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Optical Studies of Transition Metal Dichalcogenide Layer Crystals at High Pressures

By A. J. GRANT, J. A. WILSON and A. D. YOFFE
Cavendish Laboratory, University of Cambridge, Cambridge

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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 MoS₂ and WSe₂, 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 NbS₂ and the Group 4 insulators HfS₂, HfSe₂ and ZrS₂ 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 MoS₂ (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 MoS₂ 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 MoS₂-Br₂ transport—4N Mo.

WSe₂-I₂ transport—4N W.

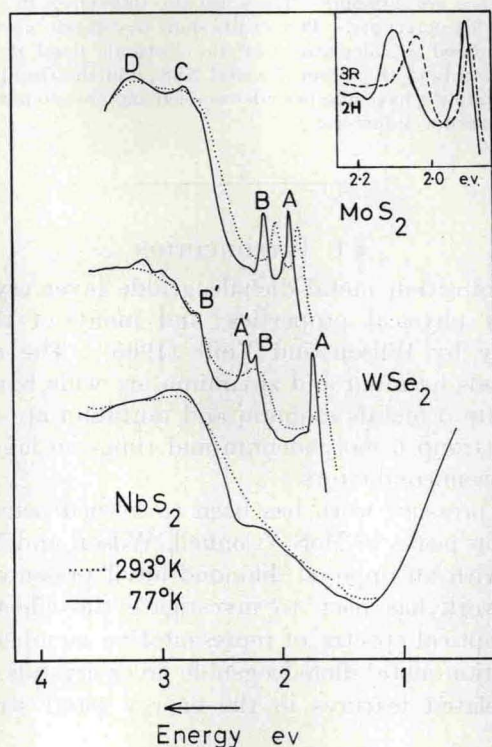
HfS₂ and HfSe₂-I₂ transport—2½% Zr present.

ZrS₂-I₂ transport—2N5 Zr.

NbS₂-I₂ 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

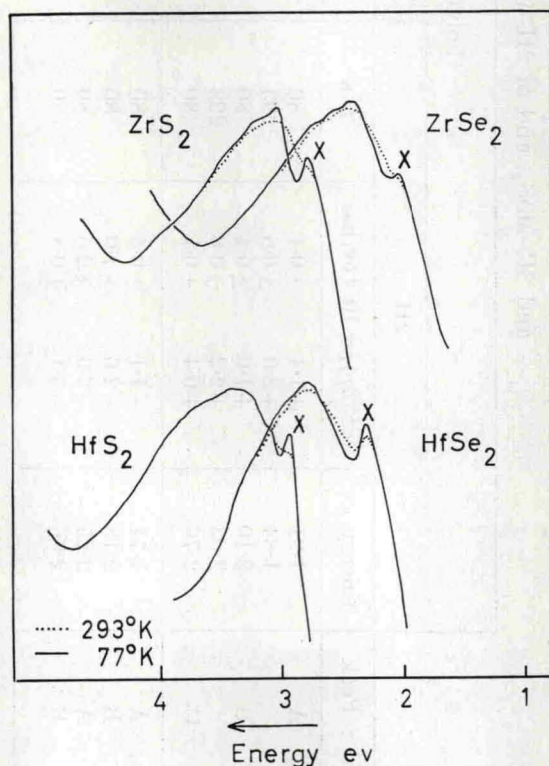


The optical transmission spectra, after Wilson and Yoffe, of MoS₂, WSe₂ and NbS₂, at room temperature and at liquid nitrogen temperature. Inset: The A and B peaks in the spectrum of 2H and 3R polytypes of MoS₂ at liquid nitrogen temperature.

One crystal of 2H-MoS_2 was peeled to a thickness of less than 400 \AA —a pale green colour—which allowed a measurement to be made of the pressure coefficient of the C peak (see fig. 1). Simultaneous observation of the A and B peaks showed that A and B were moving at a rate approximately ten times faster than the known pressure coefficients for these peaks. The crystal was presumably strained by an amount determined by the compressibility of the adhesive tape. The apparent pressure coefficient of peak C was therefore reduced by a factor of ten before inclusion in table 1. The value is so small that it probably would have been unmeasurable without this fortuitous effect. It appears that the effect of adhesive tape as a substrate is important only for crystals much thinner than 1000 \AA .

The helium gas pressure system and the optical system used in this work have been described previously (Grant, Liang and Yoffe 1970). The pressure range available was 0–6 kilobars.

Fig. 2



The optical transmission spectra, after Wilson and Yoffe, of zirconium sulphide and selenide, and of hafnium sulphide and selenide, at room temperature and liquid nitrogen temperature.

§ 3. RESULTS

Optical transmission spectra for 2H-MoS₂ and 2H-WSe₂ are given in fig. 1 after Wilson and Yoffe (1969). The upper right insert shows in detail the A and B exciton peaks in the 2H and 3R polytypes of MoS₂, measured at 77°K. The metallic layer crystal NbS₂ is included in fig. 1, with the three spectra displaced vertically for clarity, but having a common absorption coefficient of about $5 \times 10^5 \text{ cm}^{-1}$ in the region of the C peak in MoS₂.

Table 2. The hydrostatic pressure coefficient of the first peak in the optical absorption spectra of some zirconium and hafnium chalcogenides

Material : Peak	Energy (ev)	$(\partial E/\partial p)_T \times 10^{-6} \text{ ev/bar}$	$T^\circ\text{K}$
ZrS ₂ X	2.78	-0.5 ± 0.4	80
X	2.78	Not measurable, no peak	293
HfS ₂ X	2.88	-7.0 ± 0.4	80
X	2.85 (shoulder)	-10.5 ± 1.0	293
HfSe ₂ X	2.26	-9.6 ± 0.4	80
X	2.26	-12.5 ± 0.6	293

Table 3. The room-temperature compressibility values (Flack 1970) for some layer crystals parallel to, and perpendicular to, the crystallographic *c* axis.

Material	$\beta_{\parallel} \times 10^{-7}/\text{bar}$	$\beta_{\perp} \times 10^{-7}/\text{bar}$	<i>P</i> range kilobars
2H-MoS ₂	17 ± 2	3.3 ± 1.0	0-12
NbSe ₂	11 ± 1	1.5 ± 0.3	0-48
HfS ₂	19 ± 1	2.8 ± 0.5	0-35

The hydrostatic pressure coefficients which have been measured for MoS₂ and WSe₂ are presented in table 1. The possible error associated with each measurement varies according to the strength and sharpness of the particular feature (with the exception of the C peak in 2H-MoS₂, which was mentioned in the previous section).

The optical transmission spectra for the sulphide and selenide of Hf and Zr are shown in fig. 2. The pressure coefficients of the feature X for each material (except ZrSe₂, for which sufficiently large crystals were not available) are presented in table 2.

The room-temperature compressibility values of Flack (1970) for three-layer materials parallel to, and perpendicular to the crystallographic *c* axis are given in table 3. These measurements were made with an

opposed diamond anvil high pressure x-ray apparatus. Powdered samples mixed with powdered NaCl as the pressure marker were placed in a molybdenum gasket to produce quasi-hydrostatic conditions.

§ 4. DISCUSSION

It will be convenient to discuss the results for the different layer materials separately, dealing first with the semiconductors MoS₂ and WSe₂, then the metal NbS₂, and then the insulators HfS₂/Se₂ and ZrS₂.

4.1. Molybdenum Disulphide

4.1.1. Pressure coefficients in 2H and 3R polytypes of MoS₂

The pressure coefficients of exciton peaks A and B for 2H-MoS₂ bear interesting comparison with those for the 3R polytype; the (2H) coefficients are at least 50% larger in each case. This result was anticipated by Connell (1967), who found low values for the pressure coefficients of the A and B peaks in 3R-MoSe₂ and WS₂, similar to those reported here for 3R-MoS₂. This paper, however, reports the first measurements on different polytypes of the same compound.

It has been usual to suppose that the energy levels in layer crystals are adequately described in terms of the electronic interactions within a single layer, although it had been observed that the energy separation of the A and B peaks in (3R) was only about three-quarters of the separation in 2H-MoS₂ (fig. 1, inset). It is now apparent that interlayer interactions are important in determining not only the energy splitting of the band extrema but also the deformation potentials of the energy levels in the layer crystals under consideration.

The pressure coefficient of the B peak is always slightly larger than that of the A peak, in both 2H- and 3R-MoS₂, and at both liquid nitrogen and room temperatures. Band structure calculations (Bromley, Murray and Yoffe 1971) have shown that the AB energy splitting can be influenced by sulphur-sulphur interactions between adjacent layers of crystal across the van der Waals gap, and it is of interest to note that this splitting increases under pressure for both polytypes of MoS₂.

The pressure coefficient of the C peak in MoS₂ is much smaller than those of the exciton peaks A and B. The C peak has been assigned by Bromley (1971) to a density of states effect at the symmetry point Q, and calculations of the deformation potential for this transition would help to confirm this assignment.

4.1.2. Temperature variation of the pressure coefficients

The temperature variation of the pressure coefficients in 2H-MoS₂ observed previously in this laboratory (Connell *et al.* 1969) was explained at that time in terms of a reduction in the exciton binding energy due to screening of the electron-hole interaction by carriers promoted across the narrow indirect bandgap present in this material.

Recently, however, it has been established (Grant *et al.* 1970, Grant and Yoffe 1970, 1971) that pressure coefficients in a number of materials including both cubic and layer crystals (e.g. TlBr, PbI₂, As₂Se₃, etc.) do normally increase with increasing temperature. It should be possible to describe the implied temperature dependence of the deformation potential in terms of the pseudopotential model, but there is as yet to our knowledge no detailed theory to account for this effect.

We will then consider the increase in pressure coefficients between 80°K and 290°K as 'normal' behaviour, and reserve the previous explanation involving a reduction in the exciton binding energy for the non-linear region of pressure shift observed by Connell *et al.* at pressures in excess of 30 kilobars.

4.1.3. Lattice dilatation and the electron-lattice interaction

An important reason for measuring the pressure coefficient of interband transitions is to determine how much of the temperature coefficient of the energy of the interband transition in question arises from thermal expansion and how much from the electron-lattice interaction. Since the energy of a transition is a function of the pressure, temperature and volume of the solid, it may readily be shown that

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\alpha}{\beta} \cdot \left(\frac{\partial E}{\partial P}\right)_T, \quad \dots \dots \dots (1)$$

where the expansion coefficient $\alpha = 1/V \cdot (\partial V/\partial T)_P$ and the isothermal compressibility $\beta = -1/V \cdot (\partial V/\partial P)_T$.

This equation expresses the temperature coefficient of an energy gap E as the sum of two terms. The first term on the right-hand side relates to the change in energy gap with temperature at constant volume, and is a measure of the electron-lattice interaction, or the degree to which energy levels are perturbed by lattice vibrations. The second term expresses the energy change due to lattice expansion in terms of the expansion coefficient, the isothermal compressibility and the pressure coefficient. Independent measurements of the temperature and pressure coefficients therefore permit an estimate to be made of the electron-lattice interaction, provided that α and β are known.

In these layer crystals the crystallographic c axis is normal to the plane of the layers, and we may take two other equivalent directions as lying in the plane of the layers. To take account of this crystal anisotropy the last term in eqn. (1) is modified (Davies 1970, private communication) to become

$$\left(\frac{\alpha_{\parallel} + 2\alpha_{\perp}}{\beta_{\parallel} + 2\beta_{\perp}}\right) \cdot \left(\frac{\partial E}{\partial p}\right)_T, \quad \dots \dots \dots (2)$$

where the subscripts denote directions parallel \parallel and perpendicular \perp to the c axis. The pressure coefficient refers to hydrostatic pressure, and the compressibilities refer to strains produced by hydrostatic pressure. This expression naturally reduces to the original one for a cubic system.

Flack (1970) has measured β_{\parallel} and β_{\perp} for several layer crystals, and his results are presented in table 3. The compressibility is, as expected, considerably greater parallel to the c axis than in a direction lying parallel to the crystal layers. This effect is to be attributed to the easy reduction under pressure in the van der Waals gap between successive MX_2 sandwiches.

Young (1968) measured the variation with temperature of the lattice parameter in MoS_2 normal to the c axis, using crystals mounted on a cold stage in an electron microscope. The value of α_{\perp} obtained from his data is $\alpha_{\perp} = 32 \times 10^{-6}/\text{deg.}$ at 290°K .

No direct measurement of α_{\parallel} for MoS_2 has been found in the literature. Brixner (1963) has however measured α_{\parallel} and α_{\perp} for tungsten diselenide WSe_2 , which has the same crystal structure as MoS_2 . Brixner obtained $\alpha_{\parallel} = 10.6 \times 10^{-6}/\text{deg.}$; and $\alpha_{\perp} = 6.8 \times 10^{-6}/\text{deg.}$ The large discrepancy in the above values of α_{\perp} for MoS_2 and WSe_2 is surprising, but in the absence of a direct measurement, we estimate α_{\parallel} for MoS_2 , using the same ratio between α_{\parallel} and α_{\perp} as for WSe_2 , to be $\alpha_{\parallel} = 50 \times 10^{-6}/\text{deg.}$ for MoS_2 at 290°K .

The above values of expansion coefficient and compressibility, together with the pressure coefficient of peak A in 2H-MoS_2 at 293°K , lead to a lattice dilatation term of value, -1.0×10^{-4} eV/deg.

The temperature coefficient at room temperature of the A peak in 'freely mounted' crystals of 2H-MoS_2 (Frindt and Yoffe 1963) can be estimated as -3.0×10^{-4} eV/deg., so that the lattice dilatation accounts for just one-third of the temperature shift of peak A at room temperature. The electron-lattice term is left with the value (from eqn. (1)) -2.0×10^{-4} eV/deg., with the usual negative sign predicted by Fan (1951, 1967).

An estimate may be made of the electron-lattice interaction term at 80°K assuming that the ratio involving expansion coefficients and compressibilities in the expression (2) does not change significantly between 290°K and 80°K . The temperature coefficient of peak A at 80°K from Frindt and Yoffe (1963) is approximately -1.7×10^{-4} eV/deg. The pressure coefficient of peak A at 80°K given in table 1 leads to a lattice dilatation term of value -0.8×10^{-4} eV/deg., so that the electron-lattice term must have the value -0.9×10^{-4} eV/deg.

The reduction in magnitude of the electron-lattice term at low temperature is in agreement with Fan's theory of the electron-lattice interaction. Accurate measurements of expansion coefficient and compressibility as functions of temperature are required, however, before weight can be attached to the numerical value of the electron-lattice term at 80°K .

4.1.4. *The indirect gap*

The electrical energy gap of about 0.3 eV in MoS₂ has been assigned (Wilson and Yoffe 1969) to an indirect gap between a lower filled band arising from metal d_{z²} levels and that same conduction band as is involved in the direct optical absorption (i.e. peaks A and B). Electrical measurements under pressure have been made on MoS₂ crystals with the current flowing parallel to the *c* axis. The resistance fell with both increasing temperature and pressure, but there is no information on the variation of the carrier mobility in this direction with either pressure or temperature, so that an analysis similar to the above but in terms of the indirect energy gap cannot be given at present.

4.2. *Tungsten Diselenide: Pressure Coefficients and the Interlayer Interaction*

The second excitonic doublet, labelled A' and B', is well resolved at liquid nitrogen temperature in the absorption spectrum of WSe₂ (fig. 1) from the usual peaks of the stronger doublet AB. The energy splittings are similar, with 0.47 eV for AB and 0.41 eV for A'B'.

Under pressure, peaks A and B move to higher energy, with B moving somewhat faster than A, as was the case for MoS₂. Peaks A' and B' however, both move in the opposite direction, to lower energies. The pressure coefficients suggest that the two doublets should superpose, appearing as a single doublet for pressures of order 100 kilobars. The data are not sufficiently accurate to permit a definite conclusion regarding the variation with pressure of the A'B' energy splitting; the AB splitting is initially greater and increases further with pressure. Any simultaneous superposition of AA' and BB' therefore represents only a tentative possibility.

The above result is clearly of significance in connection with band structure calculations for layer crystals, since the deformation potentials of the two doublets AB and A'B' must be of opposite sign. The hypothesis (Bromley 1971) that the origin of the energy splittings AA' and BB' lies in the interlayer interaction is supported by the work of Consadori and Frindt (1970). These authors thinned crystals of WSe₂ down to only two or three molecular layers, and found that the energy of peak A increased from 1.71 eV to 1.87 eV. Unfortunately the weaker A' peak rapidly merged with B, and it was not possible to observe the likely reduction in energy of this peak on thinning. The AB splitting was however observed to be reduced for very thin specimens of WSe₂ by some 8%. In this connection we may recall that the AB splitting is less in 3R-MoS₂ than in the 2H polytype; probably the 3R material is more closely comparable to a 'single layer' crystal without interlayer interactions. The effect of thinning a 2H crystal would then be expected to lead to modification of the 2H spectrum towards that of the 3R material, namely by a reduction in the AB splitting.

4.3. Niobium Disulphide

There are no sharp features in the interband absorption spectrum of NbS₂ at energies corresponding to the allowed direct bandgap of MoS₂, since the high density of free carriers—one per Nb atom—screens out the AB excitons which might otherwise appear. With the small range of hydrostatic pressure available (0–6 kilobars) no observable change in the spectrum around 2.3 eV was found at 80°K. The basic similarity in the band structures of NbS₂ and MoS₂ has received support from intercalation studies (Acrivos, Liang, Wilson and Yoffe 1971).

The 'free carrier' region of the spectrum, below about 1.3 eV, is found to be temperature independent to within a few per cent between liquid helium and room temperatures. A similar result for NbSe₂ was found by Bachmann, Kirsch and Geballe (1971). Transmission measurements in this region are somewhat unsatisfactory because they do not distinguish between the increase in reflectivity of the metal and the intraband absorption. However qualitative measurements up to 60 kilobars, using a van Valkenburg opposed diamond anvil apparatus, established a decrease under pressure in the slope of the reflectivity versus wavelength. This may be due partly to an increase in the plasma frequency under pressure, and partly to an enhancement in the free carrier lifetime due to a decrease in lattice scattering.

An effect of particular interest is the striking increase under pressure of the superconducting transition temperature for the related compound NbSe₂, which is reported elsewhere (Jérome, Grant and Yoffe 1971).

4.4. Zirconium and Hafnium Chalcogenides

The octahedrally bonded layer crystals of Group 4 (Zr, Hf) have properties distinct from the trigonal Group 6 (Mo, W) materials. The optical spectra (figs. 1 and 2, after Wilson and Yoffe 1969) are quite different. In addition the Group 4 materials are insulators, whereas the Group 6 materials are semiconductors having a narrow filled band derived mainly from the metal d_z^2 orbitals.

The distinction is reinforced in the measurements of the pressure coefficients of the first peak X in the optical absorption spectra of ZrS₂, HfS₂ and HfSe₂, shown in table 2. The coefficients are all negative, in contrast to the positive values obtained for the spin-orbit split peaks of Group 6 materials such as MoS₂. The difference between the small negative coefficient in the case of ZrS₂, and the much larger negative coefficients for HfS₂ and HfSe₂ is unexpected, in view of the close similarity in the general shape of the optical absorption spectra. Preliminary band structure calculations for these materials (Murray 1971, private communication) indicate that the bands involved in this series of compounds are similar.

Recent electric-field-modulated transmission measurements have been made on HfS₂ and HfSe₂ in the sandwich configuration (Bordas 1971).

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 MoS₂ and WSe₂ (see fig. 1) increases with pressure, though both peaks shift to higher energy. On the other hand, the A'B' peaks in WSe₂ have pressure coefficients opposite in sign to those of the AB peaks (i.e. shift to lower energy). The pressure coefficients in 3R MoS₂ are substantially smaller than those in the 2H polytype. Furthermore the C peak in MoS₂ 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
	2.016	294	-4.8	± 0.6
				-4.0 (average between 77° and 290°K)

For the wide band gap dichalcogenides formed from Hf and Zr (octahedral coordination), corresponding to a d⁰ 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 d² type compound MoS₂, where the coordination is trigonal prismatic.

The optical properties of the metal NbS₂ 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 NbSe₂. 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 MoS₂ 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 MoS₂, 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.
- CONSDORI, 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.