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Hydrostatic-pressure coefficient of the indirect gap and fine structure of the valence band of 6*H*-SiC

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Photoluminescence measurements on 6*H*-SiC doped with nitrogen have been performed under hydrostatic pressure up to 50 kbar at low temperature ($T=29\pm2$ K). The observed emission lines S_0, R_0, P_0, S_{02}, and R_{02} are due to excitons with holes from the *A* and *B* valence bands bound to the neutral nitrogen donor. The energy shift of the P_0 line under hydrostatic pressure is used to determine the linear pressure coefficient of the indirect gap of 6*H*-SiC, which yields 0.20 eV/Mbar. The energy difference between the emission lines S_{02} (R_{02}) and S_0 (R_0) of 5.15 ± 0.1 (5.08 ± 0.1) meV gives the splitting Δ_{AB} of the topmost valence bands. We employ nonrelativistic band-structure calculations within the density-functional theory based on the local-density approximation in order to calculate the pressure coefficient of the indirect band gap of 6*H*-SiC (together with those of 4*H*, 2*H*, and 3*C*-SiC as well as those of diamond, Si, and Ge) and the crystal field splitting of the valence band. The latter, together with the experimental splitting Δ_{AB} of the topmost valence bands *A* and *B* is used to estimate the spin-orbit splitting of 6*H*-SiC to be about 7.7 meV. The calculated pressure coefficient shows good agreement with the experimental value. [S0163-1829(96)02747-6]

I. INTRODUCTION

The dependence of optical and electronic properties on hydrostatic pressure has been used in the past to obtain important information on the band structure for a vast variety of semiconductors.[1–3] However, for 6*H*-SiC no investigation of the electronic band structure under hydrostatic pressure has been reported so far, to our knowledge. In this work we determine the hydrostatic pressure dependence of the indirect gap of 6*H*-SiC in both experiment and theory.

The atmospheric pressure photoluminescence (PL) spectrum at liquid-helium temperature of *n*-type 6*H*-SiC doped with nitrogen shows three characteristic lines, called S_0, R_0, and P_0, which were attributed to the recombination of bound excitons at neutral nitrogen donors occupying the three crystallographically inequivalent carbon lattice sites in the unit cell of 6*H*-SiC in the fundamental work of Choyke and Patrick.[4] The binding energies of the S_0, R_0, and P_0 excitons were determined to be 32.1 meV, 30.4 meV and 16.0 meV, respectively,[5] using the value $E_{gx}=3.0230$ eV for the excitonic band gap. At higher temperature Choyke and Patrick found two new lines, called S_{02} and R_{02}, approximately 4.8 meV (± 0.3 meV) displaced to higher energies from the S_0 and R_0 lines, which were attributed to the bound exciton complexes with holes from the spin-orbit split-off valence band[4] (cf. Fig. 1). The energy differences between exciton states bound to neutral N donors formed from holes of the valence bands *A* and *B* in different uniaxial SiC:N polytypes are given in Table I (cf. the notation of Ref. 10).

Although all these emission lines are regularly found in low-temperature PL spectra of 6*H*-SiC doped with nitrogen, there exist only a few reports about absorption measurements of these excitons. [5–9] This is probably due to the very low absorption coefficient in the energy range of bound exciton transitions, which requires rather thick crystals for their observation. However, valuable information about the fine structure of the valence band of 6*H*-SiC could be obtained from these absorption spectra because excitons formed with holes from all three valence bands *A*, *B*, and *C* are expected to contribute to the absorption spectrum. Gorban *et al.*[9] have

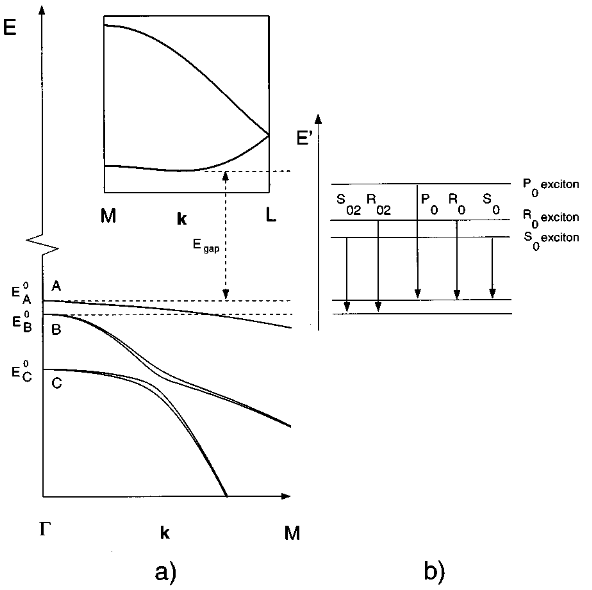

FIG. 1. (a) Electron energy band scheme in 6*H*-SiC taking into account the spin-orbit splitting of the valence band. The inset shows details of the conduction band energies in the *M*-*L* direction of the Brillouin zone. (b) Energies E' of bound excitons to the different nitrogen donors (two cubic sites and one hexagonal site) and the corresponding emission lines in the PL spectrum of 6*H*-SiC.

found strong evidence for the observation of bound excitons built from the valence band *C* (lines S_{03} and R_{03}). In PL these lines cannot be observed because of thermalization and the large energy separation of the valence band *C*.

In experiment we measured the hydrostatic pressure dependence of the exciton lines S_0, R_0, P_0, S_{02}, and R_{02} and determined their corresponding linear pressure coefficients (Sec. II). Finding the same value of the pressure coefficient for the emission lines S_0, R_0, S_{02}, and R_{02} confirms the earlier interpretation of the S_{02} and R_{02} lines as being due to the recombination of bound excitons with holes from the *B* valence band. Accordingly, we estimate the splitting Δ_{AB} of the topmost valence bands from the separation between the luminescence lines S_0 (R_0) and S_{02} (R_{02}).

Parallel to these experiments we performed *ab initio* calculations of the electronic energies of SiC polytypes under hydrostatic pressure based on the density-functional theory (DFT) using the local-density approximation (LDA) (see Sec. III). Such calculations have become standard and have been applied to SiC by several authors (see, e.g., Refs. 11–14). Although DFT-LDA calculations underestimate the energy gaps, it has been shown in the literature that calculated positions of the band extrema (e.g., the minimum of the conduction band) and pressure coefficients are in agreement with experimental data.[15] Therefore, we rely, in our investigations, on this method.

TABLE I. Energy difference between bound exciton states formed from valence bands *A* and *B* in different SiC:N polytypes (results were obtained from standard PL measurements at elevated temperatures).

Polytype	Exciton lines	ΔE (meV)
6*H*	S_{02}-S_0	5.13 ± 0.1
	R_{02}-R_0	5.08 ± 0.1
4*H*	Q_{02}-Q_0	4.50 ± 0.1
15*R*	R_{02}-R_0	4.33 ± 0.1
	S_{02}-S_0	4.59 ± 0.1

DFT-LDA calculations are designed to calculate the ground-state properties by minimizing the total energy with respect to the lattice parameters. The relative change of the volume can be related with the hydrostatic pressure by Murnaghan's[16] or Vinet's equation of state,[17,18] which contain the bulk modulus B_0 and its pressure derivative B_0'. Therefore these quantities have to be calculated to find theoretical values for the hydrostatic pressure coefficient. As the band calculations are performed in a nonrelativistic version, a comparison with the experimental splitting Δ_{AB} is possible only by employing the Bir-Pikus Hamiltonian for the valence bands of wurtzite type materials[10] and using the DFT-LDA results for the crystal field splitting together with reported values of the spin-orbit splitting from 3*C*-SiC from the literature.[19–21]

During the past years, the position of the lowest conduction-band minimum of 6*H*-SiC and the dispersion $E(\mathbf{k})$ close to it have been involved in controversial discussion. Rather contradictory results have been reported on the effective electron masses as determined in several experiments using different techniques such as Faraday rotation,[22] optically detected cyclotron resonance,[23] fitting of IR absorption data[24,25] and Raman scattering from LO-phonon-plasmon-coupled modes.[26] In a previous work[27] it was shown by a symmetry analysis of the wurtzite Brillouin zone and $\mathbf{k}\cdot\mathbf{p}$ theory that the symmetry properties of the band structure at the conduction-band minimum have to be taken into account in order to extract reliable information about the electron effective mass tensor from experimental data. From the analysis of the Zeeman pattern of the *N* donor excitation spectrum at high magnetic fields[27] it was concluded that the equivalent conduction-band minima of 6*H*-SiC are located along the line *ML* in the Brillouin zone[28] and that the effective mass tensor has three independent components. However, the exact position of the conduction-band minimum $k^{\min}$ along the line *ML* could not be determined by experiment so far.

Different results for the shape and position of the conduction-band minimum in 6*H*-SiC are reported in theoretical studies of the band structure of 6*H*-SiC too. All recent DFT-LDA band-structure calculations of 6*H*-SiC[13,29–31,33] find, like in GaP,[32] a camel's back shape for the dispersion of the lowest conduction band. The conduction-band minimum is located at about 0.4*ML* and can be approximately described with rather large effective electron masses [$1.5m_e$–$2m_e$ (Refs. 29 and 13)] in the k_z direction. In contrast, a quasiparticle calculation places the conduction-band minimum at *M* and yields a much lower effective electron mass for the k_z direction [$0.51m_e$ (Ref. 33)]. We consider this controversy when comparing experimental and theoretical results (Sec. III).

II. EXPERIMENT

The samples used in this experiment were cut from an *n*-type 6*H*-SiC crystal, grown by the modified Lely process

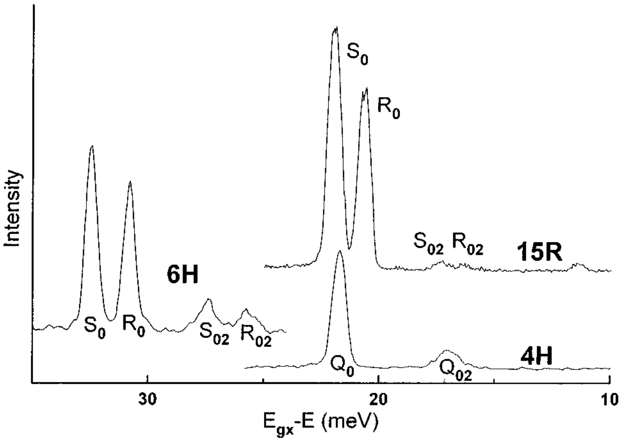

FIG. 2. Photoluminescence spectra of different SiC polytypes at atmosphere pressure ($T=29\pm 2$ K). The energies are given relatively to the excitonic energy gap E_{gx} of the corresponding polytype.

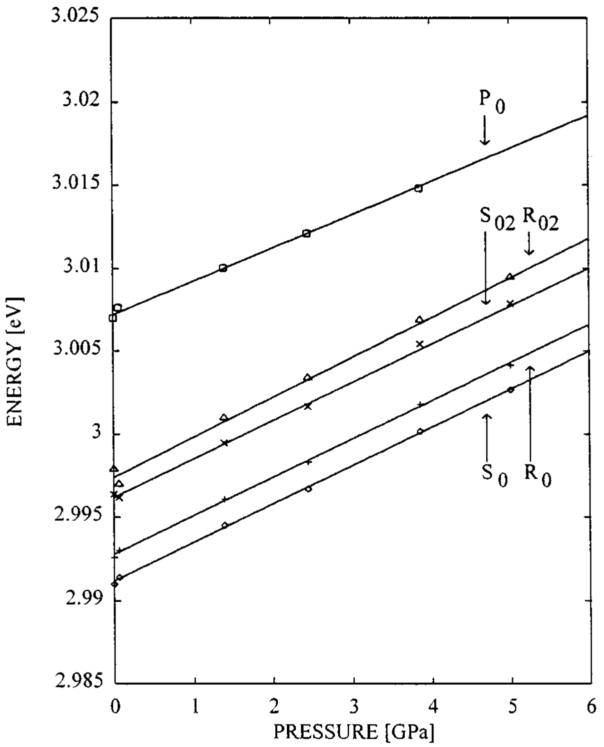

FIG. 3. Hydrostatic pressure dependence of the energies of exciton lines S_0, R_0, P_0, S_{02}, and R_{02} in the 6*H*-SiC photoluminescence spectrum ($T=29\pm 2$ K).

by Ziegler and Stein[34,35] at the Siemens Research Laboratories Erlangen, which are unintentionally doped with nitrogen. The free-electron density at room temperature as determined by a Hall effect measurement was 2.0×10^{16} cm^{-3}. The identification of the polytype was performed by analyzing the low-temperature PL spectrum due to bound excitons at neutral nitrogen donor atoms at atmospheric pressure.[36] The sample was mechanically polished down to a thickness of 50 μm and broken into sufficiently small pieces with sizes about 100 μm across.

PL was excited by the 325-nm line from a He-Cd laser directed on the sample backside and collected in the forward direction. The sample was placed in a clamp-type diamond anvil cell (DAC). A 4:1 mixture of methanol and ethanol was used as the pressure-transmitting medium. The value of the pressure was determined from the calibrated shift of the ruby luminescence line by including tiny ruby pieces in the pressure chamber along with the sample.[37] The pressure determination was accurate to ± 1 kbar. All pressure changes were made at room temperature. No pressure dependence of the PL linewidth has been detected, indicating a negligible amount of nonhydrostatic stress (< 1 kbar). The DAC was inserted in a helium flow cryostat and the temperature was measured using a platinum resistor glued to the heat sink. The temperature of the sample was $T=29\pm 2$ K during the measurements. The PL spectra were analyzed with triple spectrograph DILOR equipped with multichannel detection. The spectral resolution of the whole setup was 0.12 meV.

Typical PL spectra of 6*H*-SiC, 4*H*-SiC, and 15*R*-SiC doped with nitrogen at $T=29\pm 2$ K are shown in Fig. 2. It is noted for later discussion that the energy differences between pairs of excitons formed from *A* and *B* valence bands are about the same for a given polytype, namely, $\Delta E(S_{02}-S_0)=5.13\pm 0.1$ meV and $\Delta E(R_{02}-R_0)=5.08\pm 0.1$ meV for 6*H*-SiC.

Figure 3 shows the peak energies of the exciton lines S_0, R_0, P_0, S_{02}, and R_{02} as a function of hydrostatic pressure. All lines show a clear shift to higher energies with increasing hydrostatic pressure. The pressure dependence of these exciton lines can be fitted by the linear relation

$$E(P)=E(0)+eP, \tag{1}$$

where $E(0)$ is the energy at atmospheric pressure and e the first-order pressure coefficient. The values of $E(0)$ as well as those of the linear pressure coefficients obtained by this method are listed in Table II.

The pressure dependence of the indirect band gap is determined by assuming that the emission lines associated with the radiative decay of a free or a shallow bound exciton shift with the host semiconductor band gap under hydrostatic pressure at the same rate. This is because for weakly bound excitons the change of the binding energy due to a change of the electron and hole effective masses and of the dielectric constant under hydrostatic pressure is small compared with the pressure dependence of the band gap. This was demonstrated by Kobayashi *et al.* by simultaneous measurements of the band-gap absorption and exciton PL under pressure[38] in 3C-SiC.

It can easily be seen from Fig. 3 that the emission lines S_0, R_0, S_{02}, and R_{02} show the same shift under pressure (within experimental errors). However, the P_0 exciton line shows a slightly different behavior under hydrostatic pressure. This is remarkable because it is assumed in the literature that they are formed by the same conduction- and valence-band states. Therefore, the contribution from the shift of band states as well as the changes of the exciton binding energies with hydrostatic pressure should be the same for all excitons. We assume that the different pressure coefficients of the P_0 and the R_0 and S_0 excitons are due to

TABLE II. Pressure coefficients of the S_0, R_0, P_0, S_{02}, and R_{02} exciton lines in 6*H*-SiC ($T=29\pm21$ K). The results were obtained from least-squares fits with $E(P)=E(0)+eP$ to the experimental data.

Line	$E(0)$ (eV)	e (eV/Mbar)
S_0	2.9912	0.23
R_0	2.9928	0.23
P_0	3.0072	0.20
S_{02}	2.9962	0.23
R_{02}	2.9974	0.24

TABLE III. Bulk modulus B_0 and its pressure derivative B_0' of the indirect group-IV semiconductors diamond, Si, and Ge, and some SiC polytypes.

Material	Method	B_0 (Mbar)	B_0'	Reference
diamond				
	Expt.	4.42		53
	Present calc.	4.60	3.5	
Si				
	Expt.	0.960–0.994	3.2–4.68	53
	Present calc.	0.94	4.3	
Ge				
	Expt.	0.758		53
	Present calc.	0.768	4.7	
3*C*-SiC				
	Expt.	2.60(9)	2.9(3)	54
	Expt.	2.48(9)	4.0(3)	55
	Expt.	2.27(3)	4.1(1)	56
	Present calc.	2.22	3.9	
	Other calc.	3.08	2.1	57[a]
	Other calc.	2.00	7.3	57[b]
	Other calc.	2.494	3.159	58
	Other calc.	2.24		59
	Other calc.	2.12	3.7	60
	Other calc.	1.9621	3.5722	61
	Other calc.	2.22	3.88	29
	Other calc.	2.22		62[c]
	Other calc.	2.22		62[d]
4*H*-SiC				
	Expt.			
	Present calc.	2.24	3.8	
	Other calc.	2.23	3.66	29
	Other calc.	2.17		62[c]
	Other calc.	2.11		62[d]
6*H*-SiC				
	Expt.	2.60(9)	2.9(3)	54
	Expt.	2.302	4	63
	Present calc.	2.31	4.0	
	Other calc.	2.18		62[c]
	Other calc.	2.15		62[d]

[a] Calculation was made for the energy cutoff of 20.6 Ry in the plane-wave method.

[b] Calculation was made for the energy cutoff of 29.7 Ry in the plane-wave method.

[c] Calculated values with atomic relaxations.

[d] Calculated values without atomic relaxations.

their strongly different binding energy, which is 16.0 meV, 30.4 meV, and 32.1 meV, respectively.[5] A bound state is represented as a wave packet that for increasing binding energies involves Bloch states from an increasing volume in **k** space. These states (or corresponding transition energies) may have different pressure coefficients. The P_0 line, corresponding to the bound exciton with the smallest binding energy, has the strongest localization in **k** space. Therefore, its pressure coefficient of 0.20 eV/Mbar is closest to that of the indirect band gap.

III. RESULTS FROM NONRELATIVISTIC BAND STRUCTURE CALCULATIONS

For the strength and weakness of the DFT-LDA method, the plane-wave expansion, and the concept of norm-conserving pseudopotentials we refer to the earlier papers on SiC polytypes.[39,40,29] In our calculations we have used the parametrization of Perdew and Zunger for the exchange-correlation potential.[41] The convergence of ground-state properties, to which DFT-LDA calculations are addressed, sensitively depends on the smoothness of the pseudopotentials. For generating soft pseudopotentials we have followed the lines suggested by Troullier and Martins.[42] Integration in **k** space[43] has been performed using 12 special points for the hexagonal polytypes and 10 points for the cubic structure. Convergence for the ground-state properties (and the details of the near band-edge states) was obtained with a cutoff for the plane-wave expansion of 36 Ry for all SiC polytypes, 40 Ry for diamond, 20 Ry for Si, and of 20 Ry for Ge, respectively. The corresponding number of plane waves was kept fixed when varying the volume for a given crystal lattice. We mention, in particular, that the position of the conduction-band minimum of 6*H*-SiC at $0.4ML$ is converged. The determination of the equilibrium structures has been accomplished using the following procedure. For cubic crystals the total energy E_{tot} for different lattice constants a was fitted to the Murnaghan's[16] or Vinet's equation of state[17,18] in order to determine the ground-state values for E_{tot}, a, the bulk modulus B_0, and its pressure derivative B_0'. For hexagonal SiC polytypes the total energy has been calculated as a function of c/a for fixed values of the unit cell volume V. By fitting these energies to polynomials of c/a we have determined the minimum for fixed V with respect to c/a. Repeating this calculation for another value of V, we have found the total energy minimum at the same c/a ratio. We have fitted the values of E_{tot} for this c/a ratio but different V using again Murnaghan's equation of state. All values for the lattice constants B_0, and B_0' (Table III) obtained in this way are in good agreement with those reported from other calculations and from experiments (see Table III).

In order to determine the pressure coefficients of the band gaps we calculated the electronic band structure at equilibrium volume and at a compressed state. Thereby, for the hexagonal polytypes, we kept the c/a ratio fixed, thus taking into account a result from previous calculations.[29] The obtained volume dependence of the indirect-gap energy is converted into a pressure dependence using Vinet's equation of state and the values of B_0 and B_0' from Table III. In compar-

TABLE IV. Pressure coefficients dE_G/dP (eV/Mbar) of the indirect band gaps of the group-IV semiconductors diamond, Si, and Ge and some SiC polytypes.

Material	k_{min}	dE_G/dP Expt.	dE_G/dP Present calc.	dE_G/dP Other calc.
diamond	$0.74\Gamma X$[a]	$+0.6$[b]	$+0.59$	$+0.53-0.58$[d]
Si	$0.85\Gamma X$[a]	-1.432[e]	-1.63	-1.41[f], -1.6[g]
Ge	L	$+5.0$[a], $+4.8\pm0.2$[h]	$+4.6$	$+4.38$[i] $+4.6$[j]
3*C*-SiC	X	-0.19[k]	-0.27	-0.11[l], -0.36[m], -0.33[n,o]
4*H*-SiC	M		$+0.21$	$+0.08$[p]
6*H*-SiC	$0.4ML$[c]	$+0.20$[c]	$+0.08$	-0.03[p] (at the M point)

[a] Reference 64.
[b] Reference 65.
[c] This study.
[d] Reference 66.
[e] Reference 67.
[f] Reference 68.
[g] Reference 69.
[h] Reference 70.
[i] Reference 71.
[j] Reference 69.
[k] Reference 38.
[l] Reference 61.
[m] Reference 60.
[n] Reference 11.
[o] Reference 15.
[p] Reference 11.

ing the resulting pressure coefficients for the considered indirect-gap materials (Table IV) one finds surprisingly large differences in the values despite the fact that the involved band-edge states are p bonding and s-p antibonding states in all cases. Our calculated values are in good agreement with other theoretical work and with experimental data, the typical absolute difference being 0.1–0.2 eV/Mbar (cf. Table IV). Compared to diamond, Si, and Ge, the hydrostatic pressure coefficient of the indirect gap in SiC polytypes is close to zero; it is negative for 3*C* and positive for 4*H* and 6*H*-SiC. We have calculated also the pressure coefficients for indirect transitions to different points of the lowest conduction-band along the ML line in 6*H*-SiC and found values ranging from 0.03 eV/Mbar at M to 0.18 eV/Mbar at L.

In comparing the calculated value for the hydrostatic pressure coefficient of the indirect gap with the experimental value derived from the pressure dependence of the P_0 line, we find good agreement. In our analysis a possible change of the camel's back structure of the lowest conduction-band and its influence on the exciton binding energy under hydrostatic pressure is not considered. We find from band calculations a decrease of the camel-back height, which is 3.8 meV at equilibrium volume with a hydrostatic pressure coefficient of 0.003 eV/Mbar. However, the corresponding change of the exciton binding energy is not known. Despite the agreement between the experimental and theoretical values of the pressure coefficient, we cannot draw conclusions with respect to the position of the conduction-band minimum along the ML line.

Calculated crystal field splittings Δ_{cr} of the valence band in hexagonal SiC polytypes are rarely found in the literature. Therefore, we present our values of Δ_{cr} for 2*H*-SiC, 4*H*-SiC, and 6*H*-SiC in Table V. In accordance with existing experimental data and other calculations,[13,9,44–46] Δ_{cr} increases with the hexagonality of the polytype.

IV. ANALYSIS OF THE VALENCE-BAND FINE STRUCTURE OF 6*H*-SiC FROM THE EXCITON EXCITATION SPECTRUM AND ITS PRESSURE DEPENDENCE

A. Spectrum of the unstrained crystal

The valence-band structure of hexagonal polytypes at the Brillouin-zone center at $\mathbf{k}=\mathbf{0}$ is determined by crystal field and spin-orbit splitting as described by Bir and Pikus.[10] The three eigenvalues E_1^0, E_2^0, and E_3^0 of the Hamiltonian

$$E_1^0=\Delta_1+\Delta_2, \tag{2}$$

$$E_{2,3}^0=\frac{\Delta_1-\Delta_2}{2}\pm\left[\left(\frac{\Delta_1-\Delta_2}{2}\right)^2+2\Delta_3^2\right]^{1/2} \tag{3}$$

give the maxima of the A, B, and C valence bands, respectively. Δ_1 is the crystal field splitting (Δ_{cr} in Table V) and Δ_2 and Δ_3 are the spin-orbit parameters, which in the quasicubic approximation can be related to the spin-orbit split-

TABLE V. Crystal field splitting Δ_{cr} for several hexagonal SiC polytypes.

Polytype	Calc. (meV) this study	Calc. (meV) Ref. 13	Calc. (meV) Ref. 46	Expt. (meV)
6*H*-SiC	44	36		48.7[a], 53[b]
4*H*-SiC	74	56		88 ± 2 or 83 ± 2[c]
2*H*-SiC	145	97	120	

[a] Exciton piezoabsorption (Ref. 9).
[b] Electroabsorption (Ref. 45) [this value has to be corrected from the value of Δ_{so} according to Eqs. (2) and (3)].
[c] Electroabsorption (Ref. 49) [this value has to be corrected from the value of Δ_{so} according to Eqs. (2) and (3)].

ting Δ_{so} of the cubic polytype by $\Delta_2 = \Delta_3 = \Delta_{so}/3$. The splittings of the valence bands thus read

$$E_1^0 - E_{2,3}^0 = \frac{1}{2}\left\{ (\Delta_{cr}+\Delta_{so}) \mp \left[(\Delta_{cr}+\Delta_{so})^2 - \frac{8}{3}\Delta_{cr}\Delta_{so} \right]^{1/2} \right\}. \tag{4}$$

In the case of $\Delta_{so} \ll \Delta_{cr}$, which can be assumed for the hexagonal SiC polytypes, these expressions simplify in second order of Δ_{so}/Δ_{cr}:

$$E_1^0 - E_2^0 = \frac{2}{3}\Delta_{so} - \frac{2}{9}\frac{\Delta_{so}^2}{\Delta_{cr}^2}\Delta_{cr}, \tag{5}$$

$$E_1^0 - E_3^0 = \frac{1}{3}\Delta_{so} + \left(1 + \frac{2}{9}\frac{\Delta_{so}^2}{\Delta_{cr}^2} \right)\Delta_{cr}. \tag{6}$$

In the case of $\Delta_{so} \ll \Delta_{cr}$ the energy difference between the bands A and B ($\frac{2}{3}\Delta_{so}$) is independent of crystal field splitting Δ_{cr}. Therefore, the spin-orbit splitting Δ_{so} of the hexagonal SiC polytypes can be determined from Eq. (5) if the energy difference $E_A^0 - E_B^0$ is known.

B. Spectrum of the strained crystal

The equations that describe the hydrostatic and uniaxial pressure dependence of the three valence bands A, B, and C can been obtained from the strain Hamiltonian of Bir and Pikus.[10,47,48] Keeping only terms up to first order in the stress, these expressions at $\mathbf{k} = \mathbf{0}$ are

$$E_A = E_A^0 + D_1\epsilon_{zz} + D_2\epsilon_\perp + D_3\epsilon_{zz} + D_4\epsilon_\perp, \tag{7}$$

$$E_B = E_B^0 + D_1\epsilon_{zz} + D_2\epsilon_\perp + \alpha_+ D_3\epsilon_{zz} + \alpha_+ D_4\epsilon_\perp, \tag{8}$$

$$E_C = E_C^0 + D_1\epsilon_{zz} + D_2\epsilon_\perp + \alpha_- D_3\epsilon_{zz} + \alpha_- D_4\epsilon_\perp. \tag{9}$$

Here, D_1, D_2, D_3, and D_4 are deformation potential constants of the valence bands and ϵ_{zz} and $\epsilon_\perp = \epsilon_{xx} + \epsilon_{yy}$ denote the components of the strain tensor. In the cubic approximation $\alpha_\pm$ is given by

$$\alpha_\pm = \frac{1}{2}\left\{ 1 \pm \frac{3\Delta_{cr} - \Delta_{so}}{[(3\Delta_{cr} - \Delta_{so})^2 + 8\Delta_{so}^2]^{1/2}} \right\}. \tag{10}$$

In the case of $\Delta_{so}/\Delta_{cr} \ll 1$, as assumed for the hexagonal SiC polytypes, $\alpha_\pm$ are given to second order in Δ_{so}/Δ_{cr} by

$$\alpha_+ := 1 - \frac{2}{9}\left(\frac{\Delta_{so}}{\Delta_{cr}}\right)^2, \quad \alpha_- := \frac{2}{9}\left(\frac{\Delta_{so}}{\Delta_{cr}}\right)^2. \tag{11}$$

From Eqs. (7) and (8) it is obvious that excitons formed by the valence bands A and B have very similar pressure coefficients for both hydrostatic and uniaxial pressure.

C. Interpretation of the exciton spectra under hydrostatic pressure

According to our experimental results we give the following interpretation of the 6*H*-SiC exciton spectrum. Due to the experimentally observed thermalization, we attribute the exciton emission lines S_0, R_0, and P_0, as do the authors of Ref. 4, to excitons bound to the three crystallographically different neutral nitrogen impurities with holes from the highest valence band A. Furthermore, we confirm the interpretation of the emission lines S_{02} and R_{02} appearing at higher temperature to be due to excitons formed with thermally excited holes of the valence band B[4] because these emission lines nearly have the same hydrostatic pressure coefficient as the emission lines S_0 and R_0 [cf. Eqs. (7) and (8) and Table II] and are displaced by almost the same energy.

The energy difference between the excitons formed from the valence bands A and B can be used to estimate the spin-orbit splitting in SiC polytypes [cf. Eq. (5)]. Taking reported values of Δ_{so} that range from 10 meV (Refs. 19 and 20) to 14.4 meV for 3*C*-SiC,[21] the approximation $\Delta_{so} \ll \Delta_{cr}$ is definitely justified for 2*H*-SiC and leads for 6*H*-SiC to an error of 0.2–0.5 meV. Converting the Δ_{AB} value determined from bound exciton data, we obtain a value of $\Delta_{so} = 7.7$ meV for 6*H*-SiC (6.8 meV for 4*H*-SiC), which is smaller than the values quoted above for 3*C*-SiC. According to this analysis, Choyke and Patrick[4] were in error as they missed the factor of 3/2 when assigning Δ_{AB} to the spin-orbit splitting.

The values of the spin-orbit splitting above given are in good agreement with other values determined by electroabsorption [6*H*-SiC, 6.5 meV (Ref. 49)] and wavelength modulated absorption [6*H*-SiC, 7 meV, 15*R*-SiC, 7 meV (Refs. 19 and 20)] for the uniaxial SiC polytypes. In cubic silicon carbide (3*C*-SiC) a slightly higher value of 10 meV has been determined by wavelength modulated absorption.[19,20] A recent relativistic band-structure calculation of 3*C*-SiC gives 14.4 meV for the spin-orbit splitting of the valence bands at the Γ point.[21] Also, the empirical relation of Phillips for the estimation of the spin-orbit splitting of binary semiconductors gives a higher value ($\Delta_{so} = 21.6$ meV).[50] The above values of the spin-orbit splitting are much closer to the value of atomic carbon (5.9 meV) than that of atomic silicon (44.1 meV).[51] We assume that the spin-orbit splitting for 6*H*-SiC and 4*H*-SiC should be very similar. The small difference between hexagonal polytypes (cf. Table I) can be explained by the different hole dispersion relations of the A and B valence bands,[52] which affect the exciton binding energy. Moreover, due to the nature of an exciton and the small value of spin-orbit interaction in SiC, several electronic wave functions from the A and B bands might contribute to one exciton. Therefore, the experimental value for $E_A^0 - E_B^0$ includes some mixing between A and B bands and for this reason might be smaller than calculated values of the difference between A and B energy bands. An exact solution of the exciton problem in 6*H*-SiC is beyond the scope of this article.

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