IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

A theoretical study of the local electronic structures of SiC polytypes

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 165

(http://iopscience.iop.org/0953-8984/9/1/018)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.207
The article was downloaded on 14/05/2010 at 06:03

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **9** (1997) 165–175. Printed in the UK PII: S0953-8984(97)74253-X

A theoretical study of the local electronic structures of SiC polytypes

G Cubiotti†, Yu N Kucherenko‡ and V N Antonov‡

† Dipartimento di Fisica, Sezione di Fisica Teorica, Università di Messina, PO Box 50, 98166 S Agata di Messina, Messina, Italy, and Istituto Nazionale di Fisica della Materia, Unità di Messina, Italy

‡ Institute of Metal Physics, National Academy of Sciences of the Ukraine, Vernadsky Street 36, 252142 Kiev, Ukraine

Received 8 May 1996, in final form 15 October 1996

Abstract. The electronic structure of four SiC polytypes has been computed by means of the LMTO (ASA+CC) method. It is shown that the results of the calculations are very sensitive to the choice of the atomic sphere radii, if the combined corrections are not taken into account in the ASA. The local electronic structure shows a different behaviour between the states in the cubic bilayers and those in the hexagonal ones. It is found that the interaction of *c* and *h* bilayers plays a major role, giving rise to changes in the polarity of the Si–C bonds and to charging of bilayers. The effect of the lattice distortion on the local valence electron charge has been investigated and discussed.

1. Introduction

The current interest in silicon carbide crystals is due to their strong chemical bonding, physical stability, and other attractive electrical, optical, and thermal properties, which are very promising for high-temperature, high-frequency, and high-power semiconductor devices. SiC crystallizes in either a cubic or a hexagonal form, and exhibits polytypism [1]: more than 100 different modifications have been observed. These polytypes are natural short-period superlattices, with the electronic band structure and, in particular, the indirect fundamental gap varying remarkably with the polytype. In the last few years extensive investigations have been performed in order to improve the understanding of the dependence of the electronic band structure of SiC on the polytype.

Recently several authors have studied theoretically the electronic structure of SiC polytypes by means of *ab initio* calculations: the first-principles pseudopotential (PP) methods [2–4] and the linear muffin-tin orbital method in the atomic-spheres approximation (LMTO–ASA) [5–7] have been used. It seems reasonable to compare the calculated results provided by different methods of calculations (PP and LMTO). Because of considerable discrepancies in the results published in [5] and in [7], especially for the value of the indirect fundamental gap, the applications of the LMTO–ASA method to the calculations of the electronic structure of the SiC polytypes should be also discussed in more detail.

In this work we present the results of the theoretical study of the electronic structures of four SiC polytypes (3C, 2H, 4H, and 6H). The calculations were performed using the LMTO method taking into account the corrections to the ASA (called the combined correction (CC)

0953-8984/97/010165+11$19.50 © 1997 IOP Publishing Ltd

terms in the ASA) [8, 9]. The effects of the CC as well as the influence of other model parameters on the calculated results were studied.

The published LMTO–ASA results were used for the explanation of optical properties of the SiC crystals, such as electroreflection spectra [5] and UV reflectivity [6, 7], while the details of the electronic structures were not discussed. In our opinion the investigation of the local electronic states, especially the differences in energy and spatial distributions of the valence electrons in the different atomic layers of the SiC crystals, are very important for the understanding of their physical and chemical properties. Moreover, due to the fundamental interest in the properties of the doped and amorphous silicon carbide [10], it is useful to study the influence of the crystal lattice distortions on the valence electron distribution.

The paper is organized as follows: in the next section we give briefly the computational details. The crystal structures of the SiC polytypes are described in section 3, where results of test calculations are also presented, which show a sensitivity of the calculated results to the choice of the atomic sphere radii. The numerical results on the SiC electronic structures are given and discussed in section 4. In section 5 the effects of the crystal lattice distortions on the electronic states in 6H-SiC are presented and discussed. Finally, we give a summary of our results in the last section.

2. Computational details

The energy band structures of SiC were calculated by means of the self-consistent LMTO method in the atomic-spheres approximation and including the combined corrections (ASA+CC). A detailed description of the LMTO method is given in [8] and [9]. The present calculations were performed within the scalar-relativistic approach. For calculation of exchange and correlation effects the local density approximation (LDA) was used in the form of von Barth–Hedin parametrization for the exchange–correlation potential [11]. We used the frozen-core approximation; the core charge distribution was evaluated using the solutions of the Dirac equation for free atoms. In order to obtain a close-packed structure, empty spheres were introduced in the interstitial regions. The angular momentum expansion of the basis functions was performed up to $l = 2$ for all the spheres in the unit cell. We calculated the density of states (DOS) by using the tetrahedron method [12], choosing from 260 (for 6H-SiC) to 308 (for 2H-SiC) $\boldsymbol{k}$-points in the irreducible part of the Brillouin zone.

3. Crystal structure and parameters of the model

Silicon carbide occurs in several modifications which are similar in basic principle and closely related to one another [1]. The polytypes considered in the present work (3C, 2H, 4H and 6H) have tetrahedral bonds, their local atomic arrangements being the same up to the second neighbours. When expressed in terms of hexagonal units, all these structures have practically the same value of the lattice constant a and a value of c which is proportional to the number of molecules in the hexagonal cell. The structural difference in the polytypes is well understood by considering the stacking sequence of the hexagonal bilayers (consisting of pairs of Si and C layers). Successive bilayers are displaced sidewise so that atoms in each bilayer are characterized by one of the possible positions: A $(0, 0, z_1)$, B $(1/3, 2/3, z_2)$, and C $(2/3, 1/3, z_3)$. The vertical sequence of bilayers in the cubic polytype 3C-SiC is ABCABC... and has a non-identically placed bilayer above and below any chosen one. In this case we speak about a cubic (c) position of the bilayer. The stacking sequence for the 2H structure is of the type ABABAB.... We define the position of the bilayer

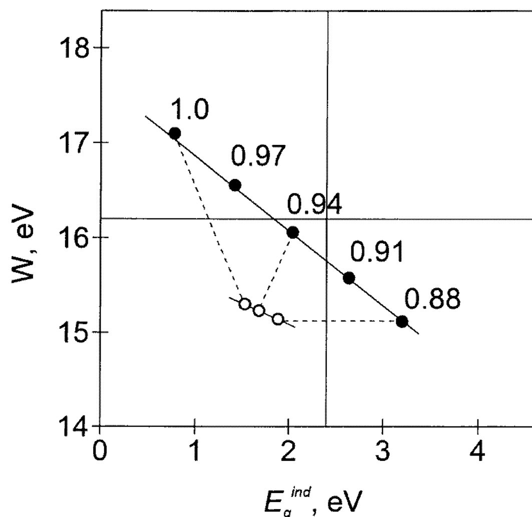

Figure 1. A plot of values of the valence band width W and the indirect energy gap E_g^{ind} in the cubic SiC calculated without (solid circles) and with combined corrections (open circles) for different ratios of ASA radii: $\alpha_1 = 1.164$, the values of α_2 are given in the figure. The experimental values $W = 16.2$ eV and $E_g^{ind} = 2.4$ eV are denoted.

as hexagonal (h) if the layers above and below it have the same displacement. Thus, all bilayers have the c position in the 3C structure and the h position in the 2H structure. The 4H structure has the sequence of bilayers ABACABAC... ($\ldots hchchc \ldots$), while the 6H structure is characterized by the stacking sequence ABCACB... ($\ldots hcchcc \ldots$). From this point of view we may speak about 50% hexagonal nature for the 4H structure and about 33.3% 'hexagonality' for the 6H structure. Note that two successive cubic bilayers in the 6H structure are not equivalent: one has the Si atoms interacting with carbon atoms in the h bilayer (we denote this as c_1), while the other one has the Si atoms interacting with carbon atoms in the c_1 bilayer (here we use the notation c_2). Thus, the sequence of bilayers in 6H-SiC is $\ldots hc_1c_2hc_1c_2 \ldots$.

In order to study *only* one effect of the different stacking on the electronic structure of the SiC polytypes, we did not take not into account the small deviations of the lattice constant a in the different structures, and the calculations were performed using the value $a = 5.823$ au for all the considered polytypes. This value corresponds to the Si–C interatomic distance in the cubic SiC crystal. The c values were chosen for each polytype so that the nearest shell of neighbours for every Si (C) atom was a perfect tetrahedron of C (Si) atoms.

The choice of sphere radii in the LMTO method, especially if in addition to the atomic spheres also the empty spheres are introduced, is a problem which up to now has not been completely clear. We studied this question in more detail.

In order to study how the results of the energy band calculations depend on the choice of the sphere radii, we have performed test calculations for the cubic SiC compound. The empty spheres were introduced in the tetrahedral interstitial sites: e_1 is the sphere surrounded by C atoms, e_2 is surrounded by Si atoms. We have characterized the choice of the atomic sphere radii by two parameters:

$$\alpha_1 = R_{Si}/R_C \qquad \alpha_2 = R_{E_1}/R_{Si} = R_{E_2}/R_C.$$

In [5] and [7] equal sphere sizes were used for carbon and silicon atoms without any explanation. However, the 2p orbitals of C atoms are more strongly localized than the Si 3p orbitals, because of the lack of p core states in the C atom. So the valence electron charge in bonds is shifted towards the C atoms, and we expect to obtain a better description of the electronic structure of the SiC crystals by using a radius for the C atomic sphere smaller than that for the Si sphere. One of the most reasonable recipes for choosing the atomic sphere radii is the following. The radii of non-overlapping 'muffin-tin' (MT) spheres are calculated under the condition that the potentials of the neighbouring atoms are equal at the MT-sphere radii and then the atomic sphere radii are obtained by a proportional enlarging of touching MT spheres. In the case of the cubic SiC this procedure gives the ratio $R_{Si}/R_C = 1.164$. Unfortunately, this procedure cannot be applied to obtain the radii of empty spheres.

Figure 1 shows the ranges of variation of the valence band width W and of the lowest indirect energy gap E_g^{ind} if the parameter α_2 is changed in the calculations. Note the strong dependence of the energy gap value on the variation of the empty sphere radii (from 0.8 to 3.2 eV if α_2 is varied between 1.0 and 0.88) in the calculations performed by using atomic sphere approximation without taking into account the combined corrections. The results of the ASA+CC calculations are not so sensitive to the choice of the atomic sphere radii, because they are corrected for both the overlap of the spheres and the failure of the spheres to cover certain interstitial regions.

We have chosen for the further calculations the value of $\alpha_2 = 0.94$, which corresponds to the point closest to the experimental value of both W and E_g^{ind} whereas the overlap of the atomic Si and C spheres does not exceed 16% (the overlap of the atomic spheres increases with decreasing α_2 value).

Table 1. Atomic sphere radii used in the calculations of the electronic structure of the SiC polytypes.

Sphere	R (au)	R/R_C
Si	2.2337	1.164
C	1.9190	1.000
E_1	2.0994	1.094
E_2	1.8039	0.940
E_3	2.3579	1.229
E_4	1.2628	0.658

For the hexagonal polytypes we have to introduce two additional empty spheres for the hexagonal bilayers (E_3 and E_4). Their radii were determined so that the overlapping with other spheres does not exceed 15%. The radii of spheres are given in table 1. We used the same sphere sizes for the calculations of all the polytypes considered. This gives us the possibility of comparing the spatial distributions of the valence electrons in the different structural SiC modifications.

4. Discussion of the calculated results

The calculated total DOSs of four polytypes of SiC are shown in figure 2. The shapes of the DOSs in the valence bands are very close for all polytypes. The dependence of the heights of several peaks (at the energies −2, −7.5, and −10.5 eV) on the hexagonal stacking nature, should be noted, especially a strong increase of peaks near −2 and −10.5 eV and decrease

of a peak at −7.5 eV as going from the 3C to the 2H structure. Both the valence band width W and the ionic gap E_g^{ion} within the valence bands (see table 2) show very small changes in going from one polytype to another. These results are in good agreement with the results of the PP calculations presented in [2] and [4]. In [2], [4] and [7] as well as in the present calculations the conduction band minimum occurs at the M point (the M_{1c} state) for the 3C (if considered in the hexagonal representation), 6H, and 4H structures, and at the K point (the K_{2c} state) for the 2H structure. The energy lowering of the K point in the 2H-SiC leads to the breaking of the approximately linear behaviour of the E_g^{ind} value with 'hexagonality' [4] between the 4H and 2H structures. Our results show (like the experimental data) a weakly increasing value of E_g^{ind} on going from the 4H structure to the 2H structure, whereas in [7], [2] and [4] this value is slightly decreasing. From the data presented in table 2 one can conclude that the LMTO method gives E_g^{ind} values larger than those obtained by PP methods. It should be noted that our results obtained by LMTO–ASA (without combined corrections) give higher values for E_g^{ind} (2.06 eV for 3C-SiC to 3.39 eV for 2H-SiC). Apparently, the differences between these results and those of Lambrecht *et al* [7] are caused by the different choices of atomic sphere radii. Including the combined corrections in the LMTO–ASA calculations reduces the E_g^{ind} values so that they become very close to those obtained in [7].

Table 2. The calculated parameters (in electron volts) of the electronic structure of the SiC polytypes.

SiC polytype	Valence band width W	Ionic gap E_g^{ion}	Indirect gap E_g^{ind}					Corrected indirect gap $E_g^{ind}+\Delta$	Indirect gap E_g^{ind}
	LMTO (ASA+CC)		PP		LMTO–ASA		LMTO (ASA+CC)	LMTO (ASA+CC)	Experiment
	Present work		[2]	[4]	[5]	[7]	Present work	Present work	[13]
3C	15.23	1.63	1.24	1.27	—	1.38	1.67	2.52	2.39
6H	15.20	1.56	1.98	1.96	2.92	2.05	2.05	2.90	2.86
4H	15.12	1.51	2.14	2.18	2.89	2.44	2.31	3.16	3.20
2H	15.13	1.76	2.05	2.10	2.76	2.17	2.48	3.33	3.33

The results calculated by Gavrilenko *et al* [5] show trends in the changes of the E_g^{ind} value that are opposite to the experimental ones. These discrepancies cannot be explained by another choice of the atomic sphere radii (they were chosen in the same manner as in [7]) and the reason for this is not clear.

The problem of underestimating band gaps by calculation methods using LDA is well known. For the correct comparison of the calculated results with the optical experiments the self-energy effects on single-particle excitations should be taken into account. Our calculations confirm the statement [7] about the single, $\boldsymbol{k}$-point-, energy-, and polytype-independent gap correction. In fact, an excellent quantitative agreement with the experimental data [13] is obtained (table 2) if the quasiparticle gap correction $\Delta = 0.85$ eV is added to the calculated LDA E_g^{ind} values. In spite of the discrepancies between the calculated and measured band gaps, the dispersion of single bands as well as the energy ordering of the conduction-band minima emerge correctly from the calculations.

The shapes of the DOS in the conduction bands differ more significantly for the SiC polytypes. Lee *et al* [3] have paid attention to the differences in the DOS near the conduction band edges. Their PP calculations show that the 6H structure exhibits a rapidly increasing

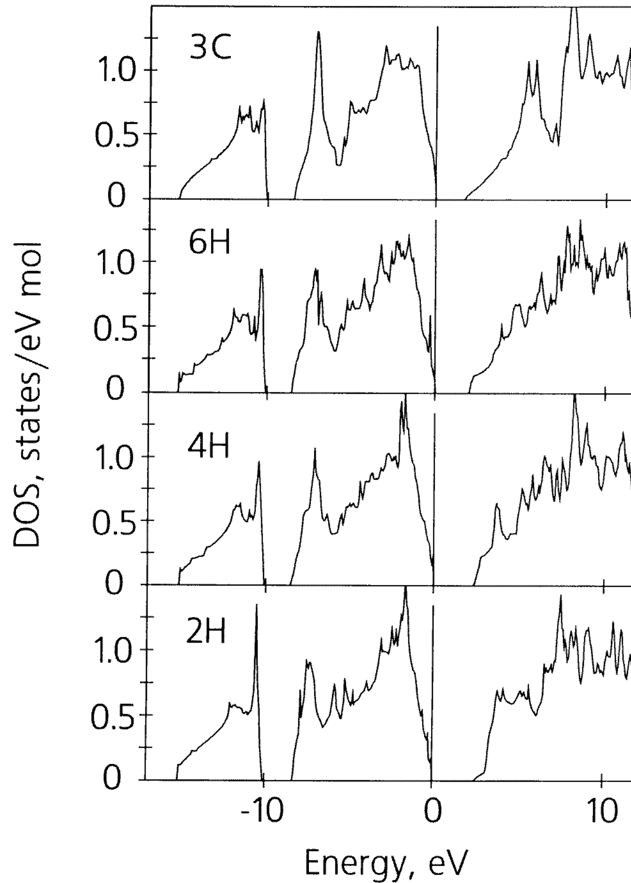

Figure 2. The calculated densities of electron states for the SiC polytypes.

behaviour of the DOS, with the largest slope. This could cause the high recombination rates in a narrow energy region and gives some possibilities for applications of the 6H-SiC. The present LMTO calculations provide the same behaviour of the DOS at the bottom of the conduction band (figure 3). From the energy band structure of the SiC polytypes it follows that the high DOS slope at the bottom of the conduction band is attributed to the flat energy bands near the M–L direction in the Brillouin zone. Most of the flattening of the conduction band states in the 6H structure is caused by the folding effect due to the large unit cell. In the case of the 2H structure the parabolic form of the energy band at the K point (this is the conduction band minimum for this polytype) gives rise to the DOS tail with a low slope from 2.5 eV upwards, while the contributions from the regions near M and L points occur at higher energies (about 3.2 eV).

Recently the effective masses at the bottom of the conduction band have been calculated for the four SiC polytypes considered [4, 14] and it has been found that the largest effective mass emerges for the 6H polytype. This correlates with the highest slope of the density of states at the 6H conduction band edge.

Our estimation of the total energies shows that the differences in these values for the four SiC polytypes are extremely small (within 10 meV/atom) and the cubic 3C-SiC structure has

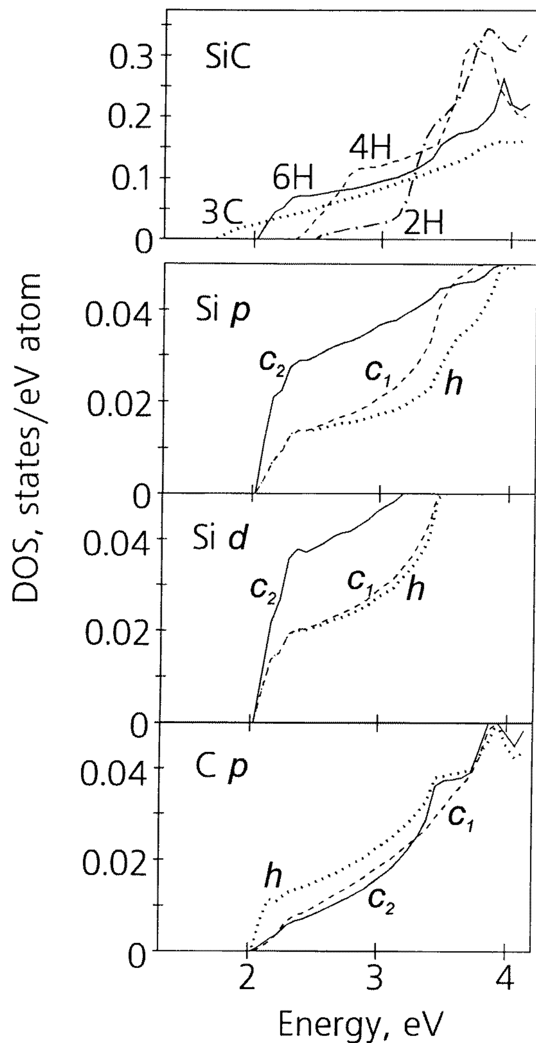

Figure 3. The shape of the total DOS at the bottom of the conduction band for the SiC polytypes and the local partial contributions from different bilayers to the DOS of the 6H structure.

the minimal value of the total energy. These results are in agreement with PP calculations [15] performed for ideal tetrahedral structures. However, taking into account the relaxations of the cell geometries leads to another ordering of the polytypes, and the minimal total energy has been found for the 4H-SiC polytype [2, 15].

It should be noted that the spherical approximation for the potential used in the ASA gives no possibility of calculating the total energy with high accuracy. Therefore we have not optimized the volume of the cells, taking for the calculations the same lattice constant a for all polytypes. This approach could be considered as a theoretical model in order to extract the effect of different stacking on the electronic structure.

The local contributions from the different bilayers of 6H-SiC to the DOS at the bottom of the conduction bands are also presented in figure 3. It can be seen that most of the

contributions to the high DOS slope are provided by the local p and d states of the Si atom located in the c_2 bilayer. In contrast, the highest contribution to the DOS from the carbon atoms is provided by the p states of the C atom in the *h* bilayer.

Table 3. The local distribution of the valence electron charge in the SiC polytypes.

SiC polytype	Type of bilayer	Q_{Si} (at. units)	Q_C (at. units)	Charge delocalization (at. units)	Q_{empty} (at. units)	Gross charges (10^{-3} at. units)
3C	c	1.400	0.063	1.463	−1.463	0
6H	h	1.508	0.065		−1.627	−54
	c_1	1.373	0.084		−1.490	−33
	c_2	1.400	0.150	1.527	−1.463	+ 87
4H	h	1.506	0.066		−1.626	−54
	c	1.378	0.151	1.551	−1.476	+ 54
2H	h	1.487	0.129	1.616	−1.616	0

Let us consider the spatial distributions of the valence electron charge, after having recalled that the values of C and Si spheres are kept fixed in the four polytypes so that changes in the electronic structure (in the spatial and energy distribution of the electron states) are due to different stacking only. It should also be noted that the following discussion on the electronic charge changes in the C and Si spheres does not concern the problem of the interatomic charge transfer in these covalent compounds. As can be seen from table 3, the silicon and carbon atomic spheres are positively charged, the rest of the valence electrons being distributed over the empty spheres. In spite of their smaller radii the C atomic spheres are almost neutral, since there are almost four valence electrons inside each C sphere. This means that the covalent Si–C bond is polarized, the electronic charge being shifted towards carbon atoms. The polarity of bonds in the bilayers ('in-bonds' aligned along the hexagonal z axis) is sensitive to the position of the bilayer. If the atoms of the c bilayer interact with the h bilayer, the electrons leave the carbon sphere and approach the silicon sphere (as compared with the 3C structure), lowering the polarity of in-bonds in the c bilayer. In contrast, the comparison of Q_{Si} and Q_C obtained for the 2H structure (h bilayers only) and for 4H and 6H structures (h bilayers adjacent to c bilayers) shows that the electrons are shifted from the silicon sphere to the carbon one, increasing the polarity of in-bonds in the h bilayer. This is in agreement with the changes of the ionic gap value E_g^{ion} presented in table 2.

The sum of charges of the Si and C atomic spheres, when averaged over the bilayers, characterizes the delocalization of the valence charge, that is the averaged number of valence electrons distributed outside the Si and C spheres (in the empty spheres). The charge delocalization increases with increasing hexagonality of the polytype. In general, as can be seen in table 3, the charges Q_{empty} in the h bilayers always exceed those in the c bilayers, in spite of the equality of volumes $E_1+ E_2$ (in c bilayers) and $E_3+ E_4$ (in h bilayers). Apparently, this delocalization of the valence charge in the h bilayers is caused by an existence of large interstices (the empty spheres E_3) in these bilayers. If we estimate the gross charges in the bilayer as a sum of charges of all spheres in this bilayer, we obtain that in the 4H and 6H structures the h bilayers become slightly negatively charged, while the c bilayers are mostly positive. These results are in contradiction with the PP calculations [2] where the hexagonal bilayers in the 4H and 6H polytypes were found to be positively charged.

The comparison of the local distributions of the valence electron charge in the 6H, 4H, and 2H polytypes with those in the cubic 3C polytype ($\Delta Q_i = Q_i - Q_i^{3C}$) shows that besides delocalization of the valence electrons the charge in the atomic spheres is redistributed. The off-bonds Si(h)–C(c) lose electronic charge, whereas a small increasing of charge on the off-bonds Si(c)–C(h) is observed.

Thus, the calculated results show the different behaviour of the c and h bilayers in the SiC structures and the important role of the interaction of the c and h bilayers in the formation of the local electronic structure of the SiC polytypes.

5. Crystal lattice distortions in 6H-SiC

In order to study the effect of the crystal lattice distortions on the local electronic structure, energy band calculations were performed for the 6H-SiC polytype with modified c/a values. We chose the structure data such that the volume of the unit cell remained constant, so that an increasing c/a ratio required a decrease of the lattice constant a, and vice versa. The sphere radii were not changed. It should be noted that the lattice distortions (5% changes in the c/a ratio) cause an increase of the total energy by about 40 meV/atom for both ‘constriction’ and ‘stretching’ of the crystal lattice.

Table 4. The calculated results for the distorted 6H structure.

		$Q - Q_0$ (10^{-3} au)	
Bilayer	Sphere	$0.95c/a$	$1.05c/a$
h	Si	−13	+10
	C	−11	+ 7
	E_3	+49	−36
	E_4	−21	+18
c_1	Si	− 3	0
	C	− 3	0
	E_1	− 1	+ 3
	E_2	0	+ 1
c_2	Si	− 1	− 1
	C	− 1	0
	E_1	+ 3	− 2
	E_2	+ 2	0
a (au)		5.924	5.730
E_g^{ind} (eV)		2.06	1.82
W (eV)		15.18	15.39

The calculated results are presented in table 4. The energy distribution of electron states (the valence band width W and the indirect energy gap E_g^{ind}) is more sensitive to the ‘stretching’ of the lattice in the z direction than to its ‘constriction’ (compare with the values for zero distorsion given in table 2). A very interesting result emerges for the spatial distribution of the valence electron charge: most of the redistribution of charge caused by the lattice distortions occurs in the h bilayer, while for the cubic c_1 and c_2 bilayers the 5% distortions have only a weak effect on the sphere charges.

The influence of the lattice distortions on the shape of the DOS at the bottom of the conduction band is different if the c/a ratio increases or decreases (see figure 4). For the ‘constricted’ lattice the DOS slope becomes higher than in 6H-SiC (as discussed above, it

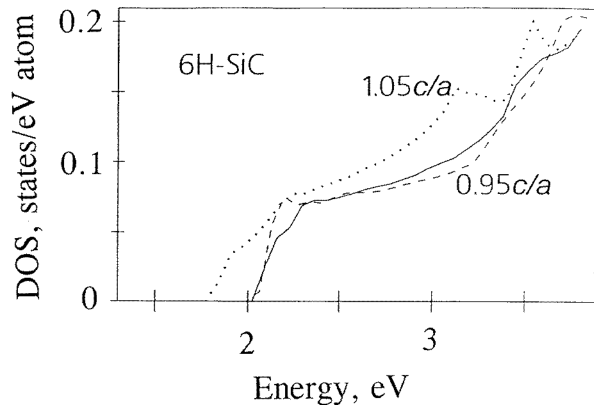

Figure 4. The modification of the 6H-SiC conduction band DOS (solid line) due to lattice distortions.

has the highest DOS slope of all SiC polytypes considered). In contrast, the 'stretched' lattice leads to a DOS shape slowly increasing with energy.

6. Conclusions

We have studied the local electronic structure of four SiC polytypes by means of the LMTO (ASA+CC) method. It was shown that the results of the ASA calculations are very sensitive to the choice of the atomic sphere radii (especially if empty spheres are introduced). Taking into account the combined corrections in the ASA leads to results which show a very weak dependence on the choice of the atomic radii. Including the combined corrections in the calculations can also significantly modify the calculated results.

The interatomic distances and the sphere radii were chosen to be equal for all SiC polytypes considered, so that the differences in the calculated electronic structure are caused only by the different stacking sequence of the hexagonal bilayers. The main feature of the local electronic structure in the SiC polytypes is an essentially different behaviour of the electron states in the *c* (cubic) and in the *h* (hexagonal) bilayers. The most interesting effects are determined by the interaction of the *c* and *h* bilayers. This leads in the 4H and 6H structures to changes in the polarities of the Si–C bonds, to the charging of bilayers, and to the high slope of the DOS at the bottom of the conduction band.

The effect of the lattice distorsion on the distributions of the local valence electron charge is found mainly for the *h* bilayers. Possibly, the changes of the DOS at the conduction band edges caused by the lattice distorsions could be observed in the optical spectra. These results are only the first step in the study of the influence of the lattice distorsions (caused by point defects, non-stoichiometry, amorphization, etc) on the electronic structure of Si–C alloys by means of the methods of computational physics. Further work is now in progress.

References

[1] Wyckoff R W G 1963 *Crystal Structures* (New York: Wiley) p 113
[2] Park C H, Cheong B-H, Lee K-H and Chang K J 1994 *Phys. Rev.* B **49** 4485
[3] Lee K H, Park C H, Cheong B-H and Chang K J 1994 *Solid State Commun.* **92** 869

[4] Kackell P, Wenzien B and Bechstedt F 1994 *Phys. Rev.* B **50** 10 761
[5] Gavrilenko V I, Postnikov A V, Klyui N I and Litovchenko V G 1990 *Phys. Status Solidi* b **162** 477
[6] Lambrecht W R L, Segall B, Suttrop W, Yoganathan M, Devaty R P, Choyke W J, Edmond J A, Powell J A and Alouani M 1993 *Appl. Phys. Lett.* **63** 2747
[7] Lambrecht W R L, Segall B, Yoganathan M, Suttrop W, Devaty R P and Choyke W J 1994 *Phys. Rev.* B **50** 10 722
[8] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[9] Skriver H L 1994 *The LMTO-Method* (Berlin: Springer)
[10] Robertson J 1992 *Phil. Mag.* B **66** 615
[11] von Barth U and Hedin L 1971 *J. Phys. C: Solid State Phys.* **4** 2064
[12] Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
[13] Madelung O, Schulz M and Weiss H (ed) 1984 *Landolt Börnstein Tables* vol 17A, (Berlin: Springer)
[14] Lambrecht W R L and Segall B 1995 *Phys. Rev.* B **52** R2249
[15] Kackell P, Wenzien B and Bechstedt F 1994 *Phys. Rev.* B **50** 17 037