

# Magneto-optical effects on shallow donor states in 6H-SiC in high magnetic fields

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Impurity excitation spectra in 6H-SiC doped with nitrogen donors are studied by infrared absorption measurements in the frequency range 200–1400  $\text{cm}^{-1}$  under the influence of high magnetic fields up to 20 T. No line splitting is observed for any orientation of the magnetic field. However, four transitions show a diamagnetic shift if the magnetic field is oriented along the crystal  $c$  axis. This diamagnetic shift is found to be anisotropic, depending on the orientation of the viewing direction towards  $c$ . From these results we conclude that the effective mass ellipsoids describing the conduction-band minima must be oriented along lines of the Brillouin zone, which are parallel to the crystal  $c$  axis, and that the effective mass tensor has three independent components. Using the symmetry properties of the Brillouin zone it is shown that the conduction-band minimum must be located somewhere along the line  $M$ - $L$  in the Brillouin zone. From the experimental results at  $B = 20$  T it is estimated that the average effective mass  $m^* = (m_x m_y m_z)^{1/3}$  must be  $m^* > 0.3m_0$ .

## I. INTRODUCTION

The increasing interest in semiconductor devices for use at high temperatures, high power, and high frequency has resulted in growing research activities in wide band gap materials during recent years. SiC is regarded as the most promising material for this purpose in the near future. It is a characteristic property of silicon carbide to form a variety of different crystallographic structures, which are called polytypes.<sup>1</sup> The most common polytype is 6H which has the stacking order  $A$ - $B$ - $C$ - $A$ - $C$ - $B$  of the C-Si layers. This arrangement of the atoms leads to a hexagonal structure with a sixfold symmetry axis along the stacking direction ( $c$  axis). The complex crystallographic structure of 6H-SiC enables the substitution of carbon and silicon atoms by impurity atoms on different nonequivalent lattice sites, which strongly complicates the interpretation of observed impurity spectra.

Infrared excitation spectra of nitrogen donor impurities in 6H-SiC have been reported by several authors since the early 1970s<sup>2-7</sup> and the absorption lines were interpreted in terms of the effective-mass theory (EMT).<sup>6,7</sup> However, neither the measured absorption spectra nor their interpretation produce a consistent picture in all points. A description of the polarization, oscillator strengths, and temperature dependence of these donor transitions has recently been given in Ref. 8. The main results are summarized in Table I, where four transition lines at 1049, 1086, 1105, and 1221  $\text{cm}^{-1}$  have been added, which are identified in this investigation as donor impurity excitations due to the effect of a magnetic field. However, due to still lacking information about the symmetry properties of the lines, it was not possible to as-

sign the observed electronic transitions uniquely so that no fit to an energy scheme for these transitions could be proposed by the authors.<sup>8</sup> Until now no examination using symmetry reducing techniques (e.g., uniaxial stress or magnetic fields) which can provide additional information on the involved donor states has been reported to our knowledge.

TABLE I. Nitrogen donor excitation transition in 6H-SiC ( $B = 0$  T). These results are taken from Ref. 8 including four new lines from this work.

Energy ( $\text{cm}^{-1}$ )	Energy (meV)	Polarization
332	41.13	$E \parallel c$
382	47.33	$E \parallel c$
405	50.18	$E \parallel c$
429	53.15	$E \parallel c$
559	69.26	$E \perp c$
571	70.75	$E \perp c$
579	71.74	$E \perp c$
581	71.99	$E \perp c$
614	76.07	$E \perp c$
622.5	77.13	$E \perp c$
632	78.31	$E \parallel c$
667	82.64	$E \perp c$
907	112.4	$E \perp c$
1049	129.9	$E \perp c$
1086	134.6	$E \perp c$
1105	136.9	$E \perp c$
1124	139.3	$E \perp c$
1162.5	144.1	$E \perp c$
1221	151.3	$E \perp c$

TABLE II. Published experimental values for the effective masses in 6H-SiC.

Technique	Effective masses	Ref.
Optically detected cyclotron resonance	$m_{\perp} = 0.42m_0, m_{\parallel} = 2.0m_0$	16
Faraday rotation	$m_{\perp} = 0.25m_0, m_{\parallel} = 1.5m_0$	17
Fitting of ir absorption data	$m_{\perp} = 0.32m_0, m_{\parallel} = 0.96m_0$	6
Fitting of ir absorption data	$m_{\perp} = 0.24m_0, m_{\parallel} = 0.32m_0$	7

The investigation of the impurity absorption lines in the spectral range of two-phonon absorption requires the use of thin samples with an approximate thickness of  $d = 100 \mu\text{m}$ . Therefore the application of uniaxial stress implies some difficulties, especially in terms of breaking the samples. For this reason, we used magnetic field techniques, which additionally give the identification of the observed absorption lines as donor-excitation transitions. The application of a magnetic field lifts all degeneracies of excited donor states in a semiconductor and has been proven to be very effective in the investigation of donor spectra of group IV and III-V compound semiconductors.<sup>9</sup> Valuable information about the conduction-band structure can be obtained from these measurements. From the orientation of the magnetic field, information about the location of the conduction-band minima in the Brillouin zone in an indirect semiconductor can be obtained. The splitting of degenerate energy states in a magnetic field provides a direct tool to determine the electron effective-mass parameters of the conduction band. To examine the effective-mass parameters was the main reason for starting this work, because values of the electron effective mass reported in the literature are not in agreement (cf. Table II).

## II. EXPERIMENT

The samples we measured were *n*-type 6H-SiC crystals doped with nitrogen grown by a modified Lely process after Ziegler *et al.*<sup>10</sup> and Stein *et al.*<sup>11</sup> The free electron density at room temperature was determined by Hall effect measurements and found to be between  $5.0 \times 10^{16} \text{ cm}^{-3}$  and  $1.2 \times 10^{17} \text{ cm}^{-3}$ . The identification of the polytype was performed by measuring low temperature photoluminescence due to bound excitons at neutral nitrogen donor atoms.<sup>12</sup>

The Zeeman spectra were recorded by using a Bruker IFS 113 Fourier transform spectrometer with a resolution of  $\pm 1 \text{ cm}^{-1}$ , which was matched to two different magneto-optical cryostat systems. We used a Ge composite bolometer placed in its own cryostat. This bolometer was specially designed to operate with a large background radiation to cover a spectral range as wide as possible from the far infrared to the near infrared. The samples were placed at the center of the magnetic field of a 13 T superconducting ( $T = 1.8 \text{ K}$ ) or a 20 T resistive magnet ( $T = 4.2 \text{ K}$ ). The radiation was transferred into the magnet and from there to the input window of the bolometer by an optical system of mirrors and radiation pipes made of polished brass. With the available setup it was possible to perform transmission measurements in the energy region from 200 to  $1300 \text{ cm}^{-1}$  with a reasonable signal

to noise ratio up to 20 T in Faraday ( $\mathbf{k} \parallel \mathbf{B}$ ) and up to 13 T in Voigt configuration ( $\mathbf{k} \perp \mathbf{B}$ ). In Faraday configuration the radiation was unpolarized, whereas in Voigt configuration the radiation was partly polarized due to a reflecting mirror placed just in front of the sample. The misorientation of the magnetic field towards a specified direction was estimated to be less than  $5^\circ$  in all configurations. The experimental error in the energy shifts was given either by the signal to noise ratio or the absorption linewidths.

## III. EXPERIMENTAL RESULTS

### A. Measurement configurations

To study the effect of the magnetic field on the donor excitation spectra it is useful first to classify all configurations (orientation of magnetic field  $\mathbf{B}$ , crystal *c* axis  $\mathbf{c}$ , propagation direction of infrared radiation  $\mathbf{k}$ , and polarization of the electrical field  $\mathbf{E}$  with respect to the crystal *c* axis and magnetic field  $\mathbf{B}$ ). Due to the results of our measurements we use a classification scheme which is based on the orientation of the magnetic field  $\mathbf{B}$  towards the crystal *c* axis (Table III). All four configurations were investigated using unpolarized radiation.

With the samples made available to us, it was not possible to realize measurements with a specified orientation of  $\mathbf{k}$  and  $\mathbf{B}$  in the plane perpendicular to the *c* axis towards lines of high symmetry in the Brillouin zone.

### B. Effect of magnetic field on the spectra

The most striking result which is common to all spectra is that no line splitting is observed irrespective of the orientation of the magnetic field  $\mathbf{B}$  in the Brillouin zone.

However, the excitation lines with the transition energies 667, 1125, 1162, and  $1221 \text{ cm}^{-1}$  show a quadratic shift to higher energies with increasing magnetic field, if  $\mathbf{B}$  is oriented along the crystal *c* axis (cf. Figs. 1–5). The quadratic shifts depend on the orientation of the mag-

TABLE III. Different orientations of magnetic field  $\mathbf{B}$  and *c* axis  $\mathbf{c}$  in 6H-SiC.

( $\mathbf{B}$ , $\mathbf{c}$ )	( $\mathbf{k}$ , $\mathbf{B}$ )		( $\mathbf{E}$ , $\mathbf{c}$ )
$\mathbf{B} \parallel \mathbf{c}$	$\mathbf{k} \parallel \mathbf{B}$	Faraday	$\mathbf{E} \perp \mathbf{c}$
	$\mathbf{k} \perp \mathbf{B}$	Voigt	$\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \perp \mathbf{c}$
$\mathbf{B} \perp \mathbf{c}$	$\mathbf{k} \parallel \mathbf{B}$	Faraday	$\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \perp \mathbf{c}$
	$\mathbf{k} \perp \mathbf{B}$	Voigt	$\mathbf{E} \perp \mathbf{c}$

netic field  $\mathbf{B}$  towards the crystal  $c$  axis. They appear in all configurations with  $\mathbf{B} \parallel \mathbf{c}$ , whereas in configurations with  $\mathbf{B} \perp \mathbf{c}$  no effect of magnetic field at all is observable.

The configurations which show an effect of magnetic field on the spectra ( $\mathbf{B} \parallel \mathbf{c}$ ) were investigated both in Faraday ( $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$ ) and Voigt ( $\mathbf{c} \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations using unpolarized radiation. These quadratic shifts have a significant anisotropy depending on the direction of  $\mathbf{k}$  in the Brillouin zone. The peak positions of the excitation lines 667, 1125, 1162, and 1221  $\text{cm}^{-1}$  are plotted as a function of magnetic field in Figs. 2–5 for  $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$  (Faraday configuration) and  $\mathbf{c} \parallel \mathbf{B} \perp \mathbf{k}$  (Voigt configuration). The coefficients  $d$  describing the diamagnetic shifts according to  $\Delta\omega = \omega(B) - \omega(0) = dB^2$  are given in Table IV including their dependence on the orientation of the wave vector  $\mathbf{k}$  towards the  $c$  axis.

The magnetic field also influences the excitation linewidths  $\Gamma$  of some of the absorption lines. The absorption lines at 1125, 1162, and 1221  $\text{cm}^{-1}$  show a quadratic line broadening with increasing magnetic field  $\mathbf{B}$ , whereas the linewidth of the transition at 667  $\text{cm}^{-1}$  is not affected by magnetic field. The coefficients  $g$  describing the magnetic field dependence of the linewidth according

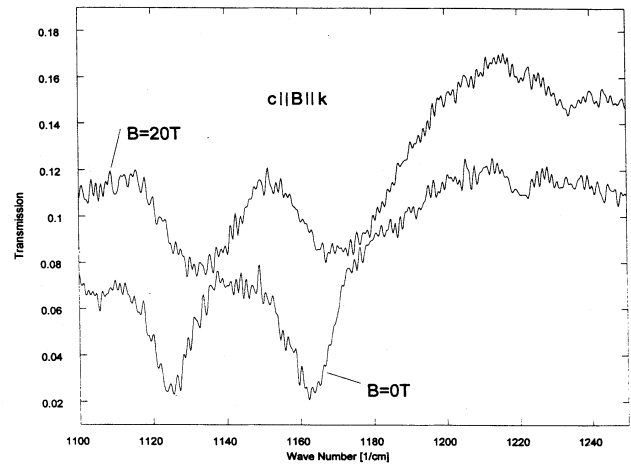


FIG. 1. Influence of magnetic field ( $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$ ) on the photoexcitation spectrum of the nitrogen donor in 6H-SiC. Shown is a part of the transmission spectrum for a sample with a nitrogen concentration of  $1.2 \times 10^{17} \text{ cm}^{-3}$  and a thickness of 120  $\mu\text{m}$ . (The spectrum at 20 T is shifted by a constant value of 0.04 towards the spectrum at 0 T.)

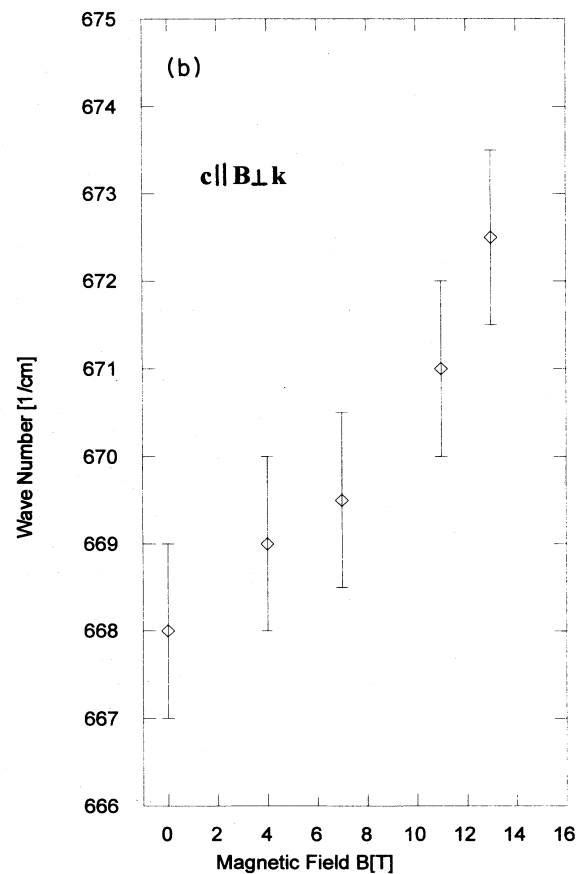
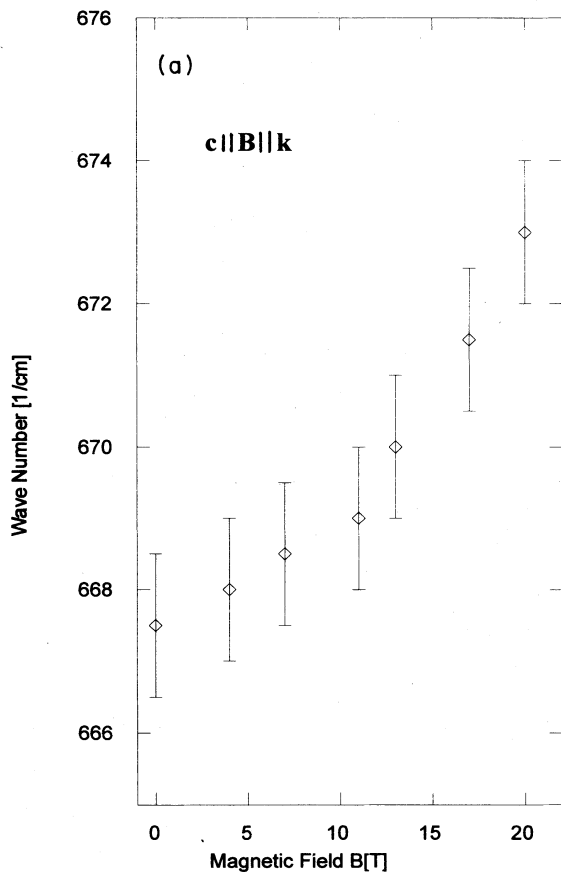


FIG. 2. Energy position of the transmission minimum of the absorption line 667  $\text{cm}^{-1}$  as a function of magnetic field for (a) Faraday ( $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$ ) and (b) Voigt ( $\mathbf{c} \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations.

to  $\Delta\Gamma = \Gamma(B) - \Gamma(0) = gB^2$  are given in Table V for the excitation lines 667, 1125, 1162, and 1221  $\text{cm}^{-1}$ .

No change of oscillator strengths up to  $B = 20$  T was detected for the transitions at 667, 1125, 1162, and 1221  $\text{cm}^{-1}$  in Faraday configuration, whereas the oscillator strengths of the transitions 623 and 1049  $\text{cm}^{-1}$  increased slightly with magnetic field. All other transitions showed no change of oscillator strength within experimental error.

It seems that there is also a weak effect of magnetic field on the transitions at 559, 579, 581, 614, 1086, and 1105  $\text{cm}^{-1}$  at  $B = 20$  T. However, it was not possible to resolve a shift or a change of oscillator strength of these lines because they partially overlap each other or coincide with strong two-phonon bands. For all other transitions, neither an energy shift nor a change of oscillator strength with increasing magnetic field  $\mathbf{B}$  was observed for any orientation of magnetic field  $\mathbf{B}$  in the Brillouin zone within experimental error.

#### IV. DISCUSSION

The experimental results can qualitatively be explained in the following way. From the fact that no line

splitting is observed with increasing magnetic field  $\mathbf{B}$  independent of the orientation of  $\mathbf{B}$  in the Brillouin zone, we conclude that the system of the excited eigenstates already has no more degeneracies at zero field. This is the reason that no linear Zeeman splitting appears. Therefore the energy spectrum is influenced only by second-order effects of the magnetic field  $\mathbf{B}$  (diamagnetic shift). To get an idea of the directional dependence of the diamagnetic shift on the orientation of the magnetic field  $\mathbf{B}$  towards the crystal  $c$  axis, it is useful to have a look at Si, where the band structure is well known and the quadratic Zeeman effect has been studied experimentally and theoretically in great detail.<sup>13</sup> In this work it has been demonstrated that the quadratic Zeeman effect on nondegenerate  $p_0$  states has a maximum for those conduction-band valleys which are oriented along the magnetic field  $\mathbf{B}$  but is much weaker for valleys perpendicularly to  $\mathbf{B}$ .

Applied to 6H-SiC one can draw the following conclusions. From the symmetry properties of the wurtzite Brillouin zone (Fig. 6) it is obvious that the effective mass ellipsoids describing the conduction-band valleys (which are assumed to lie on lines of high symmetry) are oriented either in planes which are perpendicular to the  $c$  axis or along lines which are parallel to the  $c$  axis. Different equivalent conduction-band valleys oriented perpen-

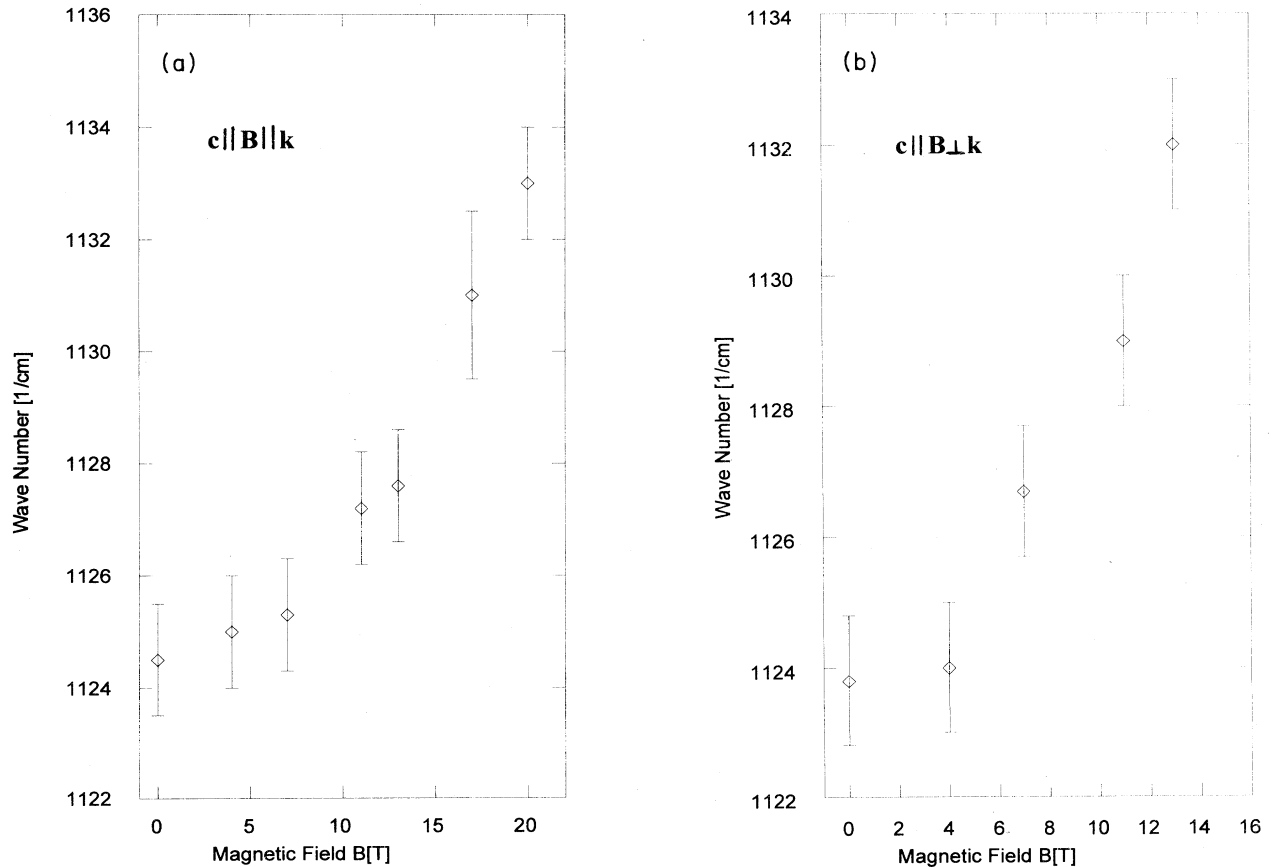


FIG. 3. Energy position of the transmission minimum of the absorption line 1125  $\text{cm}^{-1}$  as a function of magnetic field for (a) Faraday ( $c \parallel \mathbf{B} \parallel \mathbf{k}$ ) and (b) Voigt ( $c \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations.

dicularly to the  $c$  axis would contribute to the quadratic Zeeman effect if the magnetic field  $\mathbf{B}$  is oriented in the same plane, and at sufficiently high magnetic fields one would expect splittings due to the contribution from different equivalent conduction-band minima as in Si. The effect of the magnetic field is then expected also to depend on the angle between  $\mathbf{B}$  and one of the equivalent conduction-band valleys. However, in our experiments, no effect of magnetic field at all is found for the  $\mathbf{B} \perp \mathbf{c}$  configurations. Thus we can conclude that the conduction-band valleys must be oriented along a line parallel to the  $c$  axis.

To get more information on the exact position of the conduction-band minima in the Brillouin zone, effective-mass theory must be combined with the symmetry properties of the Brillouin zone.

### A. Effective mass theory (EMT)

The structure of the conduction-band minimum at  $\mathbf{k}_0$  of an arbitrary semiconductor can be discussed using  $\mathbf{k} \cdot \mathbf{p}$  theory and symmetry properties of the band extremum.<sup>14</sup> Relativistic effects are supposed to be very small in SiC due to the small spin-orbit interaction of the C and Si atoms.<sup>15</sup> Therefore the  $k$ -linear terms which are

due to these relativistic effects are neglected. Then the energy  $E_n(\mathbf{k}_0 + \mathbf{k})$  near the extremum of the conduction band can be written as

$$E_n(\mathbf{k}_0 + \mathbf{k}) = E_n(\mathbf{k}_0) + \sum_{\alpha,\beta} \frac{\hbar^2}{2m_{\alpha,\beta}} k_\alpha k_\beta. \quad (1)$$

The constants  $m_{\alpha,\beta}$  are the components of the effective-mass tensor. Thus, near the conduction-band minimum, the energy is a parabolic function of  $k_\alpha$ . The symmetric tensor  $1/m_{\alpha,\beta}$  may be reduced to principal axes and then (1) becomes

$$E_n(\mathbf{k}_0 + \mathbf{k}) = E_n(\mathbf{k}_0) + \sum_{\alpha} \frac{\hbar^2}{2m_{\alpha}} k_{\alpha}^2. \quad (2)$$

Therefore, for a nondegenerate band the surfaces of constant energy near an extremum are ellipsoidal, determined by the six components of the symmetric tensor  $1/m_{\alpha,\beta}$ , or the three principal values of  $1/m_{\alpha}$  and the three directions of the principal axes of the energy ellipsoid. The symmetry properties of the ellipsoid (1) depend only on the symmetry of the position of the band extremum  $k_0$  in the Brillouin zone. If  $k_0$  is located on a symmetry axis, one of the axes of the energy ellipsoids

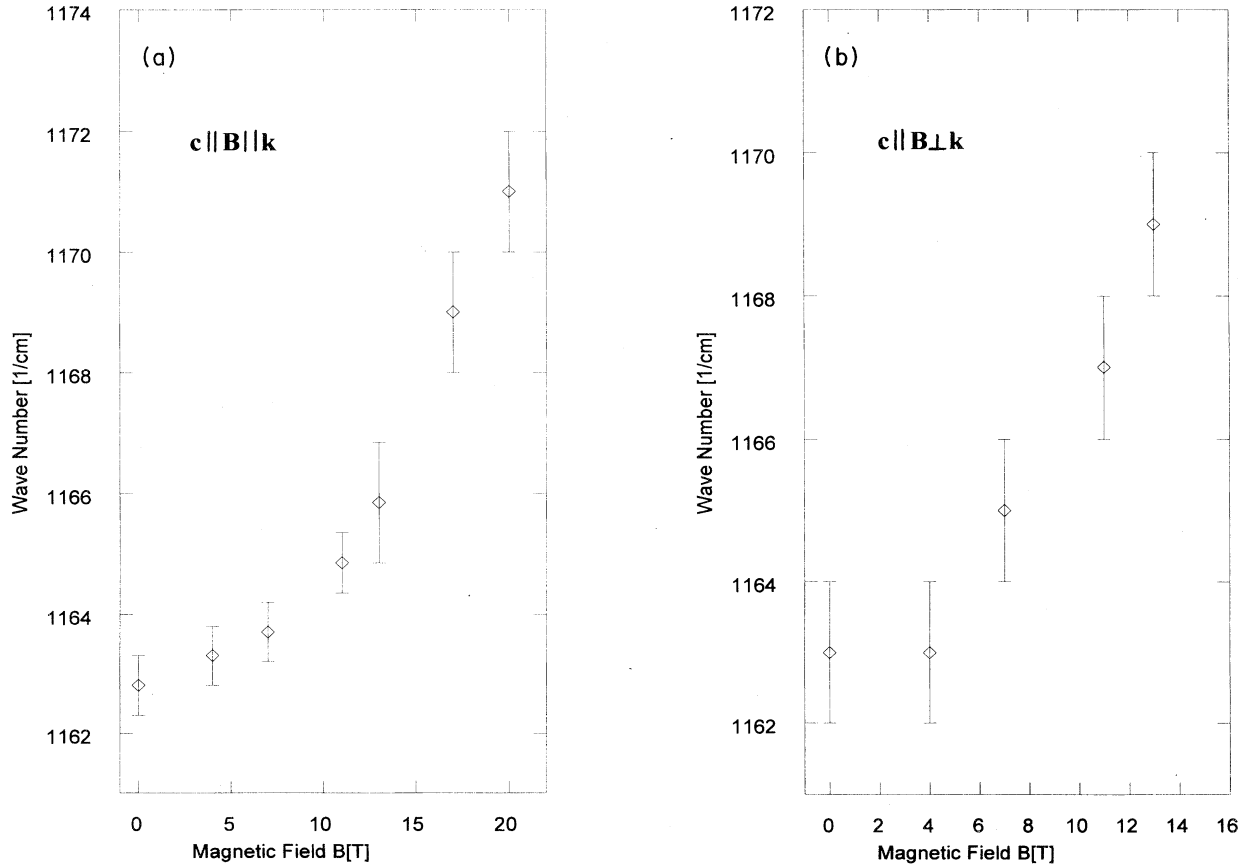


FIG. 4. Energy position of the transmission minimum of the absorption line  $1162 \text{ cm}^{-1}$  as a function of magnetic field for (a) Faraday ( $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$ ) and (b) Voigt ( $\mathbf{c} \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations.

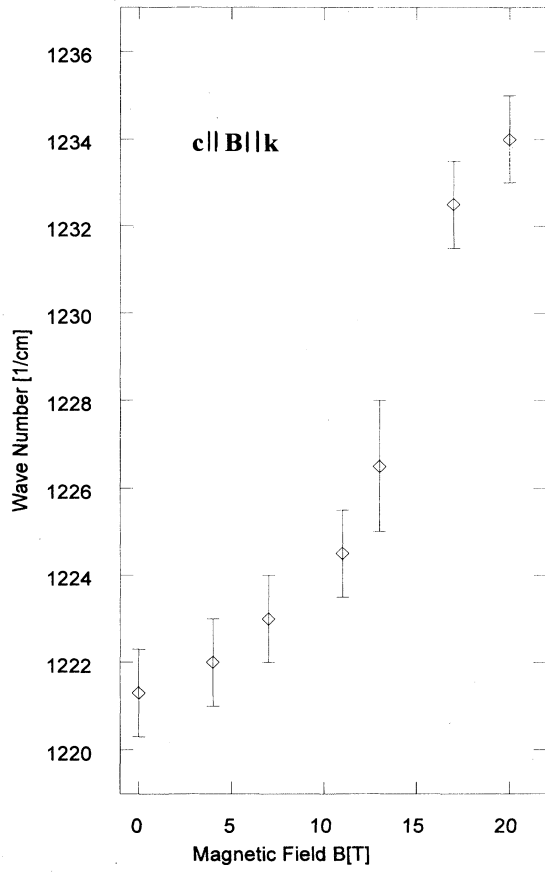


FIG. 5. Energy position of the transmission minimum of the absorption line  $1221 \text{ cm}^{-1}$  as a function of magnetic field for Faraday ( $c \parallel \mathbf{B} \parallel \mathbf{k}$ ) configurations.

coincides with this symmetry axis. Using symmetry arguments, it can be shown that, if the symmetry axis is threefold, fourfold, or sixfold, the energy ellipsoid is an ellipsoid of revolution and the other two axes can be chosen arbitrarily in a plane perpendicular to this symmetry axis. This ellipsoid is characterized by two different effective masses. If  $k_0$  lies on a twofold axis in a reflection plane  $\sigma_\nu$  (symmetry group  $C_{2\nu}$ ), the ellipsoid is characterized by three different effective masses. The results of this procedure applied to different positions of the conduction-band minima  $k_0$  on lines parallel to the  $c$  axis of  $6H$ -SiC ( $C_{6\nu}$  symmetry) are summarized in Ta-

TABLE IV. Diamagnetic shift coefficients  $d$  for Faraday ( $c \parallel \mathbf{B} \parallel \mathbf{k}$ ) and Voigt ( $c \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations:  $\Delta\omega = \omega(B) - \omega(0) = dB^2$ .

Line origin ( $\text{cm}^{-1}$ )	$d(\text{Faraday})$ ( $\frac{\text{cm}^{-1}}{\text{T}^2}$ )	$d(\text{Voigt})$ ( $\frac{\text{cm}^{-1}}{\text{T}^2}$ )
667.5	0.014	0.027
1124.5	0.0215	0.049
1162.8	0.021	0.035
1221.3	0.036	not detectable

TABLE V. Quadratic line broadening coefficients  $g$  for Faraday ( $c \parallel \mathbf{B} \parallel \mathbf{k}$ ) configuration:  $\Delta\Gamma = \Gamma(B) - \Gamma(0) = gB^2$ .

Line origin ( $\text{cm}^{-1}$ )	$\Gamma(0)$ ( $\text{cm}^{-1}$ )	$g(\text{Faraday})$ ( $\frac{\text{cm}^{-1}}{\text{T}^2}$ )
667.5	11	0.0
1124.5	9	0.023
1162.8	10.5	0.023
1221.3	6.5	0.032

ble VI. The effect of these different possible conduction-band structures on the impurity excitation spectrum is discussed in the next section.

### B. Description of shallow impurity centers

The excitation spectra of shallow donors in  $6H$ -SiC can be described within effective-mass theory (EMT) in the following way, which, neglecting polaron coupling, is the most general situation which can appear. Depending on the location of the equivalent conduction-band minima of  $6H$ -SiC in the Brillouin zone, it was shown in the previous section that the effective-mass tensor  $m_{ij}$  has either two or three independent components which are listed in Table VI. The dielectric constant has to be treated as a tensor  $\epsilon_{ij}(\omega)$  too. If there exists a common set of eigenvectors for the effective mass and dielectric tensor, which is fulfilled if the conduction-band minima are oriented along lines parallel to the  $c$  axis, they can simultaneously be diagonalized and the effective-mass Hamiltonian  $H$  of the donor problem can be written as follows:

$$H = -\frac{\hbar^2}{2} \left( \frac{1}{m_x} \frac{\partial^2}{\partial x^2} + \frac{1}{m_y} \frac{\partial^2}{\partial y^2} + \frac{1}{m_z} \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{\sqrt{\epsilon_y \epsilon_z x^2 + \epsilon_x \epsilon_z y^2 + \epsilon_x \epsilon_y z^2}}. \quad (3)$$

Using the uniaxial symmetry of the crystal field ( $\epsilon_x = \epsilon_y = \epsilon_\perp, \epsilon_z = \epsilon_\parallel$ ) the electrostatic potential  $V(\mathbf{r})$  can be rewritten as follows:

$$V(\mathbf{r}) = -\frac{e^2}{\sqrt{\epsilon_\perp \epsilon_\parallel (x^2 + y^2) + \epsilon_\perp^2 z^2}}. \quad (4)$$

The electrostatic potential  $V(\mathbf{r})$  has rotational symme-

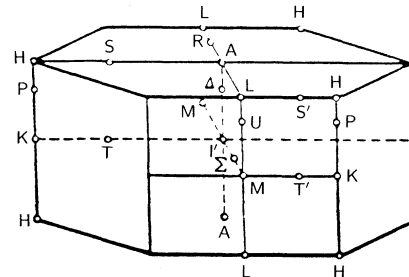


FIG. 6. Brillouin zone for wurtzite lattice.

TABLE VI. Energies as a function of  $k$  for conduction-band minima at  $k_0$  located at different points in the Brillouin zone for wurtzite type lattices (cf. Fig. 6).

Symmetry group $F_{k_0}$	Points	Energy near minimum
$C_{6\nu}$	$\Gamma, \Delta, A$	$\frac{\hbar^2}{2m_1}(k_1^2 + k_2^2) + \frac{\hbar^2}{2m_3}k_3^2$
$C_{3\nu}$	$K, P, H$	$\frac{\hbar^2}{2m_1}(k_1^2 + k_2^2) + \frac{\hbar^2}{2m_3}k_3^2$
$C_{2\nu}$	$M, U, L$	$\frac{\hbar^2}{2m_1}k_1^2 + \frac{\hbar^2}{2m_2}k_2^2 + \frac{\hbar^2}{2m_3}k_3^2$

try around the crystal  $c$  axis. The commutator of the Hamiltonian

$$H = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + \frac{p_z^2}{2m_z} - \frac{e^2}{\sqrt{\epsilon_{\perp}\epsilon_{\parallel}(x^2 + y^2) + \epsilon_{\perp}^2 z^2}} \quad (5)$$

and the  $z$  component of the angular momentum  $L_z$  is given by

$$[H, L_z] = i\hbar \frac{m_x - m_y}{m_x m_y} p_x p_y. \quad (6)$$

This means that in contrast with the case of two different effective masses ( $m_x = m_y = m_t, m_z = m_l$ ) in the case of three different effective masses the eigenvalues of  $L_z$  are no longer good quantum numbers. Thus states with magnetic quantum numbers  $m$  and  $-m$ , which are degenerate in the case of two effective masses due to time reversal symmetry,<sup>9</sup> will split at zero magnetic field. These non-degenerate states no longer are allowed to be classified using magnetic quantum numbers. However, the parity operator  $P$  which transforms  $\mathbf{r} \rightarrow -\mathbf{r}$  still commutes with the Hamilton operator and parity is a preserved quantum number of the system.

### C. Effect of a magnetic field on the donor excitation spectra

Due to the fact that the band parameters  $m_x, m_y$ , and  $m_z$  are not known we give only a short qualitative description of the Zeeman effect on shallow donors in 6H-SiC. For the Zeeman problem, the linear momentum operator  $\mathbf{p}$  has to be replaced by  $\mathbf{p} - \frac{q}{c}\mathbf{A}$ ,<sup>18</sup> where  $q = -e$  is the charge of the electron and the vector potential  $\mathbf{A}$  is

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r} \quad (7)$$

where  $\mathbf{B}$  is the applied magnetic field. The effective-mass equation (5) for donors in 6H-SiC in a magnetic field, neglecting spin effects, can be written as follows:

$$H = \frac{(p_x + \frac{e}{c}A_x)^2}{2m_x} + \frac{(p_y + \frac{e}{c}A_y)^2}{2m_y} + \frac{(p_z + \frac{e}{c}A_z)^2}{2m_z} - \frac{e^2}{\sqrt{\epsilon_{\perp}\epsilon_{\parallel}(x^2 + y^2) + \epsilon_{\perp}^2 z^2}}. \quad (8)$$

This simple form of the Hamilton operator does not take into account that we are dealing with a multivalley semiconductor. This means that intervalley couplings are ignored, which may be important if the equivalent conduction valleys are affected by the magnetic field  $\mathbf{B}$  in different ways as in Si. However, this effect is neglected here, because the equivalent conduction-band minima are supposed to lie along lines in the Brillouin zone which are parallel to the  $c$  axis, so that no effect of intervalley couplings is expected for  $\mathbf{B} \parallel \mathbf{c}$ . Equation (8) contains terms linear in the applied field of the form  $\mathbf{p} \cdot \mathbf{A}$ , and terms of the order  $\mathbf{B}^2$  (the  $\mathbf{A}^2$  terms). Since there is no first-order effect in  $\mathbf{B}$  (no Zeeman splittings appear) the system of eigenstates already possesses no more degeneracies without applied magnetic field (neglecting spin effects). Using the results which are given in Table VI it can be concluded that the conduction band minimum must be located somewhere along the line  $M$ - $L$  in the Brillouin zone so that the effective mass tensor has three independent components. The observed diamagnetic effects are either due to  $\mathbf{A}^2$  terms in first order or to  $\mathbf{p} \cdot \mathbf{A}$  terms in second order.

The directional dependence of the diamagnetic shifts  $\mathbf{B} \parallel \mathbf{c}$  on the direction of  $\mathbf{k}$  towards the crystal  $c$  axis is difficult to explain, because  $\mathbf{k}$  does not explicitly enter the effective-mass equation (8). The most obvious difference between Faraday ( $\mathbf{c} \parallel \mathbf{B} \parallel \mathbf{k}$ ) and Voigt ( $\mathbf{c} \parallel \mathbf{B} \perp \mathbf{k}$ ) configurations is the polarization of radiation towards the crystal axes. In the former we have  $x$  and  $y$  and in the latter  $x, y$ , and  $z$  components. We suppose that the anisotropy of the diamagnetic shift has to do with the anisotropy of the conduction-band valleys. The calculation of the matrix elements describing the diamagnetic shifts requires detailed knowledge of the impurity envelope functions  $F(r)$ , which strongly depend on the effective masses and the magnetic field. Therefore we do not try to estimate values for the effective masses from the experimental data.

From the fact that even at 20 T no transition from the quadratic to a linear magnetic field dependence appears, we conclude that there is no indication for the formation of Landau levels. This transition can be characterized by the parameter  $\gamma$ , which is defined by

$$\gamma = \frac{\frac{1}{2}\hbar\omega_c}{R_y^*}, \quad (9)$$

where  $\omega_c$  is the cyclotron frequency and  $R_y^*$  the effective Rydberg energy, which are given by

$$\omega_c = \frac{eB}{m^*} \quad (10)$$

and

$$R_y^* = \frac{m^*}{m_0} \frac{1}{\epsilon^2} \times 13.6 \text{ eV}. \quad (11)$$

$\gamma$  is the ratio of the energy of an electron in the lowest Landau level and the effective Coulomb binding energy. We assume that deviations from the diamagnetic shifts should be detectable if  $\gamma > 0.1$ . From the experimental

results at 20 T it is estimated that the average effective mass  $m^* = (m_x m_y m_z)^{\frac{1}{3}}$  has to be  $m^* > 0.3m_0$ .

Effective masses of 6H-SiC have been experimentally studied by several direct and indirect methods (cf. Table II). However, all of these investigations suffer from the fact that the properties of the effective-mass tensor were not discussed by taking the symmetry properties of the position of the conduction-band minimum into account. This is one of the main reasons for requiring a very careful experimental reexamination and interpretation of these experiments.

Recent band structure calculations of 6H-SiC locate the position of the conduction-band minimum along the line  $M-L$ ,<sup>19,20,22</sup> or at the point  $M$ ,<sup>21</sup> in the Brillouin zone. Käckell *et al.*<sup>19</sup> found three different values for the effective masses,  $m_{\parallel} = 0.68$ ,  $m_{\perp 1} = 1.25$ , and  $m_{\perp 2} = 0.13$ . Also, Karch *et al.*<sup>22</sup> found three different effective masses,  $m_{\parallel} = 1.2-1.5$  ( $ML$ ),  $m_{\perp 1} = 0.23$  ( $MK$ ),  $m_{\perp 2} = 0.78$  ( $MT$ ). Furthermore, Karch *et al.*<sup>22</sup> and Backes *et al.*<sup>23</sup> claim that the lowest conduction band in 6H-SiC can be described much better by a camel's back structure similar to the one in GaP (for the details see Ref. 22). These results qualitatively agree with our experimental results.

## V. SUMMARY AND CONCLUSIONS

We have studied impurity excitation spectra in 6H-SiC doped with nitrogen by infrared absorption measurements in the frequency range from 200 to 1400  $\text{cm}^{-1}$  under the influence of high external magnetic fields up to 20 T. No line splittings were observed for any orientation of the magnetic field. However, four transitions show a diamagnetic shift, if the magnetic field is oriented along the crystal  $c$  axis. This diamagnetic shift was investigated in Faraday and Voigt configurations up to 20 T and 13 T, respectively, and was found to be anisotropic, depend-

ing on the orientation of  $\mathbf{k}$  towards  $\mathbf{c}$ . Absorption lines at 1049, 1086, 1105, and 1221  $\text{cm}^{-1}$  were identified as donor impurity excitations due to the effect of the magnetic field. The results for these lines are not consistent with previously given interpretations of infrared data by Vakulenko and Guseva<sup>6</sup> and Suttrop *et al.*<sup>7</sup>

We conclude from the experimental results that effective mass ellipsoids describing the the conduction-band minima must be oriented along lines of the Brillouin zone which are parallel to the crystal  $c$  axis and that the effective-mass tensor has three different independent components (i.e., somewhere along the line  $M-L$ ). From the experimental results at  $B = 20$  T, it is estimated that the average effective mass  $m^* = (m_x m_y m_z)^{\frac{1}{3}}$  must be  $m^* > 0.3m_0$ . Recent results of band structure calculations of 6H-SiC which locate the position of the conduction-band minimum along the line  $M-L$ ,<sup>19,20,22</sup> or at the point  $M$ ,<sup>21</sup> in the Brillouin zone are in agreement with our results. Studies of cyclotron resonance or Faraday rotation data on oriented samples taking symmetry properties of the band structure at the minimum into account are necessary to get reliable experimental data for the  $E(k)$  dispersion relation of electrons (effective masses) in 6H-SiC.

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