Tight-binding study of the electronic states in GaSe polytypes

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Abstract. The electronic band structures of the β, ϵ and γ polytypes of GaSe are studied by the tight-binding method. The calculation takes into account interlayer interactions and the generally neglected lowest excited atomic states. The energy levels of the three polytypes differ from each other by 0·3 eV at most. Inclusion of excited atomic states strongly modifies the conduction bands but has little effect on all valence states. The calculated valence band structure compares well with both angular-resolved and integrated photoemission data. The electronic charge-density distribution resulting from tight-binding Bloch states confirms the chemical bonding picture proposed in recent pseudopotential investigations.

1. Introduction

The electronic band structure of the layer semiconductor GaSe has been previously investigated both by the tight-binding (TB) method (Bassani and Pastori 1967, Kamimura and Nakao 1968, McCanny and Murray 1977) and the empirical pseudopotential method (Schlüter 1973, Bourdon 1974, Schlüter *et al* 1976, Depeursinge 1977, 1978). Characteristic differences exist between the energy band structures obtained with the two methods. All pseudopotential calculations, for example, agree with each other with respect to the order and the approximate width of the lowest conduction bands whereas the TB calculations give conduction bands of larger dispersion and in different orders. The discrepancies, however, are not limited to the more delocalised conduction states whose description is more difficult in the TB scheme. In fact while the order of the valence bands is generally the same for all calculations, the shape of the two Ga–Ga valence bands located at about −6 eV from the top of the valence band was different for the pseudopotential and the TB calculations. Photoemission (Thiry *et al* 1977, Margaritondo *et al* 1977) and reflectivity (Thiry 1976) data support the pseudopotential results both for the shape of the Ga–Ga valence bands and for the small dispersion of the conduction bands.

In this paper we present the results of a new, improved TB calculation for GaSe which is in better agreement with experimental data and with the pseudopotential results. An analysis of the difficulties encountered in previous TB investigations is also given.

Our TB calculation includes all interactions between all pairs of atoms whose distance is less than 4·7 Å and also includes the 5s excited atomic orbitals of Ga and Se in addition

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to the usually considered 4s and 4p valence orbitals. Furthermore, while previous TB calculations were limited to the single-layer approximation we include the interlayer interaction and show that the TB result generally agrees with that of the pseudopotential method in predicting the energy dispersion in the direction perpendicular to the layers.

Various polytypes have been reported in the literature for GaSe (Hulliger 1976). We have limited our study to the β, ϵ and γ polytypes. Our results show that polytypism has small effects on the energies of Bloch states in GaSe in agreement with both experimental data (Aulich *et al* 1969) and recent pseudopotential investigations (Depeursinge 1977, 1978).

While the TB method is generally applied as an empirical or semiempirical interpolation scheme where overlap and interaction matrix elements are fitted to experimentally obtained band-structure parameters, we calculate the matrix elements from modified Hartree-Fock atomic orbitals and, therefore, obtain Bloch eigenstates as well as energy bands. Thus we have been able to calculate the electronic charge densities for different groups of valence bands, and obtain information on the chemical bonds in this semiconductor.

Up to now the electronic charge densities in solids have in most cases been calculated with the pseudopotential method and the results have been interpreted in the TB formalism. We show that for GaSe the TB charge density agrees with the pseudopotential results and that it is easily decomposed into contributions from different atomic orbitals. Bloch wavefunctions obtained with the TB method are, therefore a more convenient basis for the investigation of chemical bonds in solids.

2. Crystal structure and symmetry

GaSe is a layer semiconductor in which each layer consists of four mono-atomic sheets in the order Se–Ga–Ga–Se. Several polytypes have been reported in the literature (Hulliger 1976) which differ in the stacking sequence of the basic layer units. Among these, the ϵ, γ and β polytypes have been studied most. The unit cell of β-GaSe, the polytype with highest symmetry, extends over two layers and contains four Ga and four Se atoms. Its space group is D_{6h}^4 and its Brillouin zone as well as its unit cell are shown in figure 1. ϵ-GaSe has lower symmetry and its space group is D_{3h}^1. Similar to β-GaSe its unit cell extends over two layers and contains four formula units. The Brillouin zones of the ϵ and β polytypes are the same (see figure 1). The Bravais lattice of γ-GaSe is rhombohedral (trigonal R). The primitive cell contains two formula units and extends over three layers (see figure 1). The corresponding Brillouin zone has twice the volume of that of the ϵ and β polytypes.

The primitive lattice vectors and the position of the basis atoms for the three polytypes are given in table 1 as functions of the hexagonal lattice constants a and c and of the parameters z_1 and z_2 which describe the position along the c axis of Se and Ga, respectively. The values of z_1 and z_2 are related to interatomic distances within the unit cell and their experimental determination is difficult. The relative positions of the energy bands in GaSe, however, strongly depend on the parameters z_1 and z_2 (Baldereschi *et al* 1974, Schlüter *et al* 1976).

Since the experimental data for these parameters do not agree with each other (Hulliger 1976), we have used the same values (listed in table 1) as Bassani and Pastori (1967). These correspond to intralayer nearest-neighbour distances which are close to the sums of the covalent radii of the neighbouring atoms. In fact the values for the
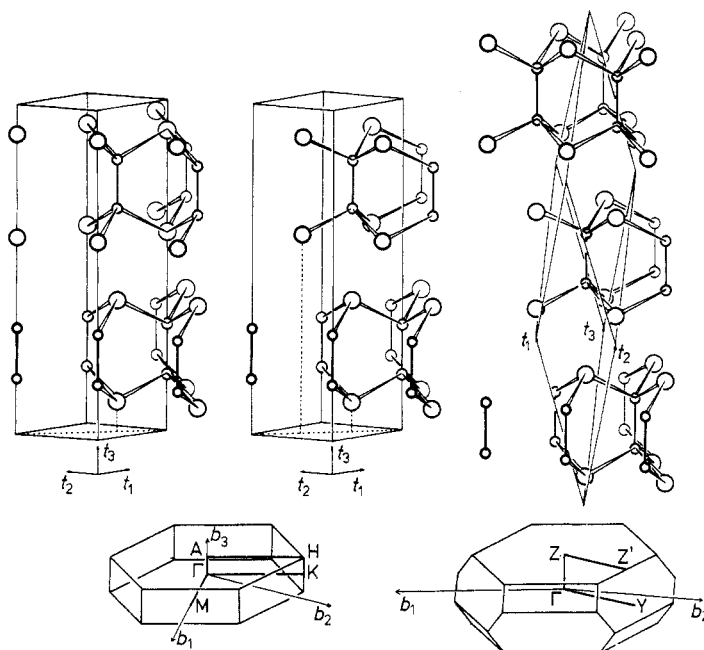
Figure 1. Unit cells and Brillouin zones for β-GaSe (left), ϵ-GaSe (middle), γ-GaSe (right).

Table 1. Primitive vectors and coordinates of the basis atoms for the β, ϵ and γ polytypes of GaSe. The values of the lattice constants a and c and of the parameters z_1 and z_2 used in the present work are also given.

β-GaSe	ϵ-GaSe	γ-GaSe
$t_1 = (-a, 0, 0)$	$t_1 = (-a, 0, 0)$	$t_1 = (-a/2, -a/(2\sqrt{3}), c/2)$
$t_2 = (a/2, a\sqrt{3}/2, 0)$	$t_2 = (a/2, a\sqrt{3}/2, 0)$	$t_2 = (a/2, -a/(2\sqrt{3}), c/2)$
$t_3 = (0, 0, c)$	$t_3 = (0, 0, c)$	$t_3 = (0, a/\sqrt{3}, c/2)$
$\mathrm{Se_I}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + z_1 t_3$	$\mathrm{Se_I}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + z_1 t_3$	$\mathrm{Se_I}: \frac{2}{3} z_1(t_1 + t_2 + t_3)$
$\mathrm{Ga_I}: z_2 t_3$	$\mathrm{Ga_I}: z_2 t_3$	$\mathrm{Se_{II}}: \frac{2}{3}(\frac{1}{2} - z_1)(t_1 + t_2 + t_3)$
$\mathrm{Ga_{II}}: (\frac{1}{2} - z_2)t_3$	$\mathrm{Ga_{II}}: (\frac{1}{2} - z_2)t_3$	$\mathrm{Ga_I}: \frac{2}{3}(\frac{1}{2} + z_2)(t_1 + t_2 + t_3)$
$\mathrm{Se_{II}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (\frac{1}{2} - z_1)t_3$	$\mathrm{Se_{II}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (\frac{1}{2} - z_1)t_3$	$\mathrm{Ga_{II}}: \frac{2}{3}(1 - z_2)(t_1 + t_2 + t_3)$
$\mathrm{Se_{III}}: (\frac{1}{2} + z_1)t_3$	$\mathrm{Se_{III}}: \frac{1}{3}t_1 + \frac{2}{3}t_2 + (\frac{1}{2} + z_1)t_3$	
$\mathrm{Ga_{III}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (\frac{1}{2} + z_2)t_3$	$\mathrm{Ga_{III}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (\frac{1}{2} + z_2)t_3$	
$\mathrm{Ga_{IV}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (1 - z_2)t_3$	$\mathrm{Ga_{IV}}: \frac{2}{3}t_1 + \frac{1}{3}t_2 + (1 - z_2)t_3$	
$\mathrm{Se_{IV}}: (1 - z_1)t_3$	$\mathrm{Se_{IV}}: \frac{1}{3}t_1 + \frac{2}{3}t_2 + (1 - z_1)t_3$	
$a = 3{\cdot}73\,\text{Å} \qquad c = 15{\cdot}9\,\text{Å}$	$z_1 = 0{\cdot}1003 \qquad z_2 = 0{\cdot}1701$	

intralayer Ga–Ga and Ga–Se distances, thus determined, are $2{\cdot}54\,\text{Å}$ and $2{\cdot}42\,\text{Å}$ respectively and compare well with the values $2{\cdot}52\,\text{Å}$ and $2{\cdot}42\,\text{Å}$ obtained from the sum of the covalent radii (Pauling 1960). Recent band-structure calculations (Schlüter 1976, Depeursinge 1977, 1978) have shown that agreement between photoemission data and the calculated valence band density-of-states can be obtained using interatomic distances close to the sum of the covalent radii.

3. Method of calculation

We expand the TB eigenstates in terms of Bloch functions $\phi_{i,v}(k, r)$ constructed from atomic orbitals $\alpha_{i,v}(r)$

$$\phi_{i,v}(k, r) = (1/N) \sum_{l=1}^{N} \exp[ik \cdot (R_l + \tau_i)]\alpha_{i,v}(r - R_l - \tau_i) \tag{1}$$

where v labels different atomic orbitals, i distinguishes different atoms in the unit cell, and the sum extends over all lattice vectors R_l. Usually v is restricted to states which belong to the valence shell of the atom under consideration. This choice gives good results for the valence bands where little admixture from higher excited states is expected, but in general it is too restrictive for the description of the conduction bands, particularly for the more ionic compounds. This difficulty can be avoided by including Bloch functions (1) constructed from excited states of the atoms. In order to test the effects of excited atomic states we have included the lowest-lying excited states, i.e. the 5s orbitals of Ga and Se, in addition to the 4s and 4p valence orbitals. The matrix elements $H_{iv, i'v'} = \langle i, v|H|i', v'\rangle$ and $S_{iv, i'v'} = \langle i, v|i', v'\rangle$ have been calculated retaining only one- and two-centre integrals. Energy eigenvectors and wavefunctions have been obtained by solving the secular equation

$$\|H_{iv, i'v'} - ES_{iv, i'v'}\| = 0. \tag{2}$$

Table 2. Values for the crystal-field integrals (a), Hartree–Fock atomic energies (b) and Gaussian exponents for the reduction of the atomic wavefunctions (c). The energy unit is the Rydberg. For comparison the crystal-field integrals used by Bassani and Pastori (1967) are given in parentheses.

		4s	$4p_x/4p_y$	$4p_z$	5s
	a	−0·080	−0·232	−0·076	−0·076
		(−0·109)	(−0·151)	(−0·115)	
Se	b	−1·500	−0·702	−0·702	−0·246
	c	0·06	0·04	0·04	0·01
	a	−0·071	−0·070	−0·070	−0·070
		(−0·188)	(−0·283)	(−0·240)	
Ga	b	−0·838	−0·362	−0·362	−0·037
	c	0·09	0·07	0·07	0·01

The expansions of the radial part of the atomic orbitals in terms of Slater functions are given by Watson and Freemann (1961). The corresponding Hartree–Fock energies have been taken from Herman and Skillman (1963) and are reported in table 2. The excited states were described by Slater functions calculated following the rules given by Burns (1964) and orthogonalised to the valence orbitals. The respective energies were taken from spectroscopic data (Condon and Shortley 1970). The analytical evaluation of the matrix elements (Taketa *et al* 1966) was performed by Gaussian expansion of the Slater-type orbitals (Stewart 1970).

It is well known from the literature (Bassani and Pastori 1967) that atomic orbitals are too extended for solid state applications and lead to TB matrix elements which are in general unrealistic. The contraction of atomic orbitals can qualitatively be under-

stood in terms of the repulsion between electrons located at adjacent atoms. Usually this effect is accounted for by reducing the calculated matrix elements by a constant scaling factor. The corresponding modification of the orbitals, however, is not specified so that the knowledge of the wavefunctions is lost. Furthermore, it is not evident that a contraction of the atomic orbitals leads to a reduction of all matrix elements. For these reasons we prefer to contract the atomic orbitals by multiplying them with Gaussian functions and renormalising afterwards. Different Gaussian exponents were used for different atomic orbitals as indicated in table 2 and their values were chosen so as to reproduce optical and photoemission data. Matrix elements were calculated both with the original Hartree–Fock orbitals and with the contracted orbitals. The resulting intralayer matrix elements between nearest neighbours are listed in table 3 together with the reduced matrix elements used by Bassani and Pastori (1967). Comparing the matrix elements calculated with the original and the contracted orbitals we notice that most matrix elements are reduced with the contraction (see for example the (s, s, σ) and (s, p, σ) matrix elements) but some (as for example the (p, p, σ) matrix elements) are increased. The simulation of orbital contraction by a reduction of all matrix elements (McCanny and Murray 1977) or the largest among them (Bassani and Pastori 1967) does, therefore, not seem satisfactory.

Table 3. Overlap integrals (S) and interaction matrix elements (H) calculated with atomic functions (af) and with contracted atomic functions (caf) for the nearest-neighbour interactions. The values used by Bassani and Pastori (1967) are given for comparison (BP). Energies are in Rydbergs.

	S			H		
	af	caf	BP	af	caf	BP
$(s_{Se}\, s_{Ga}\, \sigma)$	0·244	0·107	0·166	−0·188	−0·093	−0·0225
$(s_{Se}\, p_{Ga}\, \sigma)$	−0·425	−0·270	−0·396	0·396	0·271	0·093
$(s_{Ga}\, p_{Se}\, \sigma)$	−0·324	−0·233	−0·280	0·216	0·162	0·186
$(p_{Se}\, p_{Ga}\, \sigma)$	−0·292	−0·350	−0·330	0·240	0·292	0·240
$(p_{Se}\, p_{Ga}\, \pi)$	0·242	0·136	0·170	−0·158	−0·096	−0·100
$(s_{Ga}\, s_{Ga}\, \sigma)$	0·295	0·115	0·201	−0·196	−0·088	−0·142
$(s_{Ga}\, p_{Ga}\, \sigma)$	−0·477	−0·278	−0·336	0·372	0·254	0·123
$(p_{Ga}\, p_{Ga}\, \sigma)$	−0·278	−0·389	−0·415	0·214	0·289	0·176
$(p_{Ga}\, p_{Ga}\, \pi)$	0·362	0·156	0·230	−0·184	−0·097	−0·085

In our TB calculation we have treated the interaction between adjacent layers by including the matrix elements between the Se–Se and the Se–Ga pairs with the shortest distance. These interlayer matrix elements, which were neglected in previous calculations are listed in table 4. We notice that interlayer matrix elements are one order of magnitude smaller than intralayer ones. Furthermore, due to the different crystallographic arrangement of atoms the Se–Ga matrix elements depend on the polytype in contrast to the Se–Se matrix elements.

The TB matrix elements which involve the excited 5s orbitals are about one order of magnitude smaller than those involving valence orbitals only. As is usually the case (Bassani and Pastori 1967, McCanny and Murray 1977) the calculated crystal-field integrals are too large and therefore they have been strongly reduced. The crystal-field values used in the present calculation are given in table 2 together with the values used by Bassani and Pastori (1967).

Table 4. Largest overlap integrals (S) and interaction matrix elements (H) for the interlayer Ga–Se and Se–Se interaction. The values for the additional Ga–Se interaction present in the ϵ and γ polytypes are also given. Energies are in Rydbergs.

| | S | | H | |
	β, ϵ, γ	ϵ, γ	β, ϵ, γ	ϵ, γ
$(s_{Ga}\, p_{Se}\, \sigma)$	-0.010	-0.003	-0.007	-0.001
$(p_{Se}\, p_{Ga}\, \sigma)$	-0.036	-0.014	0.019	0.008
$(s_{Se}\, p_{Se}\, \sigma)$	-0.015		0.010	
$(p_{Se}\, p_{Se}\, \sigma)$	-0.047		0.026	

4. Band structure

The experimental values of the direct and indirect gaps of the different polytypes of GaSe (Aulich *et al* 1969, Le Chi Thanh and Depeursinge 1977) are given in table 5. These values and the energy positions of the most prominent structures in angularly integrated ultraviolet photoemission spectra (Williams *et al* 1974, Thiry *et al* 1974, Shepherd and Williams 1975, Williams *et al* 1976, Margaritondo *et al* 1977) and in XPS spectra (Kowalczyk *et al* 1975, Thiry 1976) were used as a guide for the choice of the values of the reduction parameters for the wavefunctions and the crystal-field integrals given in table 2. The data from angular-resolved photoemission (Thiry *et al* 1977, Williams 1977) were not used in the fitting procedure.

Table 5. Experimental values of the direct and indirect gaps in different polytypes of GaSe at 77 K. The energy gap values are from Aulich *et al* (1969). Their indirect gap values have been increased by 30 meV in order to account for exciton effects (Le Chi Thanh and Depeursinge 1977).

	direct gap (eV)	indirect gap (eV)
β	2.17	2.15
ϵ, γ	2.12	2.10

We first discuss the band-structure results for β-GaSe shown in figure 2. The corresponding density of states for the valence and conduction bands are given in figures 3 and 4, respectively. Some features of previous TB calculations are not present in our band structure which is in better agreement with experiment as well as with the pseudopotential results obtained by Depeursinge (1977, 1978) and by Schlüter in his more recent calculation (Schlüter *et al* 1976). Some small differences however still exist between the pseudopotential and our TB results. The total width of the valence bands belonging to the groups A, B, C and D (see the left side of figure 2 for the labelling of valence band groups) in our calculation is 7 eV in agreement with photoemission data (Thiry *et al* 1977) whereas both pseudopotential calculations predict a width of 6 eV. Differences less than 1 eV also exist between the various theoretical results in the relative positions of groups A, B and C, compared with the experimental data. The A–B separation is somewhat overestimated in Depeursinge's calculation whereas Schlüter *et al* overestimate the B–C separation. In our band structure the dispersion of group A is too large
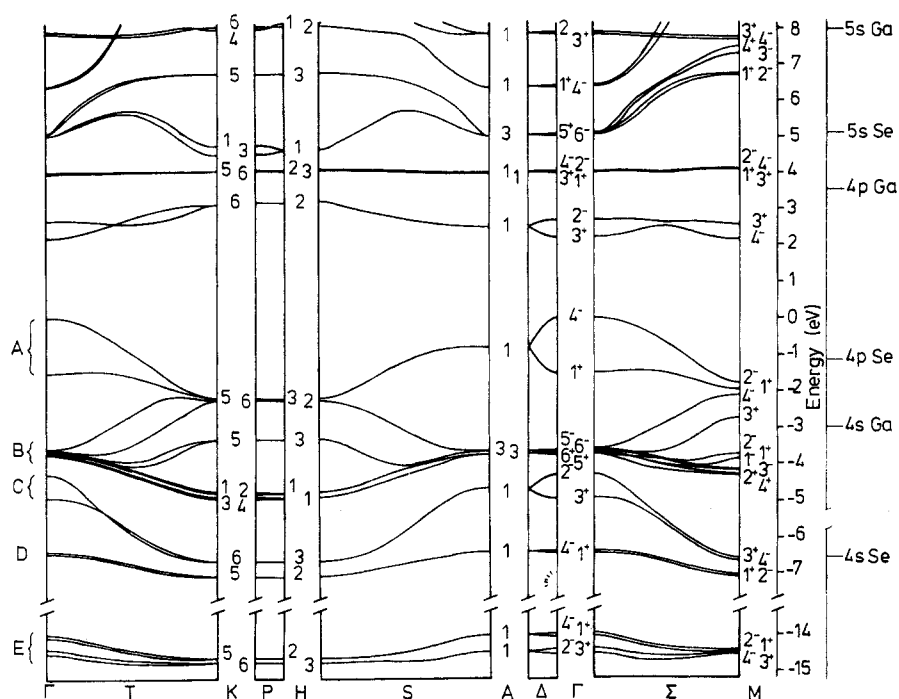
Figure 2. Band structure of β-GaSe along the main symmetry directions.
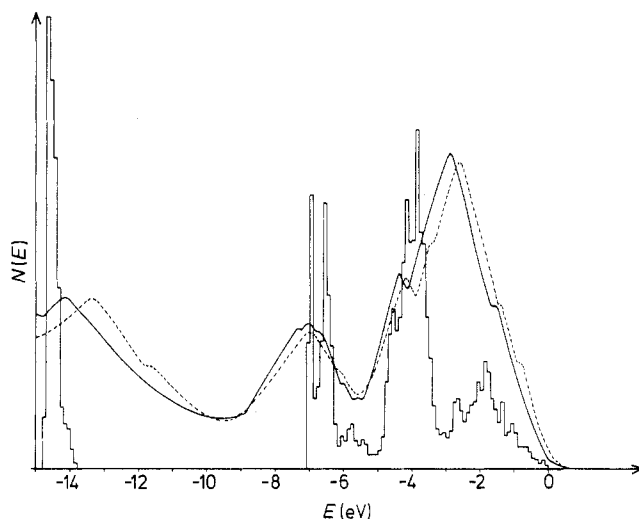

Figure 3. Calculated valence band density-of-states (histogram) compared with the XPS spectra measured by Thiry (1976) (broken line) and by Kowalczyk *et al* (1975) (full line).

by 0·5 eV. The largest difference between our band structure and the photoemission data is the position of the density-of-states peak corresponding to group B which according to our calculation is at $-3\cdot8$ eV, i.e. ~ 1 eV lower than found experimentally. This comes from our particular choice of the p_z and the p_x, p_y crystal-field integrals of Se which were mainly used to adjust the indirect band gap. At Γ the conduction band
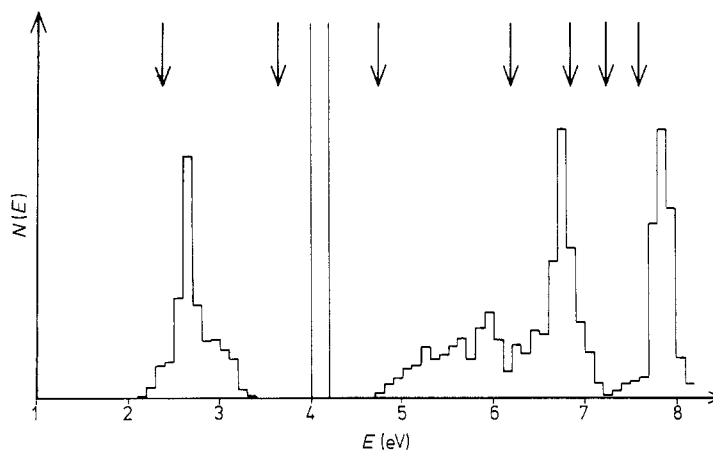
Figure 4. Calculated density of states for the conduction bands. The arrows indicate the positions of the experimentally observed maxima in the conduction band density-of-states (Thiry 1976).

contains only s and p_z states whereas at the surface of the Brillouin zone mainly the p_x and p_y states of Se contribute. In order to fix the experimental value of the indirect gap we have been forced to lower considerably the Se p_x, p_y crystal-field value. At the same time, however, this lowers the position of the valence bands of group B close to the centre of the Brillouin zone. Besides this, the general shape of these bands compares well with that obtained experimentally from angular resolved photoemission (Thiry *et al* 1977).

With respect to previous TB calculations, the present results are in considerably better agreement with experiment and with the pseudopotential studies. This is particularly true for the conduction bands where previous TB calculations did not succeed in predicting even the correct order of bands. Bassani and Pastori (1967) predict that GaSe is a direct semiconductor and that the lowest conduction band has (using the single-layer notation) Γ_3^+ instead of Γ_2^- symmetry. The Γ_2^- band which should be the lowest conduction band appears instead 11·8 eV above the top valence band. A similar result was obtained by Kamimura and Nakao (1968) whereas only the TB calculation of McCanny and Murray (1977) gives the Γ_2^- band at the right position. The failure of the Bassani and Pastori (1967) calculation is mainly a consequence of an improper choice of the $S(s_{Ga}, s_{Se}, \sigma)$ overlap and corresponding $H(s_{Ga}, s_{Se}, \sigma)$ matrix elements. The values of these elements are not the ones showing the largest difference from those used in the present work (see table 3). Nevertheless we have found that after replacing these two values only with our values in the Bassani and Pastori calculation, the Γ_2^- conduction state drops to 4·4 eV above the top valence band. With this modification all other bands keep approximately the same energy position but the corresponding wavefunctions change character. This occurs in particular for the group-D valence band which in the original Bassani and Pastori calculation has a mixed Ga–Se character and which after the modification of the matrix elements mostly becomes bonding between the two Ga 4s orbitals as is the case in our TB calculation. The strong localisation of this wavefunction between the two Ga atoms explains the very small dispersion of the D valence band shown in figure 2. The C bands on the other hand correspond to much less localised wavefunctions and show in fact much more dispersion in the Brillouin zone. Previous

TB calculations predicted identical and large dispersions for the C and the D bands. This is due to a too large admixture of Se orbitals in the D band wavefunctions and is in contradiction with angular-resolved photoemission data (Thiry *et al* 1977, Williams 1977), all pseudopotential calculations and our results. This difficulty of the previous TB calculation is not restricted to GaSe but has also been found for the layer semiconductor InSe (McCanny and Murray 1977, Balzarotti *et al* 1977). Also the low-energy position of the $\Gamma_5^\pm$ and $\Gamma_6^\pm(D_{6h}^4$ notation) conduction bands found in previous TB calculations is not a failure of the method itself since in our TB calculation these bands are more than 5 eV above the top of the valence bands in agreement with pseudopotential results, photoemission (Margaritondo *et al* 1977, Shepherd and Williams 1975) and reflectivity data (Thiry 1976) (see figure 4). In our results, however, the Γ_5^+ and Γ_6^- bands are separated from the Γ_5^- and Γ_6^+ bands (these are not represented in figure 2) by ~ 5 eV whereas in the pseudopotential calculations the absolute value of this splitting is only ~ 2 eV and the relative order of the two groups of levels is not the same in all calculations (Schlüter 1973, Schlüter *et al* 1976, Depeursinge 1977, 1978). In general the TB method gives conduction bands with much more dispersion than the pseudopotential method. Our calculation which includes excited atomic states and the interactions with rather distant neighbours provides a small dispersion of the conduction bands similar to that of the pseudopotential band structures. This result is in agreement with photoemission (Margaritondo *et al* 1977) and reflectivity data (Thiry 1976) which show very sharp structures in the density of states of the conduction bands. An additional and more important effect of the inclusion of atomic excited states is the appearance of additional bands near the bottom of the conduction band. This is the case for the very flat conduction band which appears at 4 eV in figure 2 and which is mostly formed by Se 5s orbitals. Rather flat bands with the same symmetry appear at a somewhat higher energy in the pseudopotential band structure and two corresponding peaks have been detected experimentally in the conduction band density-of-states (see figure 4). The splitting between the two experimental structures is not present in our calculation and this might be caused by our neglect of higher excited states like for example the Se 5p states which are expected to interact strongly with the Se 5s states. We find however that the inclusion of the Se and Ga 5s states does not alter the energy of the valence states.

A quantity of interest for layer materials is the strength of the interlayer interaction, a measure of which is given by the dispersion of the energy bands along the k_z axis. This dispersion is caused by the interlayer interactions between the Se–Se and Se–Ga pairs with shortest distance. The dispersion of the energy bands in figure 2 along the Δ and P axes agrees well with the pseudopotential results. In agreement with photoemission data (Thiry *et al* 1977) our results show that the A-group valence bands have the largest dispersion whereas the B- and D-group bands have two dimensional character (Schlüter 1973).

Our TB calculation of the energy bands of ϵ-GaSe and γ-GaSe follows exactly that of β-GaSe except for the additional values of the interlayer Ga–Se matrix elements as indicated in table 4. In the β polytype all interlayer Ga–Se pairs are equivalent to each other. The two atoms are aligned along the c axis and their distance is 4·30 Å. In the ϵ and γ polytypes half of the interlayer Ga–Se pairs have the same relative geometry as found in β-GaSe whereas the other half have a distance of 4·81 Å and each of these atoms has three equivalent interlayer neighbours of the other kind. The effects of polytypism on the energy bands result from the delicate balance of the energy changes produced by these two geometric factors.

A comparison between the three modifications is complicated by the fact that the

Brillouin zone of γ-GaSe is different from that of the ϵ and β modifications. As the number of atoms in the primitive cell of γ-GaSe is only one half of that in the primitive cell of β- and ϵ-GaSe the number of bands for γ-GaSe is also reduced by one half. Because of the smallness of the interlayer interaction with respect to the intralayer interaction (see tables 3 and 4) the k dependence of the energy eigenvalues is mainly determined by the properties of the single layer. For a discussion of the effect of polytypism on the band structures it is, therefore, possible to compare the eigenvalues at equivalent k points in the different Brillouin zones. Each k vector corresponding to one point in the reduced zone scheme for β- and ϵ-GaSe gives rise to two different points in the reduced zone scheme for γ-GaSe. As the rhombohedral Brillouin zone of γ-GaSe has twice the volume of the hexagonal Brillouin zone of β- and ϵ-GaSe, a folding procedure which relates each k point in the hexagonal Brillouin zone to two points in the rhombohedral Brillouin zone can be performed in a unique way. In table 6 the energy eigenvalues of ϵ-GaSe at the high symmetry points Γ, M, and A of the hexagonal Brillouin zone and of γ-GaSe at the pair of equivalent points are compared with the results obtained for the β modification for the most important bands. It is evident from the table that the effects of polytypism are small in GaSe and we find that they are ~ 0.3 eV at most.

Table 6. Energy shift due to polytypism for the valence bands of groups A to D and the lowest conduction bands (CB). The shift is measured in meV and with respect to the energies of β-GaSe. For the γ-modification the energies reported are those at the pairs of k-points corresponding to the high symmetry points Γ, M, and A in the hexagonal Brillouin zone.

| | | Γ | M | | | A | |
		ϵ, γ	ϵ	γ		ϵ, γ	
CB	Γ_2^-	-13	M_3^+	-75	-122	A_1	0
	Γ_3^+	-26	M_4^-	$+113$	$+163$		
A	Γ_4^-	$+8$	M_2^-	$+114$	$+35$	A_1	0
	Γ_1^+	-6	M_1^+	-121	$+83$		
B	$\Gamma_5^\pm \Gamma_6^\pm$	0	M_4^-	-116	-317	A_3	0
			M_3^+	$+89$	$+164$		
			M_2^-	-50	-64		
			M_1^+	$+49$	$+65$		
			M_1^-	0	-2		
			M_3^-	0	$+3$	A_3	0
			M_2^+	0	-2		
			M_4^+	0	$+1$		
C	Γ_2^-	$+5$	M_3^+	-23	-27	A_1	0
	Γ_3^+	-4	M_4^-	$+22$	$+26$		
D	Γ_4^-	0	M_1^+	-7	-11	A_1	-5
	Γ_1^+	0	M_2^-	$+7$	$+11$		

The calculated direct gap values for the three polytypes are consistent with experimental data (see table 5) which show a larger gap for β-GaSe. It is interesting to observe that the largest effects appear at the M-point and generally at points a large distance from the Δ axis. This is due to the fact that at these points the effects of polytypism result not only from the small differences in overlap and interaction energies as listed in table 4 but also from structure-factor differences. The larger effects at the border of the

Brillouin zone affect the indirect gap which in all modifications is assumed to occur between the valence band at Γ and the conduction band at k vectors corresponding to the point M in the hexagonal Brillouin zone (Aulich *et al* 1969, Le Chi Thanh and Depeursinge 1977). According to our calculation the conduction band minimum at M shifts so much to higher energies in ϵ-GaSe and γ-GaSe that the indirect gap disappears in these modifications in contrast to experimental data.
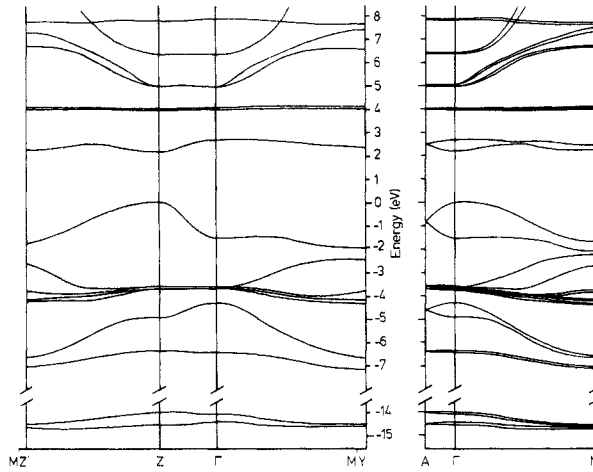
Figure 5. Band structure of γ-GaSe (left) and of ϵ-GaSe (right) along the path indicated in figure 1. The two k points for γ-GaSe which correspond to the point M in the hexagonal Brillouin zone are also indicated.

In figure 5 we represent the energy bands of γ-GaSe in the rhombohedral Brillouin zone along the cartesian y and z axes. These directions correspond to the high symmetry directions Σ and Δ, respectively, in the Brillouin zone of the β and ϵ modifications. The corresponding energy bands of ϵ-GaSe along Σ and Δ are also represented in figure 5. While the energy levels of the three polytypes (table 6) are very similar, the energy band structure of γ-GaSe looks completely different from that of β-GaSe and that of ϵ-GaSe when each is represented in its own Brillouin zone. For example, the lowest direct gap of γ-GaSe occurs at the Z point and not at Γ as for the other polytypes. As a consequence transitions which are indirect in γ-GaSe may at nearly the same energies occur as direct transitions in the ϵ and β polytypes. Thus the k-selection rule is more restrictive in γ-GaSe than in the other two modifications studied in this work.

5. Charge density

The solution of the TB eigenvalue problem (2) also provides Bloch eigenstates $\psi_n(k, r)$ for each band n and each k point

$$\psi_n(k, r) = \sum_{i, v} C_{i, v}^n (k) \, \phi'_{i, v} (k, r) \tag{3}$$

where the $\phi'_{i, v}$ differ from the functions (1) since they are superpositions of the contracted atomic orbitals. The charge density corresponding to the band n is defined in terms of

these functions as

$$\rho_n(r) = 2e \sum_k |\psi_n(k, r)|^2. \tag{4}$$

The averaging over the Brillouin zone was performed with the mean-value-point technique (Baldereschi 1973) and the representative-point technique (Chadi and Cohen 1973) which require consideration of only a few k points. Besides the 1-point average we have also tried in a few test cases the 3- and the 6-point averages (Chadi and Cohen
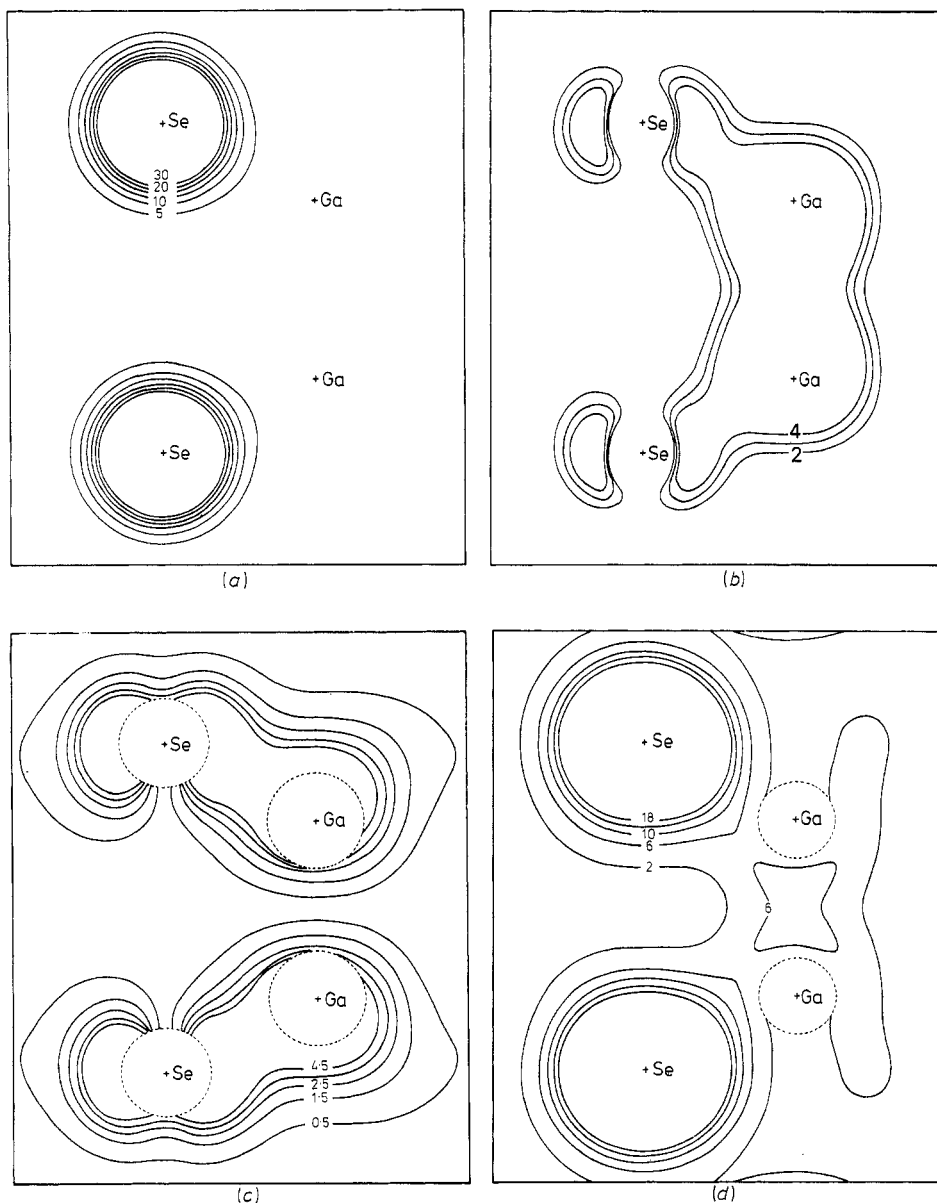

Figure 6. Charge-density distribution for different groups of valence bands (a) E, (b) D, (c) C, (d) B, (e) A and total valence charge density (f).
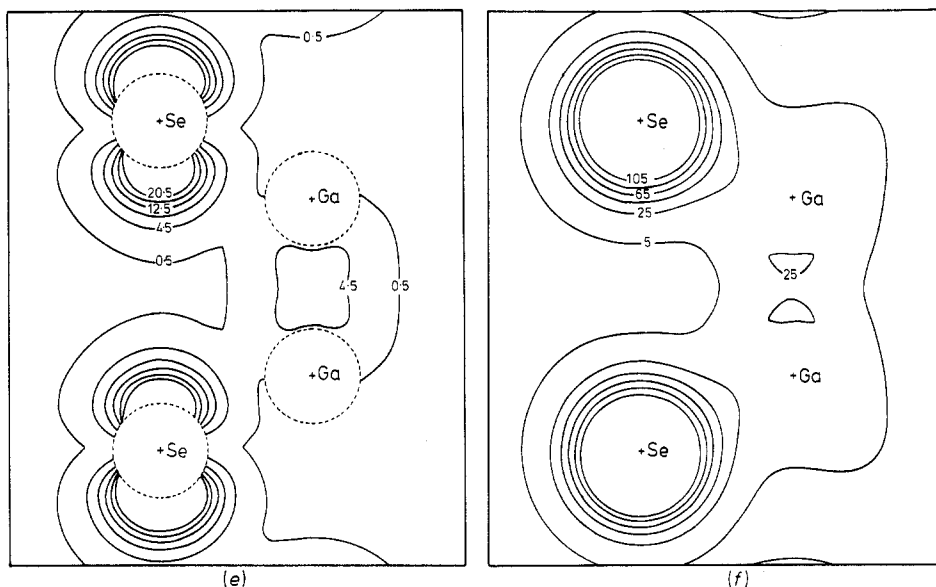
Figure 6 (*continued*)

1973). The deviations were generally less than 5% and therefore we calculated ρ for different groups of bands with the 1-point average. The results are shown in figure 6(*a–e*). The total valence charge-density is given in figure 6(f). The charge densities are in units of electrons per unit cell and the dashed circles enclose regions where the charge densities could not be plotted easily because of the rapid core oscillations.

The pseudopotential method has usually been used in band theory for the calculation of electronic charge densities. The good agreement between our TB charge densities and those obtained with the pseudopotential method (Schlüter 1973, Depeursinge 1978) shows that the TB method works as well. However, the decomposition of charge densities in terms of atomic orbitals and the interpretation of chemical bonds are much easier in the TB scheme since the Bloch eigenstates are already written as superpositions of atomic orbitals. The probability that the state $\phi'_{l,\mu}(k, r)$ derived from the contracted orbital $\alpha'_{l,\mu}(r)$ is contained in the Bloch eigenstate (3) of band n can be defined as (Bromley and Murray 1972)

$$P_n^{(l,\mu)}(k) = |\langle \phi'_{l,\mu}(k, r)| \psi_n(k, r)\rangle|^2 = |\sum_{i,v} C_{iv}^n(k) \langle \phi'_{l,\mu}(k, r)|\phi'_{i,v}(k, r)\rangle|^2 \quad (5)$$

where the matrix elements on the right side are elements of the TB overlap matrix. The sum $\sum_{l,\mu} P_n^{(l,\mu)}(k)$ is generally not equal to unity since the $\phi'_{l,\mu}(k, r)$ are not orthogonal to each other. Expression (5) has, therefore, to be normalised for each band and it can be averaged over k in the Brillouin zone with the mean-value-point technique in order to define the probability $\bar{P}_n^{(l,\mu)}$ that the atomic orbital of atom l is contained in band n. The $\bar{P}$ values for various groups of valence bands and for the lowest conduction bands are given in figure 7 as functions of all the atomic orbitals used in the present work. The quantitative information presented in the figure completely confirms the qualitative description of chemical bonds in GaSe presented by Schlüter (1973). Such a description will, therefore, not be reported here.
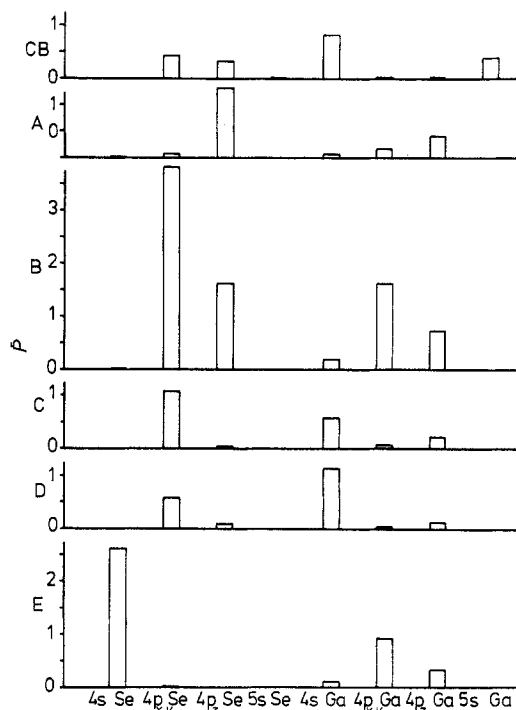
Figure 7. Average contribution of different atomic orbitals to the Bloch eigenstates of the valence bands of groups A–E and of the lowest conduction band (CB). The probabilities $\bar{P}$ are normalised for each band as explained in the text.

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