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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} 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} 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