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## EFFECTS OF PRESSURE AND TEMPERATURE ON EXCITON ABSORPTION AND BAND STRUCTURE OF LAYER CRYSTALS: MOLYBDENUM DISULPHIDE

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Abstract – The effect of pressures of up to 60 kbars on the exciton series in the spectral region of 2 eV in molybdenum disulphide has been investigated at room and liquid nitrogen temperatures, using a diamond anvil device. An electronic band model, suggested by the crystallography of the layered material and the optical spectra of the various polytypes, is made the basis for the discussion of the experimental results. An indirect energy gap of 0.25 eV determines the electrical properties of the intrinsic material, but transitions from a lower, spin-orbit split valence band produce the exciton series and fundamental absorption edge. It is shown that under these circumstances the pressure coefficient of an exciton peak can be separated into two parts; the pressure coefficient of the direct gap and the pressure dependence of the exciton binding energy which is a result of changes in the free carrier density that are necessarily related to the pressure variation of the indirect gap.

### 1. INTRODUCTION

MOLYBDENUM disulphide is a layer-type material in which, within a layer, there is trigonal prism type co-ordination between each metal atom and six sulphur atoms. The resultant sandwiches are loosely stacked into hexagonal (2H) or rhombohedral (3R) platelike polytypes[1], weakly bound together by van der Waal's forces, so that perfect cleavage occurs in (0001) planes. This allows the preparation of thin crystals which are eminently suitable for optical transmission measurements using light with the electric vector Eperpendicular to the crystal *c*-axis. The initial optical work by Frindt and Yoffe[2] indicated that the fundamental absorption edge was characterized by two series of exciton absorption bands, which later proved to be hydrogenic[3, 4], in spite of the extreme anisotropy of the crystal structure. This unlikely result led Ralph[5] to the conclusion that in molybdenum disulphide the ratio of the longitudinal and transverse exciton masses was equal to the ratio of the transverse and longitudinal dielectric constants, since under these circumstances, the excitons are much flattened in the c-direction, but their energies correspond to the isotropic case.

This paper describes an experimental investigation of the effect of 'quasi-hydrostatic' pressure at various temperatures on the two exciton series, using experimental techniques described in Section 2. A simple, zero pressure band model, developed in Section 3, in which there is full mixing between molybdenum s, p and d-orbitals and sulphur orbitals, is made the basis for the discussion of the experimental results, presented in Sections 4 and 5. In Section 4, we describe the effect of pressure on the exciton absorption bands, and indicate how the shape and position of the first exciton peak  $(A_1)$  are influenced by the presence of an indirect forbidden energy gap. Further evidence for this interpretation is presented in Section 5, where the variation in the binding energies of the A-series excitons is accounted for by a change in electron density in the conduction band.

### 2. EXPERIMENTAL TECHNIQUES

## 2.1 Apparatus

A Barr and Stroud V. L. 2 monochromator with a glass prism giving a spectral resolution of  $0.004 \,\text{eV}$  in conjunction with a quartz iodine lamp was used to provide monochromatic radiation. The light incident upon and transmitted through the crystals was monitored with an E.M.I. 9558Q photomultiplier tube, the signal from which was amplified and phase detected at a chopping frequency of 225 cps. The rectified signal was finally recorded in chart form as a function of photon energy over the region of interest.

Optical measurements were performed at high pressure and low temperature in a unit that was based upon the high pressure cell devised by van Valkenburg[6]. The specimen was cooled by heat conduction along the brass body of the apparatus and good thermal connection was ensured by intimate contact with the diamond anvils. It should be noted that at liquid nitrogen temperature the thermal conductivity of diamond is 25 times greater than that of copper. In this way, temperatures of 80°K were obtained with pressures in excess of 100 kbars.

The apparatus is shown in Fig. 1. Two gem-cut type II diamonds comprise the anvils. They are ground into square-based truncated tetrahedra, and mounted over holes in stainless steel pistons.

The pistons are free to slide in a stainless steel bearing, that sits in a brass block carrying the pressure generating equipment. One piston, which rests in a cavity in the face plate, can be tilted by levelling screws, while at the other end, a stainless steel transmission plate bears against the second piston. The force transmission lever is activated at its upper end by helium gas pressure inside a flexible stainless steel bellows.

The specimen is cooled by liquid nitrogen in the stainless steel dewar that constitutes the upper part of the apparatus. A copper radiation shield surrounds the high pressure region and the whole is encapsulated in a stainless steel tail-piece. Light enters the apparatus through spectrosil windows, mounted on O-ring seals for easy replacement.

Exciton absorption is characterized by a high absorption coefficient in the region of  $10^5$  cm<sup>-1</sup>, so that a crystal having a thickness of 2000 Å or less must be used. However, as the thickness of the specimen is reduced, it becomes impossible for a single crystal to fill the space between the diamond anvils arising from their concavitation under compression. The result is that the concavitation is reduced by an increase in pressure at the edges and a reduction near the centre, leading to a limit in the hydrostatic pressure attain-



Fig. 1. Liquid nitrogen cryostat for optical transmission measurements at high pressures.

able[7]. This problem was surmounted by incorporating a pressure transmitting medium of standard thickness between the anvils.

ZnS single crystals were chosen for several reasons. Firstly, the absorption edge occurs at about 29,000 cm<sup>-1</sup> and moves to even higher energies under pressure, until a phase change occurs at 240 kbars[8]. Consequently, its optical properties do not interfere with our work. Secondly, for a thickness of 20  $\mu$ , our standard, a centrally peaked pressure distribution is obtained, and thirdly, its refractive index is very similar to that of diamond, thereby avoiding any problems caused by interference fringes, produced by multiple reflections in the ZnS layer.

The cell arrangement is shown schematically in Fig. 2. An evaporated layer of luminescent grade ZnS, 5000 Å thick, effectively protects the specimen against disintegration, which would otherwise occur on account of the microscopic uneveness of ZnS single crystal surfaces. Calibration was effected by using as a specimen, an evporated layer of nickel dimethylglyoxime, in which an absorption peak shifts at a known rate under pressure [9].



Fig. 2. Schematic representation of the pressure cell. The diagram is not to scale.

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The light path was restricted to a small area near the centre of the specimen across which the pressure is essentially constant.

By reducing the area of the crystal under examination the pressure variation can, in principle, be made as small as required. However, signal to noise considerations in the detection system put a lower bound on the area that could be selected. Nevertheless it was shown that in a typical experiment for which  $r_s = 0.1 r_0$ , where  $r_s$  and  $r_0$  are the sampling and anvil radii respectively, the variation in pressure across the specimen was no greater than 1 per cent of the measured pressure. Moreover, the equations of Jackson and Waxman[10] suggest that whenever

$$\frac{2fr_0}{t} \gg 1$$

where f is the coefficient of friction between ZnS and diamond, and t is the ZnS thickness, the pressure at the centre of the anvils is hydrostatic for all types of centrally peaked pressure distributions. Therefore, although we are aware that a solid pressure transmitting medium may produce non-uniform strains, the experimental observations are most probably described by changes in the 'quasi-hydrostatic' pressure experienced by the specimen.

## 2.2 Material

The samples were cleaved from a large natural single crystal of  $MoS_2$  using 'Sello-tape'. Suitable specimens can then be trans-

ferred to an anvil, by dissolving away the glue with trichloroethylene, and at the same time allowing surface forces to pull the crystal down into intimate contact [11(a)]. The crystals are relatively impure, but there is no observable effect due to these impurities in the region of the excition absorption bands. This has been verified in the case of the analogous material  $WS_2$  by comparing natural and synthetic crystals.

The electrical and photoelectrical properties of these natural crystals, perpendicular to the *c*-direction, have been investigated by Wieting[12], and the carrier density at room temperature of about 10<sup>17</sup> cm<sup>-3</sup> is similar to the value  $(5 \times 10^{16} \text{ cm}^{-3})$  obtained by Fivaz and Mooser [13], for crystals grown by vapour phase transport. Therefore, the major impurities, Al and Si, in the natural crystals make little or no contribution to the electrical properties. Inspection of the effective potential in which excess carriers in a layer lattice move, reveals the explanation of this effect. Within each layer but outside the atomic cores the potential is low and varies slowly. Between the layers, however, the contributions of the different atoms add up to high and fairly wide potential barriers. The carriers therefore become localized within individual layers and thus behave as if moving through a stack of independent lamellae. Moreover, this tendency is accompanied by a strong interaction between the free carriers and the homopolar phonons, polarized at right angles to the layers, which leads to an anomalously strong temperature dependence of mobility [14]. Furthermore, impurities lying within the van der Waal's gap, cannot influence either the concentration or scattering behaviour of the charge carriers, although the existence of electrical polarization in the natural crystals and the absence of this polarization in grown crystals[12] indicates that these impurities are present as polarizable molecules, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or possibly aluminium silicate. However, substitutional impurities within a layer produce

n-type material, in which impurity scattering and extrinsic conduction occur below about 250°K (see Sections 4.3 and 5).

### 3. BAND STRUCTURE AND EXCITON ASSIGNMENT

## 3.1 Bonding considerations

In the following discussions a single layer model is used for the deduction of the relative positions of the energy bands, since interlayer interactions must produce only small perturbations on the interlayer potential [15].

The hybridisation of the atomic wavefunctions, which is required to give the MoS<sub>2</sub> layer structure has been described by Hultgren [16]. The 4d, 5s and 5p orbitals, outside the core of the Mo atom, are combined to make six equivalent cylindrical bond functions with a trigonal prism configuration, together with two degenerate (d/p)hybridisation) and one non-degenerate  $(d_{z_0})$ non-bonding orbitals. The sulphur atoms at the corners of the prisms, on the other hand, use 3p orbitals in the bonding, so that the orbitals perpendicular to the layers, which are then responsible for the interlayer van der Waal's forces, are saturated 3 s subshells. It is now necessary to consider how such hybridised orbitals give rise to a band structure.

It appears that the overlap integral between the atomic levels in the molybdenum and sulphur atoms in MoS<sub>2</sub> is so large that in the solid the outer s, p and d orbitals form filled valence bands and empty conduction bands which are separated by a large energy. Indeed, the energy of formation of MoS<sub>2</sub> is comparable to CdI<sub>2</sub>, so that the basic bonding gap is of order 5 eV. This implies that the electronic properties are imparted by electrons in bands formed from the non-bonding orbitals, which have energies that lie within the basic gap. Direct evidence for the existence of such bands comes from electron energy loss experiments in the energy range 0-60 eV, which have recently been made by Liang and Cundy [17].

In Fig. 3 are shown the relative positions of the bands, which follow directly from such considerations. The lower valence bands, labelled  $X_1$ , and the upper conduction bands  $X_1^*$  correspond to  $\sigma$  and  $\sigma^*$ -bonds between the hybridised s, p and d orbitals of molybdenum, and the p orbitals of sulphur respectively. The location of the Fermi level depends on the number of outer electrons per molecule, and in MoS<sub>2</sub> lies between the narrow nonbonding bands,  $X_2$  and  $X_3$ . The formation of bands from d-functions in this way, is not surprising as the metal-metal distance is only 3.16 Å. Furthermore, the large conductivity in NbS<sub>2</sub>, 10<sup>6</sup> times greater than in



Fig. 3. Suggested electronic band structure of  $2H-MoS_2$ . The energies and degeneracies of the levels in the Mo and S atoms, and in the hybridised Mo atom are shown in columns (a), (c) and (b) respectively. The absolute energy scale is subject to considerable error, but the relative positions of the bands,  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_1^*$  are correct to a few tenths of an eV.

 $MoS_2[18]$ , is explained by a half-filled  $X_2$ bands, since  $NbS_2$  is crystallographically similar to  $MoS_2$ . No separation of bonding and antibonding states occurs in  $X_2$  since the band is essentially equivalent to the ground state in 2-D metallic hydrogen. A separation in  $X_3$ , however, may occur, but is probably too small to be observed. Finally, an inspection of the band structure of GaS[19], in which the sulphur atoms occupy similar crystallographic positions, suggests that the sulphur 3 s subshells form a narrow valence band that lies below the other valence bands in  $X_1$ .

## 3.2 Comparison with optical data

More comprehensive optical measurements have been made by Wilson on  $MoS_2$  and the related transition metal dichalcogenides [11(b)]. A weak absorption was observed at room temperature at about 0.25 eV, showing that the direct transition between the non-bonding bands is forbidden and that the curvature of one band at k = 0 is not related to the other through the k.p perturbation. In addition, the existence of a weak shoulder at the bottom of the fundamental absorption edge in NbS<sub>2</sub>, in which band  $X_2$  is half empty, suggests that an indirect Burstein transition is involved, and the minimum gap between bands  $X_2$  and  $X_3$  is not at the  $\Gamma$ -point.

The optical spectra of the different stacking polytypes of MoS<sub>2</sub> are basically the same. The majority of transitions occur in pairs that are characteristic of a spin-orbit split valence band, although the magnitude of the splitting differs in 2H- and 3R- material as shown by the inset in Fig. 4. Group theoretic arguments, however, suggest that spin-orbit split bands can occur only along the  $\Gamma Z$  axis of the rhombohedral Brillouin zone corresponding to point group  $C_{3v}[20]$ , and therefore the majority of transitions in 3R-MoS<sub>2</sub> occur on this axis, at critical points required by the symmetry of the zone. These are situated at  $\Gamma$  and Z, but, as already emphasized, the band structure is largely determined by a single layer, so that as a first approximation, we suggest that the



Fig. 4. Some experimental absorption spectra for 2H– $MoS_2$  at 100°K and at different pressures. Curves numbered in the order in which the data were taken: (1) 0.5 kbars (2) 15.8 kbars; (3) 30.0 kbars; (4) 45.0 kbars; (5) 3.0 kbars. Intermediate and higher pressure curves were consistent with those shown. The curves have been shifted vertically for clarity from the zero pressure absorption curve. The inset shows the absorption spectra in the region of the fundamental absorption edge of 2H– $MoS_2$  and 3R– $MoS_2$ .

transitions in 2H–MoS<sub>2</sub> occur at the analogous critical points  $\Gamma$  and A, in the hexagonal Brillouin zone corresponding to point group  $D_{6h}$ .

If the exciton series are now associated with the direct gap at  $\Gamma$  between the spin-orbit split valence band in  $X_1$  and the conduction band in  $X_3$ , the remaining absorption peaks in the whole family of materials may be consistently assigned to transitions allowed by the model [11(a), 21]. Furthermore, the widths of bands  $X_2$  and  $X_3$ , the splitting of the valence band edge in  $X_1$ , and the widths of the forbidden energy gaps, all shown in Fig. 3, are determined with an accuracy of a few tenths of an eV.

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However, the work function of the material has not been measured, but it is possible to assign absolute energies to the system, by the examination of the relevant valence states in the sulphur atom and the hybridised molybdenum atom. In this approximation the work function is 8 eV, although an error of the order of an eV must be expected.

The rest of the paper describes an experimental investigation of the band model. The approach taken is to measure the effect of pressure on the exciton series and to relate the results to shifts in the various band edges.

#### 4. EFFECT OF PRESSURE ON EXCITON FORMATION

## 4.1 Introduction

Measurements on the shape and position of the  $A_1$  and  $B_1$  peaks have been made at both room and liquid nitrogen temperatures. The main features in both cases are the shift of the peak positions to higher energies and a considerable weakening and eventual disappearance of the peaks themselves at the highest pressures. However, with the reduction of pressure, the peaks reappear and return to their zero pressure positions. Figure 4 summarizes these statements for a typical run at 100°K. Intermediate and higher pressure curves were consistent with those shown, but have been omitted for clarity. The second order exciton was not observed at pressures above 5 kbars, nor after the reduction of pressure, although the resolution of the system was better than 0.005 eV in this spectral range. It will also be noticed that the absorption coefficient at the minimum the  $A_1$  and  $B_1$  peaks has increased on returning to zero pressure. Similar effects were observed previously by Evans and Young[4] when MoS<sub>2</sub> crystals were subjected to mechanical working. We suggest, therefore, that changes in the dislocation density occur during the initial application of pressure to the cell, owing to very high, though localized, stress concentrations that temporarily exist around non-uniformities in the surface of the ZnS crystal. The reversible region is reached when plastic flow has produced intimate contact throughout the cell.

## 4.2 Pressure coefficient of the A1-peak

The shift of the  $A_1$ -peak is shown at both room and liquid nitrogen temperatures in Fig. 5. In both cases a linear change occurs at



Fig. 5. The effect of pressure on the  $A_1$ -peak at 300° (1) and 100°K (2). Curve (3) indicates the relative shift of the band edges in  $X_1$  and  $X_3$  at the  $\Gamma$ -point, so that curves (4) and (5) represent the change in binding energy of the exciton with increase in pressure at 300° and 100°K respectively.

lower pressures, but at higher energies, the shift becomes non-linear. The error in positioning the exciton peak increases at these higher pressures, but is insufficient to explain the deviation from linear behaviour.

Apart from these similarities in shape, a most striking difference in pressure coefficient exists for the two temperatures. The values obtained in the linear regions are

$$\left(\frac{\partial E_{A_1}}{\partial p}\right)_{300} = (2 \cdot 0 \pm 0 \cdot 1) \times 10^{-6} \text{ eV/bar}$$
$$\left(\frac{\partial E_{A_1}}{\partial p}\right)_{100} = (1 \cdot 4 \pm 0 \cdot 2) \times 10^{-6} \text{ eV/bar}.$$

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.

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

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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

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

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



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

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

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

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

$$E(T,p) = E_d; \quad T \le 250^{\circ} \text{K} \tag{3}$$

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

$$E(T,p) = E_{x_2x_3}(T,p)/2; \quad T \ge 250^{\circ} \text{K}$$
 (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

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

With values of  $(\partial E_{x_2x_3}/\partial p)_{300}$  ranging from  $-2.0 \times 10^{-6} \text{ eV/bar}$  to  $-3.0 \times 10^{-6} \text{ eV/bar}$ , in steps of  $0.1 \times 10^{-6} \text{ eV/bar}$ , 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

$$\left(\frac{\partial E_{x_2x_3}}{\partial p}\right)_{300} = (-2.5 \pm 0.5) \times 10^{-6} \text{ eV/bar}$$

and

$$\delta(300, 0) = 0.22 \pm 0.02$$

or

$$N(300, 0) = (2 \cdot 0 \pm 0 \cdot 5) \times 10^{17} \,\mathrm{cm}^{-3}$$

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

$$\left(\frac{\partial E_{x_2x_3}}{\partial p}\right)_{300} = 2kT \frac{\partial \log_e R}{\partial p}$$
$$= (-2.0 \pm 0.5) \times 10^{-6} \,\text{eV/bar}$$

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

## 4.4 Pressure coefficient in the B<sub>1</sub>-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

$$\left(\frac{\partial E_{B_1}}{\partial p}\right)_{300} = (2 \cdot 2 \pm 0 \cdot 1) \times 10^{-6} \text{ eV/bar}$$
$$\left(\frac{\partial E_{B_1}}{\partial p}\right)_{100} = (1 \cdot 4 \pm 0 \cdot 2) \times 10^{-6} \text{ eV/bar}.$$

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  $\Gamma$ . 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  $\sigma$  are Pauli matrices, V is the electrical potential between an electron and the nuclei and p is the momentum operator. Consequently,  $\nabla V$ , 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

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be sufficient to test the theory, as indicated in Fig. 6. The temperature range over which the experiment may be carried out is unfortunately relatively narrow, since below liquid nitrogen temperatures only small changes in binding energy are expected from from the nature of the exponent in the expression for N(T, p), while above liquid nitrogen temperature, it becomes increasingly difficult to locate the position of peak  $A_2$ .

Figure 7 shows the separation of exciton peaks  $A_1$  and  $A_2$  at temperatures between 4° and 200°K. The separation at 300°K was that



Fig. 7. The variation in the separation of the  $A_1$  and  $A_2$  exciton peaks with temperature. The transition from extrinsic to intrinsic behaviour occurs at about 250°K.

deduced from the pressure measurements. As expected, the separation is reduced as the temperature is increased, but by using (1) and (2), a more quantitative analysis is possible. We can write

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$$\delta(T, 0) = \delta(T_s, 0) \left(\frac{T}{T_s}\right)^{1/4} \\ \times \exp\left[\frac{E(T_s, 0)}{2k} \left\{\frac{1}{T_s} - \frac{1}{T} \frac{E(T, 0)}{E(T_s, 0)}\right\}\right]$$
(6)

in which  $T_s$  is a specified, fixed temperature in either the extrinsic or intrinsic region and  $E(T_s, 0)$  is the activation energy, defined in Section 4, in the conduction region containing  $T_s$ . If the temperature variation of  $E_{x_2x_3}$  and  $E_d$  are neglected, then (6) may be expressed as

$$\delta(T, 0) = \delta(T_s, 0) \left(\frac{T}{T_s}\right)^{1/4} \\ \times \exp\left[\frac{E(T_s, 0)}{2k} \left\{\frac{1}{T_s} - \frac{1}{T}\right\}\right]$$
(7)

to a good degree of accuracy.

The variation  $\delta(T, 0)$ , and, accordingly in the separation of peaks  $A_1$  and  $A_2$ , owing to changes in the intrinsic carrier concentration, is shown as the dotted line in Fig. 7. In this calculation, the value of  $\delta(300, 0)$  is taken from the pressure measurements. We see that at low temperatures, the reduction in separation is underestimated, owing to the dominance of extrinsic effects. The electrical measurements available suggest that  $E_d$  is  $(0.05 \pm 0.03)$  eV, so that, with the value of  $\delta(250, 0)$  taken from the intrinsic curve, the change in binding energy, owing to an extrinsic carrier concentration, can be calculated. The calculation, however, is relatively insensitive at low temperatures to the exact value of  $E_d$ within this range, and therefore the result for  $E_d$  equal to 0.05 eV, shown as the solid curve, brings the theoretical calculations in line with the experimental observations.

#### 6. CONCLUSION

The excitonic doublet below the fundamental absorption edge of  $MoS_2$  has been explained in terms of transitions from a spinorbit split valence band  $X_1$  to a doubly degenerate conduction band  $X_3$ , lying on each side of a full narrow *d*-band  $X_2$ , (Fig. 3). The effect of pressure on the intensity and width of each absorption peak is well described by an increase in electron-hole screening, caused by a reduction of  $E_{x_2x_3}$  with pressure, and it is evident that  $E_{x_2x_3}$  is always greater than the exciton binding energy. However, at liquid helium temperatures, the free carrier density is sufficiently reduced for the binding energy of the  $B_1$  exciton to be equal to  $E_{x_2x_3}$  at about 60 kbars. Under these conditions, the original ground state is expected to become unstable against exciton formation, and a new ground state is formed[26–29]. This might be observed as a crystallographic phase change.

The pressure coefficients of the excitonic doublets in the related family of materials have also been measured, but these will be published later, together with the pressure coefficients of the absorption peaks at higher energies.

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