$$\left(\frac{\partial E_{A_1}}{\partial p}\right)_{300} = (2\cdot0\pm0\cdot1)\times10^{-6}\ \text{eV/bar}$$

$$\left(\frac{\partial E_{A_1}}{\partial p}\right)_{100} = (1\cdot4\pm0\cdot2)\times10^{-6}\ \text{eV/bar.}$$

It is now shown that these differences may be explained by a reduction in binding energy of an exciton at high pressures and that the linear region at 100°K corresponds to the relative shift of the band edges of X_1 and X_3 at $k = 0$.

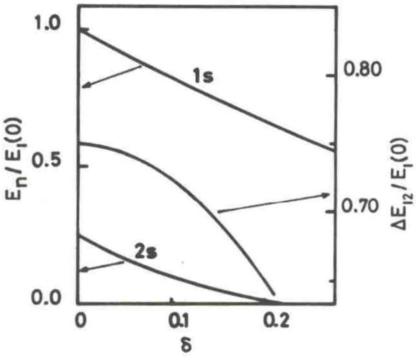

Fig. 6. The variation in the binding energy, E_n, of an n^{th} order exciton with the screening parameter δ (after Harris[25]).

4.3 *Changes in electron-hole interaction caused by increased screening*

Minomura and Drickamer[22] observed that the resistance of MoS_2 decreased under pressure. However, the mobility and effective mass of the electrons are expected to be relatively constant[21], so that an increase in carrier concentration is responsible for the decrease in resistance. As a result, the magnitude of the electron-hole interaction at a particular temperature will be reduced at high pressure, until at some critical free carrier density, exciton formation will no longer be possible.

The conditions for the existence of an exciton in such a Yukawa potential have been discussed by Casella[23] and Rawls and Schultz[24]. However, the most comprehensive treatment has been given by Harris[25], who shows that at a particular temperature T, the binding energies of 1 S and 2 S excitons are reduced by an increase in free carrier density in the way shown in Fig. 6. The screening parameter $\delta(T, p)$ is related to the free carrier density $N(T, p)$ by

$$\delta^2(T,p) = \left(\frac{a_\perp}{a_0}\right)^2 \frac{N(T,p)}{10^{23}kT\epsilon_\perp} = \left(\frac{a_\parallel}{a_0}\right)^2 \frac{N(T,p)}{10^{23}kT\epsilon_\parallel} \quad (1)$$

where a_0 is the Bohr radius, $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants parallel and perpendicular to c, $a_\parallel$ and $a_\perp$ are the exciton radii parallel and perpendicular to c in a coulombic potential and kT is measured in electron-volts. With this model, it is apparent that the non-linear behaviour of the exciton position at high pressures and low temperatures is to be attributed to a reduction in binding energy, caused by an increase in free carrier density. At room temperature, more electrons are excited for a given energy gap between X_2 and X_3, so that the exciton binding energy is already reduced at zero pressure. The magnitude of the reduction relative to the binding energy at zero pressure at both room and liquid nitrogen temperature is obtained from the difference between the experimental curves and the line corresponding to the relative shift of the band edges in X_1 and X_2 at $k = 0$. These are shown as curves 4 and 5 in Fig. 5. It may be shown that at low temperatures, the changes in effective mass of the exciton and the dielectric constant of the crystal with pressure tend to cancel, and together make a negligible contribution to the change in peak position.

The density of free carriers in a non-degenerate semi-conductor can be written as

$$N(T,p) = \text{const}\ T^{3/2} \exp\left[-E(T,p)/kT\right] \quad (2)$$

where for extrinsic conduction in a compensated material, E is the donor ionisation energy

$$E(T,p) = E_d; \quad T \leqslant 250°\text{K} \quad (3)$$

and for intrinsic conduction, E depends upon the indirect gap between bands X_2 and X_3.

$$E(T,p) = E_{x_2x_3}(T,p)/2; \quad T \geqslant 250°\text{K} \qquad (4)$$

The transition from extrinsic to intrinsic behaviour occurs at approximately 250°K, as indicated later in Section 5. This is consistent with the mobility behaviour of the less pure crystals grown by Fivaz and Mooser[13].

Using equations (1), (2) and (4), it follows that for a given temperature in the intrinsic region, the pressure coefficient of $E_{x_2x_3}$ is

$$\left(\frac{\partial E_{x_2x_3}}{\partial p}\right)_T = -\frac{4kT}{p}\log_e\frac{\delta(T,p)}{\delta(T,0)}. \qquad (5)$$

With values of $(\partial E_{x_2x_3}/\partial p)_{300}$ ranging from $-2{\cdot}0\times10^{-6}$ eV/bar to $-3{\cdot}0\times10^{-6}$ eV/bar, in steps of $0{\cdot}1\times10^{-6}$ eV/bar, the binding energy was calculated by computer as a function of pressure for a series of values of $\delta(300, 0)$ ranging from 0 to 0·35 in steps of 0·01. The best fit was obtained with

$$\left(\frac{\partial E_{x_2x_3}}{\partial p}\right)_{300} = (-2{\cdot}5\pm0{\cdot}5)\times10^{-6}\ \text{eV/bar}$$

and

$$\delta(300,0) = 0{\cdot}22\pm0{\cdot}02$$

or

$$N(300,0) = (2{\cdot}0\pm0{\cdot}5)\times10^{17}\ \text{cm}^{-3}$$

giving a value for $N(300, 0)$ in agreement with the electrical measurements of Wieting[12]. The pressure coefficient of $E_{x_2x_3}$ may also be calculated from the measurements of Minomura and Drickamer[22], since to a good approximation it may be shown that

$$\left(\frac{\partial E_{x_2x_3}}{\partial p}\right)_{300} = 2kT\frac{\partial \log_e R}{\partial p}$$
$$= (-2{\cdot}0\pm0{\cdot}5)\times10^{-6}\ \text{eV/bar}$$

in the low pressure region. ($p < 50$ kbars), further confirming our analysis.

4.4 *Pressure coefficient in the* B$_1$*-peak*

The general behaviour of the B_1-peak is very similar to that of the A_1-peak. The pressure coefficients at 300° and 100°K in the linear regions are

$$\left(\frac{\partial E_{B_1}}{\partial p}\right)_{300} = (2{\cdot}2\pm0{\cdot}1)\times10^{-6}\ \text{eV/bar}$$
$$\left(\frac{\partial E_{B_1}}{\partial p}\right)_{100} = (1{\cdot}4\pm0{\cdot}2)\times10^{-6}\ \text{eV/bar}.$$

Now it has already been assumed that the separation of the A_1 and B_1 peaks is related to the spin-orbit splitting of the band edge in X_1 at Γ. Moreover, the spin-orbit interaction term in the Hamiltonian is

$$H_{s0} = \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}V\times\boldsymbol{p})$$

where $\boldsymbol{\sigma}$ are Pauli matrices, V is the electrical potential between an electron and the nuclei and $\boldsymbol{p}$ is the momentum operator. Consequently, $\boldsymbol{\nabla}V$, and therefore H_{s0} will only be large near nuclear sites, so that little change is expected in the magnitude of spin-orbit splitting with pressure.

The experimental evidence is strongly in favour of this interpretation. The pressure coefficient of the B_1-peak at low temperatures is equal to that of the A_1-peak, while the difference that exists at room temperature is attributed to a greater reduction in binding energy of the B_1-peak for an increment of pressure.

5. TEMPERATURE DEPENDENCE OF EXCITON BINDING ENERGY

It follows from 1 that the binding energy of an exciton is a function of temperature at a given pressure. Owing to changes in the electron-phonon interaction with temperature, it is difficult to test this theory directly by an investigation of the A_1-peak alone. The second order exciton A_2, however, is also subject to changes in the screening parameter $\delta(T, p)$ so that measurements on the relative positions of the two peaks as a function of temperature would