

## Magneto-Optical Properties and Recombination Rate of the Green Luminescence in Cubic SiC

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The Zeeman effect of the recombination radiation from a shallow bound exciton in cubic SiC has been studied at 1.6 °K as a function of magnetic field strength and direction. The observed pattern of the Zeeman-split lines is consistent with the Zeeman splitting expected from an exciton bound to a neutral donor, in which the ground state has a singlet electron bound to the donor and the excited state has two paired electrons in addition to a  $j=3/2$  hole. This is consistent with a model for this transition proposed by Choyke *et al.* The measured polarizations, relative intensities, and thermalization of the split lines are also consistent with the theory for an exciton bound to a neutral donor. The measured  $g$  values are  $g_e = 1.96 \pm 0.06$ ;  $g_{h1/2} = 1.12 \pm 0.03$ ;  $g_{h3/2} = 1.10 \pm 0.03$ . No angular anisotropy was observed in the pattern of the Zeeman lines, in agreement with the theoretical angular dependence of the splittings calculated with the experimental  $g$  values for a point defect which is a neutral donor. The no-phonon line is split into two components under uniaxial stress  $\parallel \langle 110 \rangle$ , consistent with the description of the donor energy states given above. A hydrostatic-pressure deformation-potential constant  $a = -2.2 \pm 0.3$  eV was obtained. Satellites of the principal green bound-exciton lines are identified with transitions from excited states by a comparison of spectra at 1.6 and 20.6 °K in different crystals. The low photoluminescence efficiency of the green emission, and the short decay time obtained from a pulsed photoluminescence experiment, suggest that an Auger process dominates the recombination, as expected for an exciton bound to a neutral donor in an indirect gap semiconductor such as SiC.

### I. INTRODUCTION

$\beta$ -SiC is the polytype of the group-IV indirect semiconductor SiC with a cubic (zinc blende) lattice structure. Choyke *et al.*<sup>1</sup> have reported five sharp lines together with other weaker lines (see Fig. 1) in the near band gap green luminescence. They

recognized a no-phonon line 10 meV below the exciton-energy gap and four phonon replicas displaced in energy below the no-phonon line by the TA, LA, TO, and LO zone boundary phonons. They attributed this emission to four-particle nitrogen-exciton complexes. An indirect exciton energy gap of 2.390 eV was obtained from their optical absorption

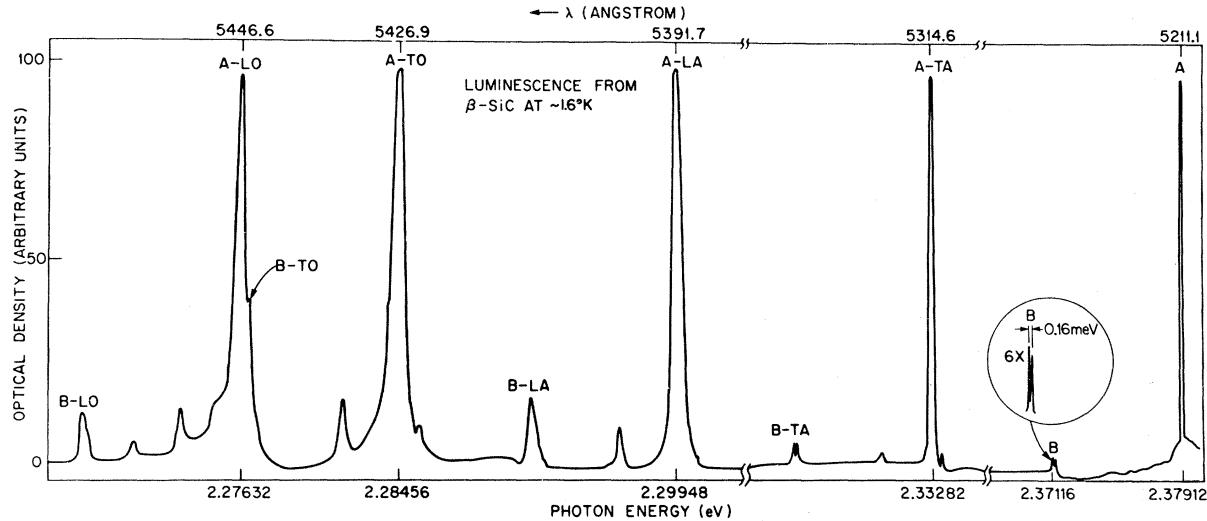


FIG. 1. Densitometer trace of the near band gap luminescence from  $\beta$ -SiC sample No. 196-1.1 at 1.6 °K. The no-phonon line reported by Choyke *et al.* is labeled A and is  $\sim 10$  meV below the exciton energy gap. The doublet labeled B is  $\sim 8$  meV below the A line. See the text for a discussion of the temperature of the sample.

measurements.

This paper contains a study of the symmetry of the optically active impurity site to which the exciton is bound through an analysis of the Zeeman-split lines in the recombination radiation. This study was partially motivated by the absence of any nitrogen spin-resonance signal<sup>2</sup> in a crystal in which the spectrum reported by Choyke *et al.* has been observed.<sup>3</sup>

The polarization, relative intensity, thermalization, and angular variation of the magnitude of the magnetically split components of the no-phonon line were measured. The interpretation of these measurements was aided by a comparison with the S donor in GaP,<sup>4</sup> which has the same type of indirect energy gap. The symmetry of the bound electrons with respect to the donor impurity was determined by a uniaxial-stress experiment. Comparisons of the spectra at 1.6 and 20.6 °K in different crystals were used to identify other lines in the green luminescence. It is concluded that the exciton is bound to a point defect which is a neutral donor. The implications of this conclusion with regard to photoluminescence efficiency are discussed and corroborated with a measurement of the decay time of the luminescence.

## II. EXPERIMENTAL DETAILS

*n*-type  $\beta$ -SiC crystals were obtained from Stanford Research Institute. The crystals were solution grown with no intentional impurities added to the melt. All the data shown in this paper were recorded from crystal No. 196-1.1,<sup>5</sup> 2 × 0.75 × 0.25 mm, the largest nontwinned single crystal available.

The photoluminescence spectra were recorded on Kodak 103 aF plates using a 2-m f/17 Bausch and Lomb grating spectrograph. A hollow cathode Fe-Ne lamp provided numerous convenient calibration lines. The sample was submerged in liquid He or H<sub>2</sub> refrigerant within a glass cryostat placed between the pole pieces of an electromagnet. Back-scattered x-ray Laue photographs were used to orient the axes of the crystal with respect to the direction of the magnetic field. The 4880-Å emission from an Ar<sup>+</sup> laser was used to excite the sample. A sharp (half-width ~150 μeV) zero-field no-phonon line was obtained for the Zeeman measurements from a strain-free portion of crystal No. 196-1.1.

Most of the Zeeman measurements were made with the crystal submerged in pumped liquid He (below the  $\lambda$  point at approximately 1.6 °K). In order to increase the population in the higher-energy states, some local heating of the crystal was produced by increasing the power in the exciting laser beam. However, the green luminescence de-

creased rapidly as the temperature of the sample increased above ~10 °K. With the temperature of the refrigerant above the  $\lambda$  point, luminescence measurements could be made only with relatively low power levels in the exciting laser beam (~25 mW) and considerably longer exposure times. Some Zeeman measurements were taken with the temperature of the refrigerant well above the  $\lambda$  point (in liquid He or H<sub>2</sub>) to study the excited states of the *A* line. Above ~10 °K, the temperature in the excited region of sample No. 196-1.1 was calculated from the ratio of the intensity of the two lines of the red *D* doublet.<sup>6</sup>

Uniaxial stress was applied to crystal No. 196-1.1 submerged in liquid H<sub>2</sub>, using a simple stress apparatus previously described.<sup>7</sup> The ends of the sample (along a ⟨110⟩ axis) were polished flat and parallel. The cross-sectional area ( $\perp$ ⟨110⟩) was not constant, varying ~10%, along the length of the sample. Therefore, the strain was not completely uniform.

The decay time of the luminescence was measured with the crystal in a variable temperature cryostat in which a flow of He vapor from a liquid-He reservoir cooled the sample. The temperature of the sample was measured with a calibrated Ge resistance thermometer. The sample was excited with pulses from an acousto-optically modulated Ar<sup>+</sup> laser operating at 4880 Å.<sup>6</sup> The photoluminescence was analyzed, with a Spex f/6.8 -  $\frac{3}{4}$ -m grating spectrometer set to have a 10-Å bandpass half-width, and detected with an EMI 9558 photomultiplier. The signal from the photomultiplier was amplified and detected with a PAR Model 160 Boxcar Integrator, the output of which was recorded and analyzed.

## III. RESULTS AND DISCUSSION

### A. Zeeman Effect

GaP and  $\beta$ -SiC have similar electronic energy bands. Their energy-band structures have three conduction-band minima located at the *X* points of the Brillouin zone, a valence-band maxima located at  $\Gamma_1$ , and indirect exciton energy gaps that are approximately the same. The principal differences in the energy-band structures are that  $\beta$ -SiC has a much larger direct energy gap (approximately 6 eV<sup>8</sup>) and a much smaller spin-orbit splitting than GaP (the spin-orbit splitting of  $\beta$ -SiC:N has been estimated as 5 meV,<sup>1,9</sup> while GaP has an ~2.88-eV direct energy gap and an 82-meV<sup>10</sup> spin-orbit splitting).

For  $\beta$ -SiC, it is assumed that only the lowest energy-band states, similar in symmetry to the lowest energy-band states in GaP, will contribute substantially to the shallow bound impurity state.

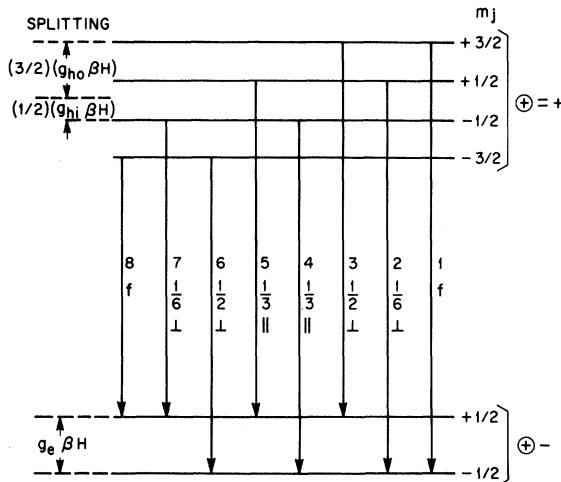


FIG. 2. Schematic energy level diagram for line *A* in a magnetic field. The ground state has a donor with a singlet electron and the excited state has two paired singlet electrons and a ( $j = \frac{3}{2}$ ) hole. The lines are numbered, corresponding to Fig. 3, with the expected polarization and strengths (*f* indicates a forbidden transition).  $\beta$  is the Bohr magneton.

Therefore, at temperatures below 20 °K a "simplified  $\beta$ -SiC"<sup>11</sup> analogous to the "simplified GaP" of Thomas *et al.* will be used to understand the radiative recombination of excitons bound to defects. For this model, the electron comes from the (twofold spin degenerate) singlet valley-orbit states and the hole comes from the (fourfold spin degenerate) *p*-like valence-band states. For an exciton bound to a neutral donor, the two electrons in the singlet valley-orbit state will pair off so that the spin and the anisotropic *g* value are due to the hole. The ground state of the neutral donor will have spin one-half and the isotropic *g* value of the electron.

The exciton causing the *C* line in GaP<sup>4</sup> has been shown to be bound (weakly, ~19 meV) to the neutral donor *S* on the *P* site. The published conclusion that an exciton bound to the neutral donor *N* causes the *A* line in  $\beta$ -SiC rests mainly on the small binding energy of the exciton (10 meV) and a comparison with data obtained for other SiC polytypes.<sup>1</sup> A comparison with the SiC polytypes also places the *N* on the *C* site,<sup>12</sup> as might be anticipated from an ionic size consideration.

The energy level scheme (see Fig. 2) for a neutral donor with a bound exciton in a magnetic field together with the expected strengths and polarizations have been given<sup>4</sup> for "simplified GaP." This scheme has been found to be valid for "simplified  $\beta$ -SiC."

At 1.6 °K (with some significant heating of the sample, perhaps a few °K, caused by the absorbed

exciting laser energy as discussed above) and *H* = 30.5 kG, the *A* line seen in fluorescence splits into five lines labeled 2, 3, 4, 6, and 7 of Fig. 3. Lines 2, 3, 4, and 7 are well resolved (see Fig. 4); it will be demonstrated that line 6, which is relatively broad and intense, is overlapping line 5. Lines 3 and 4 can be resolved because the thermalization into the lower energy  $m_j$  states of the bound exciton at this low temperature more than compensates for the greater strength of line 3. For the same reason, line 6, starting from a lower excited energy level  $m_j$  and with a greater strength than line 5, is very intense and can mask line 5. A polarizer placed before the slits of the spectrograph so that light with  $\vec{E} \perp \vec{H}$  is attenuated strongly decreased the intensity of lines 2, 3, and 7 relative to line 4. In addition, the center of density of lines 5, 6 was shifted toward higher energy, i. e., toward the much weaker line 5. These effects can be seen in Fig. 4, confirming that line 6 masks line 5 and the  $\vec{E} \perp \vec{H}$  polarizations assigned in Fig. 3. A polarizer set to attenuate light with  $\vec{E} \parallel \vec{H}$  transmitted lines 2, 3, and 7 decreased the intensity of line 4 and shifted the center of density of lines 5, 6 toward lower energy (i. e., toward line 6). Therefore, the polarization as-

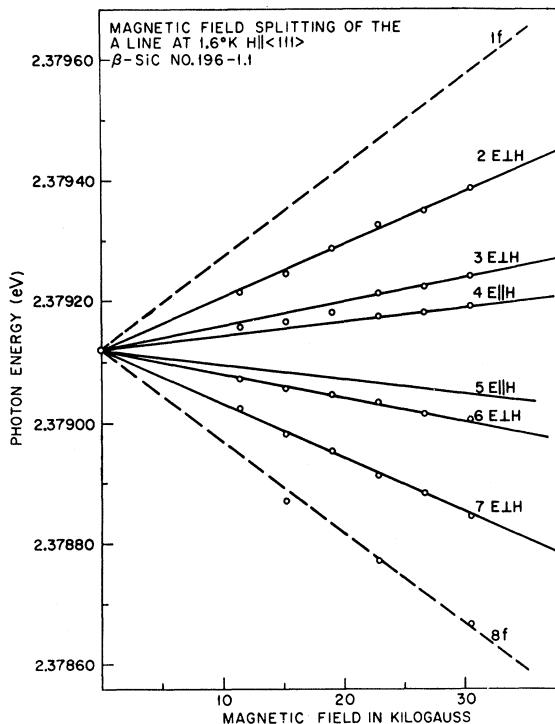


FIG. 3. Zeeman splitting of the *A* line of  $\beta$ -SiC sample No. 196-1.1 at 1.6 °K as a function of magnetic field strength. The direction of the magnetic field is along a  $\langle 111 \rangle$ . The dashed lines are calculated (see text).

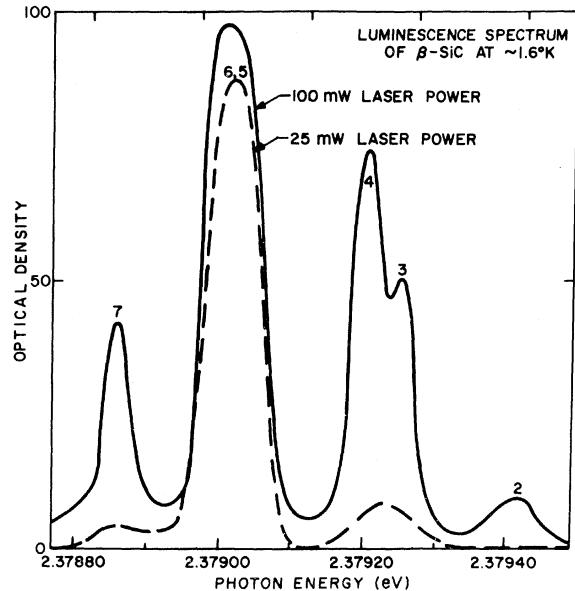


FIG. 4. Densitometer trace of the Zeeman-split  $A$  line. The dashed curve was obtained with a polarizer set to transmit  $\vec{E} \parallel \vec{H}$ , the solid curve was taken without a polarizer. The shift of the center of density of the peak corresponding to lines 5, 6 toward higher energy, i.e., toward line 5 is evident. Lines 2, 3, and 7 are attenuated by the polarizer. See the text for a discussion of the temperature of the sample.

signment of each line is consistent with the predictions from the model given in Figs. 2 and 3.

At  $20.6^{\circ}\text{K}$  and  $H = 30.5$  kG, the  $A$  line splits into a quartet, i.e., lines 3, 4 and lines 5, 6 form a pair of lines dominated by lines 3 and 6, respectively (the center of density of lines 3, 4 shifted toward higher energy, i.e., toward line 3 at  $20.6^{\circ}\text{K}$  compared to the 3, 4 line pattern at  $1.6^{\circ}\text{K}$ ). The relative intensities of lines 3, 6 to lines 2, 7 are in approximate agreement with the values in Fig. 2.

At  $1.6^{\circ}\text{K}$  and  $H = 30.5$  kG with reduced exciting energy ( $\sim 25$  mW) impinging upon the crystal, the split  $A$  line converged onto line 6 with line 4 weak and just a trace of line 7 (see Fig. 5). This is in agreement with the thermalization expected from the line strengths and energy levels shown in Fig. 2.

Figure 3 shows the splitting of the  $A$  line at  $\sim 1.6^{\circ}\text{K}$  (using  $\sim 100$ -mW excitation energy) as a function of magnetic field. Lines 3 and 4 could not be resolved below  $\sim 20$  kG, therefore, the position of the center of density is plotted. No experimental points were obtained for line 5. The forbidden transition corresponding to line 8 was very weakly seen by slightly straining the crystal (line 1, also forbidden, could not be seen at this

low temperature because of thermalization). The five measured  $A$ -line splittings can be related to the  $g$  values in Fig. 2 by

$$E_2 - E_7 = (g_{h_i} + g_e) \beta H, \quad E_3 - E_6 = (3g_{h_0} - g_e) \beta H, \\ E_4 - E_A = \frac{1}{2}(g_e - g_{h_i}) \beta H. \quad (1)$$

The  $g$  values obtained are

$$g_e = 1.96 \pm 0.06, \quad g_{h_i} = 1.12 \pm 0.03,$$

$$g_{h_0} = 1.10 \pm 0.03,$$

from which lines 1 and 8 are calculated; i.e.,  $E_1 - E_8 = (3g_{h_0} + g_e) \beta H$ . The agreement for line 8 between the measured points and the calculated values is quite good (see Fig. 3).

No angular anisotropy was observed in the pattern of the Zeeman-split components of the  $A$  line as the direction of the magnetic field was rotated in a  $\{110\}$  crystal plane from a  $\langle 100 \rangle$  direction through a  $\langle 111 \rangle$  to a  $\langle 110 \rangle$  direction (see Fig. 6). All the scatter observed in the data points at different magnetic field directions lie within the estimated experimental error of  $\pm 10 \mu\text{eV}$ .

Theoretically, any anisotropy is due to the  $g$  value of the hole since the lower-energy level (i.e., the electron with spin one-half bound to the donor) has an isotropic  $g$  factor and the electrons in the excited state are paired. Bleaney<sup>13</sup> and Yafet<sup>14</sup> have dis-

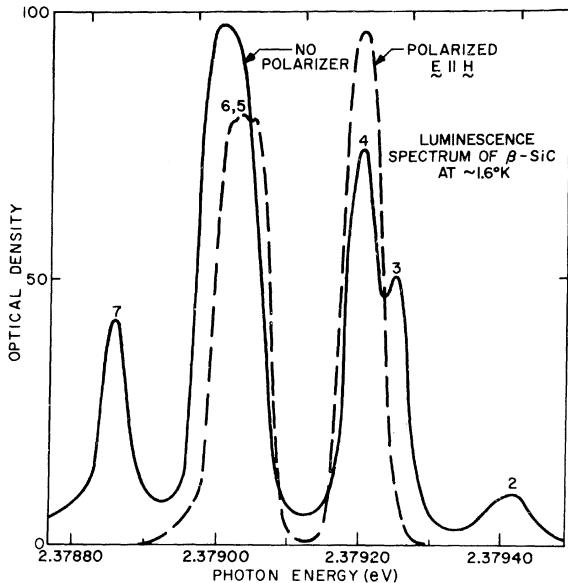


FIG. 5. Densitometer trace of the Zeeman-split  $A$  line, the dash curve was taken using 25 mW of exciting laser power, the solid curve was taken using 100 mW of laser power. The thermalization of the lines is clear. See the text for a discussion of the temperature of the sample.

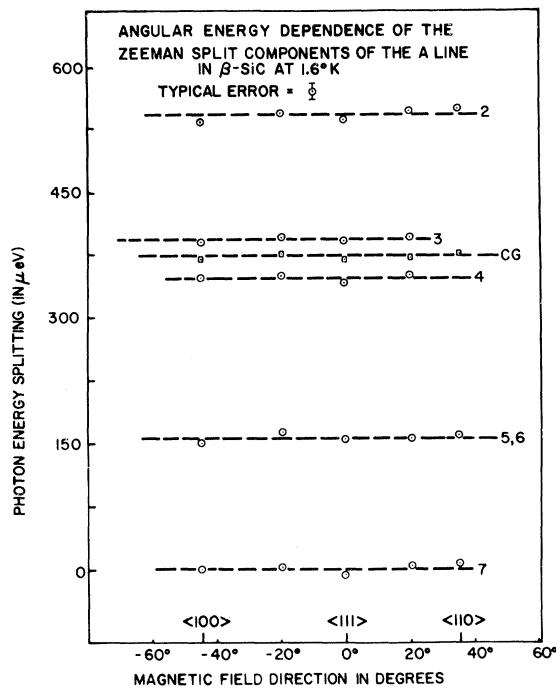


FIG. 6. The energy dependence of the Zeeman-split components of the  $A$  line at  $1.6^{\circ}\text{K}$  as the direction of the magnetic field is changed. The dashed line marked C. G. is the curve through the points (square boxes) corresponding to the center of gravity of lines 3 and 4.

cussed the anisotropy in the energy levels of the most general linear Zeeman-spin Hamiltonian

$$H = \beta [K \vec{J} \cdot \vec{H} + L (J_x^3 H_x + J_y^3 H_y + J_z^3 H_z)] \quad (2)$$

for a spin  $j = \frac{3}{2}$  particle at a site of cubic symmetry.  $\beta$  is the Bohr magneton;  $x$ ,  $y$ ,  $z$  refer to cube axes and  $K$  and  $L$  are the isotropic and anisotropic  $g$  values of the hole. For the ordering of the excited  $m_j$  states given in Fig. 2 and because the first term of Eq. (2) produces isotropic energy splitting and the second term does not, one expects  $|L/K|$  to be very small. An average  $g$  value  $M$  and a parameter to characterize the departure from spherical symmetry  $\epsilon$  are defined by

$$10M^2 = 9g_{h_0}^2 + g_{h_i}^2, \quad (3)$$

$$g_{h_i}(111)g_{h_0}(111) = M^2 \left\{ \frac{658}{9} \epsilon^2 - \frac{224}{3} \epsilon + 1 \right\}^{1/2}, \quad (4)$$

using the notation of Fig. 2.

The  $g$  values for an arbitrary direction  $\lambda$  of magnetic field have been given<sup>13,14</sup> in terms of  $M^2$  and  $\epsilon$ ,

$$9g_{h_0}^2 = M^2 \left\{ 5 + 4[1 + 15\epsilon(1 + \epsilon)] \right. \\ \left. \times \left( \sum'_{i,j=1}^3 \frac{1}{2} \lambda_i^2 \lambda_j^2 - \frac{1}{5} \right) - \epsilon^2 \right\}^{1/2}, \quad (5)$$

$$g_{h_i}^2 = M^2 \left\{ 5 - 4[1 + 15\epsilon(1 + \epsilon)] \right. \\ \left. \times \left( \sum'_{i,j=1}^3 \frac{1}{2} \lambda_i^2 \lambda_j^2 - \frac{1}{5} \right) - \epsilon^2 \right\}^{1/2}. \quad (6)$$

Using Eqs. (3) and (4) and the measured values of  $g_{h_i}$  and  $g_{h_0}$ ,  $M^2 = 1.22 \pm 0.04$  and  $\epsilon \approx 0$  (the calculated value of  $\epsilon$  is  $\epsilon = -0.0005 \pm 0.007$ , where the large error comes from the subtraction of nearly equal quantities). Therefore, the absence of anisotropy in the observed pattern of the Zeeman-split components agrees with the theoretical prediction. From the equation in the literature<sup>14</sup> relating  $M^2$ ,  $\epsilon$ ,  $K$ , and  $L$ , one obtains  $K \approx M$  and  $L \approx 0$  as expected.

#### B. Uniaxial Stress

An ESR signal has been observed at  $1.6^{\circ}\text{K}$  in crystal No. 196-1.1 and four other  $\beta$ -SiC samples.<sup>15</sup> The resonance is a narrow single line  $\sim 1.5$  g wide at half-power points with a  $g_e = 2.00495 \pm 0.0001$ , close to the optically determined  $g_e = 1.96 \pm 0.06$  given above. If this ESR signal is due to the same point-defect neutral donor involved in the green luminescence, a hyperfine interaction is expected and additional ESR lines should be observed (a three-line ESR spectrum should be seen if the neutral donor is nitrogen<sup>16</sup>) unless the electron-donor wave function is  $p$ -like with respect to the donor impurity site<sup>11</sup> or the donor has zero nuclear spin.

In order to determine whether the electron-donor wave functions are  $s$ -like or  $p$ -like, the splitting of the no-phonon line in the green luminescence was measured under uniaxial stress. If the electron states are as described above for the "simplified  $\beta$ -SiC" model, then uniaxial stress will split the fourfold-degenerate  $j = \frac{3}{2}$  valence band into two doubly degenerate states with  $m_j = \pm \frac{3}{2}$  and  $m_j = \pm \frac{1}{2}$ , respectively. The exciton bound to the neutral donor will be split under uniaxial stress corresponding to the two doubly degenerate  $m_j$  values of the hole in the excited state of the transition. The ground state of the transition will not split for any direction of uniaxial stress if the unpaired electron is in the  $1S(A_1)$  valley-orbit state, which retains only spin degeneracy. If the electron wave functions are  $p$ -like with respect to the donor impurity, the electron degeneracy due to the multivalleyed conduction band cannot be lifted by the valley-orbit interaction and both the ground state of the neutral donor and the electron states and hole state of the exciton bound to the donor will be split under uniaxial stress for orientations other than  $\parallel(111)$ , giving rise to many no-phonon lines in the radiative recombination.

Figure 7 shows an approximately linear splitting of the no-phonon line in the green luminescence into just two components for stress  $\parallel \langle 110 \rangle$ , confirming the description of the donor-electron wave functions by the "simplified  $\beta$ -SiC" model and in agreement with the NMR results of Alexander.<sup>12</sup>

If we assume that under uniaxial compression the shallow bound exciton transition moves with the band gap, then the hydrostatic-pressure deformation potential for the energy gap  $a$  can be evaluated from the expression

$$\Delta E = aX/(C_{11} + 2C_{12}),$$

where  $X$  is the stress,  $\Delta E$  is obtained from Fig. 7, and  $C_{11}$  and  $C_{12}$  are the stiffness constants. Using Tolpygo's<sup>17</sup> values for  $C_{11}$  and  $C_{12}$ ,  $a = -2.2 \pm 0.3$  eV.  $\partial E/\partial P = (-3.5 \pm 0.6) \times 10^{-7}$  eV/bar which is small compared to GaP ( $-1.1 \times 10^{-6}$  eV/bar<sup>18</sup>) but tends toward the value for diamond [ $(+5.0 \pm 1.0) \times 10^{-7}$  eV/bar<sup>19</sup>]. This pressure coefficient is expected to be small when compared to the pressure coefficients involved with transitions to other principal symmetry points of the conduction band for group IV and III-V semiconductors.<sup>20</sup>

It is not possible to draw a definite conclusion concerning the ESR signal other than to note that the above observations show that it is inconsistent with the expectation for a nitrogen donor occupying a carbon lattice site.

### C. Satellite Lines in Green Luminescence of SiC

The luminescence spectrum of  $\beta$ -SiC sample No. 196-1.1 at 1.6 °K is shown in Fig. 1. The phonon energies derived from this spectrum are  $TA = 46.3 \pm 0.1$  meV,  $LA = 79.6 \pm 0.1$  meV,  $TO$

$= 94.5 \pm 0.1$  meV, and  $LO = 102.8 \pm 0.1$  meV, in excellent agreement with the published values.<sup>1,9</sup>

Choyke *et al.*<sup>1</sup> have reported a single line  $\sim 8$  meV below the  $A$  line with relative intensity approximately 4%. This line is replicated by the zone-boundary phonons. They assign the line to two electron transitions<sup>21</sup> in which the nitrogen donor electron is left in a shallow excited state. We observe (see Fig. 1) a doublet labeled  $B$  with an energy separation of  $0.16 \pm 0.01$  meV, 7.96 meV below the  $A$  line and replicated by the zone-boundary phonons. However, the ratio of the peak intensity of the  $B$  doublet to the  $A$  line varied an order of magnitude or more over the several samples examined, with the largest ratio less than the  $\sim 4\%$  value reported by Choyke *et al.*<sup>1</sup> In addition, when the luminescence from a strained region of a crystal was studied (i. e., the  $A$  no-phonon line was split into two lines), no correlation could be found between the splitting of the  $A$  no-phonon line and the  $B$  doublet. The  $B$  doublet should also split if it is derived from a two-electron transition involving a shallow excited state of the neutral donor to which the strain split exciton is bound. These two observations suggest that the  $B$  doublet is caused by a defect not related to that responsible for the  $A$  line. This is an advantageous conclusion, because it is not obvious how a donor whose ionization energy is  $\sim 0.1$  eV<sup>1</sup> can possess an excited state shallow enough to account for the position of the  $B$  line. The effective-mass donor ionization energy in SiC is probably  $\sim 40$  meV,<sup>22</sup> in which case the lowest-lying excited state is at  $\sim 60$  meV.

The peaks which appear to be phonon replicas

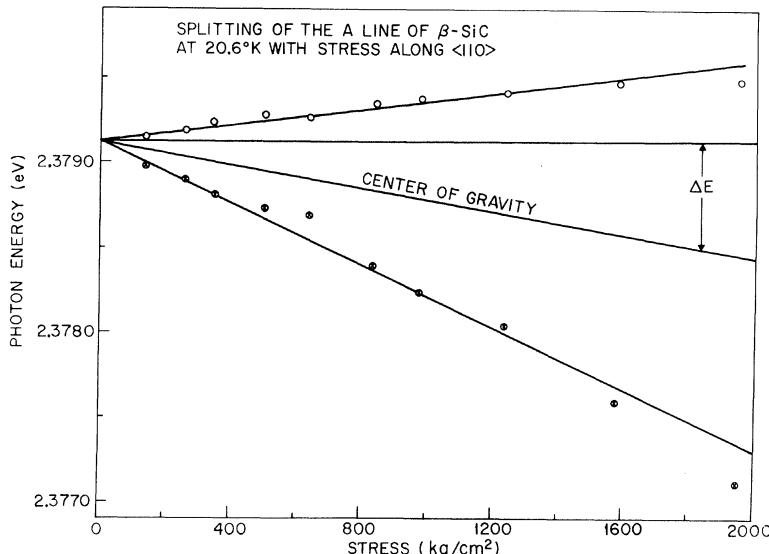


FIG. 7. The splitting of the  $A$  line of  $\beta$ -SiC taken at 20.6 °K with stress applied along a  $\langle 110 \rangle$  direction.

and are seen at slightly higher energies (~4.9 meV) than the phonon replicas of the *B* doublet (see Fig. 1) do not exhibit a detectable no-phonon component (between the *A* line and the *B* doublet), even in exposures ~30 times longer than Fig. 1. These phonon replicas do not appear in some of the crystals which have both the *A* and *B* emissions and, therefore, are thought to be a further independent system. This independent spectrum and the *B* spectrum appear to agree with two of the spectra reported by Nedzvetskii *et al.*<sup>9</sup>

The *B* series and the additional components between the *A* and *B* series (Fig. 1) cannot be seen at 20.6 °K. By contrast, the free-exciton recombination replicated by the TA phonon already reported<sup>9</sup> (the free-exciton recombination without phonon cooperation is not an allowed transition except in the presence of a major impurity perturbation) and several lines above the *A*-TA line but below  $E_{gx} - TA$  appear at 20.6 °K (Fig. 8). The temperature dependence of the intensities of these lines relative to *A*-TA indicates that they are due to recombinations from excited states of the exciton complex responsible for the *A* transition. These excited state transitions and the free-exciton recombination also occur with LA and TO phonon emission. Some of the excited state transitions can also be seen with LO phonon emission. None of these lines appeared at energies above the *A* line; i.e., recombination from these bound-exciton excited states without phonon cooperation was extremely weak, at least two orders of magnitude less intense than the replicas. The expected ratio of the intensity of excited states of the hole recombining without phonon cooperation and the intensity of the *A* line should be approximately one-fourth the ratio of the intensity of the TA replicas of these excited states and the intensity of the *A*-TA.<sup>23</sup>

Choyke *et al.*<sup>1</sup> have reported two series of lines in the 15 °K luminescence spectrum, 2 and 5 meV higher in energy than the *A* series, attributed to valley-orbit (VO) splitting and spin-orbit splitting, respectively. A TA replica of these lines at 2.2 and 5 meV is shown in Fig. 8 (the replica 5 meV above the *A*-TA line appears to be split<sup>24</sup>). The discussion of donor ionization energy given above in connection with the possibility that the *B* doublet is due to a two-electron transition again suggests that the excited state 2 meV above the *A* no-phonon line is unlikely to arise from VO splitting of the donor. From the phonon replica of the free-exciton decay, the localization energy of the exciton at the neutral donor responsible for the *A* transition is 9.6 meV, consistent with the estimate obtained by Choyke *et al.*<sup>1</sup> from comparison with the intrinsic indirect optical-absorption edge.

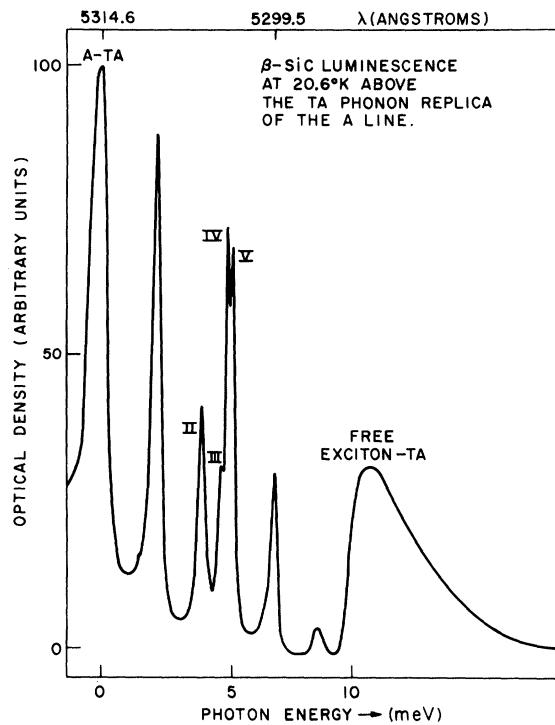


FIG. 8. Luminescence of  $\beta$ -SiC at 20.6 °K showing a portion of the spectrum immediately above the TA phonon replica of the *A* line. Lines II, III, IV, and V are 3.9, 4.7, 4.9, and 5.1 meV higher in energy than the *A*-TA line.

#### D. Auger Recombination

When three-particle wave functions overlap, a nonradiative Auger process is possible and can dominate the recombination in an indirect semiconductor. Therefore, the radiative efficiency of an exciton bound to a neutral donor in  $\beta$ -SiC is expected to be low when compared to a defect for which three carriers are not simultaneously present in the excited state. The external-photo-luminescence efficiency of the green emission of  $\beta$ -SiC at 1.6 °K was very low by visual comparison with samples of GaP of a known high photoluminescence efficiency. The efficiency of the green luminescence in  $\beta$ -SiC is roughly comparable with that for the decay of excitons bound to neutral S donors in GaP, however.

The pulsed photoluminescence decay time of the green emission was studied at 5.5 °K. Figure 9 shows that the decay of the green luminescence of  $\beta$ -SiC is exponential with a decay time  $\tau = 390$  nsec. Rethermalization of the exciton at this temperature would be negligible.

In the absence of absorption measurements on  $\beta$ -SiC crystals of known donor concentrations,<sup>25</sup>

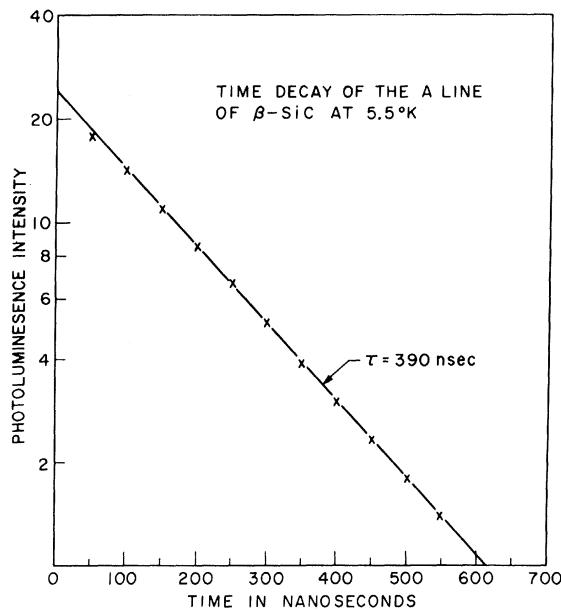


FIG. 9. Luminescent time decay from  $\beta$ -SiC at 5.5 °K for a 10-Å spectral band centered about 2.332 eV. The straight line ( $I = I_0 e^{-t/\tau}$ ) has a decay time  $\tau$  of 390 nsec.

an estimate of the radiative decay time for the  $A$  line can be made from the radiative decay time of the sulfur donor in GaP which is  $\tau_{\text{GaP:S}} = 11 \mu\text{sec}$ .<sup>26</sup> In an indirect semiconductor the lifetime of a state  $\tau$ ,<sup>27</sup>

$$\tau \propto \left| \sum_j \frac{\langle i | \sigma | j \rangle \langle j | H | f \rangle}{E_f - E_i} \right|^2 \delta(E_f - E_i + E_p - h\nu),$$

where the sum is over all intermediate states  $j$ ,  $M_R = \langle i | \sigma | j \rangle$  is the optical matrix element,  $M_S = \langle j | H | \delta \rangle$  is the impurity or phonon scattering matrix element, and  $E_p$  is the phonon energy involved (if  $M_S$  is due to phonon scattering). Assuming that the energy variation of  $M_R$  and  $M_S$  (over the states involved) is negligible compared to the energy denominator,<sup>28</sup>

$$\tau^{-1} \propto M_R^2 M_S^2 / \Delta E^2,$$

where  $\Delta E$  is the energy difference between the absolute minimum of the conduction band and the conduction-band minimum at  $\Gamma$ , i.e.,  $\Delta E$  is the energy difference between the final state and the principal intermediate state in the virtual transition. Further, assuming that  $M_R$ ,  $M_S$ , and the density of states involved in the transition are similar for  $\beta$ -SiC:N and GaP:S, then

$$\tau_{\beta\text{-SiC:N}} \sim \tau_{\text{GaP:S}} (\Delta E_{\beta\text{-SiC}} / \Delta E_{\text{GaP}})^2.$$

Using  $\Delta E_{\beta\text{-SiC}} = 3.6 \text{ eV}$  and  $\Delta E_{\text{GaP}} = 0.46 \text{ eV}$ ,  $\tau_{\beta\text{-SiC:N}} \sim 670 \mu\text{sec}$ ; or the radiative decay time of the  $A$  line is  $\sim 1700$  times longer than the measured decay time, implying that an Auger process indeed dominates the recombination rate.

#### IV. CONCLUSION

The Zeeman study has shown that the  $A$ -line luminescence is caused by the radiative recombination of an exciton bound to a point defect. This point defect is consistent with a neutral donor in which the ground state has a singlet electron bound to the donor and the excited state has two paired electrons in addition to a ( $j = \frac{3}{2}$ ) hole.

The behavior of the  $A$  line under  $\langle 110 \rangle$  uniaxial-stress measurements confirms the symmetry of the donor-electron wave function assigned in the "simplified  $\beta$ -SiC" model. A hydrostatic-pressure deformation-potential constant  $a = -2.2 \pm 0.3 \text{ eV}$  was obtained.

The luminescent spectra taken at 1.6 °K and 20.6 °K on various crystals show that the previously reported two-electron transitions ( $B$  doublet series) are most probably not part of the  $A$ -line system but are due to an independent extrinsic radiative recombination mechanism. Additional independent transitions were also observed. The energy of phonon-replicated excited states of the bound-exciton and free-exciton decay were measured and found to be consistent with previously reported values,<sup>1,9</sup> where comparison was possible.

$\beta$ -SiC was observed to have a low photoluminescence efficiency at 1.6 °K somewhat similar to GaP:S at this temperature. Comparison of the measured decay time of the green luminescence at 5.5 °K (390 nsec) and an estimate of the radiative lifetime (670  $\mu\text{sec}$ ) suggests that an Auger process dominates the recombination. The implications for the photoluminescence efficiency of an exciton bound to a point-defect neutral donor are consistent with the qualitative observations made on the  $A$ -line luminescence.

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<sup>4</sup>D. G. Thomas, M. Gershenson, and J. J. Hopfield, Phys. Rev. 131, 2397 (1963).

<sup>5</sup>Sample No. 197 of Ref. 2 and sample No. 196-1.1 of this paper came from the same melt. A low electron concentration reported for sample No. 197 ( $n = 7 \times 10^{16}$  cm<sup>-3</sup> at 300 °K) and the sharp A line observed for sample No. 196-1.1 suggests that the neutral donor concentration is in the low  $10^{17}$  cm<sup>-3</sup> for these crystals.

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<sup>7</sup>The stress apparatus was similar to that described by D. G. Thomas, J. Appl. Phys. Suppl. 32, 2298 (1961).

<sup>8</sup>F. Herman, J. P. Van Dyke, and R. L. Kartum, Mater. Res. Bull. 4, S167 (1969).

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<sup>11</sup>The bound electrons might be in a *p*-like or *s*-like state with respect to the donor impurity, depending upon which site, Si or C, the donor occupies and the difference in core potentials for Si and C. See T. N. Morgan, Phys. Rev. Letters 21, 819 (1968). If the bound electrons are in a *p*-like state, the degeneracy of the ground state of the neutral donor and the bound-exciton states are increased. In the absence of zero magnetic field splitting of the no-phonon line, the magnetic field will not remove the additional degeneracy, i.e., the Zeeman-split no-phonon luminescence line pattern will be the same for *p*-like or *s*-like electrons. However, the splitting of the no-phonon line under uniaxial stress will be different — R. A. Faulkner and J. J. Hopfield (private communication). Uniaxial stress measurements (see Sec. III B of the text) confirmed the “simplified  $\beta$ -SiC” model used in the text.

<sup>12</sup>See discussion in Ref. 1; also, M. Alexander, Phys. Rev. 172, 331 (1968); J. A. Lely and F. A. Kroger, *Semiconductors and Phosphors* (Interscience, New York, 1958), p. 525. It should be noted that in Alexander’s paper, the N donor-electron wave function is *s*-like with respect to the C site.

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<sup>15</sup>F. R. Merritt (private communication).

<sup>16</sup>A published ESR signal for nitrogen-doped 6H SiC with the magnetic field along a C axis has three almost equally intense lines, ~2 G wide at half-power points, with the *g* value of the center line equal to 2.0036. See H. H. Woodbury and G. W. Ludwig, Phys. Rev. 124,

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<sup>19</sup>P. J. Dean and P. A. Crowther, *Proceedings of the Symposium on Radiative Recombination in Semiconductors* (Dunod, Paris, 1965), p. 103.

<sup>20</sup>W. Paul, J. Appl. Phys. Suppl. 32, 2082 (1961).

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<sup>22</sup>The static dielectric constant of  $\beta$ -SiC is 10.2, slightly smaller than that of GaP. The electron effective masses  $m_i$  and  $m_t$  are not known for  $\beta$ -SiC but an average-conduction-band mass of 0.4  $m_0$  has been reported which is similar to the average-conduction-band mass for GaP. In the absence of detailed knowledge about the electron effective masses in  $\beta$ -SiC the effective-mass donor ionization energy  $(E_D)_{EM}$  of GaP [see R. A. Faulkner, Phys. Rev. 184, 713 (1969)] will be used for  $\beta$ -SiC. For a donor ionization energy  $E_D$ , the lowest-lying excited state is theoretically at  $E_D - (E_D)_{EM}$  due to valley-orbit splitting of the *s*-like ground state, i.e., at ~60 meV in the present example.

<sup>23</sup>This estimate is obtained by considering excited states of the same symmetry as the ground state ( $X_1$ ) and evaluating the change in the shape of the excited state wave function due to the decreased binding energy, R. A. Faulkner (private communication).

<sup>24</sup>The A-TA line and the lines higher in energy by 3.9, 4.7, 4.9, and 5.1 meV would appear to fit a hydrogenic series  $R_y^{\text{ex}}/n^2$  within 1%, where  $R_y^{\text{ex}}$  is an excitonic rydberg (this interpretation would assume that the two peaks at 4.9 and 5.1 meV are superimposed on the 5-meV peak reported by Choyke *et. al.* and, hence, have a smaller intensity than evident from Fig. 8). However,  $R_y^{\text{ex}}$  is then 5.25 meV, which implies a reduced exciton mass too small for this interpretation to be plausible. Assuming a static dielectric constant  $K=10.2$ , the reduced mass of the exciton would have to be ~0.04  $m_0$ . Since the conduction-band mass is ~0.4  $m_0$ , the hole mass would have to be much smaller than it is reasonable to assume.

<sup>25</sup>Absorption measurements were attempted. However, the available crystals were too lightly doped for A-line absorption to be detected at the maximum path length available (~2 mm).

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