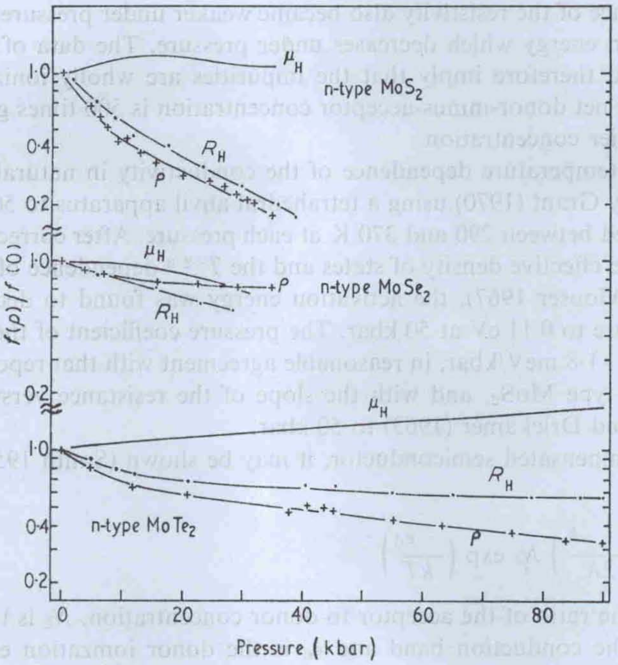

Figure 1

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
$\rho(\Omega\ \mathrm{cm})$	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
$\mu_H(10\ \mathrm{kbar})/\mu_H(0)$	1·05	0·90	0·96	1·08
$\dfrac{R_H(10\ \mathrm{kbar})}{R_H(0)} = \dfrac{n(0)}{n(10)}$	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 $T^{-2\cdot6}$ 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 $-1\cdot8$ 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

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

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

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

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

$$nK/(1-K) \ll N_A. \tag{3}$$

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