an unequivocal explanation can be given without first considering the theoretical situation very carefully. Perhaps the slightly larger increase with deformation of the energy of the $\frac{7}{2}+$ (404) Nilsson orbital[19] over that of the $\frac{5}{2}+$ (402) orbital can account for this result. Again a $d_{5/2}$ orbital is much smaller than a $g_{7/2}$ orbital, and it may be able to participate more in collective motions of the nucleus, including deformation. A similar situation is duscussed by Mottelson and Nilsson[19] in the case of Eu^{153} and they suggest that the 98-keV excited state of that nucleus may have a smaller eccentricity than the ground state.

It is most probable that the true explanation lies between these two extremes. In fact it seems likely that the two effects (single-particle and collective) might compete, since the single-particle calculation alone gives the wrong sign, with the collective effects being slightly stronger. Thus, for example, the difference in deformation may even be greater (perhaps the excited state is undeformed), with much of this effect on $\langle r^{2\rho}\rangle$ being cancelled out by the effect of the single-particle $g_{7/2}$ state.

Again we emphasize that this interpretation involves rather substantial approximations, including that of the $6s$ electron density in europium metal. On the nuclear side it should be realized that, while the simple deformation picture is probably the best that can be used at present, Eu^{151} is in a transition region where no simple model is clearly applicable and a firm interpretation of the shift must be postponed until this transition region can be understood.

Note added in proof. The half-life of the 21.7-keV level in Eu^{151} has recently been measured as[23] 9.5 ± 0.5 and 9.3 ± 0.7 msec.[24] Our estimates in this paper of $9.2<\tau<15$ would correspond to a half-life of 8.4 ± 2.1 msec, in good agreement.

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[23] D. J. Horen, H. H. Bolotin, and W. H. Kelly, Bull. Am. Phys. Soc. **8**, 127 (1963).

[24] A. C. Li, O. Kistner, and S. Monaro, Bull. Am. Phys. Soc. **8**, 332 (1963).

PHYSICAL REVIEW VOLUME 131, NUMBER 1 1 JULY 1963

Photoluminescence of Nitrogen-Exciton Complexes in $6H$ SiC

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The photoluminescence of N-doped $6H$ SiC reveals two distinct edge emission spectra, a consequence of the existence of two kinds of nitrogen-exciton complexes. This paper describes the recombination radiation of excitons bound to nitrogen ions, complementing the previously reported recombination radiation of excitons bound to neutral nitrogen. By combining data from the two spectra, we are able to estimate ionization energies of 0.17, 0.20, and 0.23 eV, for the three inequivalent nitrogen donors. Several phonon energies can be determined, and these are compared with known phonon energies in $6H$ SiC. A 90-meV phonon apparently represents a localized vibrational mode. Quenching of edge emission in impure samples is observed, and attributed to exciton hopping. Thermally excited states of the nitrogen-exciton complexes appear to be due to the valley-orbit splitting associated with a sixfold conduction-band degeneracy. A splitting of some of the states is attributed to the Jahn-Teller effect.

I. INTRODUCTION

ULTRAVIOLET illumination of N-doped $6H$ SiC creates excitons which may be captured by neutral or by singly ionized nitrogen, forming four-particle or three-particle nitrogen-exciton complexes. (The ion is considered to be one particle, and the complexes consist of the ion plus either three or two electronic particles.) The complexes decay by electron-hole annihilation, emitting photons, and, in most cases, one or more phonons. The four-particle luminescence spectrum, which lies within 0.14 eV of the exciton energy gap, has been reported by Choyke and Patrick[1] (abbreviated CP). The three-particle spectrum lies at somewhat lower energies, and is described in this paper.

Exciton-impurity complexes were first discussed by Lampert,[2] and luminescence due to the decay of four-particle complexes was first observed by Haynes,[3] who studied various donors and acceptors in Si. In both Si and SiC the transitions are indirect (phonon-assisted), resulting in series of lines from which phonon energies may be deduced. Edge emission due to three- and four-particle complexes has also been found in materials with direct transitions. A good reference is the recent paper on CdS by Thomas and Hopfield.[4]

In $6H$ SiC, nitrogen substitutes for carbon equally on each of 3 inequivalent carbon sites,[5] resulting in 3

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[1] W. J. Choyke and Lyle Patrick, Phys. Rev. **127**, 1868 (1962).

[2] M. A. Lampert, Phys. Rev. Letters **1**, 450 (1958).

[3] J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).

[4] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[5] Lyle Patrick, Phys. Rev. **127**, 1878 (1962).

TABLE I. Comparison of our notation with Lampert's. Our circled numbers are intended to suggest the number of particles in the complex.

Particle or Complex	Lampert's notation	Our notation
Electron	−	*e*
Hole	+	*h*
Exciton	+−	*x*
Donor ion	⊕	①
Unionized donor	⊕−	②
Exciton bound to donor ion	⊕+−	③
Exciton bound to un-ionized donor	⊕+−−	④

series of lines in each of the two distinct spectra (four- or three-particle). By combining data from the two spectra, we are able to find a lower limit for each of the 3 nitrogen ionization energies, E_i, and we can estimate probable values of E_i. For the 3 inequivalent nitrogen donors, we find $E_i(A)\approx 0.17$ eV, $E_i(B)\approx 0.20$ eV, and $E_i(C)\approx 0.23$ eV.

The phonon spectrum we derive from the three-particle luminescence spectrum is characteristic of a tightly bound center, with phonon energies representing a considerable part of the Brillouin zone. It is unlike the narrow-line phonon spectrum obtained in CP from the luminescence of the loosely-bound four-particle complex, in which only a special set of k vectors is represented. This difference is consistent with the fact that the binding energies of excitons to nitrogen ions are an order of magnitude greater than those to neutral nitrogen. One unusual feature in the three-particle spectrum is a narrow 90 meV phonon line. This energy appears to lie between the energies of acoustical and optical phonon branches; it may, therefore, indicate a localized vibrational mode.

On raising the temperature from 6 to 77°K, the spectrum shows additional lines, which can be attributed to thermally excited states of the three-particle complex. In order to see the origin of the excited states, the three-particle complex may be considered to be a *neutral* nitrogen plus a hole. The former can contribute valley-orbit splitting, and the latter spin-orbit splitting, to the complex. Spin-orbit splitting should be approximately the same for the three inequivalent nitrogens. However, valley-orbit splitting, in view of the very different ionization energies, should depend strongly on the particular nitrogen site involved. The data strongly suggest that valley-orbit splitting is responsible for the observed excited states.

For a probable set of 6 conduction band minima in hexagonal 6*H* SiC, one expects valley-orbit states belonging to the representations Γ_1, Γ_4, Γ_5, and Γ_6. A correlation with the 77°K spectral lines can be made if the two observed doublets are considered to arise from the doubly degenerate Γ_5 and Γ_6 states by Jahn-Teller splitting. Two of the three complexes appear to have a Γ_5 ground state; we indicate how this may result from the polar character of the SiC lattice.

Changes in the spectrum with increasing nitrogen concentration, and with increasing compensation, are discussed in Sec. IV. With large impurity concentrations we see evidence of exciton hopping, analogous to the electron hopping of impurity conduction.

Several dissociation energies must be defined, and a notation must be established, in order to discuss the quantitative results of our measurements. These topics are considered in the following section.

II. NOTATION AND DISSOCIATION ENERGIES

We are concerned with the dissociation energies required to remove electrons, holes, or excitons from Lampert's three- and four-particle complexes. To keep the notation simple we discuss only donors, and we define only the 6 dissociation energies which we need (of which only 4 are independent). Lampert's pictorial notation[2] leads to confusion when used in equations, so we have adopted the notation shown in Table I.

We now define the 6 dissociation energies by Eqs. (1) to (6).

$$\textcircled{4}\rightarrow\textcircled{3}+\mathrm{e}-E_4, \tag{1}$$

$$\textcircled{3}\rightarrow\textcircled{2}+h-E_3, \tag{2}$$

$$\textcircled{2}\rightarrow\textcircled{1}+e-E_i, \tag{3}$$

$$x\rightarrow e+h-E_x, \tag{4}$$

$$\textcircled{4}\rightarrow\textcircled{2}+x-E_{4x}, \tag{5}$$

$$\textcircled{3}\rightarrow\textcircled{1}+x-E_{3x}. \tag{6}$$

The energies required to remove excitons from three- or four-particle complexes, E_{3x} and E_{4x}, can be expressed in terms of the independent energies defined by Eqs. (1) to (4), since the exciton may be removed one particle at a time. Thus, we obtain the following relations:

$$E_{4x}=E_4+E_3-E_x, \tag{7}$$

$$E_{3x}=E_3+E_i-E_x, \tag{8}$$

where E_{3x} and E_{4x} are the quantities directly measured by the experiment. We also define the exciton energy gap, $E_{Gx}=E_G-E_x$, where E_G is the usual energy gap. $E_{Gx}=3.024$ eV for 6*H* SiC at 6°K, as measured in CP. E_G is not known precisely because the value of E_x is still uncertain. E_{3x} and E_{4x} are obtained by measuring the displacement in energy from E_{Gx} of the spectral lines identified as being due to exciton recombination, without phonon emission, at three- and four-particle complexes, respectively.

From Eqs. (7) and (8) we obtain an expression for the donor ionization energy, E_i:

$$E_i=E_{3x}-E_{4x}+E_4. \tag{9}$$

The right side of Eq. (9) is determined by experiment, except for the positive quantity E_4. Thus, we obtain a *lower limit* for E_i

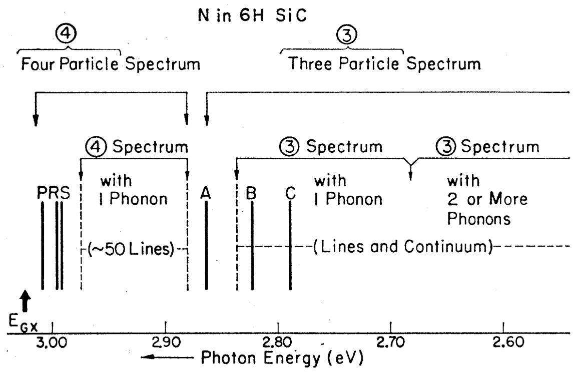

FIG. 1. Energies of phonon-free lines *P*, *R*, and *S* of the 4-particle spectrum, ④, and *A*, *B*, and *C* of the 3-particle spectrum, ③; and energy ranges of photons emitted with simultaneous phonon emission. If the lines *P* and *A* are due to the two kinds of complexes formed by *one* of the three inequivalent nitrogens, as we have assumed, then the energy difference between *P* and *A* (0.146 eV) is $E_{3x}-E_{4x}$, the lower limit of E_i for that nitrogen donor. E_{Gx} is the exciton energy gap, defined in Sec. II. Toward lower energies, at the right of the figure, the line spectrum gradually changes into a continuum.

III. EXPERIMENTAL PROCEDURES

The Dewar and the cryogenic procedures were the same as described in CP, hence, our lowest temperature was about 6°K.

To survey the spectra of more than 50 samples, we used a photographic instrument. It was an *f*/6 Littrow grating spectrograph with about 0.5 meV resolution. The spectroscopic plates were Kodak type 103a-0.

For the detailed spectra shown here, we used an f/9 Fastie-Ebert monochromator, and photon-counting equipment. The resolution of this instrument was about 0.1 meV. Both instruments were built in our laboratory.

IV. SiC SAMPLES AND EXCITON HOPPING

We used the photographic instrument for a survey (6 samples per run) of 6*H* SiC samples with various N concentrations, and various degrees of compensation.

With increasing compensation we found an increase in the intensity of the spectrum of the three-particle complex (③ spectrum) with respect to that of the four-particle complex (④ spectrum).

With increasing total impurity content we found an effect analogous to the "hopping" of impurity-band conduction. The first indication of exciton hopping was the disappearance of the *P* series of the ④ spectrum. The *P* exciton binding energy, $E_{4x}(P)$, is about half that of the *R* and *S* centers (CP). With increasing impurity concentration, the excitons on the *P* centers overlap, and can hop to, the deeper *R* and *S* centers, thus quenching the *P* series of lines. With further increase in *N* concentration and in compensating impurities, the excitons on *R* and *S* centers can eventually hop to the still deeper ionized nitrogen levels, thus quenching the entire ④ spectrum. Samples with a quenched ④ spectrum usually have the most intense ③ spectrum, and they were used in the detailed study of the ③ spectrum. The results at 6°K are given in the following section.

V. EXPERIMENTAL RESULTS AT 6°K

The 6°K results are given first, with a discussion of the phonon spectrum, and then, in Sec. VI, a calculation of ionization energies. The thermally excited states observed at 77°K are considered in Sec. VII.

Figure 1 shows the energy ranges of the two distinct luminescence spectra, due to three-particle or to four-particle nitrogen-exciton complexes (abbreviated ③ and ④). The two spectra do not overlap. The ③ spectrum continues into the lower energy region, with multi-phonon emission, and with decreasing resolution. The region of the ③ spectrum in which lines or peaks can be most clearly seen is shown in Fig. 2. Only 5 or 6 additional peaks have been recognized in the lower energy range not shown. (Lower energies lie to the right in all figures.)

The data in Fig. 2 are shown mostly in the polarization direction $E\|c$ (i.e., parallel to the *c* axis of the hexagonal crystal). The *C* peak, however, is shown in the polarization direction $E\perp c$, which brings it out most clearly. In our interpretation, we do not use the fact that many peaks are strongly polarized. In most cases we plot only the polarization direction which best emphasizes the peak positions. There appears to be some sample to sample variation in polarization ratios. Peak positions, however, were the same in all samples examined.

The phonon-free lines due to exciton recombination at the 3 inequivalent N centers are called *A*, *B*, and *C*. Each of these lines has a series of lines (or peaks) associated with it through phonon emission. The displacements of lines from *A*, *B*, or *C* are measures of phonon energies, and are the same (very nearly) in each of the 3 series. Each peak is identified by its series

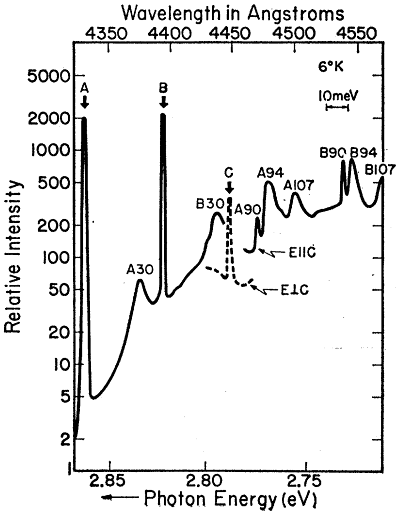

FIG. 2. A large portion of the ③ spectrum, with phonon-free lines *A*, *B*, and *C*, and some of the peaks resulting from phonon emission. Peaks are labeled with their series letter, and a number indicating the phonon energy in meV. The fine structure is not resolved in this figure.

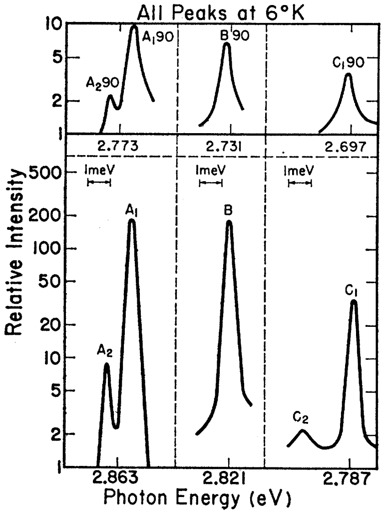

FIG. 3. *Bottom.* The phonon-free lines A, B, and C in detail at 6°K. A and C are doublets. *Top.* The 90-meV phonon peaks of the A, B, C series plotted above the phonon-free peaks on an energy scale displaced by 90 meV. The A_1-A_2 splitting of 1 MeV is reproduced exactly in A_1 90, A_2 90. The C_2 90 peak does not rise above the background at 6°K, but can be seen at 77°K.

letter, and a number indicating the phonon energy in meV. The A and B series are seen most clearly, but several C peaks have been distinguished. Some of this structure, poorly resolved, was reported earlier,[6] but at that time exciton complexes had not been reported, and the part played by N was not known.

The energy scale of Fig. 2 is too coarse to show some interesting fine structure. In Fig. 3 we show in detail the phonon-free lines A, B, and C; we observe that A and C are doublets, B a singlet. The doublet splitting is about 1 meV for A, 2 meV for C; and the higher energy components of A and C are considerably weaker because of the Boltzmann population factor at 6°K (1 meV is 11.6°K). Above A, B, and C in Fig. 3, on an energy scale displaced by 90 meV, we have plotted the narrow lines resulting from emission of a 90 meV phonon simultaneously with the photon. The splitting of A is reproduced exactly in A_1 90 and A_2 90. C_2 90 is lost in the background at 6°K, but can be seen at 77°K, at which temperature the C_1 and C_2 peaks have nearly the same strength.

Additional structure in the B series is shown in Fig. 4. The corresponding structure in the A series is more complex, and more difficult to resolve, because A is a doublet. There appear to be four components in the transverse optical (TO) peak of Fig. 4. (We recognize TO and longitudinal optical (LO) peaks by making use of the phonon spectrum of CP.) In the ④ spectrum, three TO peaks were found, and attributed to the zone structure resulting from the large unit cell of 6H SiC. The origin of the 4 TO peaks in the ③ spectrum may be the same, but two of the phonon energies (91.5 and 93 meV) are lower than the lowest TO energy found in the ④ spectrum. We find only one broad peak for LO (107 meV); this equals the energy of the highest LO mode found in the ④ spectrum.

A comparison of the ④ and ③ phonon spectra is shown in Fig. 5. The ④ spectrum, at the left, is reproduced from CP. The ③ spectrum is shown schematically at the right. The heights of the boxes indicate the approximate half-widths of the peaks in the ③ spectrum.

The broad peak attributed to the transverse acoustic (TA) branch appears to correspond to phonons of wave vector $2\pi/c$ or less, suggesting a size for the emitting complex of about $\lambda=2\pi/k=c=15$ Å. Some weak and poorly resolved structure around 60 meV (shown by the unshaded box) could be two TA phonons, or possibly a longitudinal acoustic (LA) phonon (but corresponding to a larger wave vector than that of the TA phonon).

The 90 meV phonon lines (found in A, B, and C series) are unusually narrow, and the energy is not that of any of the ④ phonons. The TO modes found in the ④ spectrum are associated with particular regions of the Brillouin zone (or extended zone). Such a restriction need not apply to the phonons emitted by the more tightly bound ③ complex. However, the infrared absorption spectrum shows 2-phonon TO peaks (see Fig. 13 of CP); these peaks span the whole zone, and do not appear to show an appreciable contribution from phonons of 90 meV. Thus, the 90 meV phonons may lie in the gap between acoustical and optical branches, and so may be localized vibrational modes.

VI. NITROGEN DONOR IONIZATION ENERGIES

In Sec. II we derived a formula for the ionization energy:

$$E_i=E_{3x}-E_{4x}+E_4. \tag{9}$$

Neglecting E_4, we have a lower limit $E_{3x}-E_{4x}$, which may be found by combining E_{3x}, from the present data, with E_{4x} from CP. The ③ center which emits the A photon corresponds to one of three ④ centers, emitting P, R, or S in the ④ spectrum, and we have not yet determined which. For the purpose of estimating E_i, we assume that the lines should be paired in the order of their energies, i.e., A with P, B with R, and C with S.

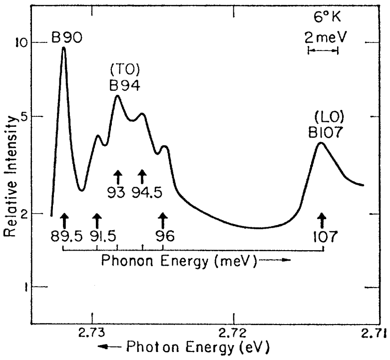

FIG. 4. Another part of the spectrum at 6°K, in greater detail, showing structure in the B 94 (TO) peak. The energies of the four TO components are shown by means of the upper energy scale, labeled *phonon energy*, which records the displacements from the phonon-free B peak.

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[6] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. **117**, 1430 (1960). Two spectra, called X and Y, were reported. The Y spectrum is the one which is now known to be due to nitrogen ③ complexes. The samples used were impure, compared with those now available; hence, the ④ spectrum had been quenched by exciton hopping. We have changed notation to one more appropriate to our understanding of the spectrum.

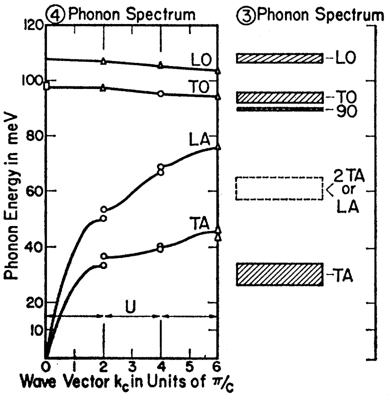


FIG. 5. A comparison of phonon energies derived from the ④ and ③ spectra. The left part of the figure, reproduced from CP, shows the energies of the ④ phonons, which have been assigned, in the figure, to specific wave vectors. The right part of the figure gives the energies of the ③ phonons, which probably do not correspond to specific regions of the zone, as the ③ complex is more tightly bound. The heights of the boxes indicate the approximate halfwidths of the spectral peaks. The 60-meV phonons are not well resolved. The narrow 90-meV phonon appears to fall between the acoustical and optical branches, and may be a localized phonon.

Since the energy separations of P, R, and S are small compared with those of A, B, and C (see Fig. 1) this assumption cannot introduce a large error.[7] The three values obtained in this way are listed in Table II under "Minimum E_i."

To obtain a "probable" value for E_i, we may make a rough estimate of E_4, the remaining term in Eq. (9), in a rather indirect way; we use the hydrogenic approximation[8] of 65 meV for the exciton binding energy E_x, and we examine the temperature stability of the ④ and ③ spectra. From Eq. (7) we find $E_4+E_3=E_{4x}+E_x$. For the P center $E_{4x}=16$ meV; hence, the sum $E_4+E_3=16+65=81$ meV. Using the hydrogen analogues of the ③ and ④ complexes,[2] one would estimate $E_4>E_3$, but the analogy is a good one only when the hole is much heavier than the electron. We show below that, for N in 6H SiC, it is more likely that $E_3>E_4$.

TABLE II. Minimum and probable values of E_i for the 3 inequivalent N donors, derived under the assumptions stated in the text. Energies are all in eV.

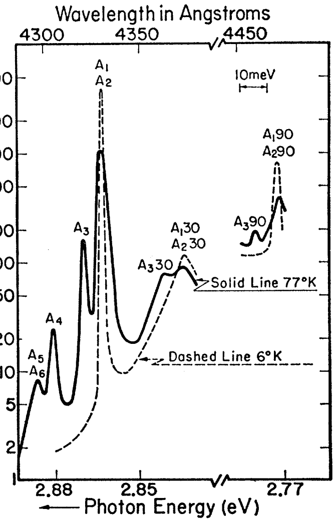
Photon energy ④ line	Photon energy ③ line	Minimum E_i $E_{3x}-E_{4x}$	Probable E_i
P 3.008	A 2.862	0.146	0.17
R 2.993	B 2.821	0.172	0.20
S 2.991	C 2.787	0.204	0.23

The ④ complex can dissociate in two ways, as shown in Eqs. (1) and (5), where the dissociation energies are E_4 and E_{4x}. The ④ spectrum has a strong temperature dependence, which was shown in CP to be consistent with the small value of E_{4x}; hence, no conclusion can be drawn as to the size of E_4, except that it is probably equal to E_{4x} or larger.

The ③ complex also can dissociate in two ways, as shown in Eqs. (2) and (6), where the dissociation energies are E_3 and E_{3x}. In this case E_3 is certainly smaller than E_{3x} [$E_{3x}(A)$ is measured by the displacement of A from E_{Gx}, and is 162 meV]. Now the temperature at which the ③ spectrum begins to fade out is at least 4 times as high as the corresponding temperature for the ④ spectrum; as an approximation, therefore, one might take $E_3\approx 4E_{4x}$. Thus, a large portion of the available 81 meV in E_3+E_4 is needed for E_3 alone, in order to explain the temperature stability of the ③ spectrum.[9] We, therefore, divide the 81 meV sum of E_3 and E_4 into the two reasonable parts, $E_3\approx 56$ meV, and $E_4\approx 25$ meV, in order to obtain the "probable" value of 0.17 eV for E_i, shown in the last column of Table II. A similar calculation is done for the other two centers.

Lely and Kröger[10] have reported, for N in 6H SiC, a value of $E_i=0.08$ eV, derived from Hall measurements. However, they considered their samples to be compensated, and therefore, equated the energy 0.08 eV to E_i rather than to $E_i/2$. It appears that their assumption of compensation was incorrect, and that the energy reported should have been $E_i=0.16$ eV, which is close to our value for the shallowest N level.

FIG. 6. A comparison of two portions of the spectrum at 6°K and at 77°K. The additional A peaks at 77°K are due to thermally excited states of the ③ complex. The A_3 peak gives rise, through phonon emission, to a new series of lines, of which A_3 30 and A_3 90 are most clearly distinguished.



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[7] For Si, Haynes found $E_{4x}\approx 0.1E_i$. Our procedure is consistent with this result.

[8] Effective masses have not been measured for SiC. We have used free electron masses (a reduced mass of $m/2$ for E_x). For the electron, this seems reasonable in view of the values of E_i shown in Table II. The static dielectric constant is 10.2, as reported by D. Hofman, J. A. Lely, and J. Volger, Physica **23**, 236 (1957).

[9] In explaining the temperature stability of the spectrum, one needs, in addition to the dissociation energy, a frequency factor which depends on the radiative lifetime of the complex. We have assumed that the radiative lifetimes of the ③ and ④ complexes do not differ by more than one order of magnitude.

[10] J. A. Lely and F. A. Kröger, in *Semiconductors and Phosphors*, edited by M. Schoen and H. Welker (Interscience Publishers, Inc., New York, 1958), p. 525.

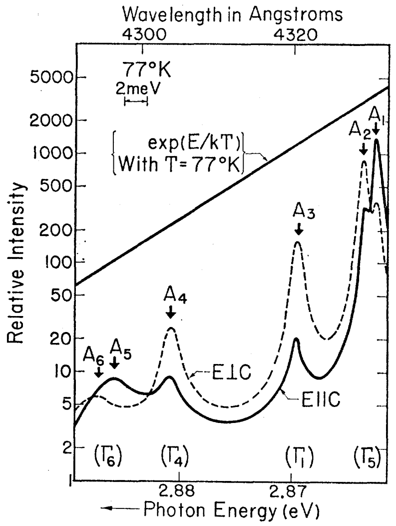

FIG. 7. The phonon-free A lines at 77°K in greater detail, shown in both polarization directions to emphasize the A_5, A_6 doublet separation. The population of excited states is determined by the Boltzmann factor, shown by the sloping straight line above the peaks. These six peaks may be associated with the representations Γ_1, Γ_4, Γ_5, and Γ_6 due to a six-valley conduction-band minimum, if the double degeneracies of the Γ_5 and Γ_6 representations are lifted by the Jahn-Teller effect. A possible assignment of the representations is shown below the peaks.

VII. EXPERIMENTAL RESULTS AT 77°K

As the temperature is increased new peaks appear in the ③ spectrum. Two portions of the spectrum in which there are additional peaks at 77°K are shown in Fig. 6. At energies higher than that of the doublet A_1, A_2 there are singlets A_3 and A_4, and a doublet A_5, A_6. These peaks fall off in intensity as their separation from A_1 increases.[11] A_2 is almost equal to A_1 at 77°K, but the 1-meV separation is too small to see in Fig. 6. Hence, A_3 is the new peak which stands out best in this group. Now A_3 is also a phonon-free line, and it gives rise to a whole new series of A_3 lines through phonon emission. Two of these, A_3 30 and A_3 90 can be seen in Fig. 6. No new lines are observed near the B peak at 77°K. The C_2 peak grows in intensity to that of C_1, but no new peaks appear. The reason for the difference between the A series and the B and C series, with respect to new peaks, is considered later.

The six A peaks are shown in greater detail, in both polarization directions, in Fig. 7. We attribute the additional peaks to exciton recombination in excited states of the A center. The population of the excited states is given by the Boltzmann factor exp $(-E/kT)$, with $T=77$°K. This is shown in Fig. 7 by the sloping straight line. The origin of the excited states is considered in the next section.

VIII. THERMALLY EXCITED STATES OF THE COMPLEX

The energy levels of a ③ complex pose a difficult problem, and the hydrogen molecule-ion analogy[2] is not very helpful. It is easier to consider the energy levels of the parts of a dissociated ③ complex. The dissociation into ion and exciton, requiring the energy E_{3x} (162 meV for A), leads one to consider excited states of the exciton. However, these lie at large fractions of the exciton binding energy, estimate to be $E_x \approx 65$ meV.

The dissociation into neutral nitrogen and hole, requiring the much smaller energy E_3 (perhaps 56 meV for A), leads one to consider the valley-orbit splitting of neutral nitrogen, and the spin-orbit splitting of the hole states. These splittings are the right order of magnitude to explain the observed excited states.[12]

Thermally excited states were found in the ④ spectrum also, and were attributed in CP to spin-orbit splitting. In the ④ spectrum, each of the three centers P, R, and S had a single excited state, within the very limited range of energy in which observations were possible. The excitation energy was 4.8 meV for all three centers. One would, indeed, expect that the differences between the 3 inequivalent nitrogen atoms should not affect the spin-orbit splitting very much. No 4.8 meV splitting is found in the ③ spectrum, nor is there *any* splitting common to all three centers A, B, and C. We interpret this to mean that peaks associated with the split-off valence band are absent, but the reason for their absence is not clear. A possible explanation is that, when bound in a ③ complex, the hole lifetime in the split-off valence band may be appreciably less than 10^{-12} sec, so that the lines emitted are broadened beyond recognition.[13]

We, therefore, attribute the observed excited states to valley-orbit splitting, which we expect to depend strongly on the particular ③ center involved. Figure 8 shows the probable ionization energies for A, B, and

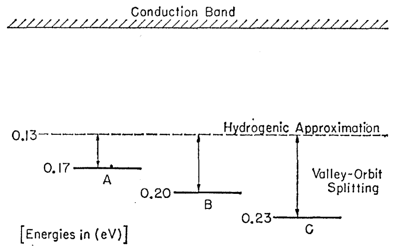

FIG. 8. Energy level diagram showing the relation of the three nitrogen donor levels to that obtained by the hydrogenic approximation. The difference between 0.13 eV and a donor level may be taken as a rough measure of the valley-orbit splitting for that donor. Hence, one expects the valley-orbit levels of A to be the most accessible to thermal excitation.

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[11] There was no evidence of peaks at still higher energy. Such peaks would be difficult to detect, however, as the luminescence intensity falls off at temperatures above 77°K. Our observations are, therefore, limited to peaks within about 30 meV of the ground state. The separation $A_1 - A_6$ is 24 meV.

[12] Spin degeneracies have not been considered, as we believe that spin forbidden transitions are too weak to observe.

[13] A lifetime broadening problem in CdS is discussed in reference 4.

C, and the dashed line indicates the ionization energy (0.13 eV) on the hydrogenic approximation (again assuming a free electron mass). The magnitude of the valley-orbit splitting is then expected to be given by the distance of the ground level from the dashed line,[14] as indicated by the arrows. Thus, one expects the A levels to be the most closely spaced, and so most likely to be appreciably populated at[15] 77°K. What we observe are excited states of a ③ complex, of course, but we consider them as arising from the excited states of neutral nitrogen.

We have used the concepts of Kohn's effective-mass theory,[14] in order to find a plausible explanation of the observed thermally excited states of the ③ complexes. A quantitative application of this theory to 6H SiC is probably not justified, as one finds a donor Bohr radius of only 5.4 Å, using the assumptions of reference 8. The second neighbor distance is 3.08 Å, hence, one can understand that second neighbor configurations and third neighbor distances[5] are important in determining the donor ionization energies.

Although our arguments are rather indirect, we conclude that, for a qualitative explanation of the ③ complex excited states, valley-orbit splitting seems most appropriate. A possible group theoretical classification of the states is considered next.

IX. THEORETICAL VALLEY-ORBIT STATES

The positions of the conduction-band minima in 6H SiC have not been determined, but evidence presented in CP leads one to think that there may be 6 minima, located on vertical mirror planes. If so, Kohn's effective-mass theory would predict a valley-orbit splitting of the sixfold degenerate ground state[16] into two nondegenerate levels Γ_1 and Γ_4, and two doubly degenerate levels, Γ_5 and Γ_6. To reconcile this set of levels with our experimental evidence, we assume that there is a Jahn-Teller splitting of the double levels into what we have called doublets, i.e., A_1, A_2 and A_5, A_6. The doublet C_1, C_2, with about 2 meV splitting, then seems also be be most plausibly labeled as a Jahn-Teller split state.

In order to make a specific assignment of labels to the A states, we assume that the Γ_1 and Γ_5 states are lower in energy than the more complex Γ_4 and Γ_6 states, in which the envelope functions have three and two nodal planes, respectively. Then the assignment indicated at the bottom of Fig. 7 follows. It is plausible then to label the B state Γ_1, and the C state Γ_5.

Kohn's theory suggests that a Γ_1 ground state should be favored. However, 6H SiC is a polar substance, and it was shown in CP that electrons may be, to a large extent, localized on the Si sublattice. Because N substitutes for C, the most favorable electronic configuration is not necessarily that which concentrates the wave function on the N atom (Γ_1), but may be one which favors the 4 Si atoms which are nearest neighbors. Thus, it does not appear implausible that the A and C ground states should be Γ_5.

It must be remembered that we observe ③ complexes, not neutral donors, and the ground states of the latter may not be those suggested here for the ③ complex. In fact, electron-spin resonance results[17] apparently show almost identical hyperfine splitting for all three donors; and the fact that an appreciable hyperfine splitting exists probably means that the donor ground states are Γ_1 (only Γ_1 wave-functions have nonvanishing amplitude at the nucleus).

X. SUMMARY

Two distinct spectra have been found in the edge emission luminescence of N-doped 6H SiC. One of these, the ④ spectrum, described by CP, is characteristic of a loosely bound exciton. The ③ spectrum, described in this paper, is characteristic of a tightly bound exciton. The phonon energies derived from it have been compared with those derived from the ④ spectrum. A localized vibrational mode is suggested by one of the energies.

Three nitrogen donor ionization energies have been found, namely, 0.17, 0.20, and 0.23 eV. In impure samples there appears to be exciton hopping from higher to lower exciton levels. This is a mechanism by which edge emission may be quenched in heavily doped materials.

The thermally excited states of the ③ complex seem to correlate with those predicted for valley-orbit splitting, on the assumption of 6 conduction band minima, is one assumes that double degeneracies are lifted by the Jahn-Teller effect.

ACKNOWLEDGMENT

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[14] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

[15] The A levels are also easiest to observe because of their position in the ③ spectrum. B excited state peaks would have to be observed against a background of the A spectrum, and C peaks against a background of both A and B.

[16] The impurity point group is C_{3v}, but we use the crystal point group C_{6v}, as Thomas and Hopfield do in the similar case of CdS. This point is discussed in reference 4. Our notation for the representations is the same as that of Thomas and Hopfield.

[17] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).