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## Optical Studies of Transition Metal Dichalcogenide Layer Crystals at High Pressures

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### ABSTRACT

The shift in the position of a number of exciton peaks seen in the spectra of the layer type transition metal dichalcogenides has been measured in a hydrostatic pressure apparatus capable of reaching pressures up to 6 kilobars, in the temperature range 80°K to 295°K. For the Group 6 materials MoS<sub>2</sub> and WSe<sub>2</sub>, the magnitude and sign of the pressure coefficients for the AB excitons and the A'B' excitons are different. There are also differences in the behaviour of the 2H and 3R polytypes. The results show that layer-layer interactions must be considered in calculations of the electronic band structure. The pressure coefficients of the Group 5 metal NbS<sub>2</sub> and the Group 4 insulators HfS<sub>2</sub>, HfSe<sub>2</sub> and ZrS<sub>2</sub> have also been determined and are compared with those of the Group 6 semiconductors.

### § 1. INTRODUCTION

THE family of transition metal dichalcogenide layer crystals exhibits a rich diversity of physical properties, and many of these have been reviewed recently by Wilson and Yoffe (1969). The chalcogenides of the Group 4 metals hafnium and zirconium are wide bandgap materials, those of the Group 5 metals niobium and tantalum are superconducting metals, and the Group 6 molybdenum and tungsten layer chalcogenides are narrow gap semiconductors.

Previous high pressure work has been concerned principally with the exciton absorption peaks in MoS<sub>2</sub> (Connell, Wilson and Yoffe 1969), and was performed with an opposed diamond anvil pressure cell. The aim of the present work has been to investigate the effect of hydrostatic pressure on the optical spectra of representative members of the Groups 4, 5 and 6 transition metal dichalcogenide layer crystals, with the object of identifying related features in the energy band structure of these solids.

### § 2. EXPERIMENTAL

The crystals of 2H MoS<sub>2</sub> used in this work were natural. The other materials were synthesized from chalcogens of 5N purity and transition

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metals of purity given below. The method by which the crystals were grown from the powder is indicated.

3R MoS<sub>2</sub>-Br<sub>2</sub> transport—4N Mo.

WSe<sub>2</sub>-I<sub>2</sub> transport—4N W.

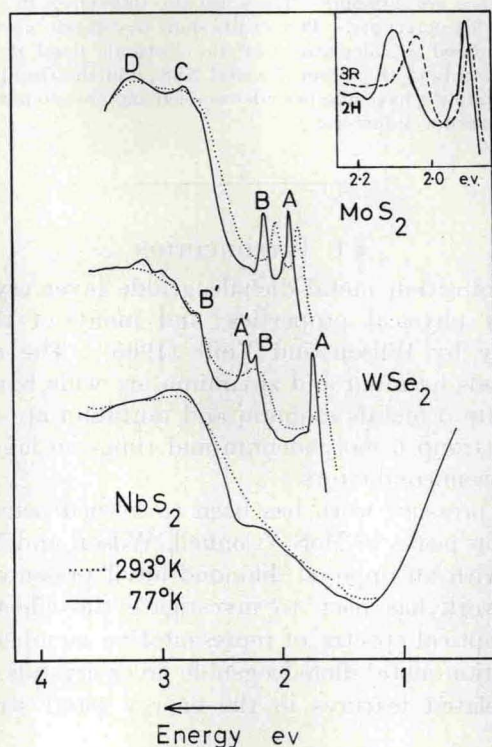
HfS<sub>2</sub> and HfSe<sub>2</sub>-I<sub>2</sub> transport—2½% Zr present.

ZrS<sub>2</sub>-I<sub>2</sub> transport—2N5 Zr.

NbS<sub>2</sub>-I<sub>2</sub> transport—2N5 Nb.

The crystals were peeled by means of adhesive tape to a thickness—usually about 1000 Å—suitable for optical transmission measurements in the desired region of the spectrum. If necessary, the crystals could be freed from the tape by dissolving the adhesive in a bath of trichlorethylene. It was found for samples 1000 Å thick that the pressure coefficients were the same whether the crystals remained on the tape or not.

Fig. 1



The optical transmission spectra, after Wilson and Yoffe, of MoS<sub>2</sub>, WSe<sub>2</sub> and NbS<sub>2</sub>, at room temperature and at liquid nitrogen temperature. Inset: The A and B peaks in the spectrum of 2H and 3R polytypes of MoS<sub>2</sub> at liquid nitrogen temperature.