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The band structures of gallium and indium selenide

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Abstract. The band structures of the group III–VI monochalcogenides GaSe and InSe have been calculated using a semi-empirical tight-binding method in a two-dimensional approximation. Many of the discrepancies between experimental work and previous calculations for GaSe have been resolved. The results for InSe appear for the first time.

1. Introduction

In recent years the layer compounds GaSe and InSe have been the subject of considerable attention. Optical transmission, reflectivity, electroreflectance and electroabsorption measurements on the former have been carried out over a large range of photon energy (Akhundov *et al* 1966, Brebner 1964, Aulich *et al* 1969, Liang 1975, Sobolev and Donetskich 1971, Suzuki *et al* 1970, Gadzhiev *et al* 1970, Wascher and Dieleman 1972, Balzarotti *et al* 1971, Balzarotti and Piacentini 1972, Mamy *et al* 1974, Leung *et al* 1966 and Fielding *et al* 1959). Complementing these are the results of photoemission and electron energy loss experiments (Williams *et al* 1976a, b, Thomas *et al* 1972, Williams *et al* 1974, Shepherd and Williams 1976, Soukiassian *et al* 1974, Lloyd *et al* 1976).

Less experimental data are available for InSe but its optical properties in transmission and reflection have been measured (Andriyashik *et al* 1968, Mushinskii and Kobolev, Akhundov *et al* 1969, Sobolev and Donetskich 1971, Fielding *et al* 1959), and photoemission experiments have recently been carried out (see following paper).

Theoretical band structure calculations on GaSe have been made previously by Schluter (1973) and by Bourdon (1974) using the pseudopotential method in three dimensions and two dimensions respectively, whilst Bassani and Pastori Parravicini (1967) and Kamimura and Nakao (1968) performed their calculations using a semi-empirical tight-binding method. We shall refer to the works of Schluter and Bassani as SCH and BPP respectively. As a result of these calculations considerable controversy has arisen over the ordering of the energy levels, particularly in the vicinity of the band gap, and it is one aim of this paper to attempt to resolve this. As far as the authors are aware, the band structure of InSe has not been calculated previously.

2. Crystal structure

The compounds GaSe and InSe are both layer materials which crystallize in a structure having the space group D_{6h}^4. The basic unit consists of two planes of metal atoms M sandwiched between two planes of selenium atoms Se with the arrangement Se–M–M–Se (see figure 1). The crystallographic data relevant to the calculation are given in table 1.
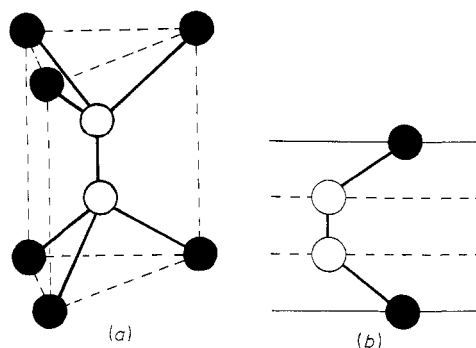

Figure 1. The crystallographic structure of GaSe (InSe). Gallium (indium) atoms are represented by open circles while the selenium atoms are represented by full circles.
Figure (*a*) shows the basic coordination unit.
Figure (*b*) shows a section through a single layer.

Table 1. Crystallographic parameters and bond lengths (in Å) for GaSe and InSe

Material	a	Metal–Se distance	Metal–metal distance	Se–Se distance	Se–Se distance across sandwich	Se–Se interlayer distance
GaSe†	3·75	2·47	2·41	3·75§	4·75	3·86
InSe‡	4·05	2·51	3·16	4·05§ (4·15)	4·82	(4·19)

† Taken from the work of Khun *et al* (1975). The values used are the means of the distances quoted for the ε, γ and δ polytypes.

‡ Taken from the work of Semiletov (1958). The Se–Se interlayer distance has been calculated from this datum.

§ In both cases this Se–Se distance has been assumed equal to the a parameter (as in an ideal coordination). The figure shown in brackets for InSe is the correct value of this distance.

Within each plane the atoms are hexagonally arranged. The bonding within the layers is normally assumed to be covalent, although SCH has suggested that it may also be slightly ionic, whilst the interlayer forces are of the van der Waals type. Four different polytypes of GaSe are believed to exist: β, γ, δ and ε. These are characterized by the different stacking sequences of their four-fold layers. We have restricted our attention to a single layer and have assumed an ideal coordination (that is one where the selenium atoms are placed at the corners of a trigonal prism with the metal atoms symmetrically situated about the centre of the prism axis).

The two-dimensional crystal structure and symmetry classification of this type of compound have already been discussed at length by BPP. Thus in this approximation GaSe and InSe have the point group D_{3h} with primitive lattice vectors

$$\tau_1 = a(\tfrac{1}{2}, \sqrt{3}/2, 0)$$
$$\tau_2 = a(-\tfrac{1}{2}, \sqrt{3}/2, 0)$$

and reciprocal lattice vectors

$$h_1 = (2\pi/a)(1, 1/\sqrt{3}, 0)$$
$$h_2 = (2\pi/a)(-1, 1/\sqrt{3}, 0).$$

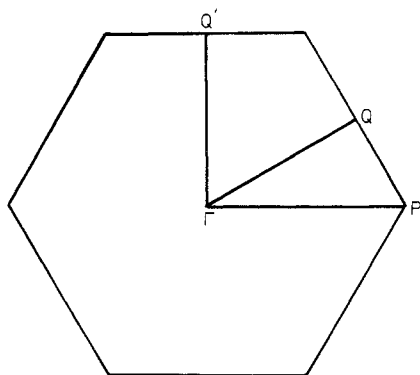This leads to a two-dimensional hexagonal Brillouin zone as illustrated in figure 2.

Figure 2. The two-dimensional hexagonal Brillouin zone for GaSe (InSe). The special symmetry points are marked.

3. Method of calculation

The calculation was carried out using the semi-empirical tight-binding approach of Bromley and Murray (1972) in a single layer approximation. Justification for this can be taken from the work of Liang (1975). He argues that the obvious similarities between the reflectivity spectra of the different polytypes of GaSe indicate that the optical selection rules are determined by the symmetry of the single layer. The selection rules have been listed by BPP.

The atomic energy eigenvalues used are given in table 2. The Bloch wavefunctions employed in the calculation were based on the 4s and 4p (5s, 5p) atomic orbitals of the gallium (indium) atoms, and the 4s and 4p orbitals of the selenium atoms. The classification of these basis functions at various symmetry points in the two-dimensional Brillouin zone is then as given by BPP. Both atomic wavefunctions and eigenvalues were computed using a program based on the work of Herman and Skillman (1963). The matrix elements were calculated using a nearest-neighbour approximation taking account of a k_z interaction. The basic differences between our calculation and that of BPP are:
(i) we have included the effects of the selenium–selenium interactions across the sandwich; and

(ii) we have used a slightly different method to compute the integrals (Bromley and Murray 1972).

The final choice of reduction parameters X, Y, Z by which effective crystal fields, bond σ and bond π integrals were reduced, was made with particular consideration being given to the recent work of Williams *et al* (1976b). Their angular x-ray photoemission work on GaSe indicates strongly that the top of the valence band is p_z-like. The strong

Table 2. Atomic energy eigenvalues in eV. These include relativistic corrections such as Darwin and mass corrections but not the spin–orbit interaction. Thus, for example, the 4p eigenvalue for gallium represents the mean of the $4p_{\frac{1}{2}}$ and $4p_{\frac{3}{2}}$ eigenvalues.

Gallium	4s	$-11{\cdot}892$	4p	$-5{\cdot}048$
Indium	5s	$-11{\cdot}170$	5p	$-4{\cdot}956$
Selenium	4s	$-21{\cdot}419$	4p	$-9{\cdot}931$

resemblance between the x-ray and ultraviolet photoemission spectra for both compounds, in particular the peak which appears in both UV spectra near the valence band edge, indicates that the same is true for InSe.

For all values of reduction parameters X, Y, and Z, it was found that the Γ_2^- band in GaSe was much lower in energy in the conduction band than was calculated by BPP. In fact it was found that the best fit occurred with the direct gap taken as the $\Gamma_1^+ \rightarrow \Gamma_2^-$ transition and this automatically produced an indirect gap $Q_1^+ \rightarrow \Gamma_3^+$. The final choices of reduction parameters were $X = 0{\cdot}9$, $Y = 0{\cdot}65$, $Z = 0{\cdot}65$ for GaSe, and $X = 0{\cdot}9$, $Y = 0{\cdot}6$, $Z = 0{\cdot}6$ for InSe. The nature of these transitions and comparisons between computed and experimental values are given in table 3.

Table 3. Optical data for GaSe and InSe at 293 K

Material	Experimental values of optical gaps (eV)	Transition	Calculated values of gaps (eV)	Nature of the transition ($E \perp c$)
GaSe	$2{\cdot}1$†	$\Gamma_1^+ \rightarrow \Gamma_2^-$	$2{\cdot}1$§	Direct forbidden
	$2{\cdot}0$†	$\Gamma_1^+ \rightarrow Q_2^-$	$2{\cdot}0$§	Indirect forbidden
	$1{\cdot}3$‡	$\Gamma_1^+ \rightarrow \Gamma_2^-$	$1{\cdot}3$§	Direct forbidden
InSe	$1{\cdot}2$‡	$Q_1^+ \rightarrow \Gamma_1^+$	$1{\cdot}2$§	Indirect forbidden
	$2{\cdot}4$‡	$\Gamma_1^+ \rightarrow \Gamma_3^+$	$2{\cdot}2$	Direct allowed

† Extracted from the references listed in § 1.
‡ Taken from the data of Andriyashik *et al* (1968).
§ Fitted in the course of the calculation.
(All figures have been rounded to $0{\cdot}1$ eV)

4. Discussion

The calculated band structures for GaSe and InSe are shown in figures 3 and 4. The similarity between them is not at all surprising. Sobolev and Donetskich (1971) found that the reflectivity spectra for both compounds are very alike and that for each reflectivity peak in GaSe there was a corresponding one in InSe. Akhundov *et al* (1966) have reported similar observations.
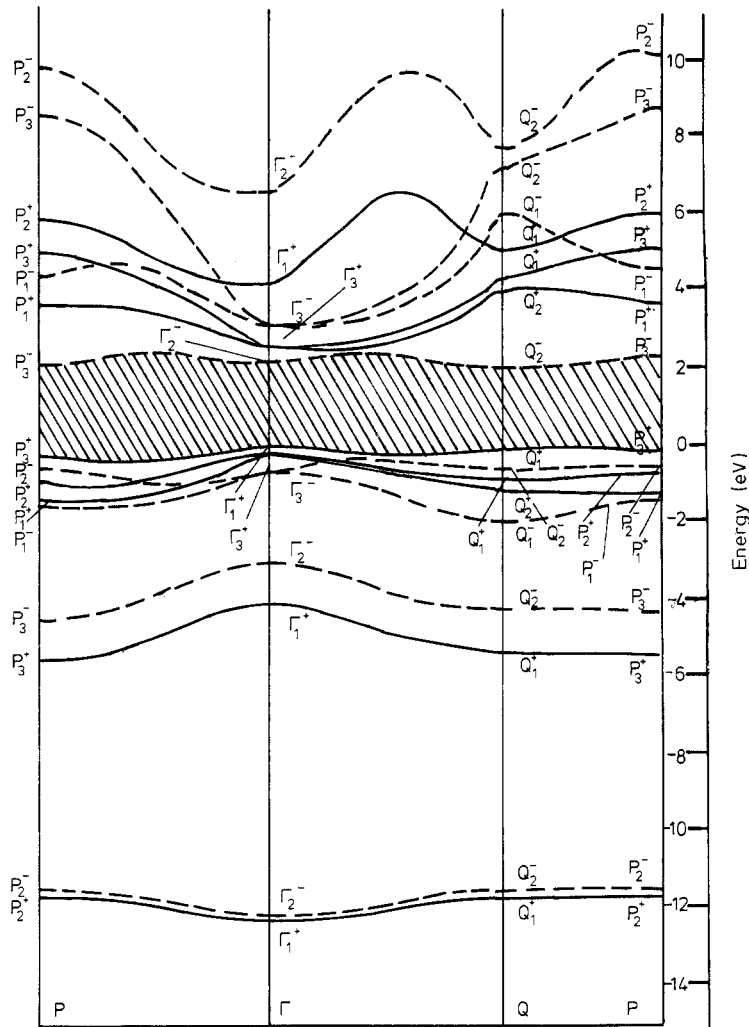
Figure 3. The band structure of GaSe. Bands which have even or odd parity with respect to the reflection operator are indicated by continuous and broken lines respectively.

In both diagrams, the lowest bands correspond to the selenium 4s atomic levels. They are widely separated from the next pair of valence bands which arise from a mixing of the selenium and gallium (indium) s and p_z states. In accordance with the charge density analysis of SCH, this gives rise to a Ga–Ga (In–In) bonding state at Γ_1^+ and an antibonding state at Γ_2^-. The uppermost valence bands are then derived mainly from the gallium 4p (indium 5p) and selenium 4p states. The crystal-field symmetry splits these into a Γ_1^+ level, which is predominantly p_z-like and forms the top valence band, and the doubly degenerate pairs Γ_3^+ and Γ_3^- which are predominantly p_x, p_y in nature. The bottom conduction band is antibonding and formed mainly from the gallium (indium) p_z level.

For GaSe the overall shape of the valence bands is in reasonable agreement with the calculation of BPP although some differences occur, mainly near the Fermi level. The main area of disagreement between our results and BPP is in the nature of the bottom

Figure 4. The band structure of InSe.

conduction band, this being Γ_2^- in our case and Γ_3^+ in theirs. The symmetry of this band is particularly important in determining the optical selection rules at the band gap, and in agreement with SCH (who finds the direct transition to be $\Gamma_4^- \to \Gamma_3^+$, in his notation for the three-dimensional case) we find the direct gap to be forbidden when the E vector of the incident light is perpendicular to the c-axis of the crystal. For the indirect gap, we have again made an equivalent assignment to SCH ($\Gamma_1^+ \to Q_2^-$ in our case, $\Gamma_4^- \to M_3^+$ in his notation) and conclude that in a two-dimensional approximation this transition must also be forbidden for $E \perp c$. BPP have not taken the indirect gap into consideration.

Wasscher and Dieleman (1972), Bourdon and Khelladi (1971) and Brebner *et al* (1967) have all measured the absorption coefficient, α, for GaSe with the plane of the E vector both parallel and perpendicular to the c-axis. They all confirm that $\alpha_\parallel$ is much greater than $\alpha_\perp$. As a result, Bourdon and Khelladi conclude that the direct transition

in GaSe is forbidden for $E \perp c$ (although weakly allowed in three dimensions when spin–orbit effects are taken into consideration), while the transition for $E \parallel c$ is allowed. Hence in a two-dimensional approximation, the transition at the gap must take place between states of opposite parity, in good agreement with our results. All the experimental evidence to support the existence of an indirect gap in GaSe has been obtained for $E \parallel c$ only (Kamimura *et al* 1969, Bourdon and Khelladi 1971, Aulich *et al* 1969) and it is generally accepted that this transition is allowed only for this particular orientation. This lends further support to our deductions.

A parallel situation is found to exist for InSe where the top valence band and bottom conduction band are of the same nature as in GaSe, so producing a forbidden direct gap (for $E \perp c$) between Γ_1^+ and Γ_2^-. The only minor difference is that we have found the indirect gap to be between the states Q_1^+ and Γ_2^-, and once again this transition is forbidden for $E \perp c$.

The analysis by Andriyashik *et al* (1968) of the absorption coefficient α of InSe in the region of the edge is in agreement with these assignments. Close comparison of their work with that of Mushinskii and Kobolev (1972) (the former measured $\alpha_\perp$, whilst in the second case $\alpha_\parallel$ was inferred) shows that for InSe, $\alpha_\parallel$ is approximately four orders of magnitude larger than $\alpha_\perp$. As in the case of GaSe this would tend to suggest that the energy levels at the band gap are of opposite parity as our calculation demonstrates.

The value 2·4 eV quoted by Andriyashik *et al* (1968) for the onset of direct allowed transitions in absorption agrees reasonably well with the calculated value of 2·2 eV ($\Gamma_1^+ \rightarrow \Gamma_3^+$). Certainly as we shall see in §6 the peak that these authors find in their reflectivity spectrum at 2·4 eV which they relate to this onset compares favourably with peak A at 2·3 eV in the joint density of states.

5. Density of states for GaSe

The calculated band structure of GaSe has been used to generate a valence band density of states which can be compared with the most recent ultraviolet photoemission data of I T McGovern and R H Williams (private communication). Both are shown in figure 5. As found in previous calculations of densities of states based on the work of BPP and SCH (Williams *et al* 1976a), the calculated widths are too narrow, particularly over the region $0 \rightarrow 7.5$ eV. The interesting point however is that all the peaks in the density of states histogram have corresponding features in the photoemission spectrum, and although their exact positions are only in fair agreement, there seems no doubt that they are equivalent.

In an attempt to resolve this discrepancy we have investigated the effect in our calculation of taking some account of the interlayer interactions. It would appear that the major effects occur via the crystal-field terms in the matrix elements, particularly those associated with the chalcogen p levels. The separations of the levels Γ_1^+, Γ_3^+ and Γ_3^- at the top of the valence bands depends mainly on the relative sizes of these crystal-field terms. and it is thought that the effect of layer–layer interactions is to increase the separations. In a three-dimensional case where the number of bands is doubled, SCH has estimated that a single level near the valence band edge splits into two levels which can be separated by up to 0·8 eV. Allowing for these shifts and splittings, in addition to experimental broadening of approximately 0·3 eV, it is plausible that the necessary shift of peaks can be accommodated. The identities of these peaks and their origins are listed in table 4.

The positions of the peak originating from the selenium 4s bands determined from x-ray photoemission experiments (Thomas *et al* 1972) and the equivalent feature in the theoretical distribution are in good agreement. The relative experimental to theoretical intensity ratios are small, but it is generally accepted that this results from the extremely low photoemission capture cross-sections which are a predominant feature of s levels. In view of this the experimental peak is poorly resolved in a region where the background due to scattering effects is high. However this, coupled with the low resolution quoted

Table 4. Assignment of the peaks in the valence density of states histogram for GaSe (see figure 5)

Peak	Bands responsible			Nature of these bands
1	Γ_1^+	Q_1^+	P_3^+	This top band is predominantly p_z-like and formed from the gallium and selenium p states.
2 } 3 }	Γ_3^+ Γ_3^+ Γ_3^- Γ_3^-	Q_1^+ Q_2^+ Q_2^- Q_1^-	P_2^+ P_1^+ P_2^- P_1^-	These doubly degenerate pairs are formed from the mixing of selenium $p_{x,y}$ and gallium $p_{x,y}$ states.
4 } 5 }	Γ_2^- Γ_1^+	Q_2^- Q_1^+	P_3^- P_3^+	These originate from a mixing of selenium and metal s and p_z states forming antibonding (peak 4) and bonding states peak 5) respectively.
6	Γ_2^- Γ_1^+	Q_2^- Q_1^+	P_2^- P_2^+	These two bands are formed from the selenium 4s levels.

for the XPS spectra of 0·5 eV, does not in total account for the difference in peak widths, but it seems likely that lifetime effects at such high binding energies may account for the extra broadening observed experimentally.

The InSe calculation has also been used to generate a valence band density of states which shows good agreement with photoemission data. These results will be presented in detail in the following paper.

6. Joint density of states

Joint density of states distributions, over the energy range 0 to 8 eV, have also been computed from the band structures of both compounds taking into account the selection rules for $E \perp c$. For this process the integration has been replaced by a summation over a large number of discrete points in k space using an energy interval of 0·1 eV, and a histogram has been built up displaying the number of states as a function of energy (see figures 6 and 7). These results can then be compared with the reflectivity spectra ($E \perp c$) of various authors (see tables 5 and 6). It must be remembered that emphasis should not be given to the relative amplitudes of features in the joint density of states distributions since no account has been taken of the matrix elements coupling the relevant valence and conduction band states.

(Strictly speaking the results obtained should be compared directly with the complex dielectric constant ε_2. To date, however, accurate and highly resolved data in the region
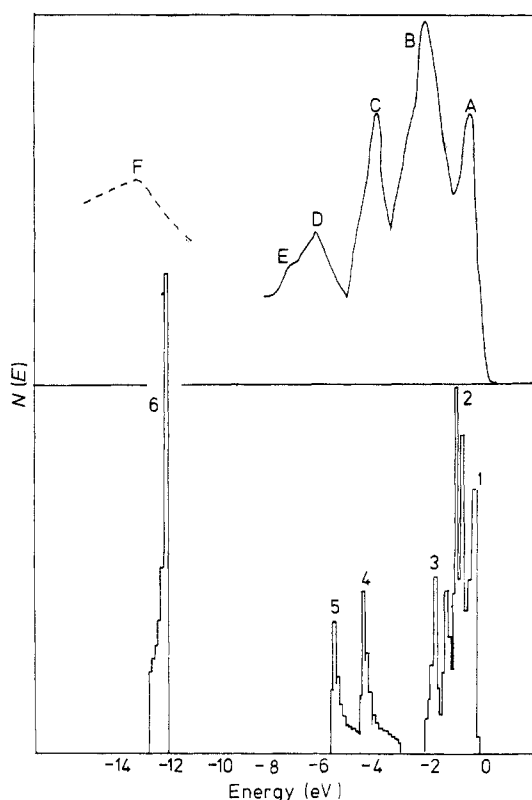
Figure 5. The valence band density of states for GaSe and the ultraviolet photoemission spectrum of I T McGovern and R H Williams (private communication) taken with an incident photon energy of 21·2 eV. The position of the selenium 4s level at about 13 eV below the valence band edge, obtained from x-ray photoemission (Thomas *et al* 1972), has been reproduced for convenience and is shown as the broken line. Peak 1 in the density of states corresponds with peak A in the photoemission spectrum, peak 2 with peak B, and so on.

Table 5. Positions (in eV) of the maxima in the reflectivity spectra of different authors as compared with the peaks in the joint density of states distributions for GaSe

	A	B	C	D		E	F	G	H	I
Theory	2·5	3·5	3·8	4·1		4·6	5·6	6·3	6·7	7·5
Liang (1975)	2·58	3·32	3·68		4·46	4·64				
Sobolev and Donetskich (1972)		3·3	3·66	4	4·56		(5·3)		6·7	8·3
Bassani *et al* (1964)			3·63	4·1		4·9		5·9	7·2	7·8
Gasanova *et al* (1966)			3·6			5				
Mamy *et al* (1974)			3·67	(4·25)		5·1	5·38	5·78	(6·5)	7·98

of interest (2 to 8 eV) are not available for both compounds. However, it is a general feature of semiconductors that in the region of the band gap and up to several eV above it, their optical properties are dominated by the effects of ε_2 (Cardona 1969). Hence structure in the ε_2 curves usually manifests itself as peaks in reflectivity spectra and direct
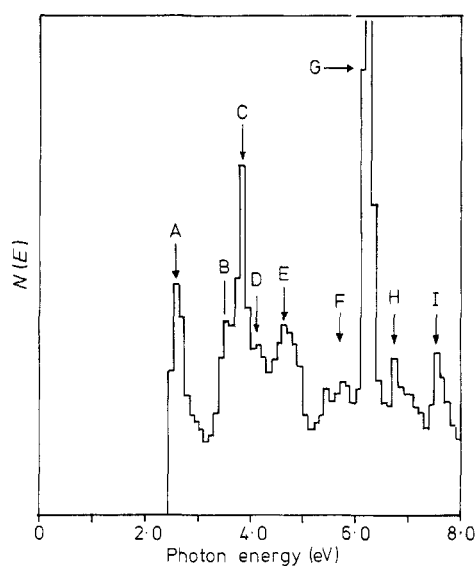
Figure 6. The joint density of states distribution of GaSe.
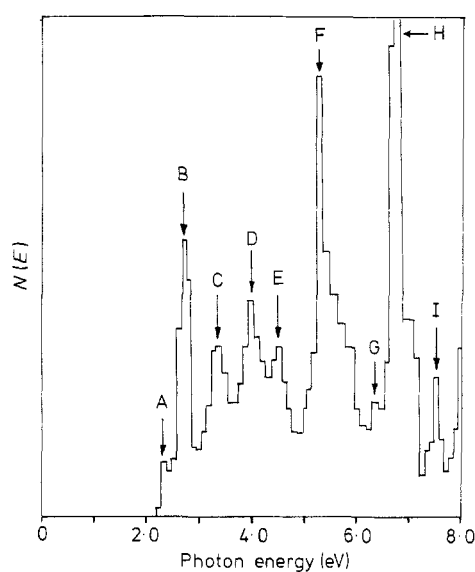

Figure 7. The joint density of states distribution of InSe.

Table 6. Position (in eV) of the maxima in the reflectivity spectra of different authors as compared with the peaks in the joint density of states distributions for InSe

	A	B	C	D	E	F	G	H	I
Theory	2·3	2·7	3·4	3·9	4·4	5·2	6·3	6·6	7·4
Sobolev and Donetskich (1972)	2·44	2·83	3·35	3·91	4·4	4·7	(6·3)		7·6
Andriyashik *et al* (1968)	2·4	2·78	3·38		4·37	4·75			
Akhundov *et al* (1969)			3·31	3·84					

comparison of the JDOS function with reflectivity measurements is to a first approximation a valid one.)

In the case of GaSe agreement between theory and experiment in the low-energy region is very good. Peak A at 2·5 eV compares well with the broad feature observed by Liang (1975) at 2·58 eV in β-GaSe, whilst the positions of peaks B, C and D agree well with the findings of many authors. Over the energy range 4·4 → 5·1 eV some disagreement exists as to the exact position and nature of the structure in the reflectivity curves. Liang (1975) has reported two peaks at 4·46 and 4·64 eV respectively, Sobolev and Donetskich (1972) reported a single peak at 4·56, whilst others such as Bassani *et al* (1964), Gasanova *et al* (1966) and Mamy *et al* (1974) find only one peak in the region of 5·0 eV. We are of the opinion that these features correspond to the broad peak E centred on 4·6 eV in the joint density of states histogram. Above about 5·0 eV comparison between theory and experiment becomes more difficult as agreement between experimental data is not nearly so good. The existence of a peak in the region of 5·3 eV had been predicted by Sobolev and Donetskich (1972) as a result of relating peaks in the spectra of GaSe to those in InSe and certainly the feature at F in the joint density of states seems compatible with this. More recently such a peak was found by Mamy *et al* (1974). The peak G at 6·3 eV, in strong evidence in the theoretical distribution, shows at best a discrepancy of 0·4 eV when compared with reflectivity measurements. However the energy loss results of Vilanove (1971) show a well marked feature at this same energy 6·3 eV. At higher energies accurate comparison between theory and experiment deteriorates, but nevertheless peaks H and I can reasonably be correlated with published data.

For InSe a similar situation exists and agreement in the region between 2 eV and 5 eV is indeed excellent. The peaks A, B, C, D and E have all been observed experimentally and rarely does the difference between experiment and theory exceed the energy resolution 0·1 eV of the theoretical curve. The peak F is obviously comparable to the structure observed at 4·7 eV, whilst the existence of the small feature at G, although not yet observed experimentally in reflectivity work, has previously been predicted by Sobolev and Donetskich (1972) using the same arguments as for GaSe. This and the large peak H at 6·6 eV would then appear to be strongly related to the strong feature at 6·4 eV in the energy loss spectrum of InSe found by Williams *et al* (see following paper). As with GaSe, agreement at high energies is poor. This is hardly surprising since at these energies we are including the effects of the higher conduction bands, accurate computation of which is a major downfall of the tight-binding approach.

References

Akhundov G A, Gasanova N A and Nizametdinova M A 1966 *Phys. Stat. Solidi* **15** K 109
Akhundov G A, Kerimova T G and Gasanova N V 1969 *Sov. Phys.–Semicond.* **3** 85

Andriyashik M V, Sakhnovskii M Yu, Timiofeev V B and Yakimova A S 1968 *Phys. Stat. Solidi* **28** 277

Aulich E, Brebner J L and Mooser E 1969 *Phys. Stat. Solidi* **31** 129.

Balzarotti A and Piacentini M 1972 *Solid St. Commun.* **9** 1715

Balzarotti A, Piacentini M, Burattini E and Picozzi P 1971 *J. Phys. C: Solid St. Phys.* **4** L273

Bassani F, Greenaway D L and Fischer G 1964 *Proc. Int. Conf. Physics of Semiconductors, Paris* ed M Balkanski (Paris: Flammarion) p 51

Bassani F and Pastori Parravacini G 1967 *Nuovo Cim.* **50B** 95

Besson J M, Jain K P and Khun A 1974 *Phys. Rev. Lett.* **32** 936

Bourdon A 1974 *J. Physique* **35** C3 261

Bourdon A and Khelladi F 1971 *Solid St. Commun.* **9** 1715

Brebner J L 1964 *J. Phys. Chem. Solids* **25** 1427

Bromley R A and Murray R B 1972 *J. Phys. C: Solid St. Phys.* **5** 759

Cardona M 1969 *Modulation Spectroscopy* (New York: Academic Press)

Fielding P, Fischer G and Mooser E 1959 *J. Phys. Chem. Solids* **8** 434

Gadzhiev V A, Sobolov V I, Subashiev V K and Tagiev B K 1970 *Sov. Phys.–Solid St.* **12** 1061

Herman F and Skillmann S 1963 *Atomic Structure Calculations* (Englewood Cliffs, NJ: Prentice–Hall)

Kamimura H and Nakao K 1968 *J. Phys. Soc. Japan* **24** 1313

Kamimura H, Nakao K and Nishina Y 1969 *Phys. Rev. Lett.* **23** 1379

Khun A, Chevy A and Chevalier J 1975 *Phys. Stat. Solidi* (a) **31** 469

Leung P C, Andermann G, Spitzer W G and Mead C A 1966 *J. Phys. Chem. Solids* **27** 849

Liang W Y 1975 *J. Phys. C: Solid St. Phys.* **8** 1763

Lloyd D R, Quinn C M, Richardson N V and Williams P M 1976 *Commun. Phys.* **1** 11

Mamy R, Martin L, Leveque G and Raisin C 1974 *Phys. Stat. Solidi* (b) **62** 201

Mushinskii V P and Kobolev V I 1972 *Sov. Phys.–Semicond.* **6** 621

Schluter M 1973 *Nuovo Cim.* **13B** 313

Semiletov S A 1958 *Kristallogra.* **3** 288

Shepherd F R and Williams P M 1976 *Phys. Rev.* in press

Sobolev V V and Donetskich V I 1971 *Phys. Stat. Solidi* (b) **45** K15

—— 1972 *Inorg. Mater.* **8** 1229

Soukiassain P, Cazaux J and Perrin J 1974 *Phys. Stat. Solidi* (b) **66** 151

Suzuki Y, Hamakawa Y, Kimura H, Komiya H and Ibuki S 1970 *J. Phys. Chem. Solids* **31** 2217

Thomas J M, Adams I, Williams R H and Barber M 1972 *J. Chem. Soc. Faraday Trans.* II **68** 755

Vilanove R 1971 *Thesis* CNRS Paris No A05885

Wasscher J D and Dieleman J 1972 *Phys. Lett.* **39A** 279

Williams R H, Kemeny P C and Ley L 1976a *Solid St. Commun.* in press

Williams R H, McGovern I T, Murray R B and Howells M 1976b *Phys. Stat. Solidi* (b) **73** 307

Williams R H, Williams G P, Norris C, Howells M R and Munro I H 1974 *J. Phys. C: Solid St. Phys.* **7** L29