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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) plate-like 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 E perpendicular 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 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^{-1} , 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-

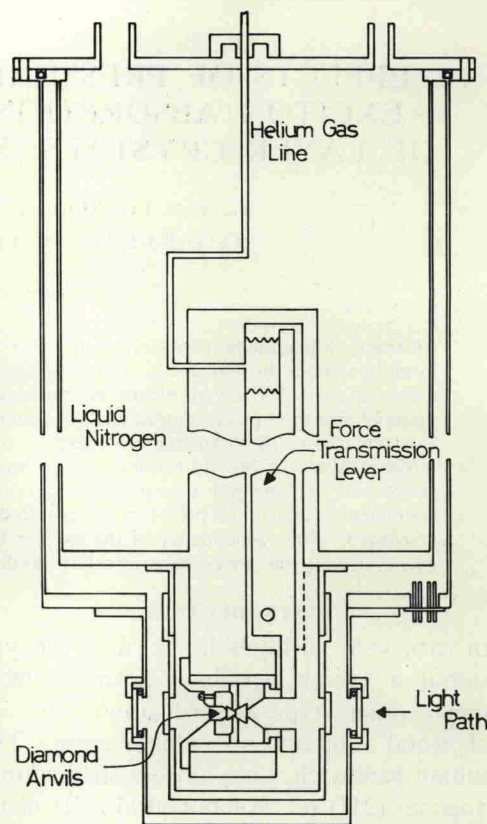


Fig. 1. Liquid nitrogen cryostat for optical transmission measurements at high pressures.

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 $29,000 \text{ cm}^{-1}$ 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 20μ , 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 unevenness of ZnS single crystal surfaces. Calibration was effected by using as a specimen, an evaporated layer of nickel dimethylglyoxime, in which an absorption peak shifts at a known rate under pressure[9].