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## Energy Band Structure and Optical Properties of Wurtzite-Structure Silicon Carbide Crystals

By

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The electroreflection spectra of hexagonal polytypes of SiC, 4H and 6H are measured in the range 1.0 to 5.6 eV. The energies of direct optical transitions are determined using a multiple oscillator model. The electronic band structures of three hexagonal polytypes of SiC (2H, 4H, and 6H) are calculated by the first-principles self-consistent linear muffin-tin orbital (LMTO ASA) method. One-electron energies and densities of states are obtained in the range  $\pm 15$  eV around the top of valence band. The results calculated are compared with experimental data measured in this work and those available in the literature.

Elektroreflexions-Spektren von hexagonalen SiC-Polytypen 4H und 6H werden im Bereich 1,0 bis 5,6 eV gemessen. Die Energien der direkten optischen Übergänge werden mit Hilfe des Viel-Oszillator-Modells bestimmt. Die elektronische Bandstruktur von drei hexagonalen SiC-Polytypen (2H, 4H und 6H) wird aus ersten Prinzipien mittels LMTO-ASA-Methode berechnet. Einlektronen-Energien und Zustandsdichten werden im Bereich  $\pm 15$  eV bezüglich der Valenzbandkante berechnet. Die Resultate werden mit experimentellen Daten verglichen, die sowohl in dieser Arbeit, als auch in der Literatur gemessen werden.

### 1. Introduction

Silicon carbide is an interesting material not only because of its traditional use as an abrasive ("carborundum"), but there is currently much interest in materials made from SiC fibres, which compare well with their carbon fibre counterparts. SiC is also a high-temperature large band gap semiconductor used primarily in light-emitting diodes [1]. In addition SiC is the only IV-IV compound to form stable and long-range ordered structures (polytypes) [2]; over 100 different such polytypes have been observed [3]. Polytypism in SiC is very interesting for a number of reasons. These polytypes are semiconductors with a varying band gap, they are natural short period superlattices and therefore attract similar interest as artificially grown superstructures [4].

The optical properties of SiC near the fundamental absorption band have been measured by several authors. Choyke and Patrick [5] reported absorption measurements up to 4.9 eV, where four thresholds (one of which may be direct) were observed. Makarov [6] has extended

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the absorption measurements in 6H SiC to 5.8 eV by using a surface-barrier diode. Reflection spectra of 6H, 15R, and 3C SiC in the range 3.0 to 13 eV have been measured in [7]. In [8] the optical constants of 6H SiC have been measured by reflectivity in the range 4 to 25 eV. The energies of direct optical transitions between subbands in the conduction band, resulting from confinement in a one-dimensional superlattice, have been measured in several polytypes of SiC by absorption [4, 9] and electroreflection [10, 11].

The electron energy band structure of SiC in the sphalerite structure (3C SiC) has been calculated by several authors (see e.g. [12 to 15]). The band structure of the wurtzite modification of SiC has been calculated in [12, 14 to 16] for 2H SiC. In [14] the band structure of 4H and 6H SiC has been calculated by the semiempirical pseudopotential method at several high-symmetry points of the Brillouin zone (BZ). LCAO calculations of 2H SiC show valence bands which agree with experiment, but unrealistic conduction bands due to the restriction to nearest neighbour interaction in the Hamiltonian matrix [16].

Recently, the first-principles local density functional technique has been applied to the *ab initio* calculation of ground-state properties of cubic [17] and 2H wurtzite polytypes of SiC [18].

In this work we have measured electroreflectance (ER) spectra of hexagonal 4H and 6H polytypes of SiC in the range 1.0 to 5.6 eV. Values of direct optical gaps have been obtained from the ER spectra using a multiple oscillator model [19, 20].

The electronic band structure of the three hexagonal polytypes of SiC (2H, 4H, and 6H) has been calculated by the first-principles self-consistent linear muffin-tin orbital (LMTO-ASA) method [21]. One-electron self-energies have been found in the whole BZ. Calculated band structure parameters have been compared with experimental data measured in this work and available in the literature.

## 2. Theory

The non-relativistic electronic band structure of SiC has been calculated by the LMTO-ASA method [21, 22].

The local-density approximation (LDA) has been used for calculation of exchange and correlation effects. It is well known that in this case the absolute values of the calculated gaps in many semiconductors and insulators turn out to be lower than the experimental values (well-known "gap problem") [23, 24]. It will be shown later that this takes place in 2H and 4H SiC.

The atomic sphere approximation is too crude for tetrahedral systems unless empty spheres, i.e. interstitials (where the potential is treated as spherically averaged rather than constant), are introduced. In the diamond or zincblende structure [23], the radii of empty spheres positioned in tetra- and octahedral cavities are usually chosen equal to those of the real atoms, and thus giving rise to rather close (CsCl-type) packing of atomic spheres, half of which are empty.

In the wurtzite structure, in spite of its similarity to the zincblende structure with respect to nearest-neighbour geometry, the above-mentioned scheme of putting the empty spheres is no longer appropriate. In order to achieve the best space filling and to reduce the overlap of the spheres at the same time, it is necessary to introduce two types of empty spheres with different radii situated as shown in Fig. 1. In higher polytypes where zincblende-like orientations of layers appear again in different combinations with wurtzite-like orientations

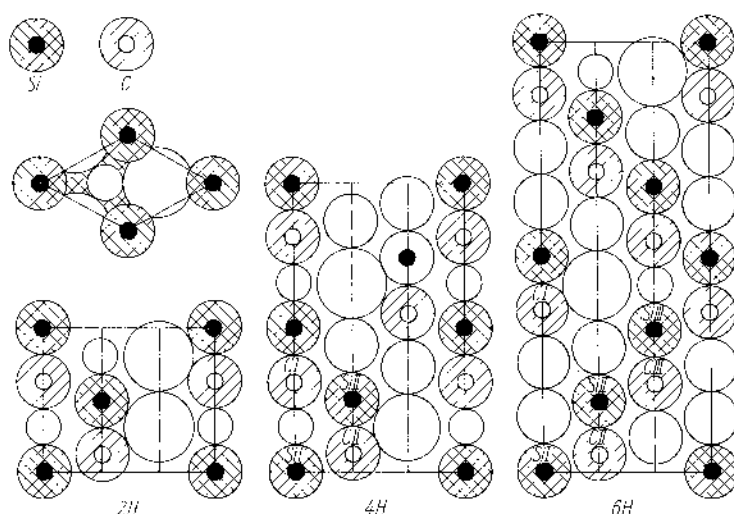


Fig. 1. Crystalline structure of SiC wurtzite polytypes, calculated in this work. Open circles show the empty spheres used in the calculations. Values of the empty sphere radii are given in Table 1

a third type of empty spheres with radii equal to those of Si and C spheres has to be introduced (see Fig. 1).

The atomic sphere radii used in the calculation are presented in Table 1. They are obtained by proportional enlarging of touching muffin-tin spheres so as to fill the whole space. The radii are slightly different for the three polytypes considered here, because of different contents of "small" and "big" interstitials per unit cell. Including empty spheres, the total number of centres per unit cell is 8 in 2H, 16 in 4H, and 24 in 6H polytypes of SiC.

Although the atoms in all these inequivalent sites have the same pattern of nearest neighbours, differences in more distant neighbours can lead to different charge distributions, therefore the potentials inside the atomic spheres of these atoms should be allowed to be different. Together with empty spheres, it gives 8 inequivalent atomic sites in the 4H structure and 12 in 6H SiC.

The calculated band structures of three hexagonal polytypes of SiC (2H, 4H, and 6H) are shown in Fig. 2. Only the band structures for the directions which are most important in applications, have been shown.

Values of lowest indirect forbidden gaps ( $E_g$ ) are listed in Table 2 in comparison with the data available in the literature and experimental results.

Table 1

Atomic sphere radii (in  $10^{-1}$  nm) in hexagonal polytypes of SiC used in the calculations

site	2H	4H	6H
Si	2.070	2.070	2.070
C	2.070	2.070	2.070
Em1	1.380	1.380	1.340
Em2	2.349	2.349	2.280
Em3	—	1.982	2.010

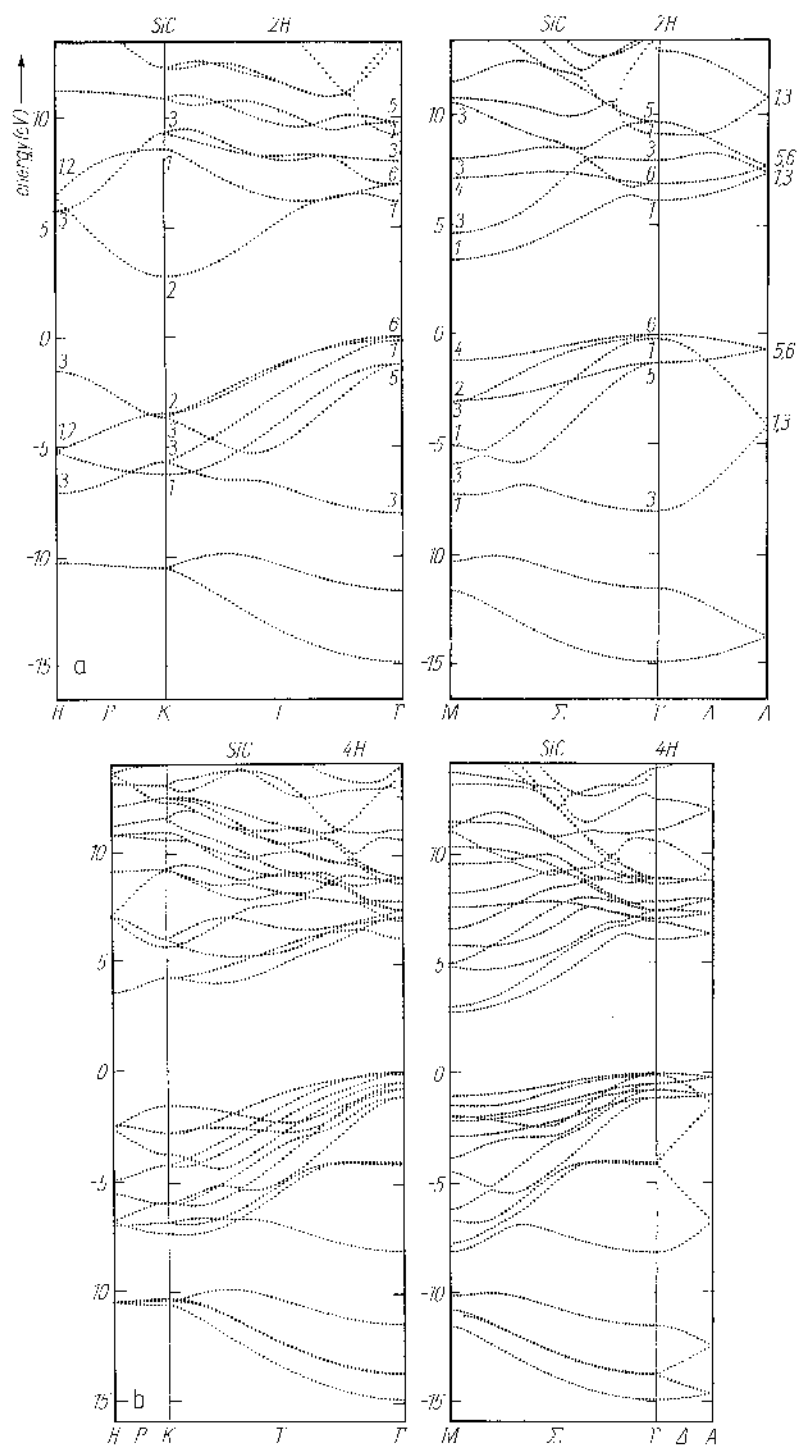


Fig. 2

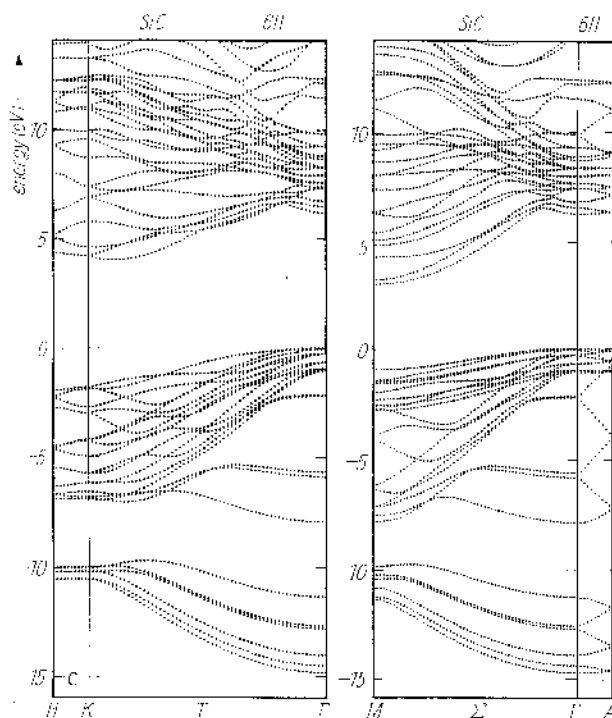


Fig. 2. Band structure of hexagonal SiC crystals. Irreducible representations are shown only for 2H SiC.

The density of states (DOS) was determined by the tetrahedron integration over a mesh that was generated by six cuts in the  $\Gamma$ -M direction of the BZ and included 112, 84, and 56 points in the irreducible part of 2H, 4H, and 6H BZ, respectively. States up to  $l = 2$  on all centres were included into the basis set. The total densities of states for 4H and 6H SiC are shown in Fig. 3, and site- and momentum-projected densities of states for 6H SiC are shown in Fig. 4. The labeling of non-equivalent sites SiI, SiII, etc. is defined in Fig. 1.

There is a noticeable difference of the p-state occupation for different polytypes and for different sites in the same polytype. States of d-symmetry are important at the Si site. Increasing the period of the superstructure along the optical axis (line  $\Gamma$ -A in the BZ) causes band folding, which can be seen for the  $\Gamma$ -A and K-H directions for the SiC polytypes shown in Fig. 2.

Table 2

Lowest (forbidden) energy gaps in hexagonal polytypes of SiC, calculated in this work in comparison with the data available in the literature

polytype	energy (eV)				
	this work	calc. [14]	calc. [15]	calc. [12]	exp. [28]
2H	2.76	3.35	3.30	3.30	3.33
4H	2.89	2.8	—	—	3.20
6H	2.92	2.45	—	—	2.86

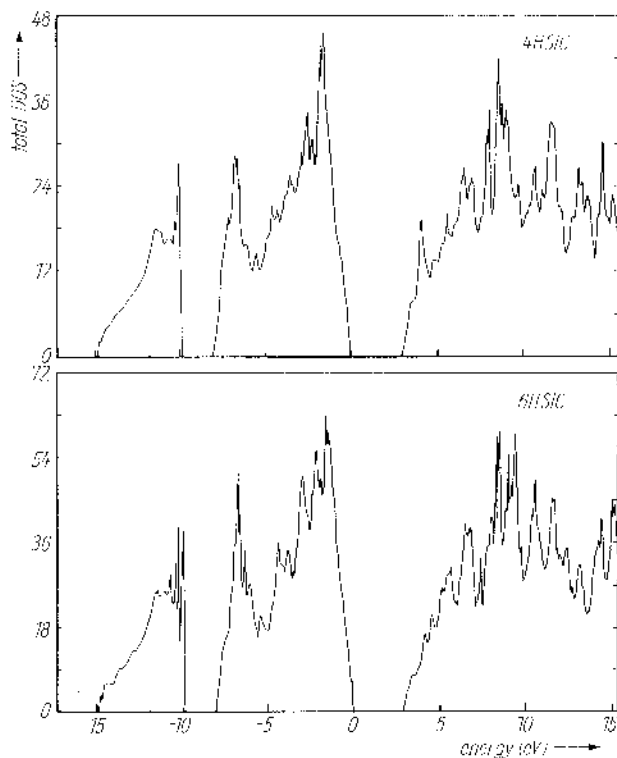


Fig. 3. Total density of states in two hexagonal polytypes of SiC.

Table 3

Values of direct optical gaps (in eV) in SiC (4H) measured in this work and those available in the literature. Calculated values of lowest direct gaps in M-point in BZ close to experimental values have been shown for comparison

No.	$e \parallel c$			$e \perp c$		
	exper.	ref.	theory (this work)	exper.	ref.	theory (this work)
1	2.10	[4]				
2	2.17	*)	2.20			
3				2.60	[4]	
4				2.60	*)	2.75
5				4.585	*)	4.65
6				4.980	*)	4.97
7	5.030	*)	5.060			
8				5.470	*)	5.33

\*) ER data, this work.

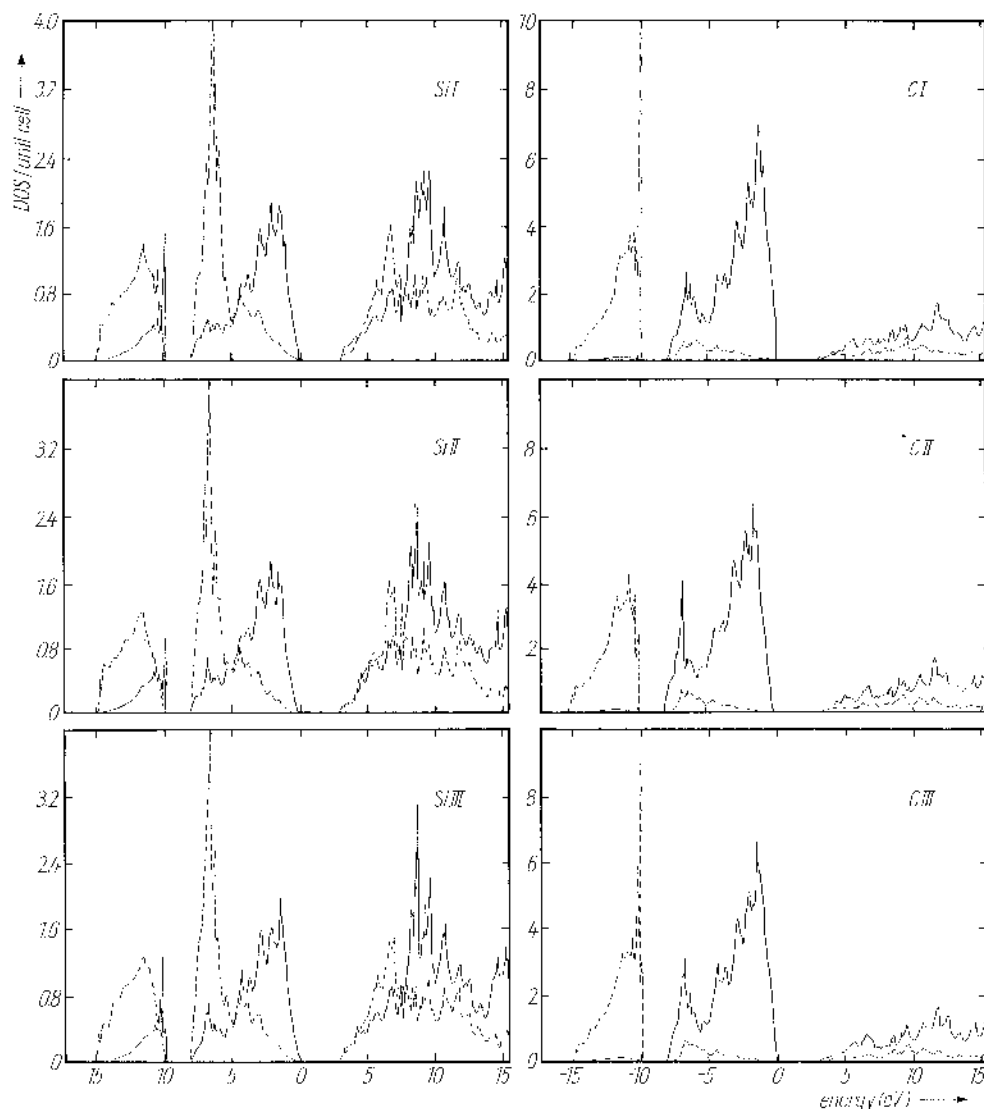


Fig. 4. Partial density of states in 6H SiC for three nonequivalent sited Si and C atoms. Solid lines represent p-electron DOS, and dashed ones correspond to s-electron DOS (look at the scale differences)

### 3. Experimental

Two hexagonal single crystal polytypes of SiC (4H and 6H) grown by the Bridgman method were investigated. Samples were cut to have surface orientations (0001) and (1 $\bar{1}$ 20). The surface treatment used in this work was the following: mechanical polishing, heating to 700 °C for 30 min, etching successively in concentrated HF and HNO<sub>3</sub>, and boiling in H<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>Cl<sub>2</sub>O. ER spectra were measured in polarized light by means of the elec-



Table 4

Values of direct optical gaps (in eV) in SiC (6H) as measured in this work and reported earlier. Comparison with calculated values of direct gaps at M-point in BZ has been shown

No.	$e \perp c$			$e \parallel c$		
	exper.	ref.	theory (this work)	exper.	ref.	theory (this work)
1	1.36	[4] *)	1.25	2.25	*)	2.042
2						
3	3.85	*)	3.92	4.07	*)	4.10
4				4.6	[5, 7]	4.55
5						
6	4.68	*)	4.58	4.71	*)	4.63
7				$5.54 \pm 0.05$	[6] *)	5.63
8						
9			5.71			

\*) ER data, this work.

trolyte technique [19, 20]. The measurement conditions corresponded to low-field ER ( $n \leq 10^{17} \text{ cm}^{-3}$ ;  $U_{pp} \leq 1 \text{ V}$ ) [20]. 0.1 KCl was used as the electrolyte. No changes in the surface quality of the samples after ER measurements were noticed.

The wurtzite structure is characterized by the lack of inversion [2]. Thus by proper choice of the geometry one can measure both linear and quadratic components of the electrooptic tensor. This has been illustrated in Fig. 5. The geometries of measurements have been given in the figure captions. In case of Fig. 5a ( $e \perp c$ ,  $F \parallel c$ ) the ER signal corresponds to both  $r_{13}$  and  $g_{13}$  components of linear and quadratic electrooptic tensors, respectively. But in cases of Fig. 5b ( $e \perp c$ ,  $F \perp c$ ) and Fig. 5c ( $e \parallel c$ ,  $F \perp c$ ) the ER signal is determined by  $g_{12}$  and  $g_{31}$  components of only the quadratic electrooptic tensor, respectively. This explains the differences of signal amplitude in both cases (see scale differences on Fig. 5a and Fig. 5b, c). Values of direct optical gaps in SiC have been obtained by us from ER spectra by means of a

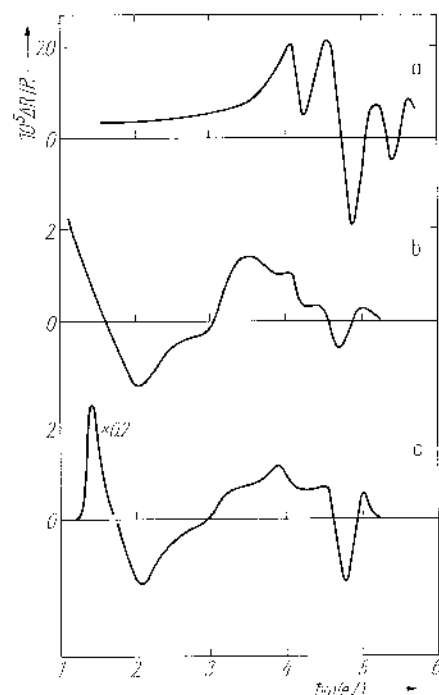


Fig. 5. Electroreflection spectra of SiC (6H). Measurements have been done on a) (0001) face with  $e \perp c$ ,  $F \parallel c$ ; b) ( $\bar{1}\bar{1}20$ ) face with  $e \perp c$ ,  $F \perp c$ ; c) ( $\bar{1}\bar{1}20$ ) face with  $e \parallel c$ ,  $F \perp c$ . Note the differences of the ER signal scale.  $F$  and  $e$  denote vectors of external electrical field and light polarization, respectively

fitting procedure which uses a linear superposition of contiguous two-dimensional oscillators (for details see [19]).

The results are summarized in Tables 3 and 4.

#### 4. Discussion

Let us now discuss the results of the calculated band structure of SiC in the light of the experimental data obtained by us and those available in the literature. Corresponding theoretical data are given in Table 2 in comparison with the data in the literature. It should be pointed out that the lowest minimum of the c-band in 2H SiC (as obtained in this work) occurs at the K-point, but in 4H and 6H SiC it lies at the M-point of the BZ. These results agree with the literature [12 to 15].

As follows from Table 2, the lowest forbidden gaps,  $E_g$ , in 2H and 4H SiC are lower than the corresponding experimental values. It has been stated earlier (see for e.g. [23] and references therein) that one of the reasons for this is the use of LDA in LMTO theory.

But relatively good agreement between calculated and experimental  $E_g$ -values is obtained in SiC 6H (see Table 2). In [25] it has been emphasized that the intrinsic failure of LDA (as far as the gaps are concerned) is much larger for third-row semiconductors and for heavy elements than in the case of Si (see also [24]). This can explain the fact that the disagreement of our results with experimental data (see Table 2) is not as large as in the case of Ge [23].

We point out further that the trend of changes of  $E_g$  (slight increase) calculated here when going from 2H to 6H SiC, is opposite to the experimental one (see Table 2), the reason for this being not clear.

The symmetry of the top of the valence band ( $\Gamma_6$ ) obtained by us agrees with [12, 15], but in [14] a  $\Gamma_1$  symmetry has been obtained for the highest valence band. The lowest direct optical transitions in 6H SiC have been reported to be near 4.6 eV [5 to 7] and 5.5 eV [7]. These values agree well with our data (see Tables 3 and 4). According to the calculations, the direct optical gaps in 4H and 6H SiC with energy lower than 6 eV are likely to take place only near the M-point in the BZ. Theory predicts the appearance of direct interband gaps in 4H and 6H SiC having other than M symmetry at  $\hbar\omega \geq 6.0$  eV (see Fig. 2b, c). This leads to the conclusion that all the transitions measured by us, with  $\hbar\omega < 6.0$  eV, have probably M symmetry. According to the selection rules ( $M_1, M_4 \leftrightarrow M_2, M_3$  for  $e \perp c$  and  $M_i \leftrightarrow M_i$  for  $e \parallel c$ , see [20]) there are many allowed direct gaps of M symmetry with energies lower than 6.0 eV. Some of them with values close to the experimental data have been listed in Tables 3 and 4 for comparison. But for an unambiguous identification of the optical data the calculation of matrix elements of direct optical transitions and optical functions (dielectric permittivity or reflection coefficient) is necessary.

The structure of ER spectra near 3.0 eV (in 6H SiC) and 3.1 eV (in 4H SiC) are interpreted as near edge electroabsorption due to reflection from the back side of the sample. These structures disappeared when the back side reflection was eliminated (as in the case of Fig. 5a). The strong increase of the ER signal when going to the IR range remains not clear.

Consider further the values of the direct optical gaps in the c-band of 4H and 6H polytypes (M-point) in comparison with experimental data, obtained by absorption [4, 9] and electrorreflection (this work and [11]) measurements (see the first two lines in Tables 3 and 4). The subband structure of the c-band in SiC is caused by the superstructure along the optical axis [4]. Good agreement between calculated and experimental values of intersubband

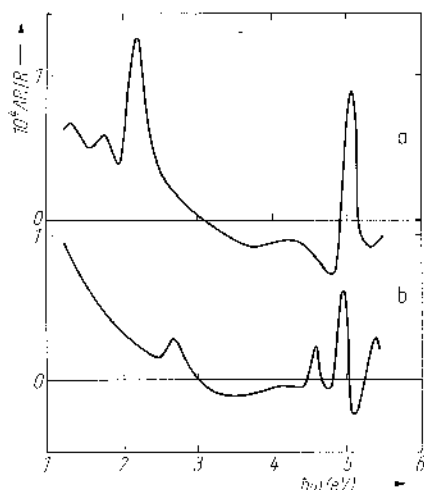


Fig. 6. Electroreflection spectra of SiC (4H). Measurements have been done on (1120)-face in a)  $F \perp c$ ,  $e \parallel c$ ; b)  $F \perp c$ ,  $e \perp c$  geometries

gaps in the c-band of SiC indicates that the orbital basis used in the present calculation is sufficient to obtain a realistic band structure of SiC.

In Fig. 3 and 4 total and partial densities of states are shown which can be used for the interpretation of photoemission spectra of SiC. The lowest valence band in 6H SiC between  $-15.0$  and  $-10.0$  eV is determined by s-electrons of Si and C. It follows from Fig. 6 that the s-electrons of C on sites I and III (see Fig. 1) dominate at the top of this band. The maximum

at 6.85 eV in the total DOS is determined by the s-electrons of Si. The upper part of the valence band of 6H SiC is determined mainly by the p-electrons of C and Si, but the C-derived orbitals dominate (see Fig. 4). The conduction band is mainly determined by the s, p, d-electrons of Si, whereas p, d-electrons of C are less dominant. The band width of the v-band agrees with [13] where 16.0 eV were obtained. Our value of the v-band width ( $\approx 15.0$  eV) of 6H SiC is lower than in cubic SiC as expected [26 to 28].

## 5. Conclusion

We have measured electroreflection spectra in the range 1.0 to 5.6 eV of 4H and 6H SiC. The energies of direct optical transitions have been determined using a multiple oscillator model. The band structure of SiC (2H, 4H, and 6H) has been calculated by the first-principles self-consistent LMTO-ASA method. The results obtained have been compared with experimental data measured by us and available in the literature.

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