These indicate that the feature X may be excitonic in character, with some evidence of a second transition, not visible in direct transmission, at an energy about 0·1 ev higher than X in each case.

§ 5. Conclusions

The optical studies under hydrostatic pressure and at low temperature have brought out a number of points connected with the band structure of these layer type materials. It has been found that the energy separation between the spin–orbit split exciton peaks A and B for the semiconductors MoS_2 and WSe_2 (see fig. 1) increases with pressure, though both peaks shift to higher energy. On the other hand, the A′B′ peaks in WSe_2 have pressure coefficients opposite in sign to those of the AB peaks (i.e. shift to lower energy). The pressure coefficients in 3R MoS_2 are substantially smaller than those in the 2H polytype. Furthermore the C peak in MoS_2 clearly corresponds to a transition different in character from those for the AB peaks. These results show the importance of including layer-layer interactions in calculations of the electronic band structure of these materials. Calculations for a single layer are not sufficient for an accurate description of the electron energy levels.

Table 4. The pressure coefficient at room and liquid nitrogen temperatures of the first exciton peak in GaSe

	Energy ev	T°K	$(\partial E/\partial p)_T \times 10^{-6}$ ev/bar		$(\partial E/\partial T)_p \times 10^{-4}$ ev/deg.
GaSe	2·102	80	−4·4	±0·4	−4·0
	2·016	294	−4·8	±0·6	(average between 77° and 290°K)

For the wide band gap dichalcogenides formed from Hf and Zr (octahedral coordination), corresponding to a d^0 electron configuration for the metal, the pressure coefficients for the peak X (fig. 2) show that the transition associated with X cannot be compared with the transitions corresponding to peaks A and B in the d^2 type compound MoS_2, where the coordination is trigonal prismatic.

The optical properties of the metal NbS_2 in the intraband region do not change appreciably with pressure. This result is unexpected, since the related physical property, namely the superconducting transition temperature, changes rather rapidly with pressure in the similar system $NbSe_2$. A neutron diffraction study of the change in the phonon energies with pressure could help to explain this result.

The shift in the exciton peak position near 2ev in GaSe has also been measured, and the results are given in table 4. The pressure coefficients are very different from those found in MoS_2 although there are structural

similarities between the two materials. These differences in the pressure coefficients reflect the fact that the transitions involve d levels in MoS_2, while in GaSe the exciton corresponds to a $\sigma\sigma$ * type transition, and should rather be compared with the α peak seen in the spectra of the Group 6 dichalcogenides.

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References

Acrivos, J. V., Liang, W. Y., Wilson, J. A., and Yoffe, A. D., 1971, *J. Phys.* C (Solid St. Phys.), **4,** L18.

Bachmann, R., Kirsch, H. C., and Geballe, T. H., 1971, *Solid St. Commun.*, **9,** 57.

Bordas, J., 1971, Ph.D. Thesis, Cambridge University.

Brixner, L. H., 1963, *J. electrochem. Soc.*, **110,** 289.

Bromley, R. A., 1971, Ph.D. Thesis, Cambridge University.

Bromley, R. A., Murray, R. B., and Yoffe, A. D., 1971 (submitted for publication).

Connell, G. A. N., 1967, Ph.D. Thesis, Cambridge University.

Connell, G. A. N., Wilson, J. A., and Yoffe, A. D., 1969, *J. Phys. Chem. Solids,* **30,** 287.

Consadori, F., and Frindt, R. F., 1970, *Phys. Rev.* B, **2,** 4893.

Fan H. Y., 1951, *Phys. Rev.*, **82,** 900 ; 1967, *Handbuch der Physik*, edited by S. Flügge (Berlin : Springer-Verlag).

Flack, H. D., 1970, unpublished work, Cambridge University.

Frindt, R. F., and Yoffe, A. D., 1963, *Proc. R. Soc.* A, **273,** 69.

Grant, A. J., Liang, W. Y., and Yoffe, A. D., 1970, *Phil. Mag.*, **22,** 1129.

Grant, A. J., and Yoffe, A. D., 1970, *Solid St. Commun.*, **8,** 1919 ; 1971, *Phys. Stat. Sol.* B, **43,** K29.

Jérome, D., Grant, A. J., and Yoffe, A. D., 1971, *Solid St. Commun.* (in the press).

Wilson, J. A., and Yoffe, A. D., 1969, *Adv. Phys.*, **18,** 193.

Young, P. A., 1968, *Br. J. appl. Phys.* (J. Phys. D), Ser. 2, **1,** 936.