On the band gap variation in SiC polytypes

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.

• The final author version and the galley proof are versions of the publication after peer review.

• The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

On the band gap variation in SiC polytypes

W.H. Backes

On the band gap
variation
in SiC polytypes

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van
Rector Magnificus, prof.dr. J.H. van Lint, voor
een commissie aangewezen door het College van
Dekanen in het openbaar te verdedigen op

donderdag 6 juni 1996 om 16.00 uur

door

Walter Heinrich Backes

Geboren te Heinsberg (Duitsland)

Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. W. van Haeringen
en
prof.dr. F. Bechstedt

Copromotor: dr. P.A. Bobbert

Contents

Chapter 1

Introduction

Silicon carbide (SiC) is a semiconductor compound occurring in many different crystal structures, called polytypes. This thesis deals with the phenomenon that different polytypes of SiC give rise to different band gap energies. These band gaps appear to vary in a broad energy range from 2.4 to 3.3 eV and are, moreover, in a systematic way related to the lattice structures of the polytypes. This relation was experimentally established in 1964 by Choyke, Hamilton and Patrick [18]. They derived band gaps from low-temperature luminescence and absorption spectra for seven different SiC polytype structures. Until recently no satisfactory theoretical description or explanation for this phenomenon has been given. This is clearly related to the relatively poor state of development of reliable band structure methods for complicated crystal structures such as the SiC polytypes, especially when conduction band states are involved. But even if band structure calculations were capable of reproducing the band gap variation, the remaining question would still be why the variation is as it is. In this thesis we therefore give an account of a study which in the first place leads to a theoretical reproduction of the different SiC band gaps, but which secondly presents a physical explanation for the observed variation by identifying the essential underlying elements.

Before doing so, we pay, in section 1.1, some attention to the phenomenon of polytypism itself. In section 1.2 a discussion is devoted to the technological relevance of SiC. After this we will devote ourselves in section 1.3 to the actual topic of the thesis, of which the set-up is given in section 1.4.

1.1   On the origin of polytypism

The ability of certain chemical substances to exist in more than one crystalline form is called polymorphism [61]. Polytypism is a one-dimensional variant of this phenomenon and distinguishes itself by the stacking in one direction of layers of possibly varying width. The polytype structures may mutually differ in the stacking sequence of these layers. Stacking the layers in a periodic way forms crystals of which the unit cells have a dimension along the stacking axis which is an integral multiple of a common unit, the so-called bilayer, consisting of Si and C atom pairs. Besides SiC, there exist several other compounds, e.g. ZnS, CdI$_2$ and GaSe, exhibiting polytypism [61, 46]. The unit cells of the polytypes can in certain cases be extremely long. There exist SiC polytypes in which these cells extend over a few hundred bilayers.

Theories aiming to explain the existence of the various polytype structures can roughly be divided in two categories [46]. The first category deals with considerations about the thermodynamic stability of the more common short-period polytype structures. The relatively stable short-period structures are then believed to act as basic structures for the generation of the long-period structures. The second category puts emphasis on the growth mechanisms for long-period structures around (screw) dislocations. It is then argued that these spiral growth mechanisms essentially provide the driving force leading to the long range ordering in long-period polytypes. It is generally believed that a satisfactory explanation will have to contain both types of considerations. The present situation is that a final decisive background theory is still missing.

Attempts to clarify the origin of polytypism have mainly concentrated on the polytype substances SiC and ZnS. Recently there has been put a lot of effort, by a number of research groups, in computing ground-state properties for short-period structures by means of *ab initio* quantum mechanical total energy calculations [23, 16, 27, 17, 41]. There is as yet no complete agreement between the various authors concerning the exact total energy values and thus of the precise energy ordering of the short-period polytypes. Nevertheless it is very illustrative to depict some of the calculated total energies for existing polytypes of SiC and ZnS as well as non-existing hypothetical polytypes of SiC, ZnS and Si. The general results are given in the diagrams of Fig. 1.1. In this figure the various polytypes are indicated by the Ramsdell notation, in which the number denotes the number of stacked bilayers in the unit cell and the letter specifies the lattice type, either cubic (C), hexagonal (H) or rhombohedral (R). Note that in some cases different polytype structures may have the same repeat period, but a different stacking sequence, such as $6H$ and (the not observed) $6H_a$ (see Chapter 2 for

Figure 1.1: *The total energies of the polytype structures 3C, 4H, 6H, 6H_a and 3C of SiC, ZnS and Si as calculated in Refs. [16, 27, 17]. For SiC also the 15R modification is indicated. The structures below the dotted line are commonly observed to be produced in a growth process. The total energies ΔE_{total} represent energy differences with respect to the polytype structure with the lowest total energy value. The units are in meV per pair of atoms.*

more details). The horizontal (dotted) line has been drawn in Fig. 1.1 to subdivide
the polytype structures in groups with relatively low and high total energies, respec-
tively. The striking feature is that commonly observed polytypes have energies below
the dotted reference line, while the less common, or even non-existing ones, have their
total energies above it. This strongly suggests that a lower total energy leads to a more
stable structure. The total energy diagram for Si reveals that its diamond structure
($3C$) is indeed far more favourable than any other structure. For SiC and ZnS on the
other hand, it is tempting to assume that there are in fact a number of favourable
structures. Indeed, since the total energy of quite a number of polytypes of SiC and
ZnS seems to be both low and almost equal, more than just one polytype structure can
be expected to be stable. It is observed that the energy spreading of ZnS structures
between commonly and not commonly observed structures is, in comparison with SiC
and Si, quite small. This indicates a possible reason why ZnS exhibits a wider variety
of polytype structures than SiC [27].

It should be realized, however, that polytypes are usually produced by means of
a sublimation process which takes place at temperatures of about 2000 to 2500°C.
This means that not the total energy but the free energy should in fact be considered
as the important thermodynamic quantity. At such high temperatures of growth the
influence of phonons might very well become important and could in principle lead to a
quite different free energy ordering of the polytypes. However, investigations regarding
this free energy of a few SiC polytypes at such temperatures, seem to indicate that no
drastic changes in preference of occurrence are to be expected [15].

1.2   Interest of SiC technology

Before SiC was investigated in view of its semiconducting properties, it was known,
already 100 years ago, for its hardness which is near that of diamond. Polycrystalline
SiC was therefore ideal for all kinds of grinding and cutting purposes in order to
substitute pricey diamond. Due to its high thermal and chemical stability SiC turned
out furthermore to be very suitable for producing crucibles in which metals could melt
and for other applications in industrial furnaces.

Although SiC's semiconducting qualities were known for a long time, serious interest
in SiC as a semiconducting device material emerged about 40 years ago when Lely [50]
introduced his sublimation method for growing relatively large crystals. Since then
intensified investigations have been carried out aiming to produce larger single polytype
crystals and to regulate the impurity contents as can be found in e.g. Knippenberg's
[43] thesis on growth phenomena of SiC. The effort to obtain single polytype crystals

of good quality, were (and today still are) to a large extent, hindered by the inability to sufficiently control impurity contents. Due to this and the apparent successes in Si technology, research and intentions for large scale device applications of SiC showed a tendency to fade away.

Currently, however, there is renewed interest in SiC as one of the wide band gap compounds with great potential for the next generation of electronic devices operating at high temperature [36, 52, 60]. SiC's intrinsic material properties as well as its existence in various polytypes have led to a revival of technological interest. Crystal growth of SiC polytypes has recently made considerable progress, the expectation now being that the manufacturing of various electronic devices becomes feasible. At present, the chemical vapour deposition (CVD) growth technique seems to be the most promising way to produce SiC wafers of reproducible properties and sufficient quality. In spite of this, still better solutions have to be found to solve the basic material problems such as reducing the source material impurities, increasing the wafer size, exploring the possibilities of different kinds of doping and an easy production process of a large number of polytypes before a definitive breakthrough will be achieved in large scale device applications.

To demonstrate that SiC has indeed superior intrinsic physical properties in comparison to traditional semiconductors as Si and GaAs we have made a comparison of material properties in Table 1.1. To be more precise, we have compared three common SiC polytypes on the one hand, with the classical semiconductors Si and GaAs on the other hand. SiC's qualities are (i) a wide band gap energy, (ii) a high breakdown field, (iii) a high carrier saturation velocity and (iv) a high thermal conductivity. In spite of the relatively low carrier mobility, these properties form a substantial advantage in many device applications under extreme conditions such as high temperatures and high voltages. SiC has, furthermore, a relatively high atomic bonding energy which is responsible for its mechanical strength and chemical stability at high temperatures. Recently realized prototype power devices of SiC, like rectifier diodes, thyristors and junction field-effect transistors, show indeed encouraging performance results under extreme conditions [36, 52]. The first SiC transistor has already made its way into the commercial market [52].

Since the various energy gap values of SiC all happen to lie in the visible range of the spectrum, SiC is an interesting optical device material as well. In fact, blue light emitting diodes were the first electronic SiC devices which found a good sale. A number of light-emitting diodes covering the entire visible spectrum have already been manufactured [59]. Some SiC polytypes are furthermore most promising as photodetective material sensitive to ultraviolet radiation. In view of the relatively wide band gaps,

Table 1.1: *Comparison of physical properties of semiconductors. This table has been drawn up by combining data as contained in Refs. [36, 52].*

	Si	GaAs	3C SiC	6H SiC	4H SiC
Band gap (eV) at room temperature	1.1	1.4	2.3	3.0	3.2
Breakdown field (MV/cm)	0.6	0.6	>1.5	3.2	3
Saturated electron drift velocity (10^7cm/s)	1	1	2.5	2	2
Electron mobility (10^3cm^2/V s)	1.1	6	0.75	0.37	0.80
Hole mobility (cm^2/V s)	0.4	0.3	0.04	0.09	0.1
Thermal conductivity (W/cm K)	1.5	0.5	5.0	4.9	4.9
Maximum operating temperature (K)	600	760	1200	1580	-
Commercial wafers (inch)	12	6	none	1.375	1.375

one could speculate about SiC as being a good candidate for a short wave length diode laser. Unfortunately, however, the band gaps of all known SiC polytypes are indirect. More realistic chances of success are possibly to be expected from a heterostructure combination with a direct band gap material like AlN [36], which has an almost perfect lattice match with SiC.

1.3   Present work

As mentioned in the introduction the main purpose of this thesis is to deal in a theoretical way with the problem of the 1 eV band gap variation in SiC polytypes. Basically, our approach to solve this problem utilizes the idea that SiC polytypes can be interpreted as electronic building-block systems. Each individual building block in it is a piece of cubic SiC and consists of a certain number of SiC bilayers in the stacking direction. The subsequently stacked blocks possibly differ in size and are mutually twisted over 60° around the stacking axis. Polytype structures then differ by different periodic stackings of blocks.

With this model representation in mind, our hypothesis is that the band gap variation can be traced back to differing sequences of blocks consisting of intrinsically the same cubic material. These differing sequences can best be described by introducing the concept hexagonality. Adapted to the building-block representation, the hexagonality can be defined as the reciprocal value of the averaged building-block size of a

Figure 1.2: *The band gap energies of seven SiC polytypes, namely 3C, 8H, 21R, 6H, 33R, 15R and 4H, as a function of the hexagonality, as measured initially by Choyke, Hamilton and Patrick [18]. The indicated line was only drawn as a guide to the eye.*

polytype, expressed in the number of bilayers. Frequently the so-called hexagonality percentage h is used, which is nothing but 100% times the hexagonality. According to this definition the cubic SiC polytype corresponds to $h=0\%$. The structural band gap relation of the SiC polytypes, as found in 1964 by Choyke *et al.* [18], then amounts to a nearly linear relationship between gap energy and hexagonality percentage up to $h=50\%$. In Fig. 1.2 we have displayed the experimentally obtained band gaps of seven SiC polytypes as a function of h. It should be noted that one polytype, namely $2H$ SiC with the largest possible hexagonality percentage $h=100\%$ (not indicated in Fig. 1.2), has a band gap which does not follow the nearly linear rule. Its gap value is 3.33 eV [55].

When calculating the electronic band structure or, in particular, the band gap of a semiconductor we are in fact dealing with a rather complicated problem, as excited electron states are involved. From first principles it has only recently become possible

to reliably calculate energies of excited one-particle states in simple crystals such as Si or GaAs [33, 30]. The complication in the case of SiC is that unit cells of SiC polytypes may contain quite a lot of atoms, possibly more than hundred. The $3C$, $4H$, $6H$ and $8H$ structures from the above set of polytypes have 2, 8, 12, and 16 atoms per unit cells, respectively. This makes the application of the above mentioned first-principles theory to obtain the band gaps practically unfeasible. Moreover, it is by no means clear whether such a theory, if separately applied to each of the relevant polytypes, could contribute to the understanding of the band gap variation. At the best it would reproduce the experimentally obtained relation.

Our idea to consider and treat SiC polytypes as superlattices consisting of cubic bulk-like blocks needs of course justification. We will have to investigate to which extent it is an acceptable approximation for truly existing polytypes when fragments of the $3C$ SiC crystal are used to represent polytype superlattices. It turns out (see Chapter 2) that this is in most cases indeed an accurate approximation, a notable exception being $2H$ SiC in which case the building blocks consist of one bilayer only. In connection to this it is worth mentioning that an earlier attempt [38] in which atomic potentials of single Si and C atoms were transferred in different polytype structures did not reproduce all band gaps correctly. The reason for this partial failure can be traced back to the fact that in this attempt the potentials were, among other things, constructed so as to reproduce the $2H$ SiC indirect band gap! In the method we use, we essentially transfer building-block layers which are assumed to be cubic. It can be shown that this procedure is very satisfactory, except if the layers are too small as e.g. in $2H$ SiC.

Starting from the above introduced building-block representation we can apply a recently developed superlattice method [21] which uses only the band structure and wave functions of the building-block material $3C$ SiC as input. Since $3C$ SiC is the simplest polytype of SiC, only having two atoms per unit cell, these ingredients are relatively easy to obtain. In the superlattice method the bulk-like $3C$ wave functions are then to be matched at the polytypic interfaces separating the successive building blocks.

It is of course possible in this approach to calculate the band structure and the wave functions of the basis material $3C$ SiC within various theoretical frameworks. More specifically, we will apply two band structure methods to the basis material $3C$ SiC. The first method is the empirical pseudopotential method (EPM). The second is the density-functional theory (DFT) in the local-density approximation (LDA) [37]. In the EPM a number of potential parameters is used as input, adjusted in such a way that relevant parts of the band structure reproduce experimental findings. It is important

to note that within this technique we *only* fit crucial parts of the band structure of the basis material 3*C* SiC. The band gaps of the other polytypes are, subsequently, calculated by means of the matching procedure within the above mentioned superlattice method. The band gaps can then be considered as resulting from the intrinsic band structure and wave functions properties of cubic SiC on the one hand and the superlattice dimensions on the other hand. In DFT (LDA) the procedure is essentially similar. However, although we are in this case dealing with a first-principles theory, very well suited to describe ground state properties, we have to realize that the band gap is in fact an excited-state property and can therefore, in principle, not be obtained within DFT. Consequently, the superlattice method will then provide only so-called Kohn-Sham gaps for the respective polytypes. They are significantly lower than the experimentally observed gaps. However, the missing part, the so-called quasiparticle energy correction, can easily be identified and shown to be almost entirely polytype independent. Therefore, in order to reproduce or predict experimentally determined excitation energies we only have to add this quasiparticle correction, the size of which is obtained in a relatively easy way.

1.4 Thesis set-up

The set-up of this thesis is as follows. In Chapter 2 we describe the specific crystal structures of the respective polytypes together with their classification schemes. Starting from cubic Si-C bilayers we show how any SiC polytype structure can be built up. We will demonstrate why polytype structures can to a large extent be approximated by a piling up of entirely bulk-like 3*C* SiC segments, by comparing the lattice constants and the charge density distribution of true and building block made SiC polytypes. It is shown, by comparing the charge-density distributions, how optimum interface positions can be chosen such that the charge density of the building-block made polytype agrees as much as possible with that of the true polytype.

Chapter 3 is mainly devoted to the actual method of calculating the band structure for SiC polytypes. We first describe how the *complex* band structure of 3*C* SiC (within the EPM) is obtained together with the related Bloch and evanescent wave functions. They form the necessary ingredients in the superlattice method. Within this superlattice method it is shown how linear combinations of both Bloch and evanescent wave functions are matched at the successive polytypic interfaces. The energy band gaps obtained within this method are compared with experimental gaps for a number of SiC polytypes. It is shown that the results reproduce the experimentally observed band gap variation in SiC polytypes almost perfectly. It is checked whether the exact position of

the interface has influence on the calculated band gaps. We also describe the results of the interface matching method for SiC within the LDA and determine the necessary quasiparticle corrections.

Since the calculations as presented in Chapter 3 are quite complicated and only re-produce the experimental band gap values, we focus in Chapter 4 on a one-dimensional model which comprises the essence of the more involved treatment in Chapter 3. With the use of this model it appears indeed to be relatively simple to explain the structural dependence of the SiC band gaps. The model is constructed by using the transmission and reflection coefficients of a Bloch wave scattering at a single polytypic interface. The actual values of these coefficients directly result from the analysis in Chapter 3. The scattering process is described in terms of envelope functions [8] obeying particular discontinuous boundary conditions at the interfaces. A previously suggested Kronig-Penney model will be shown to be incorrect. We end Chapter 4 by indicating the characteristic features of $3C$ SiC which are responsible for the strong band gap varia-tion in polytypes. To this end, we have also applied the interface matching method as described in Chapter 3 to ZnS polytypes and to hypothetical polytypes of Si, C and AlAs, which all do *not* show this band gap variation.

In Chapter 5 we apply a state-of-the-art GW calculation in order to obtain the quasiparticle band structure of $3C$ SiC from first principles [4]. There is excellent agreement between calculated quasiparticle energies and the dielectric constant on the one hand and experimental data on the other. In our GW scheme we use a recently developed physical plasmon-pole model [26] which provides us with a plasmon energy dispersion of $3C$ SiC which can be subjected to experimental verification. Finally, we conclude from our quasiparticle correction to LDA energies of $3C$ SiC, together with results of other authors obtained for other SiC polytypes, that the quasiparticle correction energy necessary to upgrade the LDA gap results for SiC polytypes, is to a large extent polytype independent. The outlook of Chapter 5 contains a discussion about the feasibility of our GW approach for more complicated SiC polytype structures than $3C$ SiC.

Chapter 2

Polytype structures

A clear survey of the various existing crystal structures of polytype compounds like e.g. SiC, ZnS and CdI_2 can best be obtained by analyzing and rubricating first of all different close packing structures of equal spheres [61]. In this way, each polytype structure can be related in a one to one correspondence to a given arrangement of the packed spheres. Incidentally, these spheres should not be identified with the atoms in the respective polytypes; the spheres merely serve to produce a classification scheme of crystal structures, which is perfectly suited to rubricate the various polytypes. It also leads to the widely applied hexagonality concept to characterize the various polytype structures. This representation of polytypes is described in section 2.1.

In section 2.2 we will introduce our so-called building-block model of the SiC polytype structures, which will form the basis of our work in the next chapters. The important observation, that has given rise to this model, is that the crystal structure of any SiC polytype can always be subdivided into fragments, closely resembling the cubic polytype $3C$ SiC. These fragments of $3C$ SiC form the so-called building blocks, from which any polytype can be made up structurally. Though all cubic-like, these fragments are mutually twisted with respect to each other. Hence, the SiC polytypes can be considered as natural superlattices, in which the successive layers consist of $3C$ SiC material of possibly different width. Section 2.2 is devoted to the description of this building-block scheme. Special attention is paid to the basic material $3C$ SiC, from which the building blocks are composed.

Finally, in section 2.3, we will explicate to what extent the building-block representation of a polytype is an accurate perception of a real polytype. This will be done by comparing lattice constants, atomic positions and electronic charge density distributions of a polytype, constructed by means of our building-block model, with those of a

Figure 2.1: The close packing of spheres. The displayed ground layer contains spheres in A-type positions. A given A-sphere is surrounded by six voids. Spheres of a second layer are situated either in the voids 1, 3 and 5 or 2, 4 and 6 and are located in B- or C-type positions, respectively. The spheres of any structure, obtained by piling up subsequent layers, have their centres all located in parallel vertical planes, whose intersection with the ground plane coincides with the indicated set of dashed parallel lines.

real polytype. From the striking resemblance of the electronic charge distributions it will be argued that our model is in fact a very accurate representation of SiC polytypes.

2.1   Crystal structures

A convenient classification scheme for the polytype structures can most easily be constructed by first considering the various close packing possibilities of a collection of equally large spheres. To this end we start by considering Fig. 2.1, in which a layer of such closely packed spheres is displayed. Addition of a second layer can be achieved in one of two ways only, either by putting the spheres in the voids indicated by 1, 3 and 5 or those by 2, 4 and 6. Denoting the sphere positions of the ground layer by an A, the possible set of sphere positions for the next layer is either B or C. Two successive layers obviously have to be unlike to keep the packing as close as possible. Proceeding in this way, it will be clear that the third layer will be either of A- or C-type (in case layer 2 is B-type) or of A- or C-type (in case layer 2 is C-type) etcetera. This obviously leads to all possible close packings of equally sized spheres. The piling direction of the spheres will be indicated as the c-, the z- or the vertical direction. We will define the c-axis as the axis which corresponds to the piling direction and goes through the centre of an A-sphere.

An important subset of the above mentioned stacking possibilities is obtained by de-
manding the resulting structure to be periodic in the piling direction. Simple examples
of such periodic stackings are $ABAB...$ and $ABCABC...$, with periodicity over two and
three layers, respectively. The first stacking gives rise to a hexagonal structure, the sec-
ond one to the face-centred cubic (fcc) one. In the latter case the c-direction coincides
with the well-known [111]-direction for cubic crystals. By exploring all possibilities, an
infinite number of periodic stacking sequences results.

Let us now choose the diameter of the spheres such that the mutual distance be-
tween two neighbouring planes of sphere centres coincides with the distance between
neighbouring Si-planes in cubic SiC. Let us furthermore place Si-atoms in the center of
each sphere, and C-atoms precisely a bond length, as valid in cubic SiC, above them.
The resulting periodic crystal structures then almost perfectly represent all *conceivable*
SiC polytypes. In Fig. 2.2 we depicted the arrangement of Si and C atoms in a stacking
with a SiC bilayer sequence ABC. Similar arrangements may be constructed repre-
senting other polytype structures. The reason that this representation is not always
entirely perfect lies in the (very) small variations in the bond lengths which may occur,
both within one given polytype and also mutually between different polytypes. Pos-
sibly not all conceivable periodic stackings can be produced in fabrication processes.
However, more than 200 different SiC polytypes have been identified thusfar.

In Fig. 2.3 five different SiC polytypes are displayed by giving the positions of Si
and C atoms in a plane going through the c-axis and one of the dashed lines in Fig. 2.1.
The possible crystal structures of polytypes of SiC belong to three types, namely those
having cubic (C), hexagonal (H) and rhombohedral (R) symmetry [61]. There is only
one cubic crystal structure possible for SiC, namely the zinc blende (or fcc) structure
$3C$ SiC, which has the repeating stacking sequence ABC consisting of 3 bilayers of Si
and C. This explains the number 3 in front. The polytypes belonging to the hexagonal
structures are quite numerous. Important examples are $2H$, $4H$ and $6H$ SiC. They
correspond to the repeating stacking sequences AB, $ABCB$ and $ABCACB$, respec-
tively. Lastly, the most commonly observed rhombohedral structure $15R$ is indicated
in Fig. 2.3, and has the repeating stacking sequence $ABCACBCABACABCB$.

There are at least three rather commonly applied notations [61] in order to distin-
guish between the large number of possible polytype structures. In Table 2.1 we have
listed ten polytype structures by making use of three different kinds of notations. In
addition to the ABC notation, we will use the notations according to Ramsdell and
that of Zhdanov.

The Ramsdell notation, like $3C$, $2H$ and $15R$ as already mentioned, consists of
a number, counting the number of bilayers within one periodically repeating block

Figure 2.2: The arrangement of Si (open circles) and C (filled circles) atoms according to the cubic stacking sequence ABC. The c-axis coincides with the z-axis of the indicated coordinate frame x, y, z.

Figure 2.3: *The arrangement of Si (open circles) and C (filled circles) atoms in the polytypes 3C, 2H, 6H, 4H and 15R SiC. The plane in which the atom centres are situated, is one of the vertical planes introduced in Fig. 2.1.*

Table 2.1: Three different notations and the percentage hexagonality h (in %) of ten SiC polytype structures [61].

Polytype Ramsdell	Polytype ABC	Polytype Zhdanov	h
3C	ABC	(∞)	0
10H	ABCABCBACB	(55)	20
8H	ABCABACB	(44)	25
6H	ABCACB	(33)	33.3
4H	ABCB	(22)	50
2H	AB	(11)	100
15R	ABCACBCABACABCB	$(23)_3$	40
33R	ABCACBABCACBCABAC BCABACABCBACABCB	$(3332)_3$	36.4
21R	ABCACBACABCBACBCABACB	$(34)_3$	28.6
24R	ABCACBACBABCBACBABCACBAC	$(35)_3$	25

in the c-direction, and a letter, specifying the type of Bravais lattice. Note that the number in the Ramsdell notation does not count the number of Si-C pairs belonging to the primitive cell. For instance, for 3C SiC and 15R SiC the numbers of Si-C pairs inside their primitive cells are 1 and 5, respectively! Furthermore we note that the Ramsdell notation is not a unique way to classify all conceivable polytype structures. For instance the periodic stacking sequences according to *ABCACB* and *ABCBAB* can both be classified as 6H. In order to distinguish such structures notationally, additional subscripts have to be attached. For the observed SiC polytype *ABCACB* we use the bare notation 6H SiC, and for the other one *ABCBAB* we use $6H_a$ SiC.

The Zhdadov notation for a specific polytype modification amounts to a combination of numbers representing the number of bilayers stacked according to the cubic stacking order before a change (or fault) occurs. After such a stacking fault the cubic stacking pattern continues, be it, however, in twisted order. In line with this, the wurtzite or 2H structure is indicated by (11), the 6H structure by (33), the $6H_a$ structure by (2211) and the 15R structure by $(23)_3$. The cubic structure is, consequently, indicated by (∞). The numbers of the Zhdanov notation are very well recognizable as the successive numbers of stacked bilayers in the zigzag pattern in Fig. 2.3.

We are now in the position to introduce the hexagonality concept. The definition,

which is most adequate for our work, uses Zhdanov's notation and runs: *the hexagonality (h) of a polytype structure equals the reciprocal value of the averaged number of bilayers, stacked according to the cubic and twisted cubic order.* The 6H structure for example consists of three cubic and three twisted cubic layers, so the averaged number of bilayers is 3 and $h = 1/3$, or expressed as a hexagonality percentage $h = 33.3\%$. Table 2.1 contains, besides the notations, the hexagonality percentage h for the polytype structures. We remark that the hexagonality, and consequently the hexagonality percentage, is not a unique quantity for polytype structures to be identified with. For instance, the polytypes 8H and 24R differ structurally, but correspond to the same hexagonality percentage $h = 25\%$.

From the arrangement of atoms, depicted in Fig. 2.3, it can be observed that not all atomic layers in a given structure, and thus also not all Si or C atoms, are equivalent. The non-equivalent atomic layers are denoted by the letters h and k. The non-equivalencies have to do with differences in the relative positioning of the two adjacent bilayers. Atoms of an h-type layer, pertaining to a certain bilayer, are surrounded by two equally positioned bilayers (e.g. B in ABA), which is typical for a hexagonal environment. On the other hand, atoms of a k-type of layer are surrounded by differently positioned bilayers (e.g. B in ABC), which is typical for a cubic environment. In line with this, the hexagonality percentage can alternatively be defined as the percentage of h-layers of the polytype structure. It is in a number of cases also possible to discriminate between *kinds* of h-type and k-type of positions. Such differences are related to differences in the kind of more distant layers. If this applies, the above h or k will be provided with a subscript (see Fig. 2.3). The existence of distinguishable atomic positions has been demonstrated experimentally for several SiC polytypes, by substituting nitrogen (N) atoms for C atoms situated at the different positions. The implantation of such N donors at different locations gives rise to a number of different binding energies showing up in luminescence spectra, equal to the number of non-equivalent possible C-atom layers in the given polytype. In this way, it has been established that 3C, 2H, 4H, 6H and 15R SiC contain 1, 1, 2, 3 and 5 non-equivalent occupied positions [59], respectively, in agreement with the number of non-equivalent layers indicated in Fig. 2.3. And this can be continued to even more distant layers.

In Fig. 2.4 the crystal structure of the zinc blende polytype is depicted in its conventional unit cell. As already mentioned, for this structure the stacking direction coincides with the [111]-direction. The successive Si-layers of this structure have been indicated in this figure by A, B and C. The three primitive vectors of the fcc Bravais lattice are: $\vec{a}_1 = \frac{1}{2}a_c(0,1,1)$, $\vec{a}_2 = \frac{1}{2}a_c(1,0,1)$ and $\vec{a}_3 = \frac{1}{2}a_c(1,1,0)$, all expressed in the Cartesian coordinate frame x', y', z' of Fig. 2.4.

Figure 2.4: *The arrangement of Si and C in the zinc blende structure of SiC. The lattice constant of the conventional face-centred cubic unit cell is denoted by a_c. With respect to the coordinate frame x', y', z' the atomic positions of the primitive cell are for the Si atom $\vec{\tau}_{Si} = (0, 0, 0)$ and for the C atom $\vec{\tau}_C = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, expressed in units of a_c. The planes indicate the bilayer types to which the Si atoms belong.*

2.2   The building-block scheme

The central idea in our approach, to be used for describing the behavior of electrons in SiC polytypes in the next chapter, comes from the insight that in all polytype structures finite parts of the cubic structure can be recognized. We will use the $6H$ configuration, with stacking sequence $ABCACB$, as an example to outline the idea in detail. For this structure the stacking sequence of the first three layers reads ABC, which is exactly the same as the stacking sequence for the cubic structure. The next three layers of the $6H$ structure correspond to ACB, which is different from the ABC sequence. However, the stacking sequence ACB is nothing but ABC rotated over 60° around the c-axis. This means that the $6H$ polytype can be represented as the periodic stacking of two equally wide parts (building blocks) of the cubic polytype. The respective cubic parts ABC and ACB are, however, *twisted* with respect to each other.

Any polytype can in fact be thought of as being built up in a similar manner. Depending on the specific polytype structure, the participating cubic and twisted cubic fragments may be different in size. The Zhdanov notation gives exactly the subsequent, mutually twisted, cubic building-block sizes, precisely counting the respective number of cubic and twisted cubic bilayers.

By following this line of thought, we obtain a model representation of the polytype structures, which will certainly not be precise enough to describe all subtle details of polytypes, but, as we will show, the model is completely adequate for our purpose of predicting band structure characteristics.

In the next section we will discuss three possible objections connected with this building-block description. In the first place we discuss the fact that actual bond lengths in hexagonal and rhombohedral polytypes differ from the $3C$ SiC bond lengths. Secondly, we pay attention to the fact that the electronic environments in $3C$ SiC are used, which especially in the h-type layers will not entirely be correct. Thirdly, we will investigate the inherent ambiguity in the choice of the start and end position of the building blocks, or, put otherwise, in the choice of the interface positions.

2.3   Discussion about the building-block model

A characteristic property of our building-block made polytypes is that the atomic positions within them, and also the electronic density distribution around the atoms, are directly related to the zinc blende structure. We will therefore critically consider in this section a few important quantities, namely the lattice constants, the positions of the atoms in the primitive cells and the charge density distributions, with the intention to

Table 2.2: The experimental lattice constants of five SiC polytypes [48, 64].

Polytype	a_h (Å)	c_n (Å)	c_n/na_h
2H	3.076	5.048	0.8204
4H	3.073	10.053	0.8178
6H	3.081	15.117	0.8178
8H	3.079	20.147	0.8179
15R	3.073	37.70	0.8179

illuminate possible differences between a building-block polytype and a true polytype.

The two hexagonal lattice constants a_h and c_n of a hexagonal building-block poly-type with periodicity over n bilayers are by construction related to the lattice constant a_c of the underlaying cubic lattice. These relations are $a_h = a_c/\sqrt{2}$ and $c_n = na_c/\sqrt{3}$. This implies that the bilayer thickness c_1 and the lattice constant a_h are related by $c_1/a_h = \sqrt{2/3} \approx 0.8165$, which we will refer to as the ideal ratio of c_1 and a_h. In Table 2.2 we have summarized the experimental [48, 64] lattice constants a_h and c_n and the ratio c_n/na_h of a number of SiC polytypes, all measured near $T = 300$ K. The experimental lattice constant of the cubic modification of SiC is $a_c = 4.3596$ Å, which implies that the corresponding ideal hexagonal lattice constant is $a_h = 3.0827$ Å. From the listed experimental lattice constants it turns out that deviations from the constructed lattice constants are less than 0.5 %. Further on in this section we will estimate the influence of such relaxations to the energy band gap of SiC polytypes.

Besides the dimensions of the primitive cells, also the actual positions of the C and the Si atoms inside the primitive cells of SiC polytypes are of influence on the energy band structure. It has recently been shown, both theoretically [41] and experimentally [56], that atomic relaxations in the primitive cells of polytypes do indeed take place. This means, among other things, that the bonding configuration between neighboring Si and C atoms deviate from the ideal tetrahedral configuration. These deviations however, appear to be extremely small. Recent investigations have concentrated on the short-period polytypes 2H, 4H and 6H SiC, revealing that the bond lengths deviate at most 0.5 % from their ideal tetrahedral values, which are approximately 1.88 Å.

A rough estimation of the influence of atomic relaxations on the band gap values of SiC polytypes, can be obtained by considering the case of the (hydrostatic) pressure derivative of the band gap of 3C SiC. Since the pressure derivative dE/dp of the band

gap, as well as the equilibrium bulk modulus $B_0 = -\Omega_c dp/d\Omega_c$, and the primitive-cell volume Ω_c are known, we have

$$\frac{dE}{da_c} = \frac{dE}{dp}\frac{dp}{d\Omega_c}\frac{d\Omega_c}{da_c}. \tag{2.1}$$

The primitive cell volume equals $\Omega_c = \frac{1}{4}a_c^3$, yielding $d\Omega_c/da_c = \frac{3}{4}a_c^2$. The experimental values for dE/dp and B_0 in $3C$ SiC are -0.34 meV/kbar and 2.2 Mbar, respectively. Making use of these values, we find that the energy band gap for $3C$ SiC increases approximately 10 meV if the lattice constant is elongated 0.5 % or by 0.02 Å. A more proper estimate would include the derivatives pertaining to the respective polytypes. However, according to recent pseudopotential calculations of Park *et al.* [53], the polytype dependent quantities in Eq. (2.1) are generally smaller. Only for the $2H$ polytype they may be a factor of two higher than the ones for the $3C$ structure, but the $2H$ structure is an exceptional case, which is not very well covered by our approach anyhow. For the other polytype structures, our estimation reveals that the influence on the band gap of atomic relaxations in SiC polytypes with respect to the ideal positions is in the order of 10 meV, or appreciably less, i.e. small enough to justify our approach to the determination of band gaps.

Apart from the atomic relaxations and their small influence on the band gap, it is also observed that the actual charge density distribution around the Si and the C atoms in a given polytype is surprisingly similar to that of the related building-block system. This was already noticed by Denteneer *et al.* [23, 24], who mapped the $3C$ SiC density to a $2H$ SiC structure. More specifically, when comparing the theoretically obtained valence-charge density of actual $6H$ SiC with that of the related building-block system (both structures with the same bond lengths) the differences turn out to be minor, if the interface position in the building-block system is chosen precisely in between a Si and a C atom of an h-type bilayer. Let us denote the valence-charge density of the $6H$ building-block system by $\tilde{\rho}^{6H}(\vec{r})$, in agreement with Denteneer *et al.*. To obtain this building-block density in the $6H$ unit cell, the density of $3C$ SiC, denoted as $\rho^{3C}(\vec{r})$, is transformed into the density $\tilde{\rho}^{6H}(\vec{r})$ by

$$\tilde{\rho}^{6H}(\vec{r}) = \begin{cases} \rho^{3C}(\vec{r}) & \text{if } 0 \leq z - z_j < c_6/2 \\ \rho^{3C}(\mathcal{T}\vec{r}) & \text{if } c_6/2 \leq z - z_j < c_6 \end{cases}, \tag{2.2}$$

where $\mathcal{T}$ denotes the twisting operation, which is a rotation over 60° around the c-axis. The interface position is denoted by z_j. The actual valence-charge density of $6H$ SiC will be denoted by $\rho^{6H}(\vec{r})$. In Fig. 2.5 intersections are given of the corresponding density functions of $6H$ SiC. We have listed in Table 2.3 the most important plane-wave Fourier components $\rho_{\vec{Q}}^{6H}$ and $\tilde{\rho}_{\vec{Q}}^{6H}$ of the valence-charge densities. The reciprocal

Table 2.3: *The absolute values of the largest Fourier components of the valence-charge density of* $6H$ *SiC:* $|\rho_{\vec{Q}}^{6H}|$ *from a self-consistent supercell calculation and* $|\tilde{\rho}_{\vec{Q}}^{6H}|$ *by piling up (mutually twisted) the self-consistently obtained density of* $3C$ *SiC. The unit in which the Fourier components are expressed is the number of valence electrons per* $6H$ *unit cell. The reciprocal lattice vectors* $\vec{Q}$ *are given as sets of integral components* n_1, n_2 *and* n_3 *with respect to the basis vectors* $\vec{b}_1$, $\vec{b}_2$ *and* $\vec{b}_3$ *of the* $6H$ *structure.*

$\vec{Q}$	$|\rho_{\vec{Q}}^{6H}|$	$|\tilde{\rho}_{\vec{Q}}^{6H}|$
000	48.000	48.000
006	11.822	12.013
012	6.006	6.002
103	4.840	4.900
011	4.420	4.478
104	3.365	3.389

lattice vectors $\vec{Q}$ of $6H$ SiC in Table 2.2 are integral multiples of the reciprocal basis vectors $\vec{b}_1, \vec{b}_2$ and $\vec{b}_3$, which can be expressed in the Cartesian coordinate frame x, y, z of Fig. 2.2 as $\vec{b}_1 = \frac{2\pi}{a_h}(\frac{2}{\sqrt{3}}, 0, 0), \vec{b}_2 = \frac{2\pi}{a_h}(\frac{1}{\sqrt{3}}, 1, 0)$ and $\vec{b}_3 = \frac{2\pi}{c_6}(0, 0, 1)$. The plane-wave expansion relating the density and its Fourier components reads

$$\rho(\vec{r}) = \sum_{\vec{Q}} e^{i\vec{Q}\cdot\vec{r}} \rho_{\vec{Q}}. \tag{2.3}$$

The calculations were performed in the local-density approximation of the density-functional theory, using norm-conserving pseudopotentials for the Si and the C ions [11]. The actual valence-charge densities of $3C$ and $6H$ SiC were self-consistently calculated, starting in the first iteration cycle with a homogeneous valence-charge density for both structures. For both crystal structures $3C$ and $6H$ was taken the same $6H$ unit cell, to exclude computational convergence dissimilarities of different primitive cells. The position of the interface in the $6H$ building-block system has been situated, as a neutral guess, exactly in the middle of a Si-C bond pertaining to an h-type bilayer ($z_j = \frac{3}{8}c_1 + \frac{1}{2}jc_6$). The largest plane-wave Fourier components of the valence-charge density of the mapped density and the actual one, see Table 2.3, deviate less than 2% compared with each other. So, the agreement is good. This is of course the reason why there is hardly any noticeable difference in the charge density distributions between the building-block charge density distribution and the actual $6H$ one in Fig. 2.5.

Figure 2.5: Contour plot of the valence-charge density distribution of actual (unre-laxed) 6H SiC (left) and of the corresponding building-block polytype (right). The three successive interfaces are indicated by horizontal (dashed) lines. The plane of intersection is comparable to the one of Fig. 2.3, however the Si and the C atoms are interchanged. The lowest contour corresponds to 10 valence-electrons per 6H unit cell. The successive contours increase gradually by 20 valence-electrons per 6H unit cell.

In the above comparison the interface positions of the building-block system have been chosen exactly in the middle of a Si-C pair of an h-type bilayer. We may in fact investigate the possibility of finding a better interface position, such that the density of the building-block system fits best with the actual density. We may find this optimum interface position by demanding that the differences in charge density are minimal, the criterion being that $\sum_{\vec{Q}} |\bar{\rho}_{\vec{Q}} - \rho_{\vec{Q}}|^2$ should be as small as possible. To this end, we have calculated the building-block density of $6H$ SiC at various interface positions and found that the minimum deviation from the actual $6H$ density was indeed obtained by choosing the interface position as we did. Carrying through this same analysis for $2H$ SiC, also taken in the same $6H$ cell, we found that the minimum deviation between ρ^{2H} and $\bar{\rho}^{2H}$ is obtained for nearly the same interface position. The magnitude of the minimum deviation was, however, noticeably larger for the $2H$ than for the $6H$ case.

Although the building-block made density and the actual density of $6H$ are in good agreement with each other, there are obviously remaining differences. The interface locations are the most likely places where the differences will arise. It is hard, but not impossible, to see these differences in Fig. 2.5 by eye. In order to display the differences we have investigated [5] the charge density distributions planewise as a function of z by expanding the difference of the building-block and the actual valence-charge density in two-dimensional plane-wave Fourier components, using the set of two-dimensional reciprocal lattice vectors $\vec{Q}_\|$ parallel to the interface planes. The expansion of this difference in valence-charge density $\Delta\rho(\vec{r})$ reads

$$\Delta\rho(\vec{r}) = \sum_{\vec{Q}_\|} e^{i\vec{Q}_\| \cdot \vec{r}_\|} \Delta\rho_{\vec{Q}_\|}(z), \qquad (2.4)$$

in which $\vec{r}_\|$ is the two-dimensional component of $\vec{r}$ parallel to the interface planes. Fig. 2.6 shows two plane Fourier components $\Delta\rho_{\vec{Q}_\|}$ as a function of the z-coordinate along the c-axis. From Fig. 2.6 it can be deduced that $\Delta\rho_0(z)$, which is the z-dependent plane average of the valence-charge density difference, is at most 0.2 % of the value $48/c$, where c is the $6H$ unit cell length and 48 the number of valence electrons per cell. The fact that this Fourier component $\Delta\rho_0(z)$ is small but non-zero, is exhibited by the presence of a small dipole lying across Si-C bonds at the boundary between a k- and an h-type of bilayer. Due to this dipole moment per unit cell the polarization field does not vanish and therefore are non-cubic polytypes of SiC pyroelelectric materials [56, 42]. Also relevant, as can be seen in Fig. 2.6 is the next non-zero plane Fourier component $\Delta\rho_{\vec{Q}_\|}(z)$. The important insight gained from Fig. 2.6 is that the Fourier-components, $\Delta\rho_{\vec{Q}_\|}(z)$ (also the Fourier components not shown in this figure), are clearly largest within a region of approximately one bilayer centred around the interface positions. This allows us to say that the $6H$ SiC polytype can to a large extent be considered

to contain four out of six bilayers which to a high degree are not only structurally but also electronically cubic-like. The $2H$ polytype of SiC is observed to contain bilayers which are appreciably less cubic-like. In Chapter 3 we will estimate the effects of the potential deviations within the LDA, which are connected to the presented charge density deviations, on the calculated band gap energies.

Figure 2.6: The difference in valence-charge density $\Delta\rho_{\vec{Q}_\parallel}(z)$ between the actual density and the building-block density of 6H SiC, as calculated within the LDA for two $\vec{Q}_\parallel$ vectors. The solid line represents the Fourier component $\Delta\rho_{\vec{Q}_\parallel}(z)$ with $\vec{Q}_\parallel = 0$. The dashed line represents the Fourier component $\Delta\rho_{\vec{Q}_\parallel}(z)$ with the smallest non-zero $\vec{Q}_\parallel$. The 6H unit cell length is equal to c. Furthermore we indicated for each bilayer whether its type is h or k.

Chapter 3

The interface matching method

In this Chapter we will describe and apply a method [3], which predicts the relevant parts of the band structure and, more in particular, the band gaps of SiC polytypes. The validity of this method finds its basis in the idea that any SiC polytype may be regarded as a building-block system (see Chapter 2), in which the building blocks are $3C$ SiC bulk-like to a large extent. Our method is closely related to a method applied to e.g. GaAs/AlAs superlattices [10, 44, 22, 34] and twinned superlattices of Si and Ge [35], in which the layers are likewise assumed to be entirely bulk-like. For heterostructures this assumption is widely known as the flat-band approximation. It will be clear that the idea of building blocks discussed in Chapter 2 forms in fact the basis for this approximation. Polytypic superlattices, in comparison with heterostructure superlattices, have two important additional features, namely (i) the polytypes are perfectly lattice-matched superlattices and (ii) the polytypes have an energy band offset between adjacent (mutually twisted) layers which is zero by definition.

With the building-block idea in mind, we have as only ingredient, the complex band structure of the basis material $3C$ SiC with accompanying wave functions. As a matter of course the complex band structure of $3C$ SiC can be arrived at starting from different theoretical frameworks. In this thesis, we will apply our method starting from a $3C$ SiC band structure either obtained within the empirical pseudopotential method (EPM) or within the local-density approximation (LDA) of the density-functional theory (DFT).

Section 3.1 is devoted to the description of the way in which a complex band structure may be obtained, first for the empty-lattice case in section 3.1.1 and second for the case of bulk $3C$ SiC in section 3.1.2. It will appear further on that both the Bloch wave functions, which are related to the real part of the band structure, *and*

the evanescent wave functions, which are related to the complex part of the band
structure, form necessary ingredients in our superlattice method. As neighbouring
layers in polytypes are twisted with respect to each other, we need apart from the
complex band structure of the basis material also the complex band structure of the
twisted material. Although this is of course the same band structure, we face the
problem that the coordinate systems of the two adjacent layers are rotated with respect
to each other. In section 3.1.3 it is explained how to deal with this problem.

In section 3.2 we will present the method of calculating the band structure for the
entire building-block system. We will describe the procedure in which electronic Bloch
and evanescent wave functions, all pertaining to the $3C$ SiC material in the successive
layers, are properly matched at the interfaces, in order to make up the wave functions of
the superlattice (i.e. the polytype under consideration). Along with the wave functions
for the polytype we will obtain its energy band structure and therefore also its energy
gap.

In section 3.3 we will estimate the effect of the deviations from the flat-band ap-
proximation within the LDA. This will be done by considering the difference between
the actual potential of $6H$ SiC and the potential of the $6H$ SiC building-block system,
and by calculating to first order its effect on the obtained electron energies.

Section 3.4 is devoted to a number of remaining remarks about the method.

The conclusions are given in section 3.5.

3.1 The complex band structure

The energy band structure of a given crystal depends both on the underlying lattice
structure and its electronic potential distribution. To single out the structural de-
pendence, we will first analyse the complex band structure of $3C$ SiC in its so-called
empty-lattice approximation, i.e. with the electronic potential set equal to a constant,
after which we will turn to the band structure pertaining to an actual $3C$ SiC crystal.

3.1.1 Empty-lattice

The empty-lattice approximation refers to the electronic band structure analysis of
a crystal in which the electrons are assumed to move in a constant potential. This
leads to an infinite set of energy bands for which the dependence of the energy E on
wave vector $\vec{k}$, lying in the first Brillouin zone (1BZ) of the adopted underlying Bravais

lattice, can be expressed as

$$E_{\vec{G}}(\vec{k}) = U_0 + \frac{\hbar^2}{2m}\left(\vec{k} + \vec{G}\right)^2.$$ (3.1)

Here $\vec{G}$ represents a respective reciprocal lattice vector related to the Bravais lattice, for which we choose the face-centred cubic (fcc) lattice pertaining to $3C$ SiC. In Fig. 3.1 we have depicted the 1BZ of $3C$ SiC. If we furthermore choose the z-direction as in Fig. 2.4, we may write $\vec{k} = \vec{k}_{\parallel} + k_z\vec{e}_z$ and $\vec{G} = \vec{G}_{\parallel} + G_z\vec{e}_z$, the symbol $\parallel$ denoting vectors in the x, y-plane and $\vec{e}_z$ being the unit vector in the z-direction. Relation (3.1) can now be rewritten as

$$E_{\vec{G}_{\parallel}, G_z}(\vec{k}_{\parallel}, k_z) = U_0 + \frac{\hbar^2}{2m}\left\{\vec{k}_{\parallel} + \vec{G}_{\parallel} + (k_z + G_z)\vec{e}_z\right\}^2.$$ (3.2)

In both Eq. (3.1) and Eq. (3.2) we have added a constant U_0 to the free electron energies. The value of this constant U_0 is arbitrary and can for semiconducting crystals for instance be chosen such that the energy of the highest valence band edge at $\vec{k} = 0$ is zero.

Figure 3.1: First Brillouin zone pertaining to the face-centred cubic Bravais lattice with symmetry points Γ, X, U, W and L. The [111]-direction (corresponding to the cubic lattice) runs parallel to the ΓL-line and is indicated as the k_z-axis. In this thesis the complex band structure is always calculated, for a fixed $\vec{k}_{\parallel}$, along a path parallel to this k_z-direction. The path λ that includes the X-point and runs parallel to the ΓL-line is indicated by the dotted line (inside the 1BZ) and the thicker solid line (outside the 1BZ).

It will be clear from (3.2) that, at fixed energy E and fixed parallel wave vector $\vec{k}_\parallel$ there are precisely two solutions for k_z (either real or complex) for each value of the reciprocal lattice vector $\vec{G}_\parallel + G_z \vec{e}_z$. However, at fixed E and $\vec{k}_\parallel$ it is only relevant to consider those k_z-values which are such that $\vec{k}_\parallel + (\mathrm{Re}\, k_z)\vec{e}_z$ lies in the 1BZ or that k_z is as close as possible to $k_z = 0$. If N denotes the number of plane waves (i.e. $\vec{G}$-vectors) taken into account, and M denotes the number of different projections $\vec{G}_\parallel$ of the $\vec{G}$-vectors on the x, y-plane, it has been proved in Ref. [21] that at given E and $\vec{k}_\parallel$ there are only $2M$ relevant k_z-values (out of $2N$) to be taken into account. All other possible values of $\vec{k}_\parallel + k_z \vec{e}_z$ differ from the selected ones by some reciprocal lattice vector and are therefore superfluous. For the cases in which $\vec{k}_\parallel \neq 0$ it may happen that not all of the $2M$ solutions $\vec{k}_\parallel + (\mathrm{Re}\, k_z)\vec{e}_z$ lie in the 1BZ. In these cases it is always possible to reduce these solutions into the 1BZ by addition of some $\vec{G} = \vec{G}_\parallel + G_z \vec{e}_z$. However, there is no reason to do so because the wave functions pertaining to the two considered $\vec{k}$-points are equal. (If we had calculated the complex $3C$ SiC band structure in a hexagonal Brillouin zone we would not encounter this representation problem.)

The relations $E_{\vec{G}_\parallel, G_z}(\vec{k}_\parallel, k_z)$ in which k_z may be complex are called the complex band structure. In Fig. 3.2 this band structure is displayed for the choice $\vec{k}_\parallel$ equal to $\vec{k}_M = (2\pi/a_h\sqrt{3})\vec{e}_x$ with $a_h = a_c/\sqrt{2}$ (see Chapter 2). Note that this M-point is equivalent to the X-point of the Brillouin zone of a fcc lattice.

In Fig. 3.3 we have depicted sets of $\vec{G}_\parallel$ for the fcc structure, obtained by projecting $\vec{G}$-vectors contained in $|\vec{G}|^2 \leq g_0$, where g_0 is some constant. This set is the best choice for a proper description of the complex band structure if we choose $\vec{k}_\parallel = 0$. In Fig. 3.3 g_0 is chosen such that the number of $\vec{G}$-vectors involved is 113, and the related number of $\vec{G}_\parallel$-vectors is 31. Note that also 1, 7 and 13 are consistent choices for the number of $\vec{G}_\parallel$-vectors. However, if we aim at a proper description of the band structure for the choice $\vec{k}_\parallel = \vec{k}_M$ (see Fig. 3.3) it is best to use a set of $\vec{G}_\parallel$-vectors derived from $\vec{G}$-vectors centred around the point $-\vec{k}_M$, i.e. the set contained in $|\vec{G}_\parallel + \vec{k}_M|^2 \leq g_M$. It is shown in Fig. 3.3 that for this case 2, 4, 8 and 12 are consistent choices for the number of $\vec{G}_\parallel$-vectors to be taken into account. If for instance the number of 8 is adopted, we have according to the above reasoning to deal with 16 relevant k_z-values at each value of E. Most of them are complex. In this case the complete complex band structure therefore consists of 16 $E_s(\vec{k}_\parallel, k_z)$-curves ($s = 1, 2, \ldots 16$). It is easily proved that they occur in pairs, such that each curve $E_s(\vec{k}_\parallel, k_z)$ has a counterpart $E_{s'}(\vec{k}_\parallel, k_z)$ with $E_{s'}(\vec{k}_\parallel, k_z) = E_s(\vec{k}_\parallel, k_z^*)$. The related electronic wave functions are free electron wave functions, which can be exponentially growing or decaying in the z-direction due to the possibly complex k_z-value.

The empty-lattice description of the complex band structure is of course not realis-

Figure 3.2: Complex band structure for the empty-lattice along the [111]-direction and through the X-point of the cubic Brillouin zone; k_z is in units of π/c_1 with $c_1 = a_c/\sqrt{3}$. The depicted path through $\vec{k}$-space extends outside the 1BZ, because $\vec{k}_\parallel = \vec{k}_M$. The solid lines denote Bloch states, while the dashed and dotted lines denote the real and imaginary parts, respectively, of k_z of the evanescent states.

Figure 3.3: The projection of the reciprocal lattice of a face-centred cubic crystal structure on a plane, perpendicular to the [111]-direction of the cubic structure. The 113 used $\vec{G}$-vectors have resulted in 31 $\vec{G}_\parallel$-vectors, which are depicted as lattice points (squares). The two-dimensional Brillouin zone is depicted by the shaded area. For $\vec{k}_\parallel = 0$ two (solid) circles centered at Γ with increasing radii are indicated, containing 7 and 13 $\vec{G}_\parallel$-vectors, respectively. For $\vec{k}_\parallel = \vec{k}_M = (2\pi/a_h\sqrt{3})\vec{e}_x$ also two (dashed) circles centred at -M with increasing radii are indicated, containing 8 and 12 $\vec{G}_\parallel$-vectors, respectively. We note that the points Γ and M are quite important, because these are the locations in the hexagonal Brillouin zone where the valence band maxima and the conduction band minima, respectively, occur for most SiC polytypes.

tic. After turning on the electron potential, the $E_s(\vec{k}_\parallel, k_z)$ curves will change drastically. However, the number of independent solutions k_z as well as the number of $E_s(\vec{k}_\parallel, k_z)$ curves will not change, if the same set of projected reciprocal lattice vectors $\vec{G}_\parallel$ is chosen.

3.1.2 Bulk $3C$ SiC

Ions in a bulk crystal are arranged in a periodic way. The ion and electron potentials follow this periodicity of the crystal and, therefore, the electronic wave function $\phi_{l,\vec{k}}$ can generally be expressed in the Bloch form:

$$\phi_{l,\vec{k}_\parallel,k_z}(\vec{r}_\parallel, z) = e^{i(\vec{k}_\parallel \cdot \vec{r}_\parallel + k_z z)} u_{l,\vec{k}_\parallel,k_z}(\vec{r}_\parallel, z), \tag{3.3}$$

in which $u_{l,\vec{k}_\parallel,k_z}(\vec{r}_\parallel, z)$ is the periodic part of the wave function with band index l and wave vector $\vec{k} = \vec{k}_\parallel + k_z \vec{e}_z$. The periodic part of the wave function can be expanded in the complete set of plane waves $e^{i\vec{G}\cdot\vec{r}}$ as

$$u_{l,\vec{k}_\parallel,k_z}(\vec{r}_\parallel, z) = \frac{1}{\sqrt{\Omega_c}} \sum_{\vec{G}} d_{l,\vec{k}_\parallel,k_z}(\vec{G}) e^{i(\vec{G}_\parallel \cdot \vec{r}_\parallel + G_z z)}, \tag{3.4}$$

where Ω_c is the volume of the primitive fcc cell and $d_{l,\vec{k}_\parallel,k_z}(\vec{G})$ denotes a plane-wave coefficient of the wave function. For infinite bulk crystals only real components of $\vec{k}$ are allowed, since the probability density of the wave function has to follow the crystal periodicity. If e.g. k_z is complex, the wave function increases or decreases exponentially in the z-direction. Wave functions for which the imaginary part of (at least) one wave vector component is non-zero are called evanescent waves. The amplitudes of evanescent waves decay and grow exponentially in opposite directions. In the SiC superlattices this applies to the c-direction in the separate $3C$ SiC building blocks. The reason is that in the building-block systems the translation symmetry along the c-axis, with respect to bulk $3C$ SiC, is broken. The translation symmetry parallel to the stacking planes, on the other hand, is not changed with respect to bulk $3C$ SiC and the component $\vec{k}_\parallel$ remains real. It will be our task to construct wave functions for polytypes by matching all types of Bloch and evanescent waves in adjacent building blocks. In this way acceptable wave functions for the polytypes as a whole may easily be constructed.

Bloch wave functions (real k_z) and evanescent wave functions (complex k_z) are both solutions of the crystal Schrödinger eigenvalue problem. The conventional way in which the one-particle energies and the related wave functions are obtained for a given (possibly complex) three-dimensional $\vec{k}$-vector, is by diagonalizing the Hamilton

matrix in e.g. the plane-wave representation of expression (3.4). For our situation (see section 3.2), however, it is more convenient to use a reverse procedure: the calculation of *all complex k_z-values* and related wave functions for a *given combination E and $\vec{k}_\parallel$*. The procedure by which we will solve this problem will be outlined for the EPM and the LDA separately.

Within the EPM, the Hamilton matrix, expanded in a plane-wave basis set, reads

$$H_{\vec{G},\vec{G}'}(\vec{k}) = \left\{ \frac{\hbar^2}{2m} \left(\vec{k} + \vec{G}\right)^2 + U_0 \right\} \delta_{\vec{G},\vec{G}'} + V^{\mathrm{EPM}}\left(\vec{G} - \vec{G}'\right), \qquad (3.5)$$

in which $V^{\mathrm{EPM}}(\vec{G})$ is a Fourier component of the empirical pseudopotential, which here is assumed to be local. For $3C$ SiC these Fourier components can be written as

$$V^{\mathrm{EPM}}(\vec{G}) = \frac{1}{2}\left(v_{\mathrm{C}}(\vec{G})e^{i\vec{G}\cdot\vec{\tau}_{\mathrm{C}}} + v_{\mathrm{Si}}(\vec{G})e^{i\vec{G}\cdot\vec{\tau}_{\mathrm{Si}}}\right), \qquad (3.6)$$

i.e. in terms of atomic pseudopotential form factors $v_{\mathrm{C}}(\vec{G})$ and $v_{\mathrm{Si}}(\vec{G})$ for C and Si, respectively. In Eq. (3.6) $\vec{\tau}_{\mathrm{C}}$ and $\vec{\tau}_{\mathrm{Si}}$ indicate the positions of the C and the Si atom inside the primitive cell, respectively (see Fig. 2.4). The values of the form factors $v_{\mathrm{C}}(\vec{G})$ and $v_{\mathrm{Si}}(\vec{G})$ have been determined for $3C$ SiC in Ref. [38] and are valid for the lattice constant $a_c = 4.35$ Å.

One important advantage of the EPM is that the very convenient diagonalization scheme of Chang and Schulman [13] can be used to yield all necessary complex k_z-values and accompanying wave functions in a straightforward way, as we will show. The eigenvalue equation for the Hamilton matrix $\underline{H}$ reads

$$\left[\underline{H}(\vec{k}_\parallel + k_z\vec{e}_z) + (U_0 - E)\underline{I}\right]\underline{d} = 0, \qquad (3.7)$$

in which the elements of the column $\underline{d}$ are $d_{l,\vec{k}}(\vec{G})$ and $\underline{I}$ denotes the unit matrix. Within the EPM case the Hamilton matrix can exactly be written as a second order polynomial in k_z. It is the kinetic operator that causes this k_z-dependence, since the empirical pseudopotential V^{EPM} is a local potential and does not depend on $\vec{k}$. The matrix on the left-hand side of Eq. (3.7) can, therefore, be written as

$$\underline{H}(\vec{k}_\parallel + k_z\vec{e}_z) + (U_0 - E)\underline{I} = \underline{H}^{(0)}(\vec{k}_\parallel, E) + \underline{H}^{(1)}k_z + \frac{\hbar^2}{2m}\underline{I}k_z^2. \qquad (3.8)$$

The elements of the matrices $\underline{H}^{(0)}$ and $\underline{H}^{(1)}$ are given by

$$H^{(0)}_{\vec{G},\vec{G}'}(\vec{k}_\parallel, E) = \left\{ \frac{\hbar^2}{2m}\left(\vec{k}_\parallel + \vec{G}_\parallel\right)^2 + \frac{\hbar^2}{2m}G_z^2 + U_0 - E \right\}\delta_{\vec{G},\vec{G}'} + V^{\mathrm{EPM}}\left(\vec{G} - \vec{G}'\right) \quad (3.9)$$

and

$$H^{(1)}_{\vec{G},\vec{G}'} = \frac{\hbar^2}{m}G_z\delta_{\vec{G},\vec{G}'}, \qquad (3.10)$$

respectively. Now, the Chang-Schulman scheme amounts to solving the eigenvalue problem

$$
\begin{bmatrix} \underline{0} & \underline{I} \\ -\frac{2m}{\hbar^2}\underline{H}^{(0)} & -\frac{2m}{\hbar^2}\underline{H}^{(1)} \end{bmatrix} \begin{bmatrix} \underline{d} \\ k_z\underline{d} \end{bmatrix} = k_z \begin{bmatrix} \underline{d} \\ k_z\underline{d} \end{bmatrix}, \tag{3.11}
$$

which is, of course, nothing but a rewritten form of Eq. (3.7). In this expression $\underline{0}$ stands for the zero matrix. The matrix in Eq. (3.11) is called the Chang-Schulman matrix. In Eq. (3.11) we encounter k_z as the eigenvalue and $d_{l,\vec{k}}(\vec{G})$ and $k_z d_{l,\vec{k}}(\vec{G})$ as elements of the eigenvector columns. It is relatively easy to solve Eq. (3.11) numerically. Assuming that the wave functions, through expression (3.4), are expanded in, say, N plane waves, the dimensions of the Hamilton matrix and the Chang-Schulman matrix are $N \times N$ and $2N \times 2N$, respectively. The number of eigenvalues k_z, which we obtain by solving Eq. (3.11), is therefore equal to $2N$, which is in agreement with the number of solutions k_z for the empty-lattice case given by Eq. (3.1). However, as mentioned in section 3.1.1, $2N - 2M$ of the $2N$ eigenvalues k_z are in fact periodic continuations. So, we have to select precisely $2M$ solutions k_z to be obtained from Eq. (3.11) with related wave functions. This selection is made by taking those k_z-values such that $\vec{k}_{\parallel} + (\text{Re } k_z)\vec{e}_z$ lies in the 1BZ or that k_z is as close as possible to $k_z = 0$.

We have depicted in Fig. 3.1 the 1BZ of the $3C$ structure. In Fig. 3.4 we have displayed a part of the complex band structure of $3C$ SiC, calculated within the EPM and using Eq. (3.11). In this band structure calculation we used $N = 113$. The displayed $\vec{k}$-direction in Fig. 3.4 coincides with the path indicated by λ in Fig. 3.1. Note that the displayed band structure includes the X-point and that the depicted $\vec{k}$-path partly sticks out of the 1BZ. The characteristic features for $3C$ SiC, which can be seen in Fig. 3.4, are the energy of the lowest conduction band edge, which is approximately equal to 2.4 eV, and the non-degeneracy of this band. The value of U_0 has been adjusted in such a way that the top of the valence bands at $\vec{k} = 0$ (or Γ) corresponds to the energy $E = 0$ eV. Note that $\vec{k} = 0$ is not included in Fig. 3.4. Consequently, all displayed valence bands have negative energy values.

Within the LDA, the calculation of the complex band structure is less straightforward than within the EPM. It is impossible to use the Chang-Schulman scheme within the LDA, because of the complicated analytical form of the non-local ion potentials of Si and C [2, 23]. Approximating these ion potentials by a second order Taylor expansion in k_z turns out to be very inaccurate. Moreover, due to the deep p-potential of the C ions, the plane-wave expansion of the wave functions requires at least about 350 plane waves, before the diagonalization procedure of the Hamilton matrix yields sufficiently accurate energy eigenvalues. This means that the dimensions of the Chang-Schulman matrix would become very large, namely 700×700, and that

Figure 3.4: Complex band structure for 3C SiC along the [111]-direction and through the X-point of the cubic Brillouin zone; k_z is in units of π/c_1. The depicted path through $\vec{k}$-space extends outside the 1BZ, because $\vec{k}_\parallel = \vec{k}_M$. The solid lines denote the Bloch states, while the dashed and dotted lines describe the real and imaginary parts, respectively, of k_z of the evanescent states.

the diagonalization, already for this reason, would anyhow be unmanageable from a computational point of view. In spite of this, we succeeded in calculating the relevant parts of the complex band structure of 3C SiC. We accomplished this by calculating in the first place the Bloch band structure with pertaining wave functions of 3C SiC within the LDA, by means of the usual diagonalization procedure of the Hamilton matrix. This ensures that the energy and the k_z-values are accurate. Subsequently, we used the already calculated complex band structure from the EPM as a guide to locate globally the complex branches of the LDA band structure. The precise location of the complex LDA branches $k_z^s(E)$ were then subsequently found with help of a trial and error method. In order to achieve this, we adjusted the complex k_z-values in such a way that the energy eigenvalue of the (now non-Hermitian) Hamilton matrix gives rise to a real energy (i.e. Im $E = 0$). Within this method we have therefore performed many successive diagonalizations of the Hamilton matrix at slightly different complex $\vec{k}$ to obtain accurate (real) energies and (complex) k_z-values. The accompanying wave functions at complex $\vec{k}$ directly follow from the eigenvectors of the Hamilton matrix.

For the calculation of the 3C SiC Hamilton matrix within the LDA we made use of the *ab initio* norm-conserving ionic pseudopotentials for C and Si of Bachelet *et al.* in Ref. [2] and the experimental lattice constant ($a_c = 4.3596$ Å) [48]. Furthermore, we used the exchange potential of Kohn and Sham in Ref. [45] and the correlation potential given by the Wigner interpolation formula in Ref. [28].

3.1.3 Twisted band structure

As already mentioned, besides the complex band structure of the untwisted basis material 3C SiC, we need also the complex band structure, with accompanying wave functions, of the twisted material. A straightforward way in which this so-called twisted band structure can be obtained, is by performing a completely similar band structure analysis as for the basis 3C SiC material, however, with all atoms rotated over 60°, 180° or 300° around the c-axis.

It is easier, however, to obtain this twisted complex band structure by exploiting the symmetry properties of the Hamiltonian of the untwisted material. The reasoning goes as follows: At real $\vec{k}$ the Hamiltonian $H(\vec{k})$ is Hermitian, but at complex $\vec{k}$ it is not. However, H always satisfies the property $H^\dagger(\vec{k}) = H(\vec{k}^*)$. By restricting ourselves to real energies E and real wave vector components $\vec{k}_\parallel$ this property implies that $E(\vec{k}_\parallel + k_z \vec{e}_z) = E(\vec{k}_\parallel + k_z^* \vec{e}_z)$. This means that a fixed combination of E and $\vec{k}_\parallel$ gives rise to the solution pair k_z and k_z^* (see also section 3.1.1). The wave functions have the property of invariance under time reversal, which implies that whenever $\psi_{\vec{k}}$ is a stationary solution

also $\psi_{\vec{k}}^*$ is one with the same energy $E(\vec{k}) = E(-\vec{k}^*)$. The combination of these two properties yields $E(\vec{k}_\parallel + k_z\vec{e}_z) = E(\vec{k}_\parallel + k_z^*\vec{e}_z) = E(-\vec{k}_\parallel - k_z^*\vec{e}_z) = E(-\vec{k}_\parallel - k_z\vec{e}_z)$. So, if we found all k_z-solutions for a certain E and $\vec{k}_\parallel$, all solutions for the same E but $-\vec{k}_\parallel$ are likewise found.

This is of interest, since the twisted $3C$ material becomes identical to the untwisted $3C$ material after a rotation over $180°$ around the c-axis. Thus, the relevant solutions k_z of the Schrödinger problem for the twisted layer at E and $\vec{k}_\parallel$ can be obtained by solving the problem for the untwisted layer at the same E but $-\vec{k}_\parallel$! Hence, for a common E and $\vec{k}_\parallel$ this implies that if k_z and k_z^* are two solutions belonging to the untwisted layer, then $-k_z$ and $-k_z^*$ are two solutions for the twisted layer. For Fig. 3.4, in which the complex band structure of untwisted $3C$ SiC is displayed, this implies that the complex band structure for the twisted material can be obtained by reflecting this figure with respect to the axis $k_z = 0$.

The necessary wave functions of the twisted material can be obtained by transforming the corresponding wave functions of the untwisted material. From the time reversal property it followed that the wave functions are connected as $\psi_{E,-\vec{k}_\parallel,-k_z^*}(\vec{r}) = \psi_{E,\vec{k}_\parallel,k_z}^*(\vec{r})$. If, for a certain combination of E and $\vec{k}_\parallel$, a solution k_z with related $\psi_{E,\vec{k}_\parallel,k_z}(\vec{r}) = e^{i(\vec{k}_\parallel \vec{r}_\parallel + k_z z)} u_{E,\vec{k}_\parallel,k_z}(\vec{r})$ is already found for the untwisted basis material $3C$ SiC, then the transformed solution for the twisted material is $-k_z^*$ with related wave function $e^{-i(\vec{k}_\parallel \vec{r}_\parallel + k_z^* z)} u_{E,\vec{k}_\parallel,k_z}^*(\vec{r})$, which is the complex conjugate of (the already found) $\psi_{E,\vec{k}_\parallel,k_z}(\vec{r})$. By this, every k_z (being part of $2M$ solutions) with related wave function of the untwisted basis material corresponds to exactly one k_z-solution, with related wave function, of the twisted material.

3.2   Superlattice band structure method for polytypes

In section 3.2.1 we will present the method which we will use to calculate the band structure of polytypic superlattices. In a way, this method can be regarded as a generalization of the one-dimensional Kronig-Penney model to a real (three-dimensional) *crystal*. We use the polytypic superlattice $6H$ SiC as an example to demonstrate the determination of the characteristic equation, from which the superlattice band structure results. The determination for the other polytypic superlattices runs in a analogous way. In section 3.2.2 we will present the results of our calculations.

Figure 3.5: *The indexing of the layers and the interfaces for the 6H structure.*

3.2.1 Interface matching of wave functions

We start by giving indices to the successive layers in the $6H$ SiC polytype. In Fig. 3.5 we have indicated three successive layers (or building blocks) of the superlattice, by $j = 1, 2$ and 3. The layers $j = 1$ and $j = 3$ consist each of 3 bilayers of twisted $3C$ SiC material (indicated by ACB). Layer $j = 2$ consists of 3 bilayers of untwisted $3C$ SiC material (indicated by ABC). Note that $z_{j-1} \leq z \leq z_j$ defines the region of layer j, where $z_j = z_0 + 3jc_1$ gives the successive interface positions. We choose z_0 to be equal to $z_0 = -3c_1$.

Via the complex band structure analysis of $3C$ SiC we have for each layer j in principle at our disposal all possible and independent k_z^j-solutions, with related wave functions, for any combination of energy E and parallel wave vector $\vec{k}_\parallel$. We will use these solutions to construct wave functions pertaining to the superlattice, which can generally be written as

$$\psi_{l, \vec{k}_\parallel, K_z}(\vec{r}_\parallel, z) = e^{i(\vec{k}_\parallel \cdot \vec{r}_\parallel + K_z z)} u_{l, \vec{k}_\parallel, K_z}(\vec{r}_\parallel, z), \qquad (3.12)$$

with $\vec{k}_\parallel + K_z \vec{e}_z$ as the wave vector of the superlattice wave function. In each layer j the superlattice wave function at given E and $\vec{k}_\parallel$ can quite generally be written as a linear combination of the $3C$ (basis) wave functions $\phi^j_{E, \vec{k}_\parallel, k_z^{j,s}}$, i.e.

$$\psi^j_{E, \vec{k}_\parallel}(\vec{r}_\parallel, z) = \sum_{s=1}^{2M} \alpha^j_s \phi^j_{E, \vec{k}_\parallel, k_z^{j,s}}(\vec{r}_\parallel, z), \qquad (3.13)$$

where in all wave functions we have replaced the band index by the corresponding energy E. The unknown variables in Eq. (3.13) are the coefficients α^j_s. The $3C$ wave

functions in Eq. (3.13) can be written as

$$\phi^j_{E,\vec{k}_\parallel,k^{j,s}_z}\left(\vec{r}_\parallel,z\right) = \sum_{\vec{G}_\parallel}^{M} e^{i\left(\vec{k}_\parallel+\vec{G}_\parallel\right)\cdot\vec{r}_\parallel} v^{j,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}\left(z-z_{j-1}\right), \tag{3.14}$$

i.e. in terms of M z-dependent two-dimensional Fourier-components $v^{j,s}$, which are

$$v^{j,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}(z) = e^{ik^{j,s}_z z} \sum_{G_z(\vec{G}_\parallel)} d_{E,\vec{k}_\parallel+k^{j,s}_z\vec{e}_z}(\vec{G}_\parallel + G_z\vec{e}_z)\, e^{iG_z z}. \tag{3.15}$$

In this expression the summation is meant to take place over all G_z pertaining to the indicated $\vec{G}_\parallel$. Note in Eq. (3.14) that we shifted the arguments of each $v^{j,s}$ towards its left interface position z_{j-1}. Such a shift in the [111]-direction of $3C$ SiC is allowed, as far as it concerns a distance that is equal to an integral multiple of the $3C$ period length of ABC, which is $3c_1 = a_c\sqrt{3}$. We have applied these shifts to keep the values of the arguments of the $v^{j,s}$ functions relatively small. Otherwise numerical problems will arise, since the functions $v^{j,s}$ in expression (3.15) contain exponential parts $e^{ik^{j,s}_z z}$, in which the complex $k^{j,s}_z z$-values can have (extremely) large imaginary parts. Now, by replacing z by $z - z_{j-1}$ in each $v^{j,s}$, as we have done in Eq. (3.14), we avoid large values $|\mathrm{Im}\, k^{j,s}_z z|$ and therefore circumvent numerical problems. Substituting Eq. (3.14) in Eq. (3.13) yields for the superlattice wave function in layer j

$$\psi^j_{E,\vec{k}_\parallel}\left(\vec{r}_\parallel,z\right) = \sum_{\vec{G}_\parallel}^{M} e^{i\left(\vec{k}_\parallel+\vec{G}_\parallel\right)\cdot\vec{r}_\parallel} \sum_{s=1}^{2M} \alpha^j_s v^{j,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}\left(z-z_{j-1}\right). \tag{3.16}$$

In order to properly connect the wave functions in the three layers $j = 1, 2$ and 3, we have to specify matching prescriptions for the superlattice wave function at the three interfaces $z = z_1 = 0$, $z = z_2 = 3c_1$ and $z = z_3 = 6c_1$, respectively. The matching prescriptions (i.e. the boundary conditions) have in the first place to be such that the constructed superlattice wave function is continuous and continuously differentiable at any position $\vec{r}_\parallel$, located on the interface planes at $z = z_1$ and $z = z_2$. To achieve this, we have to demand that each of the M Fourier-coefficients appearing in Eq. (3.16) is continuous and continuously differentiable at these two interfaces. Imposing these boundary conditions, we obtain for each $\vec{G}_\parallel$

$$\sum_{s=1}^{2M} \alpha^j_s v^{j,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}(3c_1) = \sum_{s=1}^{2M} \alpha^{j+1}_s v^{j+1,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}(0) \tag{3.17}$$

and

$$\sum_{s=1}^{2M} \alpha^j_s \frac{\partial v^{j,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}(3c_1)}{\partial z} = \sum_{s=1}^{2M} \alpha^{j+1}_s \frac{\partial v^{j+1,s}_{E,\vec{k}_\parallel,\vec{G}_\parallel}(0)}{\partial z}, \tag{3.18}$$

which we apply for $j = 1$ and $j = 2$. This gives $4M$ conditions for $6M$ unknown coefficients α_s^j. In the second place we have to demand that the wave function to be constructed satisfies the Bloch condition for the $6H$ superlattice, which condition reads

$$\psi_{E,\vec{k}_\parallel}(\vec{r}_\parallel, L) = e^{iK_z L}\psi_{E,\vec{k}_\parallel}(\vec{r}_\parallel, 0), \tag{3.19}$$

where $\vec{k}_\parallel + (\mathrm{Re}\,K_z)\vec{e}_z$ is a wave vector lying in the 1BZ of $6H$ SiC and the length $L = 6c_1$ represents the period of the $6H$ supercell in the c-direction (see Fig. 3.5). Eq. (3.19) gives the remaining $2M$ conditions for the $6M$ unknowns.

The boundary Eqs. (3.17) and (3.18) can be written in matrix form:

$$D^j(3c_1)\underline{\alpha}^j = D^{j+1}(0)\underline{\alpha}^{j+1}, \tag{3.20}$$

in which the dimensions of D are $2M \times 2M$ and the subscripts E and $\vec{k}_\parallel$ have been omitted. The elements of the matrices D follow in an obvious way from Eqs. (3.17) and (3.18). Imposing the superlattice Bloch condition between the boundaries at $z = z_1$ and $z = z_3$ yields the characteristic equation

$$\left[D^2(0)\right]^{-1} D^1(3c_1)\underline{\alpha}^1 = e^{iK_z L}\left[D^2(3c_1)\right]^{-1} D^3(0)\underline{\alpha}^1, \tag{3.21}$$

which is a generalized eigenvalue equation with $e^{iK_z L}$ as the complex eigenvalue. The coefficients α_s^1, pertaining to layer $j = 1$, appear in Eq. (3.21) as the elements of the eigenvector columns $\underline{\alpha}^1$. The coefficients for the next two layers, $j = 2$ and 3, can subsequently be obtained by substituting $\underline{\alpha}^1$ in Eq. (3.20). Consequently, we can construct the superlattice wave function throughout the entire superlattice. For cases in which $|e^{iK_z L}| = 1$ we have in fact constructed a Bloch wave function, which is propagating through the entire superlattice without loosing its amplitude. From the eigenvalue $e^{iK_z L}$ we can deduce K_z, which represents the thus far unknown wave vector component in expression (3.12). Obviously, in this case K_z is real and the *superlattice Bloch band structure* is given by $E(\vec{k}_\parallel, K_z)$. If, on the other hand, $|e^{iK_z L}| \neq 1$ we have found a complex solution K_z related to a wave function which does not have a constant amplitude and, consequently, is a part of the *complex* band structure of the superlattice.

3.2.2 Band structure results

By solving the characteristic Eq. (3.21) for different combinations of energy E and wave vector component $\vec{k}_\parallel$ it is in fact possible to obtain the complete (complex) band structure of the superlattice. To confine this superlattice band structure to the 1BZ of the superlattice, it is necessary to restrict $\vec{k}_\parallel$ to its hexagonal ground plane, which

Figure 3.6: First Brillouin zone pertaining to the hexagonal Bravais lattice with symmetry points Γ, M, L, A, K and H. The cubic [111]-direction runs parallel to the ΓA-line and is indicated as the k_z-axis. The complex band structure in this thesis is always calculated for a fixed $\vec{k}_\parallel$, along a path parallel to this k_z-axis.

we have indicated in Fig. 3.3 by the shaded area. The 1BZ of a hexagonal polytype superlattice is depicted in Fig. 3.6. In Fig. 3.7 we have displayed a part of the calculated complex superlattice band structure for $6H$ SiC in the energy region between -4 and 5 eV. For this calculation we have chosen the component $\vec{k}_\parallel$ equal to $\vec{k}_M = (2\pi/a_h\sqrt{3})\vec{e}_x$. The reason for this choice is that we are interested in finding the band edge of the lowest conduction band in $6H$ SiC. This band edge is expected to lie in or near $\vec{k}_M$, as it is known that in $3C$ SiC it lies in $\vec{k}_X$. It is easily shown that if we consider $3C$ SiC in the larger $6H$ SiC cell, the point $\vec{k}_X$ (of the 1BZ of $3C$ SiC) reduces to $\vec{k}_M$ (of the 1BZ of $6H$ SiC). Indeed, by choosing other $\vec{k}_\parallel$ vectors it is invariably found that always higher conduction band states of $6H$ SiC are found. Fig. 3.7 represents the complex band structure along the M-L symmetry axis of the $6H$ Brillouin zone. For this superlattice calculation we used the EPM for the basis material $3C$ SiC. In the calculations all interface positions have been assumed to be located in the middle of a Si-C pair pertaining to the h-bilayers (see Chapter 2). The number of $3C$ wave functions used in this calculation is $2M = 16$.

By calculating the $6H$ SiC band structure along a variety of parallel directions as well, we are able to find those points $\vec{k} = \vec{k}_\parallel + K_z\vec{e}_z$ at which the valence bands have their energy maximum and the conduction bands have their energy minimum. We have found that the top of the valence band for $6H$ SiC, as in fact for all other polytypes, is located at the Γ-point of the 1BZ, albeit with a very small energy shift with respect to the valence top energy in $3C$ SiC. The bottom of the lowest conduction band for $6H$

Figure 3.7: Complex band structure for 6H SiC along the ML-axis of the 1BZ, as obtained by the described transmission method; K_z is in units of $\pi/6c_1$. The solid lines denote Bloch states, while the broken and dotted lines describe the real and imaginary parts, respectively, of K_z of the evanescent states. A camel's back type of minimum is visible (arrow) for the lowest conduction band.

SiC has been found not precisely in the point $\vec{k}_{\mathrm{M}}$, but on the ML-axis, shifted by 40 % to the L-point. Such a type of minimum is called a camel's back and has been indicated by the arrow in Fig. 3.7. Experiments [19, 54] seem to confirm that this minimum is located between $\vec{k}_{\mathrm{M}}$ and $\vec{k}_{\mathrm{L}}$. The conclusion is that the calculated band gap of $6H$ SiC is indirect, i.e. between $\vec{k} = 0$ (valence band maximum) and $\vec{k}$ on the ML-axis (conduction band minimum). We note furthermore that due to the appearance of this camel's back in $6H$ SiC, both the theoretical and the experimental band gap energy slightly deviate from the interpolating line in Fig. 1.2. The value of $2M$, used in our calculation in order to obtain well-converged results, appears to be dependent on the magnitude and the direction of the particular $\vec{k}_{\parallel}$ and satisfies generally $2M < 30$. The wave functions of the basis material have been expanded in 113 plane waves. It has been checked that incorporation of more plane waves has only minor influence on our results. In this way, convergence of the indirect gap value has been achieved within 0.02 eV.

A noteworthy way of checking our superlattice method is by using untwisted $3C$ SiC material in our $6H$ superlattice configuration. Replacing in the $6H$ SiC building-block system the twisted layers by untwisted layers, we have nothing but pure $3C$ SiC material. The result of applying the method to this system should therefore be identical to the input band structure of $3C$ SiC! In Fig. 3.8 we have displayed the result of this calculation, in which we fixed $\vec{k}_{\parallel} = \vec{k}_{\mathrm{M}}$ and varied the energy between -4 and 5 eV, again. Note that the complex $3C$ SiC band structures depicted in Fig. 3.8 and Fig. 3.4 have a different appearance. This is, however, completely due to the fact that the $3C$ band structure depicted in Fig. 3.8, has been folded into the $6H$ Brillouin zone.

The complex band structure of all other polytypic superlattices of SiC can be calculated in a way completely similar to the above procedure for the $6H$ case. In Table 3.1 we give a summary of the calculated band gaps within the EPM for ten polytypes, together with the available experimental values. Note from Table 3.1 that the variation of the calculated band gaps among the superlattices results for the main part from the clearly significant shift of the energy position of the lowest conduction band with respect to the one of $3C$ SiC. The energy variation of the highest valence band, with respect to the one of $3C$ SiC, though present, is of minor importance.

Comparing our results, obtained within the EPM, with the experimental gap values as obtained by Choyke *et al.* [18, 55], it should be remarked that the values according to these authors suffer from inaccuracies in the order of 0.015 eV. Their reported values refer, moreover, to exciton gaps, which are typically up to 0.03 eV [48] lower than the electronic band gaps. In view of this, the agreement between our EPM results, as presented in Table 3.1, and the experimental data is very satisfactory indeed, except

Figure 3.8: *Complex band structure for 3C SiC along the ML-axis of the 1BZ, as obtained by the described transmission method; K_z is in units of $\pi/6c_1$. The displayed band structure is the result of folding the 3C SiC band structure into the 1BZ of the 6H structure. The indicated M-point is equivalent to the X-point of the fcc Brillouin zone. The solid lines denote Bloch states, while the broken and dotted lines describe the real and imaginary parts, respectively, of K_z of the evanescent states.*

Table 3.1: *The hexagonality h (in %) and the band gaps $E_c - E_v$ (in eV) of ten SiC polytypes, as obtained by our superlattice method within the EPM and as found in experiment. We have also tabulated the energy levels (in eV) of the highest valence band edge E_v (at Γ) and the lowest conduction band E_c (at M, except for 6H) with respect to the energy levels in 3C SiC. The conduction band edge for 2H SiC is found to be located in M, the experimental gap value, however, is found at K. (The gap value of 2.40 eV for 3C SiC has been obtained to check our procedure, by performing the superlattice method in the 6H unit cell for merely untwisted layers.)*

Polytype	h	E_v	E_c	Calc. gap $E_c - E_v$	Expt. gap; Refs.[18, 55]
3C	0	0	2.40	2.40	2.390, 2.389, 2.416
24H	8.3	-0.04	2.41	2.45	
18H	11.1	0.00	2.47	2.47	
12H	16.7	0.03	2.60	2.57	
10H	20	0.04	2.70	2.66	
8H	25	0.04	2.80	2.76	2.80, 2.86
6H	33.3	0.04	3.09	3.05	3.023, 2.86
15R	40	0.05	3.08	3.03	2.986, 3.05
4H	50	0.06	3.34	3.28	3.265, 3.20
2H	100	0.10	4.14	4.04	3.330

for $2H$. This agreement implies that we find an almost linear relationship between gap and hexagonality percentage for $15\% \lesssim h \leq 50\%$. In Fig. 3.9 we have displayed the relationship between band gap and hexagonality. For very small h-values $h \lesssim 15\%$ we predict, however, deviations from the "linear" behavior. All considered polytypes happen to be indirect. Except for the $2H$ and the $6H$ case, the band gap is between the Γ- and the M-point. For $6H$ SiC the conduction band minimum lies on the ML-axis, as mentioned above, while it is located in the K-point for $2H$ SiC. The deviation between our calculated $2H$ gap and the experimental gap within the EPM is considerable. This is not unexpected, as $2H$ SiC is the only case, considered by us, in which the layers are as small as one bilayer. Indeed, the assumption that single bilayers exhibit $3C$ SiC character is rather provocative, as we already noticed in Chapter 2. Because the $2H$ polytype itself is an exception, hypothetical SiC superlattices which are composed of this $2H$ polytype are exceptions to our $3C$ building-block approach as well. In this connection it is worth mentioning that Käckell and Bechstedt [42] have recently calculated band gaps for the hypothetical SiC superlattices $(3C)_4(2H)_3$ and $(3C)_2(2H)_6$ but also $(3C)_2(4H)_3$ and $(3C)_2(6H)_2$ which are *smaller* than the $3C$ SiC band gap.

In Table 3.2 we give a summary of the band gaps, as calculated within the LDA (so-called Kohn-Sham gaps), for eight polytypes and a comparison with other theoretically obtained values, as obtained within the LDA. The LDA results yield the same almost linear relationship between (Kohn-Sham) gap and h. When raised by a *common* constant value of 1.2 eV the experimental gaps are reproduced! This necessary energy shift of 1.2 eV, indicated in Fig. 3.9, and suggestively called the quasiparticle shift Δ_{QP} is to be identified with the self-energy correction obtained within the GW theory and has to be added due to an inherent failure of the DFT. This failure arises because LDA (and DFT) is a theory about the ground state and does not cover excited-state properties as band gaps. In Chapter 5 we will pay attention to, and actually calculate, the so-called quasiparticle shift for $3C$ SiC. Our LDA gaps, as given in Table 3.2, agree reasonably well with the LDA gaps obtained from other theoretical investigations, in which the band gaps were calculated in a self-consistent way. We will comment on this in the next section.

3.3 Deviations from the flat-band approximation

So far, our calculations have been performed by assuming the successive layers (the building blocks) to be entirely $3C$ SiC bulk-like. This assumption is widely known as the flat-band approximation. In Chapter 2 we have already argued that this building-block representation of the SiC polytypes is not completely perfect. One of the differences

Figure 3.9: The band gaps of SiC polytypes as a function of the hexagonality h, as obtained by experiment (filled circles), by EPM matching (open circles), by LDA matching (open squares) and by a self-consistent LDA calculation [41] (asterisks). Note the overall shift Δ_{QP} bringing the LDA results in accordance with experiment, as well as with the results obtained within EPM. The depicted interpolating curves are the result of the analysis of Chapter 4.

Table 3.2: *The hexagonality h (in %) and the Kohn-Sham energy gaps (in eV) of eight SiC polytypes, as obtained by our superlattice method within the LDA and by other authors.*

Polytype	h	Present theory	Ref.[41]	Ref.[53]	Ref.[47]
$3C$	0	1.22	1.27	1.24	1.38
$24H$	8.3	1.26			
$18H$	11.1	1.32			
$12H$	16.7	1.41			
$10H$	20	1.51			
$8H$	25	1.62			
$6H$	33.3	1.83	1.96	1.98	2.0
$4H$	50	2.05	2.18	2.14	2.4

between a true polytype and a building-block one manifests itself in the charge-density, which most notably differs near the interfaces. We have estimated in Chapter 2 that this charge density difference is relatively small, but we did not actually estimate its influence on the band gap. One of the reasons why we have applied our superlattice method within the LDA is that it yields more reliable potential distributions so that effects due to the difference potential can be determined with much more precision than within the EPM.

Due to limitations within the LDA-method itself, the difference potential between a true polytype and a building-block (made) one can only be calculated for those SiC polytypes with relatively small unit cells, $3C$, $2H$, $4H$ and $6H$, say. We will restrict our investigation of the difference potential and its effect on certain energy levels to the $6H$ superlattice. We have therefore determined both the $6H$ SiC and the $3C$ one-electron potential by performing (full) self-consistent LDA calculations. This potential is the sum of the contributions of all the Si and the C ion potentials, the Hartree, the exchange and the correlation potential. The difference potential has been obtained by subtracting the building-block potential, which is derived from the self-consistent potential of $3C$ SiC, from the $6H$ potential. As already noted in Chapter 2, it appears that the calculated difference potential is quite small with respect to the amplitudes of the $6H$ and $3C$ potentials and is only appreciably non-zero near the interfaces (at most

2 % of the amplitudes) in those regions. In order to guarantee a proper subtraction procedure the potentials of $3C$ and $6H$ SiC have both been calculated in the $6H$ unit cell. In our building-block calculations we positioned, as usual, the interface exactly in the middle of a Si-C bond of an h-bilayer.

Since the potential difference appears to be quite small, we will treat it as a perturbing potential. We estimate the correction to the indirect band gap energy value due to this perturbing potential by calculating its effect on energy levels to first order, i.e. by taking the expectation value of the difference potential in the relevant electron states. For the calculation of this expectation value we use the superlattice wave functions at the valence band maximum and the conduction band minimum, obtained from our interface method. The calculated correction for the $6H$ band gap amounts to 0.06 eV. This gap correction is small in comparison to the building-block (LDA) gap value of 1.83 eV. The small increase of the band gap due to the difference potential is due to a lowering of the valence band top by 0.04 eV and a rise of the lowest conduction band edge by 0.02 eV. These corrections to the energy levels of the band edges are the result of differences in the *local* parts of the potentials. Effects due to the *non-local* parts, which arise in the ionic potentials, can be estimated to be completely negligible if the interface is positioned in the middle of an h-type of Si-C pair. The spatial range of the non-local parts of the C and Si ion potentials, in which their contributions are significant to the total potential, is of the order of 0.8 Å. This range is smaller than the distance from a Si or a C atom to the nearest interface, which is 0.94 Å. This implies that possible effects due to the non-local parts of the ion potentials can safely be neglected.

Considering the self-consistent calculations obtained by other authors in Table 3.2, our correction result explains partly why our calculated $6H$ Kohn-Sham gap is somewhat lower than the self-consistent $6H$ results of other authors. The other part of the discrepancy comes from our calculated band gap value for $3C$ SiC, which is somewhat smaller than that of other authors. This discrepancy is caused by differences in the used lattice constant and the utilized ion, exchange and correlation potentials for the LDA calculation of $3C$ SiC. Anyhow, keeping in mind that the experimental variance for SiC band gaps is of the order of 0.1 eV, we conclude that the above estimated band gap correction is small and relatively unimportant. For $2H$ SiC this correction is expected to be rather large.

3.4 Remaining remarks

So far we have demonstrated the applicability of our superlattice method to the building-block made SiC polytypes as well as its justification in predicting energy eigenvalues. In this section we will pay attention to (i) an alternative for the presented superlattice band structure method, (ii) the influence of the choice of the interface position on the gap results (within the EPM), (iii) the influence of the choice of the $3C$ SiC form factors within the EPM and (iv) differences in the application of the method within either EPM or LDA.

(i) The method presented in section 3.2 is not the only possible method to calculate electronic properties of building-block made polytypes. An alternative method is to start again with the building-block representation for a certain SiC polytype. Subsequently we determine for any SiC polytype the building-block potential in exactly the same way as we have done for the $6H$ building-block valence-charge density in Eq. (2.2). The Fourier components of this building-block potential can now be used to calculate the matrix elements of the Hamilton matrix, pertaining to the polytype under consideration. Diagonalization of this matrix yields all energy eigenvalues and related wave functions of the considered polytype superlattice. It will be clear, due to the possibly large supercell dimension along the c-axis, that this alternative method requires a large number of plane waves in order to obtain sufficiently converged results. This alternative method is applicable both within the EPM and the LDA, albeit somewhat complicated in the LDA case due to the occurrence of non-local parts of the ion potenials. We applied this alternative method to the case of $6H$ SiC and found results completely similar to the earlier obtained results.

(ii) Our superlattice method contains one parameter, the interface position, which has to be chosen. The effect of varying this position is that the shape of the building-block potential in the very vicinity of the interface planes is modified. To this end, we have investigated for $6H$ and $2H$ SiC the dependence of the gap value and the location of the conduction band edges on the position choice of the interface planes. In previous calculations we have always positioned the interfaces exactly in the middle of a Si-C pair of an h-bilayer, as we found for this position that both the charge density (see Chapter 2) and the potential of the building-block system agree best with the ones of the true polytype. By varying the interface position over one bilayer we have observed that the $6H$ gap value varies at most 0.1 eV. Moreover, we have observed that the location of the conduction band edge hardly changed for $6H$. The location of the valence band edge remained at Γ. These observations hold for other polytypes as well, except for $2H$. We recall, however, that the difference between our previously calculated

2H gap and the experimental gap is anyhow considerable. Neither the location of the lowest conduction band nor the energy value is in agreement with experimental results. We have observed that the 2H gap value strongly depends on the interface position. Varying the interface position over a distance of one bilayer changed the 2H gap by no less than 1 eV. Actually, we could reproduce the experimental gap value of 3.3 eV *as well as* the location by shifting the interface planes somewhat towards the C planes, the distance ratio to C and Si being roughly 3/7 instead of the earlier 1/1 ratio. The location of the indirect minimum changes from M to K, which is in agreement with experiment! This means that the experimental band gap value of 2H SiC is within the reach of our building-block description. However, there is no *a priori* reason for the choice 3/7 and therefore we must conclude that the validity of our building-block representation for 2H is doubtful.

(iii) In our EPM approach to 3C SiC we made use of the form factors of Ref. [38]. These form factors were determined with the help of experimental energy levels of 3C SiC which were available at that time. Recent experimental investigations, however, lead to different values of some energy levels. For instance, new measurements [47] of the *direct* band gap (at Γ) of 3C SiC give 7.59 eV, where earlier measurements [48] gave 6.0 eV and even 4.6 eV. This new experimental value of the direct band gap is, among other energy gap values in 3C SiC, in very good agreement with the theoretical result of our *GW* calculation, which we will present in Chapter 5. In view of this we have determined a whole new set of form factors, in such a way that the 3C SiC energy levels of the lowest conduction band and the two highest valence bands are in good agreement with our *GW* results and (new) experimental data. Using these new form factors, we have obtained for 3C SiC a new complex band structure, with new wave functions. Application of these new ingredients in our superlattice method, however, yields almost the same *indirect* band gap values for the polytypes with $h \leq 50\%$. This proves that the previous calculation, which made use of the form factors of Ref. [38], can be considered reliable.

(iv) We first recall the laborious way (see section 3.1.2) in which the relevant parts of the complex band structure with related wave functions were calculated within the LDA. Secondly, we remark that the number of plane waves necessary to expand the 3C wave functions in the LDA is about 350, contrary to the EPM in which we need only 113 plane waves. Carrying out the matching procedure with 350 plane waves gives rise to problems concerning the convergence of the derivatives of the wave functions. The higher plane-wave coefficients (say those beyond the first 113) are not as well converged as the lower ones. This causes inaccuracies in the wave functions and, especially, in their derivatives. The result of this was sometimes that the absolute values of the

calculated eigenvalues $e^{iK_z L}$ deviated more than 10% from ideal value of 1. Strictly speaking this means that an evanescent state has been found with a small (not zero) imaginary value of K_z but, nevertheless, can be identified with a superlattice Bloch state with wave vector component Re K_z. Omitting the higher plane-wave coefficients appeared to remedy this problem. Therefore, we have calculated the complex band structure and the Bloch and the evanescent wave functions using 387 plane waves for $3C$ SiC, but used only 113 plane-wave coefficients in the matching procedure, which is in accordance with the EPM. These first 113 plane-wave coefficients are sufficiently converged. We have confirmed this consideration by a calculation of the $3C$ wave functions using approximately 660 plane waves and using only 169 of them in the matching procedure.

3.5 Conclusions

In conclusion, we have successfully applied our superlattice method to several building-block made SiC polytypes. For the EPM we can say that our band gap results for the SiC polytypes with $h \leq 50$ % are in good agreement with the experimental data. The validity of our building-block representation for $2H$ SiC, which contains building blocks as small as one bilayer, is doubtful and the superlattice method does not yield the experimental gap value of $2H$ SiC. Ignoring the generally known underestimation of the band gap within the LDA, we have also obtained good gap results within the LDA for SiC polytypes with $h \leq 50$ %. From the LDA gap results we have observed the necessity of a common quasiparticle energy correction to bring the calculated Kohn-Sham gaps in agreement with experiment for polytypes with $h \leq 50$ %. We may pose that the experimentally observed behavior, of increasing polytype band gap with increasing hexagonality up to $h \leq 50$ % has been theoretically reproduced by our superlattice method. Our calculations confirm the experimental observation of a nearly linear relation between band gap and hexagonality for SiC polytypes with 15 % $\lesssim h \leq 50$ %. We predict, furthermore, that for SiC polytypes with small hexagonalities $h \lesssim 15$ % the band gaps are smaller than the ones predicted by the linear interpolation of Choyke *et al.*. This prediction for small hexagonalities can be considered to be reliable, since small hexagonalities correspond to relatively large building blocks, for which the method should work best.

Chapter 4

The band gap variation in SiC polytypes

So far, we have successfully calculated the band gaps of SiC polytypes with $h \leq 50$ % and reproduced the experimental gap variation. This reproduction confirms our central assumption that these polytypes can to a high degree be considered as building-block structures, in which the building blocks are mutually twisted *bulk-like* fragments of $3C$ SiC. The band gap of a SiC building-block system appears to be dependent on the sizes of the participating building blocks. Thus far, however, we have not yet answered the questions (i) how the band gap variation comes about for a piling-up of differently sized building blocks and (ii) which characteristic features of $3C$ SiC can be held responsible for the band gap variation.

To answer the first question, we will give in the present chapter a description of the polytypic dependence of the SiC band gaps in terms of a one-dimensional model [6]. In this description emphasis is put on the essential transmission characteristics at interfaces which, together with the variation in building-block sizes in the polytypes, form the basis for the understanding of the band gap variation phenomenon. Our model comprises the essence of the formation of the lowest conduction band state in the polytypes. The polytypic dependence of the energy of the highest valence band states, which in principle has to be considered as well, happens to be of much less importance (see Chapter 3), and can safely be neglected.

The rise of the energy level of the lowest conduction band with decreasing building-block sizes, which is the striking phenomenon for SiC polytypes, is at first sight similar to the quantum mechanical behavior of the energy of a particle which is confined to a box (or quantum well) for changing box (or well) sizes. In line with this idea, Dubrovskiĭ and Lepneva [25] proposed a one-dimensional model to explain the variation of the

lowest conduction band energy, namely a Kronig-Penney model with a periodic array of rectangular potential barriers. They assumed that the potential barriers are located in the h-layers and used barrier heights of about 2 eV. To check whether this can be justified we have calculated the difference of the x, y-averaged potential between the h- and k-layers. The result of this calculation in $6H$ SiC is that this difference potential is less than 0.1 eV. This means that the use of their Kronig-Penney model cannot be justified, as the average potential in h- and k-layers do not differ as much as 2 eV. Moreover, their model cannot be considered as predictive anyhow, as for each polytype the rectangular potential wells and the effective mass of the electrons have to be adjusted in order to achieve best agreement with experimental data. The band gap variation in differently sized SiC building-block systems clearly has a different origin.

In order to understand the band gap variation in the SiC building-block systems it is essential to deal with the electronic scattering properties at one polytypic SiC interface. To be more precise, we need to investigate the behavior of an electronic Bloch wave, pertaining to the lowest conduction band of $3C$ SiC, when it enters the adjacent twisted material. In section 4.1 we will describe the scattering properties of such a Bloch wave at a single interface in terms of transmission and reflection coefficients. We will then subsequently demonstrate that these scattering properties can be translated into *discontinuous* boundary conditions for one-dimensional envelope wave functions. With this we have a one-dimensional model at our disposal in which no difference potential either between h- and k-layers or between twisted and untwisted material is introduced.

In section 4.2 we will apply this one-dimensional model for envelope wave functions to periodic stackings, in order to describe the band gap variation among different polytypes of SiC.

To answer the second question we will emphasize in section 4.3 the characteristic features of $3C$ SiC that give rise to this model and are responsible for the apparent gap variation. We will also make a comparison with the polytype material ZnS, as well as with hypothetical polytypes like those constructed from cubic AlAs, Si and C.

4.1   Modeling the single-interface scattering

In order to understand the band gap variation in polytypic superlattices, the central question to be answered is what happens to an electronic Bloch wave in $3C$ SiC with energy close to the minimum of the conduction band of $3C$ SiC, when it enters the twisted counterpart. The wave vector of the incoming wave is decomposed as $\vec{k} = \vec{k}_\parallel + k_z \vec{e}_z$. Because only the translational symmetry along the stacking direction z is broken,

the wave vector component $\vec{k}_\parallel$ transverse to the stacking axis is a good quantum label both for $3C$ SiC and the polytype to be considered. The lowest conduction band state appears at the transverse wave vector component $\vec{k}_\parallel = \vec{k}_M$. We therefore concentrate on the Bloch electrons in $3C$ SiC with $\vec{k} = \vec{k}_M + k_z\vec{e}_z$, and investigate how such electrons are scattered at an interface. It should be realized that, if the band structures of both the cubic and the twisted cubic configuration are represented in a common hexagonal Brillouin zone, the twisted layer has its conduction band minimum at exactly the same energy value and $\vec{k}$-point $\vec{k}_M$. Nevertheless, a conduction electron approaching with $\vec{k} = \vec{k}_M + k_z\vec{e}_z$ from one building block to the next one is obstructed in its propagation through the structure, due to the fact that the concerning wave functions in the two neighboring layers are dissimilar and mismatch at the interfaces. Hence, the electron will be scattered to other states having the same $\vec{k}_\parallel = \vec{k}_M$ and energy. It will therefore not freely propagate through the twisted layer. To quantify the mismatch between the relevant wave functions of two mutually twisted materials we should in fact compare the precise values of the wave functions and their derivatives of the untwisted and twisted material at the interface. This comparison should furthermore not be made for just one interface position but for all possible positions in a region with a width of about one bilayer. This amounts in fact to a comparison of the wave functions through both bilayers. Therefore we rather choose to use the overlap integral between the lowest conduction Bloch states of the untwisted and the twisted material slightly above the conduction band minimum at $\vec{k}_X$ (equivalent to $\vec{k}_M$) to quantify the mismatch. We define this overlap integral $\sigma_{l,\vec{k}}$ as

$$\sigma_{l,\vec{k}} = \left| \int_{\Omega_c} d^3r \, \phi^*_{l,\vec{k}}(\vec{r}) \phi_{l,T\vec{k}}(T\vec{r}) \right|, \qquad (4.1)$$

in which $\phi_{l,\vec{k}}$ denotes the wave function of lowest conduction band state in the cubic material and T is the twisting operation (see Chapter 2). For a free propagation of the incoming Bloch wave through the interface this integral has to be equal to 1. We have calculated this integral and found it to be 0.13, which indicates that the concerning Bloch wave functions are indeed highly dissimilar.

To demonstrate that an incoming Bloch wave is scattered at the interface, instead of freely propagating through the crystal, we have depicted in Fig. 4.1 the scattering of the wave function for a case in which the electron energy is slightly above the conduction band minimum. For the description of this scattering we use Eq. (3.20) in the rewritten form

$$\begin{bmatrix} D^{j,\rightarrow}(3c_1) & D^{j,\leftarrow}(3c_1) \end{bmatrix} \begin{bmatrix} \underline{\alpha}^{j,\rightarrow} \\ \underline{\alpha}^{j,\leftarrow} \end{bmatrix} = \begin{bmatrix} D^{j+1,\rightarrow}(0) & D^{j+1,\leftarrow}(0) \end{bmatrix} \begin{bmatrix} \underline{\alpha}^{j+1,\rightarrow} \\ \underline{\alpha}^{j+1,\leftarrow} \end{bmatrix},$$

$$(4.2)$$

Figure 4.1: *The scattering at a polytypic SiC interface of an incoming Bloch wave, with an energy slightly above the conduction band minimum of 3C SiC. Depicted is the probability density $|\psi|^2$ in arbitrary units, x, y-averaged as a function of the SiC bilayer number (i.e. z/c_1) of the wave function (solid line) and the incoming Bloch wave (dotted line). The material on the left ($z < 0$) is untwisted 3C SiC and on the right ($z > 0$) twisted 3C SiC. The polytypic interface highly reflects the incoming Bloch wave. The incoming and reflected waves interfere and form a standing wave at the left side of the interface. Note from the inset that the evanescent waves contribute only near the interface ($0 \leq z < 1.5c_1$) to the transmitted part of the wave function and that there is a small part of the incoming Bloch wave that still propagates through the interface at the right side.*

where $D^{j,\rightarrow}(z)$ and $D^{j,\leftarrow}(z)$ are $2M \times M$ matrices. The right (left) arrow in Eq. (4.2) stands for Bloch or evanescent waves travelling or decaying, respectively, to the right (left). We separate the waves in- and outcoming from the interface j by

$$
\left[\begin{array}{cc} -D^{j+1,\rightarrow}(0) & D^{j,\leftarrow}(3c_1) \end{array} \right] \left[\begin{array}{c} \underline{\alpha}^{j+1,\rightarrow} \\ \underline{\alpha}^{j,\leftarrow} \end{array} \right] = \left[\begin{array}{cc} -D^{j,\rightarrow}(3c_1) & D^{j+1,\leftarrow}(0) \end{array} \right] \left[\begin{array}{c} \underline{\alpha}^{j,\rightarrow} \\ \underline{\alpha}^{j+1,\leftarrow} \end{array} \right],
$$
(4.3)

in which $\underline{\alpha}^{j+1,\rightarrow}$ and $\underline{\alpha}^{j,\leftarrow}$ represent all outcoming waves and $\underline{\alpha}^{j,\rightarrow}$ and $\underline{\alpha}^{j+1,\leftarrow}$ represent all incoming waves. In order to describe the scattering of one incoming Bloch wave we take in Eq. (4.3) the coefficient of the incoming Bloch wave equal to 1. All other coefficients, either related to evanescent waves with increasing amplitudes from the interface (either to the left or to the right) or Bloch waves travelling to the left in layer $j + 1$, are put equal to zero. Since the right-hand side of (4.3) is now completely known, it is possible to calculate the coefficients in the left-hand side related to the reflected part (in layer j) and the transmitted part (in layer $j + 1$) of the wave function. In particular, we are able to calculate the coefficient in $\underline{\alpha}^{j+1,\rightarrow}$ corresponding to the Bloch wave travelling in layer $j + 1$ to the right. It is this coefficient which we will refer to as the (complex) transmission coefficient T. In line with this, we refer to the coefficient in $\underline{\alpha}^{j,\leftarrow}$ corresponding to the reflected Bloch wave in layer j as the (complex) reflection coefficient R.

For the incoming Bloch wave (dotted line in Fig. 4.1) we have chosen an energy slightly above the conduction band minimum (see Fig. 3.8), at $\vec{k} = \vec{k}_M + k_z \vec{e}_z$ such that $k_z = 0.064\pi/c_1$. Consequently, the probability density $|\psi|^2$ of the constructed wave function ψ for this scattering case exhibits a modulation of wave length $\lambda_z = 2\pi/k_z$. For the above choice of k_z we find $\lambda_z \approx 31c_1$ (see Fig. 4.1).

As explained in Chapter 3, the complete polytype wave function at given $\vec{k}_\| = \vec{k}_M$ and energy E can be constructed as a linear combination of cubic Bloch wave functions in each layer, with real k_z, and evanescent wave functions, with complex k_z. If the situation were such that one pair of Bloch waves with $\vec{k} = \vec{k}_M \pm k_z \vec{e}_z$ in one layer coupled either to one pair of evanescent waves or to one pair of Bloch waves in the next layer then the adjacent (mutually twisted) layers could be represented as regions of different constant potentials. However, for reasons of symmetry it can be seen that there is no reason why one of the layers would act as a barrier with respect to the next! Put otherwise, there are no constant potential barriers by definition. In line with this, it appears that both types of waves, Bloch and evanescent, contribute considerably in each building block in the making up of the wave function of the superlattice. Our analysis of Chapter 3 reveals, more in particular, that the participating evanescent waves in the linear combination play an important role in the matching of the wave function

at an interface. However, for the energy range slightly above the conduction band minimum of $3C$ SiC these evanescent waves, decaying from some interface, extinguish almost completely over distances larger than c_1, because for these waves we find in our scattering analysis that $|\text{Im } k_z| \gtrsim 0.7/c_1$ (see Fig. 3.4). These waves therefore do not contribute to the propagating part of the wave function of the polytype at the next interface. Only for distances $z \lesssim c_1$ these evanescent waves are not yet extinguished at the next interface. For example in $2H$ SiC, the separate layers are of size c_1, which implies that in this case both Bloch and evanescent waves contribute to the propagating part of the wave function at any position. This will imply that the one-dimensional model, to be introduced below, does not apply to the $2H$ case.

In this model, to be applied to the periodic polytype superlattices in section 4.2, the key element is that only the *effective* coupling of two participating Bloch waves in each of the adjacent layers with $\vec{k}_M \pm k_z \vec{e}_z$ is accounted for. Though the evanescent waves are left out of this model, for the above mentioned reason, they are in fact, very relevant for the matching of the wave function at the interfaces. This matching can, however, fully be accounted for by restricting the description to the Bloch waves and demanding these waves to obey *discontinuous* boundary conditions. The Bloch waves of the superlattice can then most conveniently be described in terms of envelope functions $\mathcal{F}^j(z)$ for each layer j obeying the following boundary conditions at the interface $z = z_j$:

$$\begin{cases} \mathcal{F}^{j+1}(z_j) = \beta \mathcal{F}^j(z_j) & + \gamma c_1 \frac{\mathrm{d}}{\mathrm{d}z}\mathcal{F}^j|_{z=z_j}, \\ \mathcal{F}^j(z_j) = \beta \mathcal{F}^{j+1}(z_j) & - \gamma c_1 \frac{\mathrm{d}}{\mathrm{d}z}\mathcal{F}^{j+1}|_{z=z_j}. \end{cases} \tag{4.4}$$

The particular form of the boundary conditions in Eq. (4.4) is completely determined by the invariance under change of layer indices and substitution of $-z$ for z. All effects due to the participating evanescent waves are incorporated in the values of the coupling parameters β and γ. These both have to be real in order to conserve the probability flow across the interfaces.

The envelope function we use can in a formal way [21] be related to the superlattice wave function by

$$\psi^j_{\vec{k}_\parallel}(\vec{r}) = e^{i(\vec{k}_\parallel - \vec{k}_M) \cdot \vec{r}_\parallel} \sum_l \mathcal{F}^j_l(z) \phi^j_{l,\vec{k}_x}(\vec{r}), \tag{4.5}$$

in which the summation runs over all wave functions $\phi^j_{l,\vec{k}_x}(\vec{r})$ of $3C$ SiC with band index l and wave vector $\vec{k}_X$. In this expression the function $\mathcal{F}^j_l(z)$ with band index $l = 5$ represents the envelope function of the lowest conduction band state which we simply denote as $\mathcal{F}^j(z)$. This $\mathcal{F}^j(z)$ approximately obeys the Schrödinger-like equation $(-\hbar^2/2m^*)d^2\mathcal{F}^j(z)/dz^2 = E\mathcal{F}^j(z)$ in which m^* represents the effective mass of the lowest conduction band state at X and the energy E is measured relatively to the energy level of the conduction band edge in $3C$ SiC.

The relation between the coefficients β and γ on the one hand and the complex transmission coefficient T on the other hand can be determined as follows: Consider an incoming wave $e^{ik_z z}$ in the untwisted material j. It leads to a reflected wave $Re^{-ik_z z}$, where R is the complex reflection coefficient. The envelope function in the layer j then reads $\mathcal{F}^j(z) = e^{ik_z z} + Re^{-ik_z z}$. For the outcoming wave, in the twisted material $j+1$, we find $\mathcal{F}^{j+1}(z) = Te^{ik_z z}$, where T is the complex transmission coefficient. Substituting these expressions for $\mathcal{F}^j(z)$ and $\mathcal{F}^{j+1}(z)$ in Eq. (4.4) at $z = z_j = 0$ yields

$$\begin{cases} T & = \beta(1+R) \ + \ ik_z \gamma c_1 (1 - R), \\ (1+R) & = \beta T \qquad - \ ik_z \gamma c_1 T, \end{cases} \tag{4.6}$$

which gives

$$T = \left(\beta - i\frac{1 - \beta^2 + (\gamma c_1 k_z)^2}{2\gamma c_1 k_z} \right)^{-1}. \tag{4.7}$$

On the other hand this transmission coefficient T can also be calculated from the *complete* matching analysis in Chapter 3. The actual values of the parameters β and γ can therefore be directly derived from the energy dependent transmission properties of a single interface by fitting the right-hand side of Eq. (4.7) to the complex transmission amplitude as obtained from the analysis which uses Eq. (4.3).

In the energy region of interest the conduction band in $3C$ SiC is nearly parabolic (see Figs. 3.4 and 3.8) and can accurately be represented by $E = \hbar^2 k_z^2 / 2m^\star$ with $m^\star = 0.48m$. The dependence of T on k_z in Eq. (4.7) can therefore easily be transformed into a dependence of T on E. A full calculation of the energy dependence of the transmission probability $|T|^2$ shows that $|T|^2$ increases from 0 at the conduction band minimum to a maximum value of $1/\beta^2$ at some higher energy. Slightly above the conduction band minimum of $3C$ SiC the coupling parameters appear to be $\beta = 1.63$ and $\gamma = 0.88$. In the relevant region from 2.4 to 3.3 eV the parameters appear to increase slightly, with $\beta = 1.76$ and $\gamma = 0.93$ as average values. The fact that these parameters vary only weakly with the energy is not unexpected since the relevant k_z-branches (see Fig. 3.4) are quite steep and the periodic parts of the wave functions $u_{l,\vec{k}}$ (see expression (3.3)) do not vary much with the energy. The present model would be of much less use if β and γ were strongly energy dependent.

4.2 The band gaps in the one-dimensional model

It is convenient to write the envelope function for layer j generally as

$$\mathcal{F}^j(z) = A^j e^{ik_z(z - z_{j-1})} + B^j e^{-ik_z(z - z_{j-1})}, \tag{4.8}$$

Figure 4.2: The indexing of the successive layers for polytypes with alternating building-block sizes a and b, respectively.

where layer j corresponds to the region $z_{j-1} \leq z \leq z_j$. Substitution of Eq. (4.8) in the boundary conditions (4.4) between layer j and $j + 1$ yields

$$\mathcal{D}^j(z_j - z_{j-1}) \begin{pmatrix} A^j \\ B^j \end{pmatrix} = \mathcal{D}^{j+1}(0) \begin{pmatrix} A^{j+1} \\ B^{j+1} \end{pmatrix}, \qquad (4.9)$$

The matrix elements of the 2×2 matrices $\mathcal{D}^j$ follow in an obvious way from the Eqs. (4.4).

A polytype is built up from a number of layers of varying size. In Fig. 4.2 we have depicted the labeling of the set of polytypes with alternating building-block sizes a and b. Both the hexagonal polytypes such as $8H$ (in which case $a = b = 4c_1$) and the rhombohedral polytypes such as $24R$ (in which case $a = 3c_1$ and $b = 5c_1$) fall in this category. For all these cases the one-dimensional band structure is obtained as follows: First we demand the boundary conditions (4.4) at the interfaces located at $z = z_0$ and $z = z_1$ (see Fig. 4.2). Secondly, we impose the Bloch condition between $z = z_2$ and $z = z_0$. Combining these we then straightforwardly obtain the generalized eigenvalue equation

$$\left[\mathcal{D}^2(0)\right]^{-1} \mathcal{D}^1(z_1 - z_0) \begin{pmatrix} A^1 \\ B^1 \end{pmatrix} = e^{iKL} \left[\mathcal{D}^2(z_2 - z_1)\right]^{-1} \mathcal{D}^3(0) \begin{pmatrix} A^1 \\ B^1 \end{pmatrix}, \qquad (4.10)$$

in which e^{iKL} is the eigenvalue and $L = z_2 - z_0$. Note that this equation is very similar to Eq. (3.21). Because the dimensions of the matrices $\mathcal{D}^j$ are only 2×2 it is possible to

solve Eq. (4.10) analytically. After a tedious but straightforward calculation we obtain

$$\cos KL = \frac{1}{(2\gamma c_1 k_z)^2} \Biggl\{ \left(1 - \beta^2 - (\gamma c_1 k_z)^2\right)^2 \cos k_z(b-a) - \Biggl[\left(1 - \beta^2 + (\gamma c_1 k_z)^2\right)^2$$

$$- (2\gamma c_1 k_z \beta)^2 \Biggr] \cos k_z L - 4\gamma c_1 k_z \beta \left(1 - \beta^2 + (\gamma c_1 k_z)^2\right) \sin k_z L \Biggr\}, \qquad (4.11)$$

for the rhombohedral $(a \neq b)$ and the hexagonal case $(a = b)$. For the hexagonal structures $(a = b = L/2)$ the equation simplifies to

$$\cos \frac{KL}{2} = \beta \cos \frac{k_z L}{2} - \frac{[1 - \beta^2 + (\gamma c_1 k_z)^2] \sin \frac{k_z L}{2}}{2\gamma c_1 k_z}. \qquad (4.12)$$

In Fig. 4.3 the band gap predictions are displayed as following from Eq. (4.11) for hexagonal structures and for rhombohedral structures with $a = 1.3b$ and $a = 1.5b$, as a function of the hexagonality percentage h. The prediction is that R structures generally have smaller gaps. For not too small $h \gtrsim 15\%$ the calculated relation for H structures is linear and reproduces the experimental results found by Choyke *et al.* [18] within 0.1 eV. For smaller hexagonalities $h \lesssim 15\%$ the earlier calculated band gaps for H structures, see Chapter 3, nearly coincide with the predictions of the one-dimensional model. They are about 0.1 eV lower than the ones predicted by the empirical linear relation (i.e. the solid line in Fig. 4.3). Note, however, that the experimental spreading of the band gaps is also typically 0.1 eV [18, 48].

In order to elucidate the difference in predicted gap values for H and R structures, we have depicted in Fig. 4.4 the complex band structures, resulting from our one-dimensional model, for two structures with the same hexagonality percentage $h = 25\%$, namely $8H$ and $24R$. The sizes of the adjacent bilayers are $a = b = 4c_1$ for $8H$ and $a = 5c_1$ and $b = 3c_1$ for $24R$. Due to the unequal layer configuration in $24R$, the symmetry under translation over $L/2$ in our one-dimensional model is broken and the two lowest conduction bands repel each other. Consequently, the lowest conduction band in $24R$ lies lower than the one in $8H$.

In conclusion, we have presented a one-dimensional model that explains the differences in band gaps among the SiC polytypes for $h \leq 50\%$. The model focusses on the formation of the lowest conduction band in a polytype. This formation can be traced back to *periodic frustration* of propagating waves in the respective cubic building blocks. The calculated band gaps of R structures and the band gaps at low hexagonality values deviate slightly from the empirical Choyke-Hamilton-Patrick relation. Unfortunately, the number of experiments on electronic energy gap values of SiC polytypes is rather low and the experimental spreading is relatively large. So, there is a clear need for more, as well as more refined energy gap determinations in order to check our predictions.

Figure 4.3: The band gap values as a function of the percentage hexagonality (h) as calculated in our one-dimensional model. Three ratios of layer sizes are indicated: $a = b$ (dashed-dotted line), $a = 1.3b$ (dashed line) and $a = 1.5b$ (dotted line). The empirical linear relation given by Choyke, Hamilton and Patrick [18] is also indicated (solid line). The available experimental gaps [48] for hexagonal (filled squares) and rhombohedral (open squares) structures are depicted. Furthermore we depicted the (EPM) gap results of our matching procedure (circles). Note that the slight deviation from the nearly linear behavior due to the camel's back of 6H SiC is not covered by our one-dimensional model.

Figure 4.4: *The one-dimensional band structure $E(K)$ according to the one-dimensional model for envelope wave functions for $8H$ (solid line) and $24R$ (dashed line) SiC.*

4.3 Comparison with other polytype materials

Although we have given a description of the band gap variation among polytypes of SiC it is of interest to identify the characteristic parameters responsible for this phenomenon in SiC. To this end, it is helpful to compare with other materials, such as ZnS (which is also a polytype material) and hypothetical polytypes of Si, C and AlAs. In all these four cases the band gap variation is essentially absent.

ZnS is a polytype compound of which the band gaps are experimentally known for quite a number of different polytype structures. All these experimental band gap values appear to be (within 0.1 eV) the same, namely 3.7 eV. An important difference with SiC is that ZnS is a *direct* semiconductor with the band gap located at the Γ-point. In order to make a comparison with the SiC case we have applied the interface matching method as described in Chapter 3 to the three ZnS polytypes $3C$, $6H$ and $4H$. We have chosen the $4H$ and the $6H$ structure because in SiC they have relatively small building-block sizes with band gaps that differ considerably from the $3C$ SiC band gap. In the calculation we have utilized the empirical pseudopotential form factors of Ref. [20]. We find the direct band gaps of 3.64, 3.65 and 3.64 eV for $3C$, $6H$ and $4H$ ZnS, respectively. Our calculations therefore confirm that the band gaps of ZnS polytypes are (almost) independent of the polytype structure. The extremely small variation

of the lowest conduction band edge in ZnS is clearly related to the fact that the two wave functions of the lowest conduction band state, pertaining to the two adjacent and mutually twisted layers, happen to be highly similar. For SiC this is not at all the case, the overlap integral between the two lowest conduction band states at $\vec{k}_M$ being equal to 0.13, only. For ZnS, on the other hand, the corresponding overlap integral at $\vec{k}_\Gamma$ is equal to 0.95, implying that the wave functions almost perfectly match, in contrast to the SiC case. Completely in line with this, we find (i) that the single-interface transmission analysis, as described in section 4.2, yields a transmission probability of 98 % for the lowest conduction band state in ZnS, in contrast to the lowest conduction band state of SiC which is almost completely reflected, and (ii) that in the construction of the superlattice Bloch wave functions of $6H$ and $4H$ ZnS evanescent waves hardly contribute, in contrast to SiC where the influence of evanescent states is considerable.

The conclusion therefore seems to be that in order to obtain a strong variation of the conduction band edge in building-block polytypes it is necessary that the related Bloch wave functions in the mutually twisted cubic basis materials are highly dissimilar. This leads to a strong frustrated transmission, which makes it difficult to construct propagating waves in the polytype.

In order to investigate whether possibly other features can be held responsible for a strong variation of band gaps we have also investigated a number of hypothetical polytypes of silicon (Si), diamond (C) and AlAs. The reason behind these choices is that all these materials have indirect band gaps. For $3C$ AlAs the lowest conduction band arises at X, like for $3C$ SiC. For C and Si the lowest conduction band occurs at the ΓX-axis near the X-point. Because the lowest conduction band energy levels in Si and C near X do not differ much (less than 0.1 eV) from the values at X, we will focus in all three cases on the X-point. The three materials have in common with $3C$ SiC that the overlap integral between the Bloch wave functions related to the two conduction band minima (at X) in twisted and untwisted material is quite small (in all cases smaller than for $3C$ SiC). From the correspondence with the SiC case, one would therefore expect some band gap variation among different (hypothetical) polytypes of Si, C and AlAs. Nevertheless, contrary to the SiC case, we observe no appreciable band gap variation! In applying the interface matching method, as described in Chapter 3 using the empirical pseudopotential form factors of Refs. [20, 7], to the $3C$, $6H$ and $4H$ polytypes of Si, C and AlAs we obtained band gaps at $\vec{k}_M$ for the polytypes $3C$, $6H$ and $4H$ of 2.08, 2.14 and 2.11 eV for AlAs, 1.17, 1.03 and 1.00 eV for Si and 5.48, 5.53 and 5.38 eV for C, respectively. Moreover, all these (rather) small band gap differences are mainly due to small energy shifts of the valence band tops. The energy levels of the lowest conduction band states at $\vec{k}_M$ vary at most 0.03 eV for Si, C and

AlAs! Apparently the small overlap between related conduction band wave functions is not the only deciding feature. We believe that the difference with the SiC case can be traced back to the difference in the (complex) cubic band structures of these substances. To this end we have depicted in Fig. 4.5 the relevant part of the (complex) Si band structure. In Si (and also in C) the lowest conduction band at the X-point has a twofold degeneracy. This means for the matching procedure that at $\vec{k}_{\parallel} = \vec{k}_{\mathrm{M}}$ four Bloch waves participate, in contrast to $3C$ SiC, where only two Bloch waves participate. In AlAs, see Fig. 4.6, this lowest conduction band is not degenerate. However, in AlAs the splitting between the two lowest conduction band edges is approximately equal to 0.5 eV, which is quite small in comparison with $3C$ SiC, where it is approximately equal to 3.5 eV. As for $3C$ SiC, in AlAs only two Bloch waves participate considerably in the matching procedure at $\vec{k}_{\parallel} = \vec{k}_{\mathrm{M}}$. But in AlAs there are two evanescent waves involved with relatively small values of $|\mathrm{Im}\ k_z|$, unlike in $3C$ SiC, where all involved evanescent waves have relatively large imaginary parts of k_z! This implies that in the making up of the superlattice Bloch wave function for AlAs weakly decaying evanescent states contribute significantly to the propagation. Due to the absence of these in $3C$ SiC the formation of propagating waves in SiC polytypes is strongly frustrated. The origin of the size of the energy splitting between the two lowest conduction bands at X can be traced back to the properties of the constituting atoms. The large antisymmetric parts of the lowest Fourier components $v_{\mathrm{C}}(\vec{G}) - v_{\mathrm{Si}}(\vec{G})$ of the empirical pseudopotential with $|\vec{G}| > 0$ in comparison with those of cubic Si, C and AlAs are responsible for the rather large energy splitting between the two lowest conduction bands at X in $3C$ SiC. These antisymmetric parts are relatively small in cubic AlAs and exactly zero in cubic Si and C crystals.

Let us once more consider the behavior of a Bloch electron, with $\vec{k} = \vec{k}_{\mathrm{M}}$ and an energy slightly higher than the lowest conduction band energy, entering the twisted material (of either cubic Si, C, AlAs or SiC). For $3C$ SiC we know that this wave is hardly transmitted (see Fig. 4.1) and that the transmitted wave has an evanescent part which is appreciable in the twisted counterpart only over a distance of approximately one bilayer (i.e. c_1). This occurs due to the rather large imaginary parts of k_z of the most relevant evanescent wave component in the relevant energy region from 2.4 to 3.4 eV. These large values of $|\mathrm{Im}\ k_z|$, which are about $0.7/c_1$ or larger, cause a low penetrability of the incoming Bloch wave into the twisted layer. So, the interface frustrates the transmission, as if the twisted material acts as a strong barrier. Now, the smaller the splitting between the two lowest conduction bands at $\vec{k} = \vec{k}_{\mathrm{M}}$ is, the smaller the *smallest* values of $|\mathrm{Im}\ k_z|$ near the conduction band minimum. For AlAs we can observe from Fig. 4.6 that there is a complex k_z-branch with $|\mathrm{Im}\ k_z| \lesssim 0.3/c_1$, slightly above the

conduction band minimum of $E = 2.1$ eV. This implies that the wave transmitted from an incoming Bloch wave has an evanescent part that is appreciable in more than three bilayers of the twisted AlAs material. For e.g. $4H$ AlAs this rather strong penetrability implies that two evanescent waves, each emerging from two respective interfaces, can cause an appreciable overlap and, therefore, considerably participate in the propagating part of a superlattice Bloch wave. As a result, a propagating wave through the superlattice (i.e. a superlattice Bloch wave function) is easily formed at or slightly above the conduction band minimum of cubic AlAs and the energy level of the lowest conduction band in a hypothetical $4H$ AlAs building-block polytype hardly differs from that of the cubic basis material. We note, incidentally, that our one-dimensional model is not applicable for e.g. $2H$, $4H$ and $6H$ AlAs, because the participating evanescent waves, emerging from one interface, are not sufficiently extinguished at the next interface. For Si and C the situation at $\vec{k}_M$ is even so (because of the band degeneracy) that a Bloch wave takes over the role of the most important evanescent wave with the smallest value of $|\text{Im } k_z|$. Consequently, polytypic Si or C interfaces hardly obstruct an incoming Bloch wave and the band gaps of different (hypothetical) building-block polytypes are nearly the same.

For the valence band top in SiC polytypes the situation is in fact comparable to the situation for the conduction band edge in Si and C. Remind that the valence band top has a threefold degeneracy in $3C$ SiC. This means that in order to make up the wave functions of the valence band top of the superlattice we deal with, depending on the energy, either six propagating waves or six very weakly evanescing waves. The superlattice Bloch wave function of the valence band top is therefore quite easily formed by a linear combination of the six evanescent states, at an energy slightly above the energy of the valence band edge of the $3C$ material.

In conclusion, in order to explain the strong band gap variation in SiC polytypes it is not enough to have a considerable mismatch between the two Bloch wave functions related to the conduction band minima of the two mutually twisted $3C$ SiC layers. It is also essential to have a rather large splitting of the two lowest conduction bands at $\vec{k}_M$ (i.e. $\vec{k}_X$), as this hampers the role of evanescent waves in the formation of Bloch waves for polytypes at energies close to the $3C$ SiC conduction band minimum.

Figure 4.6: The complex band structure of cubic AlAs along its [111]-direction. The wave vector component k_z is expressed in units of π/c_1, with $c_1 = 5.66/\sqrt{3}$ Å for AlAs.

Figure 4.5: The complex band structure of cubic silicon (Si) along its [111]-direction. The wave vector component k_z is expressed in units of π/c_1, with $c_1 = 5.43/\sqrt{3}$ Å for Si.

Chapter 5

Quasiparticle effects in SiC

With Hedin's GW approximation [31] we have a method at our disposal which has the ability to accurately predict excited-state properties for a variety of semiconductors, insulators and metals. In this Chapter we will apply this method to $3C$ SiC in order to obtain the quasiparticle band structure and, more in particular, the band gap.

We will start in section 5.1 by giving a formal introduction to the GW scheme by introducing the basic quantities and equations as they apply to semiconductors and insulators. The central quantity in the GW scheme is the electron self-energy operator Σ. The GW approximation refers to the lowest order expansion of Σ in terms of the Green's function G and the dynamically screened Coulomb interaction W. Within this so-called GW approximation it is customary to rely on specific approximations for G (the LDA) and W (the random-phase approximation).

Section 5.2 is devoted to the description of a plasmon-pole model, which, first of all, serves to approximate the energy dependence of the screened Coulomb interaction W. Within this model it is possible to represent the energy dependence of W in a computationally advantageous way. Moreover, the model enables us to obtain plasmon energies and plasmon dispersion relations which can be subjected to experimental verification.

In section 5.3 we discuss the procedure of obtaining the quasiparticle band structure of $3C$ SiC, and verify whether there is agreement with experimentally observed excitation spectra.

In section 5.4 we will discuss the $\vec{k}$-dependence of the calculated quasiparticle corrections to the earlier obtained LDA energies of $3C$ SiC. We find that the quasiparticle shift to a large extent amounts to a uniform (i.e. $\vec{k}$-independent) energy shift of the

conduction bands with respect to the valence band top. The question whether the obtained quasiparticle shift applies to the Kohn-Sham gaps of other SiC polytypes as well will be discussed. We end this section by giving an outlook on the feasibility of our *GW* method to more complicated SiC polytypes than 3C SiC.

5.1   Formal *GW* scheme

In many-body theory quasiparticle wave functions $\psi_{n,\vec{k}}$ and energies $E_{n,\vec{k}}$ can in principle be obtained by solving a Schrödinger-like equation

$$\left(\hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{H}}\right)\psi_{n,\vec{k}}(\vec{r}) + \int d^3r'\Sigma(\vec{r},\vec{r}',E_{n,\vec{k}})\psi_{n,\vec{k}}(\vec{r}') = E_{n,\vec{k}}\psi_{n,\vec{k}}(\vec{r}), \qquad (5.1)$$

in which $\hat{T}$ is the kinetic energy operator, $\hat{V}_{\text{ext}}$ is the external potential operator due to, e.g., the ions, $\hat{V}_{\text{H}}$ is the Hartree potential due to the Coulomb interactions between the electrons and Σ is the electron self-energy operator. The operator Σ contains both the exchange and the correlation effects of the electrons. It takes over the role of the exchange-correlation potential V^{XC} which is accounted for in usual LDA band structure calculations. The essential difference with the exchange-correlation potential $V^{\text{XC}}(\vec{r})$ is not only that $\Sigma(\vec{r},\vec{r}',E_{n,\vec{k}})$ is non-local, but also energy dependent and non-Hermitian. Because of this non-Hermiticity the eigenvalues $E_{n,\vec{k}}$ of Eq. (5.1) are generally complex. The real part of $E_{n,\vec{k}}$ is then interpreted as the energy of the quasiparticle and the imaginary part is proportional to its inverse lifetime.

The *GW*-scheme is based on an approximation of $\Sigma(\vec{r},\vec{r}',E)$ to first order in the Green's function G and the screened Coulomb interaction W. The *GW* approximation for Σ reads [31]

$$\Sigma(\vec{r},\vec{r}',E) = i\int \frac{d\omega}{2\pi} G(\vec{r},\vec{r}',E-\omega)W(\vec{r},\vec{r}',\omega)e^{-i\eta\omega}, \qquad (5.2)$$

where η is an infinitesimally positive number and ω is an energy variable. It is usual to express the Green's function G in terms of LDA energies $E_{n,\vec{k}}$ and wave functions $\psi_{n,\vec{k}}$ as

$$G(\vec{r},\vec{r}',E) = \sum_n \int_{1\text{BZ}} \frac{d^3k}{(2\pi)^3} \frac{\psi_{n,\vec{k}}(\vec{r})\psi^*_{n,\vec{k}}(\vec{r}')}{E - E_{n,\vec{k}} + i\eta\text{sgn}(E_{n,\vec{k}} - \mu)}, \qquad (5.3)$$

where μ is the chemical potential, which lies between the valence and the conduction bands of the electrons. For reasons of convenience we will frequently use Fourier transformed quantities. For functions which separately depend on $\vec{r}$ and $\vec{r}'$, as e.g. $W(\vec{r},\vec{r}',\omega)$, the Fourier transformation is given by

$$W(\vec{r},\vec{r}',\omega) = \int_{1\text{BZ}} \frac{d^3q}{(2\pi)^3} \sum_{\vec{G},\vec{G}'} e^{i(\vec{q}+\vec{G})\cdot\vec{r}} W_{\vec{G},\vec{G}'}(\vec{q},\omega)e^{-i(\vec{q}+\vec{G}')\cdot\vec{r}'}, \qquad (5.4)$$

where $\vec{G}$ and $\vec{G}'$ are reciprocal lattice vectors. The screened interaction W is related to the bare Coulomb interaction v by means of the inverse dielectric function ϵ^{-1}. The Fourier transformed relation reads

$$W_{\vec{G},\vec{G}'}(\vec{q},\omega) = \epsilon^{-1}_{\vec{G},\vec{G}'}(\vec{q},\omega)v_{\vec{G}'}(\vec{q}), \tag{5.5}$$

in which $W_{\vec{G},\vec{G}'}(\vec{q},\omega)$ and $\epsilon^{-1}_{\vec{G},\vec{G}'}(\vec{q},\omega)$ are the matrix elements of $\underline{W}(\vec{q},\omega)$ and the inverted dielectric matrix $\underline{\epsilon}^{-1}(\vec{q},\omega)$, respectively, while $v_{\vec{G}'}(\vec{q}) = 4\pi e^2/(\vec{q} + \vec{G}')^2$.

The dielectric matrix $\underline{\epsilon}$ is related to the irreducible polarizability matrix $\underline{P}$ by

$$\underline{\epsilon} = \underline{1} - \underline{v}\,\underline{P}. \tag{5.6}$$

Here $\underline{1}$ represents the unit matrix with elements $\delta_{\vec{G},\vec{G}'}$ and $\underline{v}(\vec{q})$ is the bare Coulomb interaction matrix with elements $v_{\vec{G},\vec{G}'}(\vec{q}) = 4\pi e^2\delta_{\vec{G},\vec{G}'}/|\vec{q} + \vec{G}|^2$. Within the random-phase approximation (RPA) the expression for the matrix elements of the irreducible polarizability P is given by [1, 63]

$$P_{\vec{G},\vec{G}'}(\vec{q},\omega) = 2\int_{\mathrm{1BZ}}\frac{d^3k}{(2\pi)^3}\left(\sum_{l_1\in\mathrm{CB}}\sum_{l_2\in\mathrm{VB}} - \sum_{l_1\in\mathrm{VB}}\sum_{l_2\in\mathrm{CB}}\right)\frac{1}{\omega - E^{\mathrm{LDA}}_{l_1,\vec{k}} + E^{\mathrm{LDA}}_{l_2,\vec{k}-\vec{q}}}$$
$$\times\left(\sum_{\vec{G}''}d_{l_1,\vec{k}}(\vec{G}'')d^*_{l_2,\vec{k}-\vec{q}}(\vec{G}'' - \vec{G})\right)\left(\sum_{\vec{G}''}d^*_{l_1,\vec{k}}(\vec{G}'')d_{l_2,\vec{k}-\vec{q}}(\vec{G}'' - \vec{G}')\right), \tag{5.7}$$

where CB denotes the conduction bands, VB denotes the valence bands and $d_{l,\vec{k}}(\vec{G})$ denotes a plane-wave coefficient of the wave function $\psi_{l,\vec{k}}$ (see the expressions (3.3) and (3.4)).

The self-energy operator Σ is obtained by using LDA obtained energies and wave functions in (5.3) as well as (5.7). The usual GW approach to the band structure of semiconductors is then to calculate expectation values of the operator $\Sigma - V^{\mathrm{XC}}$ and to consider these as quasiparticle corrections to the LDA energies. We will follow this approach in section 5.3.

5.2 Plasmon-pole model

Plasmon-pole models may be very useful in the context of the above GW scheme, as they allow us to model the energy dependence of the screened Coulomb interaction W in such a way that the energy integral in Eq. (5.2) can be carried out analytically. Such models circumvent the necessity to invert the dielectric matrix $\underline{\epsilon}$ for many values of energy ω and wave vector $\vec{q}$, which is computationally very costly.

Recently, Engel and Farid [26] have developed a plasmon-pole model which not only provides an extremely useful analytic approximation of the energy dependence of the various dielectric response functions of a crystalline material, but also directly leads to a description of the plasmon band structure of the crystal under consideration. This latter property does not hold true for a number of other plasmon-pole models known to us [33, 51, 65, 58], which were merely developed to model the energy dependence of the screened interaction. Engel and Farid start by considering the full polarizability matrix $\underline{\chi}$, which is related to the dielectric matrix $\underline{\epsilon}$ by

$$\underline{\epsilon}^{-1} = \underline{1} + \underline{v}\,\underline{\chi}. \tag{5.8}$$

In their model $\underline{\chi}$ is approximated by

$$\underline{\tilde{\chi}}(\vec{q}, \omega) = \left\{ \omega^2 \underline{M}^{-1}(\vec{q}) + \underline{\chi}^{-1}(\vec{q}, \omega = 0) \right\}^{-1}, \tag{5.9}$$

which obviously coincides for $\omega = 0$ with the full static polarizability matrix $\underline{\chi}(\vec{q}, \omega = 0)$. Furthermore, by taking the matrix elements of $\underline{M}(\vec{q})$ equal to

$$M_{\vec{G}, \vec{G}'}(\vec{q}) = \frac{\epsilon_{\text{pl}}^2}{4\pi e^2} (\vec{q} + \vec{G}) \cdot (\vec{q} + \vec{G}') \frac{\rho(\vec{G} - \vec{G}')}{\rho(0)}, \tag{5.10}$$

it is also guaranteed that $\underline{\tilde{\chi}}$ has the correct asymptotic behavior $\frac{1}{\omega^2} \underline{M}(\vec{q})$ for $\omega \to \infty$ (the f-sum rule [39]). In (5.10) $\rho(\vec{G})$ is a Fourier component of the electron density and $\epsilon_{\text{pl}} = \hbar \sqrt{4\pi e^2 \rho(0)/m}$ is the plasma energy of a homogeneous electron gas with electron density $\rho(0)$. Taking the average charge density of $3C$ SiC, we find that $\epsilon_{\text{pl}} = 23.1$ eV. It follows from the relations (5.6) and (5.8) that the full polarizability $\underline{\chi}(\vec{q}, \omega)$ is related to the irreducible polarizability $\underline{P}(\vec{q}, \omega)$ by $\underline{\chi}(\vec{q}, \omega) = \underline{P}(\vec{q}, \omega) \left[\underline{1} - \underline{v}(\vec{q})\underline{P}(\vec{q}, \omega) \right]^{-1}$. Plasmon energies $\omega_m(\vec{q})$ as a function of reciprocal lattice vector $\vec{q}$ in this model are obtained from the generalized eigenvalue problem:

$$\underline{\chi}(\vec{q}, \omega = 0)\, \underline{x}_{m, \vec{q}} = -\frac{1}{\omega_m^2(\vec{q})} \underline{M}(\vec{q})\, \underline{x}_{m, \vec{q}}. \tag{5.11}$$

If the eigenvectors $\underline{x}_{m, \vec{q}}$ of Eq. (5.11), with components $x_{m, \vec{q}}(\vec{G})$, are normalized according to $\underline{x}_{m, \vec{q}}^\dagger \underline{M}(\vec{q}) \underline{x}_{n, \vec{q}} = \delta_{m,n}$, the model full polarizability[26]

$$\tilde{\chi}_{\vec{G}, \vec{G}'}(\vec{q}, \omega) = \sum_m \frac{z_{m, \vec{q}}(\vec{G}) z_{m, \vec{q}}^*(\vec{G}')}{2\omega_m(\vec{q})} \left\{ \frac{1}{\omega - \omega_m(\vec{q}) + i\eta} - \frac{1}{\omega + \omega_m(\vec{q}) - i\eta} \right\}. \tag{5.12}$$

In this expression $\underline{z}_{m, \vec{q}} = \underline{M}(\vec{q}) \underline{x}_{m, \vec{q}}$. Combining (5.5), (5.8) and (5.12), the plasmon-pole approximation for W now reads

$$W_{\vec{G}, \vec{G}'}(\vec{q}, \omega) = v_{\vec{G}, \vec{G}'}(\vec{q}) + \sum_m w_{m, \vec{q}}(\vec{G}) w_{m, \vec{q}}^*(\vec{G}') \left\{ \frac{1}{\omega - \omega_m(\vec{q}) + i\eta} - \frac{1}{\omega + \omega_m(\vec{q}) - i\eta} \right\}, \tag{5.13}$$

where the components $w_{m,\vec{q}}(\vec{G})$ of $\underline{w}_{m,\vec{q}}$ are related to the eigenvectors $\underline{x}_{m,\vec{q}}$ through

$$\underline{w}_{m,\vec{q}} = \frac{1}{\sqrt{2\omega_m(\vec{q})}} \underline{v}(\vec{q}) \underline{M}(\vec{q}) \underline{x}_{m,\vec{q}}. \tag{5.14}$$

Since $\underline{\chi}(\vec{q}, \omega = 0)$ is a Hermitian and negative definite matrix [12], whereas $\underline{M}(\vec{q})$ is Hermitian and positive definite [26], the eigenvalue problem defines real-valued quantities $\omega_m(\vec{q})$. We may interpret them as plasmon frequencies, if taken positive. Calculations for Si have shown that the two lowest plasmon bands obtained with this model compare favorably with experiment [26].

In Fig. 5.1 we have plotted the lowest lying plasmon bands for $3C$ SiC as obtained from Eq. (5.11) along two symmetry axes in the 1BZ. In calculating these we used energies and wave functions obtained from a self-consistent LDA calculation, in which a cut-off energy of 40 Ry was taken (609 plane waves). The calculation was performed for the experimental lattice constant of 4.36 Å. The ionic *ab initio* norm-conserving pseudopotentials were obtained from Bachelet, Greenside, Baraff and Schlüter [2]. The exchange potential was represented in the Kohn-Sham form [45] with the Wigner interpolation formula [28] for the correlation potential. The number of plane waves taken into account in the calculation of the dielectric response matrices is 229. The Brillouin zone integration appearing in the RPA expression for $\underline{P}(\vec{q}, \omega = 0)$ was replaced by a summation over a regular grid of $\vec{k}$-points. It appeared that the plasmon bands were fully converged if only 216 $\vec{k}$-points (16 points in the irreducible wedge) were taken, except for the Γ-point, in which case we needed approximately 3000 $\vec{k}$-points (149 points in the irreducible wedge).

The lowest plasmon energy, which occurs at the Γ-point, is calculated to be 22.4 eV, which is in very good agreement with an electron energy loss measurement of 22.1 eV [57]. We are not aware of any measurements of the plasmon dispersion away from the Γ-point. It would be interesting of course to compare such measurements with our predictions.

We also calculated the static electronic macroscopic dielectric constant, defined as $\epsilon_M = 1/\tilde{\epsilon}_{\vec{G}=0, \vec{G}'=0}^{-1}(\vec{q} \to 0, \omega = 0)$, where the (symmetrized) inverse dielectric matrix is given by $\tilde{\epsilon}_{\vec{G}, \vec{G}'}^{-1}(\vec{q}, \omega) = \delta_{\vec{G}, \vec{G}'} + 4\pi e^2 \chi_{\vec{G}, \vec{G}'}(\vec{q}, \omega)/(|\vec{q} + \vec{G}||\vec{q} + \vec{G}'|)$. The calculated value is $\epsilon_M = 6.85$, which is in fairly good agreement with the experimental value of 6.5 [48] and another recently calculated value of 6.7 [58].

Figure 5.1: The calculated dispersion of the lowest plasmon bands along the ΓL- and the ΓX-axis by the generalized eigenvalue problem for 3C SiC.

5.3   Quasiparticle band structure of $3C$ SiC

The plasmon-pole model of Engel and Farid also allows very efficient GW calculations of quasiparticle energies [4]. Namely, by applying Eq. (5.13) the energy integration in the GW expression for the self-energy can be done analytically [26]. Writing

$$\underline{W}(\vec{q}, E) = \underline{v}(\vec{q}) + \underline{W}^{\mathrm{scr}}(\vec{q}, E), \qquad (5.15)$$

the first term in this equation leads to the energy independent Fock-contribution $\underline{\Sigma}^{\mathrm{Fock}}(\vec{k})$ to the self-energy $\underline{\Sigma}(\vec{k}, E)$. The second term, the screening part, leads to an energy dependent contribution $\underline{\Sigma}^{\mathrm{scr}}(\vec{k}, E)$.

Since the GW quasiparticle wave functions are practically indistinguishable from the LDA wave functions, which we also explicitly checked for $3C$ SiC, it is sufficient to calculate expectation values of the self-energy matrix for the LDA wave functions [33]. By taking expectation values in the original LDA eigenstates $\mid n, \vec{k} >$ we obtain the following relations for the desired quasiparticle energies $E_{n,\vec{k}}^{\mathrm{QP}}$

$$
\begin{aligned}
E_{n,\vec{k}}^{\mathrm{QP}} = \ & E_{n,\vec{k}}^{\mathrm{LDA}} - < n, \vec{k} \mid V^{\mathrm{XC}} \mid n, \vec{k} > + < n, \vec{k} \mid \Sigma^{\mathrm{Fock}}(\vec{k}) \mid n, \vec{k} > \\
& < n, \vec{k} \mid \Sigma^{\mathrm{scr}}(\vec{k}, E_{n,\vec{k}}^{\mathrm{LDA}}) + (E_{n,\vec{k}}^{\mathrm{QP}} - E_{n,\vec{k}}^{\mathrm{LDA}}) \left. \frac{\partial \Sigma^{\mathrm{scr}}}{\partial E} \right|_{E=E_{n,\vec{k}}^{\mathrm{LDA}}} \mid n, \vec{k} > . \quad (5.16)
\end{aligned}
$$

In this expression a correction term (last term) has been added in order to account for the fact that the expectation values are calculated at the original LDA energy levels. This is sufficiently corrected for by the first term in a Taylor expansion around $E = E_{n,\vec{k}}^{\mathrm{LDA}}$. Eq. (5.16) can be rewritten in the form

$$E_{n,\vec{k}}^{\mathrm{QP}} = E_{n,\vec{k}}^{\mathrm{LDA}} + Z_{n,\vec{k}} < n, \vec{k} \mid -V^{\mathrm{XC}} + \Sigma^{\mathrm{Fock}}(\vec{k}) + \Sigma^{\mathrm{scr}}(\vec{k}, E_{n,\vec{k}}^{\mathrm{LDA}}) \mid n, \vec{k} > , \qquad (5.17)$$

where $Z_{n,\vec{k}}$ is the so-called wave function renormalization factor, given by

$$Z_{n,\vec{k}} = \frac{1}{1 - < n, \vec{k} \mid \left. \frac{\partial \Sigma^{\mathrm{scr}}}{\partial E} \right|_{E=E_{n,\vec{k}}^{\mathrm{LDA}}} \mid n, \vec{k} >}. \qquad (5.18)$$

The expectation value of the contribution of Σ^{scr}, occurring in (5.17), in terms of the plasmon pole model parameters, introduced in section 5.2, reads

$$\langle n, \vec{k} \mid \Sigma^{\mathrm{scr}}(\vec{k}, E) \mid n, \vec{k} \rangle = \int_{\mathrm{1BZ}} \frac{d^3 q}{(2\pi)^3} \sum_{l,m} \frac{\left| \sum_{\vec{G}} w_{m,\vec{q}}^*(\vec{G}) \sum_{\vec{G}'} d_{l,\vec{q}-\vec{k}}(\vec{G}') d_{n,\vec{k}}(\vec{G} - \vec{G}') \right|^2}{E - E_{l,\vec{k}-\vec{q}}^{\mathrm{LDA}} + (\omega_m(\vec{q}) - i\eta)\mathrm{sgn}(\mu - E_{l,\vec{k}-\vec{q}}^{\mathrm{LDA}})} . $$
$$(5.19)$$

This expression and its energy derivative have both to be evaluated at the LDA energies $E = E_{n,\vec{k}}^{\mathrm{LDA}}$. The coefficients $d_{l,\vec{q}}(\vec{G})$ are the plane-wave coefficients of the LDA wave

Table 5.1: The expectation values of $-V^{\mathrm{XC}}$, Σ^{Fock} and Σ^{scr} (in eV), the wave function renormalization factor Z and the quasiparticle shift ΔE (in eV) of 3C SiC for the highest valence band and the lowest conduction band at three $\vec{k}$-points.

$n, \vec{k}$	$-V^{\mathrm{XC}}$	Σ^{Fock}	Σ^{scr}	Z	ΔE
Γ_{15v}	14.32	-17.25	1.51	0.8082	-1.15
Γ_{1c}	12.99	-7.53	-5.65	0.8048	0.10
X_{5v}	13.13	-17.16	2.29	0.8002	-1.50
X_{1c}	10.54	-6.42	-4.16	0.8314	0.00
L_{3v}	13.95	-17.25	1.77	0.8062	-1.27
L_{1c}	11.98	-6.89	5.15	0.8179	0.15

functions. We note that Eq. (5.19) leads to real quasiparticle energies in a broad region around the gap of the order of the minimum plasmon energy of 22.4 eV. For the Brillouin zone integration occurring in Eq. (5.19) a grid of 64 $\vec{k}$-points was used. The number of reciprocal lattice vectors and bands taken into account was 229. With these values the quasiparticle energy differences were converged within 0.05 eV.

We emphasize the numerical efficiency with which Eq. (5.19) can be evaluated. In particular, the structure of the numerator as the square of the inner product of the vector $\underline{w}_{m,\vec{q}}$ with the convolution of $\underline{d}_{l,\vec{q}-\vec{k}}$ and $\underline{d}_{n,\vec{k}}$ and the fact that the plasmon-pole energies do not depend on the reciprocal lattice vectors allow a very fast algorithm. Furthermore, the convolution can be performed with a fast Fourier transform algorithm.

In Table 5.1 the expectation values of $-V^{\mathrm{XC}}$, Σ^{Fock} and Σ^{scr} are given together with the Z factors and the quasiparticle energy corrections $\Delta E = E^{\mathrm{QP}} - E^{\mathrm{LDA}}$ at three $\vec{k}$-points in the 1BZ for the highest valence band and the lowest conduction band. In Fig. 5.2 the calculated quasiparticle band structure is displayed. For comparison the band structure as obtained within the LDA as well as the valence band data as measured by Hoechst et al. [32], using photoemission spectroscopy, and the data from Ref. [48] are given. The experimental valence band dispersions of Ref. [32] are in good agreement with both the GW and LDA obtained dispersions. The indirect band gap of 3C SiC is calculated to be 2.37 eV. In Table 5.2 we give the LDA energies and our quasiparticle energies at high symmetry points in the 1BZ, together with recently calculated values by Rohlfing et al. [58] and Wenzien et al. [62] and some known experimental values. The main differences between the present work and the work of Rohlfing et al. [58] concern the use of a different plasmon-pole model, of different ionic pseudopotentials

Table 5.2: The LDA and the quasiparticle energies (in eV) for 3C SiC. The experimental are from Ref. [48], except for the ones marked with an asterisk which are from Ref. [47].

$n, \vec{k}$	LDA	Present	Ref.[58]	Ref.[62]	Expt.
Γ_{1v}	−15.07	−16.13	−16.44	−16.92	
Γ_{15v}	0.00	0.00	0.00	0.00	0.00
Γ_{1c}	6.57	7.81	7.35	7.67	7.59*
Γ_{15c}	7.24	8.66	8.35	8.72	7.75, 8.74*
X_{1v}	−10.12	−11.19	−11.24	−11.67	
X_{3v}	−7.70	−8.38	−8.64	−8.38	
X_{5v}	−3.06	−3.42	−3.62	−3.40	−3.6
X_{1c}	1.22	2.37	2.34	2.59	2.390, 2.389, 2.416
X_{3c}	4.14	5.55	5.59	5.56	5.5,4.7
X_{5c}	13.93	16.05	15.78	16.10	
L_{1v}	−11.57	−12.65	−12.75	−13.19	
L_{1v}	−8.45	−9.15	−9.42	−9.12	
L_{3v}	−0.98	−1.11	−1.21	−1.14	−1.16
L_{1c}	5.46	6.76	6.53	6.73	4.2
L_{3c}	7.12	8.68	8.57	8.73	8.5
L_{1c}	10.14	12.08	12.04	11.96	

Figure 5.2: *The calculated band structure for 3C SiC along the ΓL- and the ΓX-axis within the LDA (dotted line) and the GW method (solid line). We have also indicated the experimental (open circles) valence band data of Ref. [32] and conduction band data of Ref. [48].*

and of Gaussian orbitals as basis functions instead of plane waves. The approach of Wenzien *et al.* [62] differs from ours by the use of a model dielectric function (instead of a directly calculated dielectric matrix), in which the experimental dielectric constant is incorporated. Further differences appear in the LDA-like treatment of the local-field effects and the use of different ionic pseudopotentials. The agreement between our calculated quasiparticle energies, the experimental values and the quasiparticle energies calculated by Rohlfing *et al.* [58] and Wenzien *et al.* [62] is on the whole very good. Completely in line with these authors we find a clear disagreement between the experimental and calculated electron energy $E(L_{1c})$ of the lowest conduction band. New measurements could decide whether the failure is on the theoretical or the experimental side.

5.4 Quasiparticle effects for other SiC polytypes

5.4.1 Discussion about a uniform quasiparticle shift

The obtained quasiparticle corrections to the lowest conduction band of $3C$ SiC amount to an average increase of 1.23 eV, compared to the quasiparticle valence band top, with a variation over the 1BZ not larger than 0.08 eV. Note that only relative energy shifts of conduction bands in relation to the valence band top are relevant for the gap determination. In Ref. [58] and [62] this upward shift is found to be 1.01 ± 0.07 and 1.37 ± 0.07 eV, respectively. So, since the variation of this shift through the 1BZ in all cases is found to be small, we may pose that the "scissor" operation for only the lowest conduction band works rather well.

In line with this, Käckell, Wenzien and Bechstedt [40] have, first, assumed a rigid shift of the lowest conduction bands against the valence bands for *all* SiC polytypes. Other authors make this suggestion as well [47, 14, 49]. Käckell *et al.* have actually determined this general shift to be $\Delta_{QP} = 1.13$ eV. To achieve this, they used a very simplified GW calculation in which dynamical screening and effects of the off-diagonal elements of the dielectric matrix (i.e. local-field effects) were neglected. Their result differs about 0.1 eV from our rigorous full GW result for the quasiparticle correction throughout the Brillouin zone of $3C$ SiC.

Additionally, Wenzien, Käckell and Bechstedt [62] have recently performed more accurate GW calculations to obtain the band gaps of the $3C$, $6H$ and $4H$ SiC polytypes separately. In these calculations they found quasiparticle corrections (to their calculated Kohn-Sham gaps) of 1.30, 1.26 and 1.35 eV, respectively. Our calculated quasiparticle correction to the band gap of $3C$ SiC, on the other hand, was found to be 1.15 eV which is 0.15 eV smaller than their result for $3C$ SiC. Wenzien *et al.* ascribe this discrepancy to the use of a different dielectric constant and a different kind of approximation for W. Anyhow, most important is that they found no systematic tendency of the quasiparticle corrections with hexagonality h. This gives support to the assumption of a polytype independent quasiparticle energy shift.

From the results of our LDA calculations in Chapter 3 for the building-block representations of the respective SiC polytypes we came to the conclusion that a rigid energy shift of $\Delta_{QP} = 1.2 \pm 0.1$ eV was sufficient in order to bring the calculated Kohn-Sham gaps into agreement with the experimental gaps of the polytypes with $h \leq 50\%$. This shift closely resembles both the value of 1.13 eV [40], as obtained from the very simplified (static) GW calculation, and the average value 1.3 eV [62], as obtained from more accurate calculations on $3C$, $6H$ and $4H$ SiC.

From the interface matching method of Chapter 3 a few insights about the superlat-

tice wave functions can be derived that make it possible to reason why the quasiparticle energy corrections for the other polytypes of SiC should approximately be the same to the quasiparticle correction for $3C$ SiC. To explain this nearly polytype independent shift, we have to argue why the expectation values of Σ for the lowest conduction and the highest valence band states in different polytypes are not much differing. To this end, we first of all note that the non-locality of $\Sigma(\vec{r}, \vec{r}', E)$ in $3C$ SiC is essential to reproduce the experimental energy levels. The spatial range of the non-local part of Σ in $3C$ SiC is approximately $0.2a_c$, which is comparable to the wave length of the wave functions and therefore yields an important contribution to the expectation values of Σ. This was already noted by Godby, Schlüter and Sham in Refs. [29, 30] for other semiconductors. Because the wave function of the lowest conduction band state is more rapidly oscillating than the highest valence band wave functions, the expectation value of Σ is smaller (i.e. less negative) for the lowest conduction band state then for the highest valence band states. Consequently, the band gap energy increases. The appearance of $\Sigma(\vec{r}, \vec{r}', E)$ in the cubic segments of the polytype superlattices is expected to be quite similar to $\Sigma(\vec{r}, \vec{r}', E)$ of untwisted or twisted bulk cubic SiC. First we focus on the quasiparticle correction to the energy level of the wave functions of the LDA valence band top. From the interface matching method we have observed that the superlattice wave functions pertaining to this valence band top are made up by a linear combination of the six very weakly evanescing waves (see Fig. 3.4). This means that other (strongly evanescing) waves hardly contribute and can be left out of the consideration. Since the six weakly evanescing waves all have an energy value slightly above the valence band top of $3C$ SiC, each of them is highly resembling one of the six Bloch waves related to, or near to, the valence band top of the basis material. For these six related Bloch wave functions of $3C$ SiC we have properly calculated the quasiparticle energy corrections. We found that these corrections are all approximately equal to -1.15 eV and not significantly deviating among the six Bloch wave functions for the energies somewhat different from $E^{\mathrm{LDA}} = 0$ (see Fig. 5.2). Therefore we think it is plausible that the quasiparticle energy corrections to the superlattice wave functions, which are related to the the valence band top, are of comparable sizes. Next we consider the conduction band minimum of the polytype superlattices. The wave function at the conduction band edge of the superlattice happens to be made up by a linear combination of $3C$ waves in which Bloch waves as well as evanescent waves considerably contribute. However, since the evanescent waves are strongly evanescing from the interface, they hardly contribute to the superlattice wave function inside the $3C$ building blocks. So, inside the $3C$ building blocks the superlattice wave function is made up by a linear combination of two Bloch waves, which pertain to the lowest

conduction band of 3*C* SiC. Therefore we expect that it is, as a good first approximation, sufficient to calculate the quasiparticle correction to this linear combination of the 3*C* Bloch waves. Since the scissor operator works rather well for the lowest conduction band of 3*C* SiC, the quasiparticle correction for this linear combination of two Bloch waves is nearly equal to the quasiparticle correction for the 3*C* SiC conduction band minimum itself. And because in 3*C* SiC the value of the quasiparticle shift has appeared to be quite small (see Table 5.1) no drastic differences for the polytype superlattices are expected.

The above results lead to the conclusion that the addition of quasiparticle corrections to the Kohn-Sham band gaps of polytypes of SiC implies an almost rigid shift of about 1.2 ± 0.1 eV for all polytypes. This implies, among other things, that the band gap variation between polytypes of 1 eV is in no way related to quasiparticle corrections. This variation already completely results from LDA calculations, or, alternatively, from or matching procedure to building-block made polytype superlattices.

5.4.2 Outlook

In order to accurately determine whether indeed the deviations from the rigid quasiparticle shift for each polytype are small, we suggest to apply a state-of-the-art *GW* scheme, as e.g. presented in this chapter, to at least those non-cubic polytypes which have the smallest unit cells. In applying our scheme to non-cubic polytypes of SiC we should, however, first be aware of the complications connected with the different crystal symmetry.

Problems may arise due to the fact that the non-cubic crystals have anisotropic dielectric constants. For hexagonal polytypes the longitudinal (i.e. parallel to the *c*-axis) dielectric constant ϵ_{Mz} is different from the transversal (i.e. perpendicular to the *c*-axis) dielectric constant $\epsilon_{Mx} = \epsilon_{My}$. For instance, for 6*H* SiC these values are $\epsilon_{Mz} = 6.70$ and $\epsilon_{Mx} = 6.52$, while for 3*C* SiC the isotropic value $\epsilon_M = 6.52$ [48]. One of the computational consequences of this anisotropy is that the $\vec{q}$-integration appearing in expression (5.19) cannot be performed in the same way as for the cubic case. Formally, for $\vec{q} \to 0$ we have to perform this integration numerically along each direction. It is true that the anisotropy is quite small (3% for 6*H* SiC), but it should nevertheless be dealt with in a proper way. Wenzien *et al.* [62] have performed *GW* calculations for the polytypes 3*C*, 2*H*, 4*H*, 6*H* SiC in which some anisotropic effects of the dielectric constants were explicitly incorporated. In their *GW* scheme the above mentioned experimental dielectric constants of 6*H* and 3*C* SiC were used to obtain the dielectric constants of 2*H* and 4*H* SiC by interpolating and extrapolating the experimental constants as a function

of hexagonality. These constructed dielectric constants were then incorporated in the
dielectric response functions to calculate the quasiparticle energies of the four poly-
types. Satisfying quasiparticle energy results were found with this scheme. However,
it is not clear whether the dielectric constants of hexagonal polytypes do indeed vary
linearly with hexagonality. Because of this, together with the fact that the anisotropy
is small, a better approach is possibly to neglect the anisotropy for a particular poly-
type for $\vec{q} \to 0$ by calculating the quasiparticle energies according to our GW scheme
in which averaged plasmon poles for $\vec{q} \to 0$ are taken into account. Note in proposing
so, that we intend to use wave functions and energies obtained from (anisotropic) LDA
calculations and that the integrations over $\vec{k}$ along the three directions throughout the
entire Brillouin zone are performed in the usual way.

The major problem in calculating the quasiparticle energies in SiC polytypes arises
from the fact that the primitive cells of non-cubic polytype structures are larger than
the primitive cell of cubic SiC. An increase in primitive cell volume involves an approx-
imately linear increase in the number of plane-wave basis functions (N) to be dealt
with in the calculations. This will computationally restrict the application of our GW
scheme to a limited set of polytype structures. We expect that the GW scheme of this
chapter can indeed be applied to the structures $2H$, $4H$ and possibly $6H$ SiC. The
most important computational restrictions due to the number of plane waves arise in
the calculation of the static polarizability matrix $\underline{P}(\vec{q}, \omega = 0)$ and in the determination
of the expectation values of the self-energy operator. The required time to calculate
the static polarizability matrix by means of the expression (5.7) increases with N^3.
The required time to calculate the expectation values of Σ by means of expression
(5.19) also increases with N^3. Adopting the minimum number of plane waves required
for $3C$ SiC to be 137, and taking the same number of $\vec{k}$-points for the Brillouin zone
integration for any polytype, the computation times for the quasiparticle corrections
for $2H$, $4H$ and $6H$ would increase by a factor of about 2^3, 4^3 and 6^3, respectively.
In view of the fact that the computation of one quasiparticle correction (i.e. for one
band index and one $\vec{k}$-point) for $3C$ SiC with $N = 137$ takes about five minutes (for
a IBM RS/6000 system), we believe that the calculation for $2H$, $4H$ and possibly $6H$
is feasible, at least for a few important $\vec{k}$-points and band indices. GW calculations
according to the scheme of this chapter for more complicated polytypes should, how-
ever, be considered as temporarily unfeasible. Such state-of-the-art calculations make
sense in our opinion, as a means to verify the reliability of less sophisticated methods
such as the one advanced in Chapter 3. Apart from that we do not expect to obtain
interesting new features from such calculations, which are not already obtained by our
method.

Bibliography

[1] S.L. Adler, Phys. Rev. **126**, 413 (1962).

[2] G.B. Bachelet, H.S. Greenside, G.A. Baraff and M. Schlüter, Phys. Rev. B **24**, 4745 (1981).

[3] W.H. Backes, P.A. Bobbert and W. van Haeringen, Phys. Rev. B **49**, 7564 (1994).

[4] W.H. Backes, P.A. Bobbert and W. van Haeringen, Phys. Rev. B **51**, 4950 (1995).

[5] W.H. Backes, P.A. Bobbert, W. van Haeringen and J.T. Devreese, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors*, Vancouver, edited by D.J. Lockwood (World Scientific, Singapore), p. 385 (1995).

[6] W.H. Backes, F.C. de Nooij, P.A. Bobbert and W. van Haeringen, Physica B 217, 207 (1996).

[7] A. Baldereschi, E. Hess, K. Maschke, H. Neumann, K.-R. Schulze and K. Unger, J. Phys. C **10**, 4709 (1977).

[8] G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les éditions de physique, Paris, 1988).

[9] O. Brafman and I.T. Steinberger, Phys. Rev. **143**, 501 (1966).

[10] S. Brand and D.T. Hughes, Semicond. Sci. Technol. **2**, 607 (1987).

[11] P.E. van Camp, V.E. van Doren and J.T. Devreese, unpublished.

[12] R. Car, E. Tosatti, S. Baroni and S. Leelaprute, Phys. Rev. B **24**, 985 (1981).

[13] Y. Chang and J.N. Schulman, Phys. Rev. B **25**, 3975 (1982).

[14] J. Chen, Z.H. Levine and W. Wilkins, Phys. Rev. B **50**, 11514 (1994).

[15] C. Cheng, V. Heine and I.L. Jones, J. Phys.: Condens. Matter **2**, 5097 (1990).

[16] C. Cheng, R.J. Needs and V. Heine, J. Phys.: Solid State Phys. **21** 1049 (1988); C. Cheng, V. Heine and R.J. Needs, J. Phys.: Condens. Matter **2**, 5115 (1990).

[17] M.Y. Chou, M.L. Cohen and S.G. Louie, Phys. Rev. B **32**, 7979 (1985).

[18] W.J. Choyke, D.R. Hamilton and L. Patrick, Phys. Rev. **133**, 1163 (1964).

[19] W.J. Choyke and L. Patrick, Phys. Rev. **127**, 1868 (1962).

[20] M.L. Cohen and T.K. Bergstrasser, Phys. Rev. **141**, 789 (1966).

[21] J.P. Cuypers, *Scattering of electrons at heterostructure interfaces*, PhD thesis, Eindhoven University of Technology, 1992.

[22] J.P. Cuypers and W. van Haeringen, J. Phys. C **4**, 2587 (1992).

[23] P.J.H. Denteneer, *The pseudopotential-density-functional method applied to semiconducting crystals*, PhD thesis, Eindhoven University of Technology, 1987.

[24] P.J.H. Denteneer and W. van Haeringen, Solid State Comm. **65**, 115 (1988).

[25] G.B. Dubrovskiĭ and A.A. Lepneva, Sov. Phys. Solid State **19**, 729 (1977).

[26] G.E. Engel and B. Farid, Phys. Rev. B **47**, 15931 (1993).

[27] G.E. Engel and R.J. Needs, J. Phys.: Condens. Matter **2**, 367 (1990).

[28] M. Gell-Mann and K.A. Brueckner, Phys. Rev. **106** 364 (1957); E.P. Wigner, Phys. Rev. **46**, 1002 (1934).

[29] R.W. Godby, M. Schlüter and L.J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[30] R.W. Godby, M. Schlüter and L.J. Sham, Phys. Rev. B **37**, 10159 (1988).

[31] L. Hedin, Phys. Rev. **139**, A796 (1965); L. Hedin and S. Lundqvist, Solid Sate Phys. **23**, 1 (1969).

[32] H. Hoechst, M. Tang, B.C. Johnson, J.M. Meese, G.W. Zajac and T.H. Fleish, J. Vac. Sci. Technol. A5, 1640 (1987).

[33] M.S. Hybertsen and S.G. Louie, Phys. Rev. B **35**, 5585 (1987).

[34] Z. Ikonic, G.P. Srivastava and J.C. Inkson, Phys. Rev. B **46** 15150 (1992).

[35] Z. Ikonic, G.P. Srivastava and J.C. Inkson, Solid State Commun. **12**, 799 (1993).

[36] P.A. Ivanov and V.E. Chelnokov, Semicond. Sci. Technol. **7**, 863 (1993).

[37] R.O. Jones and O. Gunnarsson, Rev. Mod. Physics **61**, 689 (1989).

[38] H.-G. Junginger and W. van Haeringen, Phys. Stat. Sol. **37**, 709 (1970).

[39] D.L. Johnson, Phys. Rev. B **9**, 4475 (1974).

[40] P. Käckell, B. Wenzien and F. Bechstedt, Phys. Rev. B **50**, 10761 (1994).

[41] P. Käckell, B. Wenzien and F. Bechstedt, Phys. Rev. B **50**, 17037 (1994).

[42] P. Käckell and F. Bechstedt, Phys. Rev. Lett. **75**, 2180 (1995).

[43] W.F. Knippenberg, Philips Res. Rep. **18**, 161 (1963).

[44] D.Y.K. Ko and J.C. Inkson, Phys. Rev. B **38**, 9945 (1988).

[45] W. Kohn and L.J. Sham, Phys. Rev. **140** A1133 (1965).

[46] P. Krishna, *Crystal growth and characterization of polytype structures* (Pergamon Press, Oxford, 1983).

[47] W.R.L. Lambrecht, B. Segall, M. Yoganathan, W. Suttrop, R.P. Devaty, W.J. Choyke, J.A. Edmond, J.A. Powell and M. Alouani, Phys. Rev. B **63**, 2747 (1993); Phys. Rev. B **50**, 10722 (1994).

[48] *Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vols. 17a and 22c (Springer, Berlin, 1982 and 1986).

[49] Keun-Ho Lee, C.H. Park, Byoung-Ho Cheong and K.J. Chang, Solid State Commun. **11**, 869 (1994).

[50] J.A. Lely, *Berichte der Deutchen Keramischen Gesellschaft e.V.*, **32**, 229 (1955).

[51] W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988).

[52] P.G. Neudeck, J. of Electronic Materials, Vol. 24, No. 4 (1995).

[53] C.H. Park, Byoung-Ho Cheong, Keun-Ho Lee and K.J. Chang, Phys. Rev. B **49**, 4485 (1994).

[54] L. Patrick, Phys. Rev. B **5**, 2198 (1972).

[55] L. Patrick, D.R. Hamilton and W.J. Choyke, Phys. Rev. **143**, 526 (1966).

[56] A. Qteish, V. Heine and R.J. Needs, Phys. Rev. B **45**, 6376 (1992).

[57] H. Raether, *Excitations of Plasmons and Interband Transitions by Electrons*, Springer Tracts in Modern Physics No. 88 (Springer, Berlin, 1980).

[58] M. Rohlfing, P. Krüger and J. Pollmann, Phys. Rev. B **48**, 17791 (1993).

[59] Y.M. Tairov and Y.A. Vodakov, in *Topics in Applied Physics*, edited by J.I. Pankove, Vol. 17 (Springer-Verlag, Berlin, 1977).

[60] S. Tyc and C. Arnodo, Revue Technique Thomson-CSF, Vol. 26, No. 2 (1994).

[61] A.R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, New York, 1966).

[62] B. Wenzien, P. Käckell, F. Bechstedt and G. Cappellini, Phys. Rev. B **52**, 10897 (1995).

[63] N. Wiser, Phys. Rev. **129**, 62 (1963).

[64] R.W.G. Wyckoff, *Crystal Structures*, Vol. 1 (Interscience Publishing, New York, 1963).

[65] S.B. Zhang, D. Tomanék, M.L. Cohen, S.G. Louie and M.S. Hybertsen, Phys. Rev. B **40**, 3162 (1989).

Summary

In this thesis we describe a theoretical method which enables us to determine the behavior of electrons in polytypes of silicon carbide (SiC). Polytypes are different crystal structures of one chemical substance (e.g. SiC or ZnS). A striking and experimentally observed property of SiC polytypes is that they exhibit a strong variation (1 eV) in band gap energy which systematically depends on the lattice structure. Up to now theoretical methods to calculate and explain the gap variation were missing. The method we use gives in to this.

Our idea to this is to interpret polytypes of SiC as superlattices of which the stacked sublattices consist of cubic SiC. Cubic SiC is the polytype with the least complicated crystal structure and acts as the basis material to build up the other polytypes. The characteristic feature of the polytype superlattices is that adjacent sublayers are mutually rotated over 60° around the stacking axis. These rotations give rise to new crystals with electronic properties which are rather different from the basis material. Differences between polytypes are in this representation the result of differences in widths of the sublayers.

By representing the polytypes as superlattices we can apply a particular method which purely departs from the intrinsic electronic properties of the basis material and the dimensions of the superlattice. For this we only need the complex band structure and the related electron wave functions of cubic SiC. Within the method we take for each sublayer linear combinations of all wave functions of cubic SiC which are subsequently matched at the interfaces to similar combinations in the adjacent (rotated) sublayers by means of continuous boundary conditions. The wave functions which we need for this are not only the Bloch waves, but also the evanescent waves related to the complex part of the band structure of cubic SiC. With this superlattice method we are able to calculate the Bloch wave functions, the band structure and particularly the band gaps of all SiC polytypes.

To justify the application of the superlattice method, the separate sublayers have to be highly bulk-like cubic SiC. Not only the crystal structure but also the distribution of the electrons in the sublayers has therefore to resemble the one of cubic SiC. Our

investigation demonstrates that this approximation is good for those SiC polytypes which have sublayers wider than one Si-C-layer. For the one existing polytypes ($2H$ SiC) in which the sublayers purely consist of one Si-C-layer, the validity of this method has appeared to be doubtful.

The band gap variation, as obtained with this method, appears to agree well with the measured variation. This means that our superlattice representation of the SiC polytypes contains all elements that can explain the variation of the band gaps. Furthermore, it appears that the band gap variation mainly arises due to energy shifts of the conduction band minimum and not due to possible changes of the valence band maximum.

In order to understand why different superlattices show mutually different band gaps and, in particular, different band gaps from the basis material, we have developed a one-dimensional model. In this model we use the scattering properties of a Bloch wave which is approaching the interface. This incoming Bloch wave pertains to the minimum of the conduction band of cubic SiC. The band gap is determined by interpreting the superlattice as a periodic array of interfaces where the Bloch waves scatter. These scatterings are described by means of particular discontinuous boundary conditions for the envelope functions of the Bloch waves. These discontinuous boundary conditions are derived from the reflection and transmission properties of a Bloch wave at a single interface of the polytypic superlattice. Depending on the distances between the interfaces resonances arise at certain energies of the Bloch waves. The lowest energy for which these resonances arise represents the band gap energy. As the layer widths decrease it appears that the gap energy increases. The fact that the band gaps of SiC polytypes, contrary to the ZnS polytypes and hypothetical polytypes of Si, C and AlAs, vary in a rather broad region of 1 eV can be explained from the characteristic band structure properties of the basis material cubic SiC.

We have obtained the complex band structure and the related wave functions of cubic SiC, which we use in the superlattice method, from the empirical pseudopotential method on the one hand and from the *ab initio* LDA band structure method on the other hand. The EPM results for the band gaps of the polytypes excellently agree with the experimentally found data. For the LDA method as a ground-state theory on the other hand it is known to predict a too small value for the band gap energy. This appears also from the calculated LDA band gap of cubic SiC. We find that the LDA method underestimates the experimental band gaps of all SiC polytypes by an almost constant energy value. Anyhow, this means that the quasiparticle effects hardly exert influence on the variation of the band gaps in SiC polytypes.

In order to find in a non-empirical way the experimental band gap, we calculate for

the cubic polytype the necessary quasiparticle correction to the LDA band gap. This correction is necessary to include excitation effects which are not present in the LDA ground-state theory. Within this so-called *GW* calculation we have used a physical plasmon-pole model to approximate various dielectric response functions by a convenient mathematical expression. This expression enables us to carry out particular integrations analytically, which is very advantageous considering the numerical complications of the *GW* calculation. An other advantage of this is that the plasmon dispersion can be calculated and compared with an experiment. The lowest plasmon energy appears to be in excellent agreement with the experimentally found value. The thus calculated quasiparticle correction excellently agrees with the value which is necessary to reproduce the experimental band gap.

Samenvatting

In dit proefschrift wordt een theoretische methode beschreven waarmee we het gedrag van elektronen bepalen in polytypen van siliciumcarbide (SiC). Polytypen zijn verschillende kristalstructuren van één bepaalde chemische verbinding (bijv. SiC of ZnS). Een opvallende en experimenteel vastgestelde eigenschap van SiC polytypen is dat ze een sterke variatie (1 eV) in bandgapenergie vertonen die op een systematische manier afhangt van het kristalrooster. Tot voor kort ontbrak een theoretische methode om de gapvariatie te kunnen berekenen en verklaren. De methode die we in dit proefschrift gebruiken komt hieraan tegemoet.

Ons idee daartoe is de polytypen van SiC op te vatten als superroosters waarvan de gestapelde deelroosters (deellagen) bestaan uit kubisch SiC. Kubisch SiC is het polytype met de minst gecompliceerde kristalstructuur en fungeert als basismateriaal om de superroosters van alle andere polytypen op te bouwen. Het kenmerkende van de polytype-superroosters is dat aangrenzende deellagen 60° om de stapelas ten opzichte van elkaar zijn gedraaid. Door deze draaiingen ontstaat een nieuw kristal dat geheel andere elektronische eigenschappen heeft dan het basismateriaal. Verschillen tussen polytypen zijn in deze voorstelling het gevolg van verschillen in de breedtes van de deellagen.

Door de polytypen als superroosters voor te stellen kunnen we een bepaalde methode toepassen die louter van de intrinsieke elektronische eigenschappen van het basismateriaal en de afmetingen van het superrooster uitgaat. We hebben daarvoor alleen de complexe bandstructuur en de bijbehorende elektrongolffuncties nodig van het kubisch SiC. In de methode worden voor elke deellaag lineaire combinaties van alle golffuncties van kubisch SiC genomen die vervolgens met behulp van continue randvoorwaarden op de scheidingsvlakken worden aangesloten op soortgelijke lineaire combinaties in de naburige (gedraaide) deellagen. De golffuncties die we daarvoor nodig hebben zijn niet alleen de Blochgolven maar ook de uitdovende golven behorende bij het complexe gedeelte van de bandstructuur van kubisch SiC. Met deze superroostermethode kunnen we de Blochgolffuncties, de bandstructuur en in het bijzonder de bandgaps van alle SiC polytypen berekenen.

Om de toepassing van de superroostermethode op polytypen te rechtvaardigen moeten de afzonderlijke deellagen van de polytypen in hoge mate bulkachtig kubisch SiC zijn. Niet alleen de kristalstructuur maar ook de elektronenverdeling van de deellagen moet daarom veel lijken op die van kubisch SiC. Ons onderzoek toont aan dat deze benadering goed is voor die SiC polytypen waarvan de deellagen breder zijn dan één Si-C-laag. Voor het ene bestaande polytype ($2H$ SiC) waarin de deellagen louter bestaan uit slechts één Si-C-laag is deze methode van twijfelachtige waarde gebleken.

De met deze methode berekende bandgapvariatie blijkt uitermate goed overeen te stemmen met de gemeten variatie. Dit betekent dat onze superroostervoorstelling van de SiC polytypen alle elementen bevat die de bandgapvariatie kunnen verklaren. Verder blijkt dat de bandgapvariatie in hoofdzaak tot stand komt door energieverschuivingen van het geleidingsbandminimum en niet door eventuele veranderingen van het valentiebandmaximum.

Om nu te begrijpen waarom verschillende superroosters bandgaps vertonen die onderling, en in het bijzonder van het kubisch basismateriaal, verschillend zijn, hebben we een eendimensionaal model ontworpen. In dit model worden de verstrooiingseigenschappen van een Blochgolf die het scheidingsvlak nadert gebruikt. Deze inkomende Blochgolf behoort tot het minimum van de geleidingsband van kubisch SiC. De bandgap wordt bepaald door het superrooster op te vatten als een periodieke serie van scheidingsvlakken waaraan Blochgolven verstrooien. Deze verstrooiingen worden beschreven aan de hand van bepaalde discontinue randvoorwaarden voor de envelope-functies van de Blochgolven. Deze discontinue randvoorwaarden zijn afgeleid uit de reflectie- en transmissie-eigenschappen van een Blochgolf aan één enkel scheidingsvlak van het polytype-superrooster. Afhankelijk van de afstanden tussen de scheidingsvlakken treden er dan bij bepaalde energieën van de Blochgolven resonanties op. De laagste energie waarbij deze resonantie optreedt geeft de bandgapenergie. Het blijkt dat naarmate de laagbreedtes kleiner worden de gapenergie toeneemt. Dat de bandgaps van SiC polytypen, in tegenstelling tot ZnS polytypen en hypothetische polytypen van Si, C en AlAs, in een nogal breed gebied van 1 eV variëren, is te verklaren aan de hand van de karakteristieke bandstructuureigenschappen van het basismateriaal kubisch SiC.

De complexe bandstructuur en bijbehorende golffuncties van kubisch SiC, die we in de superroostermethode gebruiken, hebben we verkregen uit enerzijds de empirische pseudopotentiaalmethode (EPM) en anderzijds uit de *ab initio* LDA-bandstructuurmethode. De EPM-resultaten voor de bandgaps van de polytypen stemmen uitermate goed overeen met de experimenteel gevonden waarden. De LDA-methode daarentegen staat er als grondtoestandstheorie bekend om een te kleine waarde te voorspellen voor de bandgapenergie. Dit blijkt dan ook uit de berekende LDA-bandgap voor kubisch

SiC. We vinden dat de LDA-methode de experimentele band gaps voor alle SiC poly-
typen met een nagenoeg constante energiewaarde onderschat. Dit betekent in ieder
geval dat de quasideeltjeseffecten nauwelijks van invloed zijn op de variatie van de
band gaps in SiC polytypen.

Om toch op een niet-empirische manier de experimentele bandgap te vinden, bereke-
nen we voor het kubisch SiC polytype de nodige quasideeltjescorrectie op de LDA-
bandgap. Deze correctie is noodzakelijk om excitatie-effecten mee te nemen die niet in
de LDA-grondtoestandtheorie aanwezig zijn. In deze zogenaamde *GW*-berekening is
gebruik gemaakt van een fysisch plasmonpoolmodel om diverse diëlektrische respons-
functies te benaderen met een handige mathematische uitdrukking. Deze uitdrukking
stelt ons namelijk in staat bepaalde integraties analytisch uit te voeren, hetgeen zeer
voordelig is gezien de numerieke gecompliceerdheid van de *GW*-berekening. Een ander
voordeel hiervan is dat een plasmondispersie kan worden berekend die met een experi-
ment kan worden vergeleken. De laagste plamonenergie blijkt goed in overeenstemming
te zijn met de experimenteel gevonden waarde. De aldus berekende quasideeltjescorrec-
tie stemt uitstekend overeen met de waarde die nodig is om de experimentele bandgap
op te leveren.

Dankwoord

Voor de totstandkoming van dit proefschrift en de daaraan verbonden artikelen ben ik aan een aantal mensen dank verschuldigd. Op de eerste plaats is dit mijn promotor Wim van Haeringen die mij enthousiast begeleidde gedurende de promotieperiode en mij de vrijheid gaf de lerarenopleiding te voltooien. Ten tweede is dit Peter Bobbert met name vanwege zijn kritische kijk op de diverse manuscripten. Verder ben ik prof.dr. J.T. Devreese, dr. V. van Doren en dr. P. van Camp uit Antwerpen erkentelijk voor het leveren van de noodzakelijke gegevens voor de figuren 2.5 en 2.6. Tot slot dank ik Herman de Groot, omdat mijn promotiewerk zeker niet zo vlot verlopen zou zijn als hij mij niet op computer-technisch gebied had ondersteund.

Curriculum vitae

Geboorte   7 september 1966 te Heinsberg (Duitsland)

- 1978-1982   R.K. MAVO te St. Odiliënberg

- 1982-1986   Middelbaar Laboratorium Onderwijs te Sittard,
Laboratoriumtechniek (met lof)

- 1986-1987   Hogeschool Eindhoven,
Technische Natuurkunde, propadeuse

- 1987-1991   Technische Universiteit Eindhoven (TUE),
Technische Natuurkunde (met lof),
afstudeerrichting: Vaste Stof,
afstudeerlokatie: Universitaire Instellingen Antwerpen,
afstudeerscriptie: 'Longitudinale plasmonen in overgang
van een quasi-tweedimensionaal naar een driedimensionaal
elektrongas' onder begeleiding van prof.dr. J.T. Devreese

- 1991-1992   Militaire dienst

- 1992-1996   Promotieonderzoek aan de TUE onder begeleiding van
prof.dr. W. van Haeringen en dr. P.A. Bobbert
in de vakgroep Theoretische Natuurkunde van de
faculteit Technische Natuurkunde

- 1994-1995   Universitaire lerarenopleiding, natuurkunde

STELLINGEN

behorende bij het proefschrift

On the band gap variation in SiC polytypes

van

W.H. Backes

Eindhoven, 6 juni 1996

I.

De variatie in bandgapenergie die wordt aangetroffen onder polytypen van SiC kan niet worden verklaard met behulp van het Kronig-Penney-model.

[1] G.B. Dubrovskiĭ and A.A. Lepneva, Sov. Phys. Solid State **19**, 729 (1977).

[2] Dit proefschrift, hoofdstuk 4.

II.

Hexagonale polytypen van SiC met een lange eenheidscel hebben een bandgapenergie die afwijkt van de waarde die de lineaire Choyke-Hamilton-Patrick-relatie voorspelt.

[1] W.J. Choyke, D.R. Hamilton and L. Patrick, Phys. Rev. **133**, 1163 (1964).

[2] Dit proefschrift.

III.

SiC gaat een rijke toekomst tegemoet als halfgeleidermateriaal voor transistoren.

[1] P.A. Ivanov and V.E. Chelnokov, Semicond. Sci. Technol. **7**, 863 (1993).

[2] P.G. Neudeck, J. of Electronic Materials, Vol. 24, No. 4, 283 (1995).

[3] S. Tyc and C. Arnodo, Revue Technique Thomson-CSF, Vol. 26, No. 2, 467 (1994).

IV.

Het axial nearest neighbour Ising (ANNI) model, waarmee de totale-energieordening van SiC polytypen wordt berekend in termen van wisselwerkingsenergieën tussen bilagen op verschillende afstanden, gaat voorbij aan het netto ladingsverschil tussen hexagonale en kubische bilagen.

V.

De voorstelling van ZnS polytypen als periodieke stapelingen van kubische en hexago-
nale ZnS-bilagen biedt geen verklaring voor de (subtiele) variatie in bandgaps.

[1] O. Brafman and I.T. Steinberger, Phys. Rev. **143**, 501 (1965).

[2] Z.Z. Bandić and Z. Ikonić, Phys. Rev. B **51**, 9806 (1995).

VI.

Het verdient aanbeveling het gebruik, binnen de vaste-stoffysica, van het sommatiesym-
bool $\sum_{\vec{k}}$ in definities van grootheden expliciet vergezeld te laten gaan van de factor $1/\Omega$,
waarbij Ω het kristalvolume is.

VII.

Wetenschappers zouden moeten leren zich te beperken in de hoeveelheid informatie die
ze willen aanbieden tijdens voordrachten.

VIII.

Door de toename van opvoedende taken die scholen op zich nemen zou niet het gezin
maar de school steeds meer de hoeksteen van de samenleving genoemd kunnen worden.

IX.

Recente vernieuwingen in het vak natuurkunde binnen het VWO leiden ertoe dat dit
vak een bredere inhoud heeft doch zijn voorbereidende functie voor een universitaire
studie natuurkunde aan het verliezen is.

X.

Een wetenschapsquiz zal er niet toe leiden dat een breder publiek geïnteresseerd raakt
in wetenschap.

XI.

Fietsend neemt men een bocht naar rechts (links) het meest comfortabel door eerst
naar links (rechts) te sturen.