four small gold contacts were evaporated on the corners of one face of each crystal, and four fine copper wires were indium soldered to these contacts to allow measurement of the resistivity in the plane of the crystal layers by the van der Pauw (1958) technique. It was necessary to clean the surface of $MoSe_2$ crystals to obtain ohmic contacts. The sample mounting technique is described by Pitt (1968) and Pitt and Gunn (1970).

Resistivity and Hall effect data obtained under hydrostatic pressure for all four sample types is given in table 1. The data obtained in the Bridgman apparatus to higher pressures is shown in figure 1 for n-type MoS_2, $MoSe_2$ and $MoTe_2$. The normalized resistivity and Hall coefficient ($R_H = 1/ne$) are shown together with the calculated Hall mobility. No Bridgman run was made on the As-doped p-type MoS_2. The Bridgman and hydrostatic pressure data were in good agreement for all three n-type semiconductors in the 0–15 kbar range.

In each material, the resistivity and the Hall coefficient decrease under pressure, which indicates an increase in the carrier concentration under pressure and a relatively pressure-independent Hall mobility. The decrease in the rate of change of ρ and R_H with increasing pressure may be attributed to a decrease under pressure in the compressibility of the sample.

In natural n-type MoS_2, the carrier concentration at room temperature and pressure is usually of order $10^{16}\ \mathrm{cm}^{-3}$ (Mansfield and Salaam 1953, Fivaz and Mooser 1967, this work), and we have shown that the mobility is almost pressure-independent at least to 35 kbar. An estimate of the concentration of impurity levels in MoS_2 may be made from the work of Minomura and Drickamer (1963) if we assume that the mobility remains

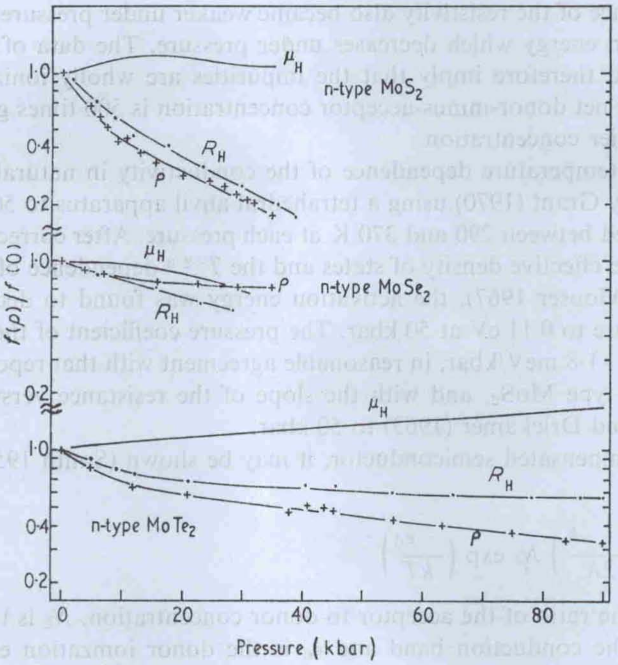

Figure 1

Table 1. Resistivity and Hall effect data from hydrostatic pressure measurements. Also included are the donor activation energy, the intrinsic (indirect) bandgap inferred from high temperature conductivity, photoemission, and optical absorption measurements, the direct optical gap and its pressure dependence.

Material	MoS$_2$	MoS$_2$	MoSe$_2$	MoTe$_2$
Carrier type	n	p	n	n
$\rho(\Omega\ \text{cm})$	18	2·0	1·0	0·1
Carrier concentration (cm^{-3})	6×10^{15}	$1{\cdot}6 \times 10^{17}$	$1{\cdot}6 \times 10^{17}$	6×10^{18}
Hall mobility μ_H (cm^2 V^{-1} s^{-1})	57	20	40	10
$\mu_H(10\ \text{kbar})/\mu_H(0)$	1·05	0·90	0·96	1·08
$\dfrac{R_H(10\ \text{kbar})}{R_H(0)} = \dfrac{n(0)}{n(10)}$	0·35	0·75	0·78	0·79
ϵ_d(eV)	0·20	—	0·1	0·01
$\dfrac{d\epsilon_d}{dp} = kT\dfrac{d \ln n}{dp}$ (meV kbar^{-1})	−2·6	−0·7	−0·7	−0·7
E_{indirect}(eV)	1·6	1·6	1·1	1·0
E_{optical}(eV)	1·9	1·9	1·6	1·1
dE_{opt}/dp(meV kbar^{-1})	+2·0	—	+1·2	—

relatively pressure-independent to higher pressures and that changes in the conductivity reflect corresponding changes in the carrier concentration. Minomura and Drickamer observed a 500-fold decrease at room temperature in the resistivity of natural MoS$_2$ under pressure to 150 kbar, followed by a region of constant resistivity at higher pressures to 380 kbar. (We quote here the revised pressure calibration of Drickamer 1970). The temperature dependence of the resistivity also became weaker under pressure, suggesting an impurity activation energy which decreases under pressure. The data of Minomura and Drickamer would therefore imply that the impurities are wholly ionized at high pressure, and that the net donor-minus-acceptor concentration is 500 times greater than the zero pressure carrier concentration.

The pressure and temperature dependence of the conductivity in natural MoS_2 has also been measured by Grant (1970) using a tetrahedral anvil apparatus to 50 kbar. The temperature was cycled between 290 and 370 K at each pressure. After correction for the $T^{3/2}$ dependence of the effective density of states and the $T^{-2\cdot 6}$ dependence of the carrier mobility (Fivaz and Mooser 1967), the activation energy was found to decrease from 0·20 eV at zero pressure to 0·11 eV at 50 kbar. The pressure coefficient of the activation energy was therefore −1·8 meV/kbar, in reasonable agreement with that reported in this paper (table 1) for n-type MoS_2, and with the slope of the resistance versus pressure curve of Minomura and Drickamer (1963) to 50 kbar.

For a partially compensated semiconductor, it may be shown (Smith 1959) that the carrier concentration

$$n = \left(\frac{1-K}{2K}\right) N_c \exp\left(\frac{-\epsilon_d}{kT}\right) \qquad (1)$$

where $K = N_A/N_D$, the ratio of the acceptor to donor concentration. N_c is the effective density of states for the conduction band and ϵ_d is the donor ionization energy. The position of the Fermi level relative to the conduction band edge is given by

$$E_F = kT \ln\left(\frac{n}{N_c}\right) \qquad (2)$$

and the approximation which leads to the solution (1) is valid provided

$$nK/(1-K) \ll N_A. \qquad (3)$$

If we take the value $n = 6 \times 10^{15}\ \mathrm{cm}^{-3}$ from table 1, and suppose, following the work of Minomura and Drickamer (1963) that $(N_D - N_A)/n \approx 500$, we may solve for ϵ_d, N_D and N_A for various values of the compensation K (table 2). A compensation of 0·5 gives a value of ϵ_d (0·20 eV) in agreement with the value obtained experimentally by Grant (1970), if the donor concentration is $6 \times 10^{18}\ \mathrm{cm}^{-3}$ and with the inequality (3) adequately satisfied, assuming a value $3 \times 10^{19}\ \mathrm{cm}^{-3}$ for N_c (Smith 1959). This solution is not to be considered as universally applicable to all MoS_2 samples, but is rather intended to demonstrate that a model for extrinsic conduction can be found to fit the available data for these particular samples. The consistency of the data would however support the idea of a common impurity level in the natural MoS_2 studied by each of these authors.

Table 2. Possible values of the donor activation energy and of the donor and acceptor concentrations, for various values of the compensation K, in MoS_2.

K	ϵ_d(eV)	$N_D(10^{18}\mathrm{cm}^{-3})$	$N_A(10^{18}\mathrm{cm}^{-3})$
0·01	0·31	3·0	0·03
0·1	0·25	3·3	0·33
0·5	0·20	6·0	3·0

In the case of $MoSe_2$, 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 $1\cdot3 \times 10^{17}\ \mathrm{cm}^{-3}$ at 290 K and a resistivity of 0·5 Ωcm, 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 $MoSe_2$ and $Nb_{0.05}Mo_{0.95}Se_2$. 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 $MoSe_2$. 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 $MoSe_2$ to the valence band edge in the Nb (acceptor) doped material. The intrinsic bandgap would then be 0·93 eV, since E will lie 0·13 eV below the conduction band in n-type $MoSe_2$ if $n = 1\cdot6 \times 10^{17}$ and $N_c = 3 \times 10^{19}\ \mathrm{cm}^{-3}$.

This hypothesis leaves unexplained the energy interval of about 0·5 eV in Nb doped $MoSe_2$ 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 (~0·09 eV) reported for Nb-doped WSe_2 (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 $MoTe_2$ 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 $10^{19}\ \mathrm{cm}^{-3}$ with compensation $K \sim 0\cdot8$ 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 (~1000 Ωcm at 300 K) than that studied by Lepetit (~0·3 Ωcm at 300 K) and by the present authors (~0·1 Ωcm at 300 K).

In the $MoTe_2$ studied in this work, R_H (and hence the carrier concentration) was observed to saturate at the highest pressures used (figure 1), whereas ρ 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 $n = 6 \times 10^{18}\ \mathrm{cm}^{-3}$ at 1 bar and 300 K (table 1) and $(N_D - N_A) = 1\cdot1 \times 10^{19}\ \mathrm{cm}^{-3}$ (from the high pressure value of R_H), the approximate expression (1) given earlier no longer holds. The donor ionization energy is given by

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

and therefore depends on the compensation $K = N_A/N_D$. The range of positive values for ϵ_d varies from 12·8 meV when $K = 0$, to zero when $K = 0\cdot27$, 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 $E_H m^*/K^2$ where $E_H = 13{\cdot}6$ 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 ϵ_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 ϵ_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_2, $MoSe_2$ and $MoTe_2$ 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_2 and $MoSe_2$. This weak absorption begins around 1·3 eV in MoS_2 and 1·2 eV in $MoSe_2$. 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.

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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.* **a24** 181–92
Evans B L and Young P A 1965 *Proc. R. Soc.* **A284** 402–22
Fivaz R and Mooser E 1967 *Phys. Rev.* **163** 743–55
Frindt R F and Yoffe A D 1963 *Proc. R. Soc.* **A273** 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.* **B66** 377–85
Mattheiss L F 1973 *Phys. Rev.* **B8** 3719–40
——1973 *Phys. Rev. Lett.* **30** 784–7
Minomura S and Drickamer H G 1963 *J. Appl. Phys.* **34** 3043–8

Murray R B and Williams R H 1974 *Phil. Mag.* **29** 473–92
Paul W 1968 *Proc. 9th Int. Conf. on Physics of Semiconductors, Moscow* (Leningrad: Nauka)
Pitt G D 1968 *J. Phys.* E: *Sci. Instrum.* **1** 915–7
Pitt G D and Gunn D A 1970 *High Temp.–High Press.* **2** 547–52
Revolinsky E and Beerntsen D 1964 *J. Appl. Phys.* **35** 2086–9
Shepherd F R and Williams P M 1974 *J. Phys.* C: *Solid St. Phys.* **7**, 4416–40
Shepherd F R, Williams P M, Young D A and Scruby C B 1974 *Proc. 12th Int. Conf. on Physics of Semiconductors, Stuttgart* ed M Pilkuhn (Stuttgart: Teubner–Verlag)
Smith R A 1959 *Semiconductors* (London: Cambridge UP)
Title R S and Shafer M W 1972 *Phys. Rev. Lett.* **28** 808–10
——1973 *Phys. Rev.* **B8** 615–20
van der Pauw L J 1958 *Philips Res. Rep.* **13** 1–9
Wertheim G K, Di Salvo F J and Buchanan D N E 1973 *Solid St. Commun.* **13** 1225–8
Williams P M and Shepherd F R 1973 *J. Phys.* C: *Solid St. Phys.* **6** L36–40
Williams R H 1973 *J. Phys.* C: *Solid St. Phys.* **6** L32–5
Wilson J A and Yoffe A D 1969 *Adv. Phys.* **18** 193–335
Wood K and Pendry J B 1973 *Phys. Rev. Lett.* **31** 1400–3
Yoffe A D 1973 *Festkorperprobleme* **13** ed H J Queisser (Vieweg: Braunschweig) pp 1–29
——1974 *Proc. 12th Int. Conf. on Physics of Semiconductors* ed M Pilkuhn (Stuttgart: Teubner)