The technique presented here is based on the realization that the normalization integral depends only on the expected value of the first and second moments of certain cell variables. Because the potential in a cell is, by assumption, independent of its neighboring potentials, the relation (14) permits us to calculate the first moments directly. For the second moments, we are forced to increase the dimensionality of the transfer matrices (by introducing $\overleftrightarrow{M}$ and $\overleftrightarrow{S}$) so that we may again use the relation (14). This technique may be extended to other one-dimensional problems such as chains of coupled oscillators and wave propagation in layered media.

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Efficient Luminescence Centers in H- and D-Implanted 6*H* SiC†

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The luminescence center formed in SiC by H implantation and annealing is an H atom bonded to a C atom at a Si vacancy. It has high radiative efficiency at low temperatures because of the absence of Auger recombination. This model is derived from an annealing study and by an analysis of the three components of the phonon spectrum, (i) a 370-meV CH bond-stretching mode, (ii) two Si-vacancy localized modes, and (iii) many momentum-conserving modes. The change of frequency of these components on substituting D for H is large for (i), small for (ii), and zero for (iii). Inequivalent sites in 6*H* SiC permit three axial and three nonaxial centers, and five of the six expected spectra were observed. The site dependence of the polarization of localized-mode lines indicates a breakdown of the effective-mass approximation at the defect, for the polarization of momentum-conserving phonon lines is site *independent*. The H and D spectra are contrasted with the spectrum of the donor N. At 1.3 °K very nearly all the luminescence is due to the nonaxial centers, for recombination from the ground states of axial centers is spin forbidden. Thermally excited states were observed at various temperatures up to 26 °K. H and D luminescence was observed in 15*R* and 4*H* polytypes, but not in 3*C*. It is suggested that the usual defect is formed in 3*C* SiC but does not bind an exciton.

I. INTRODUCTION

In a recent letter[1] we gave a preliminary account of the strong 1.3 °K luminescence of H- and D-implanted 6*H* SiC. The main point emphasized in the letter was the presence of high-energy vibrational modes (370 and 274 meV in H- and D-implanted samples, respectively) that were identified as the CH and CD bond-stretching modes. This identification, together with an annealing study, led to the suggestion that the implanted H or D atom diffuses to a bombardment-induced Si vacancy to form a CH or CD bond with one of the four neighboring C atoms.

The present paper discusses the full range of phonon energies and the additional spectra observed at higher temperatures. These observations support and extend our model. We show that the bound exciton is sensitive to three scales of size, the CH bond (1.1 Å), the Si vacancy (~ 3 Å),[2] and the unperturbed lattice (> 3 Å), and that certain phonons can be associated with each. Differences between the H and D spectra reflect these three size scales, for the ratio of H- to D-phonon energies correlates with the degree of localization of the phonon, and reduces to unity for the momentum-conserving (MC) lattice modes. The MC modes predominate, for the 3.024-eV exciton energy gap of 6*H* SiC is indirect,[3] and excitons are loosely bound to the centers.

6*H* SiC is uniaxial (space group $P6_3mc$) and has three inequivalent sites for Si or C atoms, hence three inequivalent Si vacancies.[3] At each Si vacancy, an H atom may form a CH bond with one of the four neighboring C atoms. Of the four possible bonds, one is axial (aligned with the crystal *c* axis), and three are nonaxial. Thus, crystal symmetry permits three axial and three nonaxial H or D centers. We have observed the spectra of five of the six centers in both H- and D-implanted samples. The axial centers have the higher symmetry and show a 1.4-meV spin splitting, with the ground-state spin forbidden. The spectrum due to recombination in the allowed spin state is not observed at 1.3 °K and was therefore not shown in Ref. 1. However, strong luminescence of the axial centers is observed at 3 °K and above, up to the thermal quenching temperature of about 30 °K.

The multiple centers of 6*H* SiC tend to clutter up the spectrum, but they do have the advantage of showing what properties are site dependent. For example, the polarization of no-phonon and localized-phonon lines is found to be different for each of the three inequivalent nonaxial centers, whereas the polarization of MC lines is independent of the center. This indicates that the effective-mass approximation gives a fair description of the total exciton wave function but breaks down close to the center.

The H and D centers are the most efficient luminescence centers we have observed in SiC. They are approximately 100 times as efficient as the neutral-donor N centers that luminesce in the same spectral region.[3] The extra electron present in the excited state of the N center leads to radiationless Auger recombination.[4,5] The absence of an extra electron in the H or D center is the principal factor in its high efficiency. In this respect it is like the isoelectronic centers that have been studied in GaP.[6,7]

Each of the many H and D spectra has ten or more resolvable phonon lines in it, many of them strongly polarized ($\vec{E}\perp\hat{c}$ or $\vec{E}\parallel\hat{c}$). Each spectrum has been recorded at several luminescence temperatures. Only a summary of our observations can be given here, with figures showing representative portions of the data. In some cases the experimental results can be stated in terms of predictions of the model. We therefore start in Sec. II with further evidence for our model and a fuller description of it. The experimental results at 1.3 °K are then given in Sec. III and discussed in Sec. IV. Finally, results are given for luminescence at higher temperatures and for other SiC polytypes.

II. MODEL OF H AND D LUMINESCENCE CENTERS

Our model of the luminescence center is based on the observation of CH and CD bond-stretching-mode frequencies,[1] and on a study of luminescence intensities as a function of annealing temperatures. We shall supplement the brief description of sample preparation and annealing given in Ref. 1, indicating how the annealing results support our model. Additional implications of the model will then be considered. In particular, we shall discuss the role of site symmetry in distinguishing axial from nonaxial centers.

A. Sample Preparation and Annealing

An ion accelerator equipped with beam scanner and magnetic separator was used to implant H or D atoms in 6*H* SiC samples held at room temperature. The fluence was usually 3×10^{14} cm^{-2} at 150 keV. With a projected range[8] of 0.73 μ, the H density was about 4×10^{18} cm^{-3}. The density of Si vacancies before annealing is not known. Each H or D atom displaces perhaps 20 or 30 Si and C atoms, but some recombination occurs, and some vacancies are captured by impurities, forming luminescent impurity-vacancy centers.[9] In any case the lattice damage is small compared with that produced by the same fluence of heavy ions, and narrow-line luminescence spectra are obtained even without annealing. The luminescence was excited by uv light from a mercury lamp, the penetration of the light being kept to about the implantation depth by using filters to exclude wavelengths greater than 3100 Å. This reduced the background luminescence from the unimplanted crystal.

The 1.3 °K luminescence of the unannealed H-implanted samples showed both H and N spectra with about equal intensities. Both spectra are sensitive to sample purity and were absent from impure samples. After a 15-min anneal at 300 °C the N spectrum intensity was unchanged but the H spectrum had grown much stronger. After a 500 °C anneal the H spectrum overwhelmed the N spectrum, and it kept increasing in strength with annealing to about 800 °C. We estimate that it was then about 100 times the N spectrum intensity.

The increase of H intensity with annealing was not due to a repair of lattice damage, for the N intensity remained unchanged. It must therefore have been due to the formation of the H luminescence centers. The H was probably present in interstitial sites initially, near C atoms of the lattice. These C atoms are fully bonded to Si atoms and cannot form CH bonds. However, C atoms with broken bonds are present near Si vacancies, and the need for annealing shows that diffusion enters into the process of luminescent-center formation. The observation of the standard CH and CD stretching-mode frequencies of 2980 and 2210 cm^{-1} shows that the H atom is simply attached to a C atom and is not strongly perturbed by any other atom. Thus, our model is a logical one. Some samples were held at 750 °C during implantation, effectively combining the implantation and annealing steps. A comparable luminescence intensity was obtained by this method.

The H luminescence was greatly reduced after a 1-h anneal at 1000 °C, and was absent after an anneal at higher temperatures. Hart *et al.*[10] showed that the SiC lattice is almost completely repaired at these temperatures. When a Si atom appears at a Si vacancy it restores all four broken bonds. This is much more favorable energetically than the single CH bond, and we expect the H atom to be ejected from its position. Perhaps the H ends up in H_2 molecules (interatomic spacing 0.74 Å) which would readily fit into the interstitial positions of the SiC lattice.

The strongest line of the H spectrum, H_3^0 at 4193 Å, had been observed several years ago, for it showed very faintly in the spectra of some unimplanted crystals grown in a hydrogen atmosphere.[11] If our speculation of the preceding paragraph is correct, these crystals may contain hydrogen in the form of H_2 molecules. There would be few Si vacancies or H atoms, hence very few H luminescence centers. After such crystals were bombarded with heavy ions at 750 °C, a moderately strong H spectrum appeared, presumably because the bombardment had produced Si vacancies and had dissociated H_2 molecules.

Finally, we note that the *relative* strengths of the five H or D spectra are only weakly dependent on annealing temperature. All spectra grow with annealing at approximately the same rate, and all decrease with annealing at 1000 °C. We conclude that essentially only one kind of center is produced. For this reason, and because no SiH bond-stretching mode was observed, we disregard the complementary model of H or D bonded to a Si atom at a C vacancy. If such centers are formed, it is not apparent in the luminescence. The multiplicity of six implied in our CH bond model is discussed in Sec. II B, and a probable reason why one of the six spectra is not observed is given in Sec. VII.

B. Implications of Model

The CH and CD bond lengths are both approximately 1.12 Å.[12] In SiC the C-Si distance is 1.89 Å, and the C-C distance is 3.08 Å.[13] Thus, the H or D atom in the luminescence center does not occupy the site of the missing Si atom but is held closely to a particular one of the four C atoms, and is otherwise well isolated from its surroundings. Apparently, there is little difference in the bond energies at different sites, or at axial and nonaxial positions, for the five spectra are all of comparable intensities, implying that the centers are formed in comparable numbers.

In the *axial* center the CH bond and the crystal *c* axis are aligned, hence the center has C_{3v} site symmetry, just as a substitutional atom has. If the exciton is not strongly bound to the center, the macroscopic crystal symmetry C_{6v} may be more appropriate for analyzing the spectrum. The possible electron, hole, and exciton symmetries in the group C_{6v} will be considered briefly. The positions of the conduction-band minima are not yet certain,[14] but the wave function of the electron bound to a center is a linear combination of the wave functions at the separate minima, and for the donor N this combination has the symmetry Γ_7.[15] The valence-band order is thought to be Γ_9, Γ_9, and Γ_7 as in CdS,[16] and excitons formed from a Γ_9 hole and a Γ_7 electron may be either Γ_5 or Γ_6, the recombination of the former being allowed with $\vec{E} \perp \hat{c}$, and the latter being spin forbidden. If Γ_6 is the ground state of the axial center, the strength of the Γ_5 spectrum will depend on its thermal excitation.

The *nonaxial* centers have only C_{1h} symmetry. Locally there are two possible axes for the center, the CH axis and the crystal *c* axis. The perturbing CH axis mixes the crystal angular momentum or spin states. Consequently, the ground state of the nonaxial center may not show a spin splitting, and recombination may occur at this center without thermal excitation.

There is only one nonaxial center per Si vacancy, for the three C atoms involved in nonaxial CH or CD bonds are equivalent. Thus, the threefold inequivalence of the Si vacancies permits the formation of three axial and three nonaxial centers in either H- or D-implanted samples. The very different symmetry of the axial and nonaxial centers will be used to distinguish them.

III. EXPERIMENTAL RESULTS AT 1.3 °K

Most of the spectra were recorded photographically on Kodak 103 plates, and the portions shown here were copied from densitometer traces. Figure 1 shows part of the 1.3 °K luminescence spectrum of a D-implanted sample. This complex set of lines can be resolved into three similar spectra, each associated with one of the no-phonon lines D_1^0, D_2^0, and D_3^0. In our notation D means deuterium, the subscript indicates one of several inequivalent sites, and the superscript indicates the phonon energy (zero in this case). The superscript is omitted in references to a complete spectrum consisting of a no-phonon line plus associated phonon-emission components. A phonon energy scale with origin at D_3^0 shows the lattice phonon limit at 120.5 meV[17] and the gap between acoustic and optic branches from 80 to 91 meV. The predominantly momentum-conserving phonon lines of the D_3 spectrum are identified, using the large-zone division into acoustic (*A*) and optic (*O*) modes, as in Ref. 3, and the

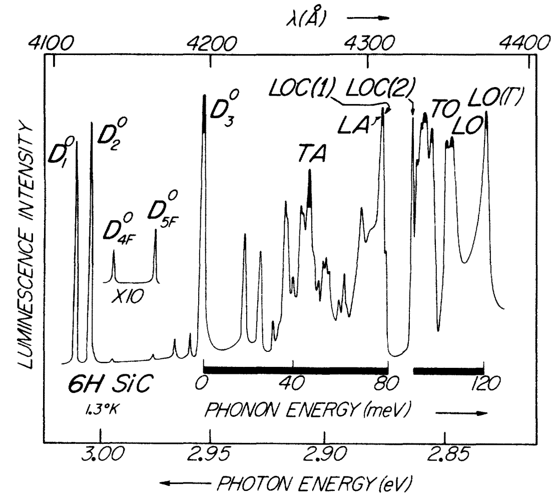

FIG. 1. Photoluminescence spectrum of D-implanted 6*H* SiC at 1.3 °K. There are five no-phonon lines (zero superscripts) but all the resolved phonon structure belongs to the spectra of the three nonaxial centers, D_1, D_2, and D_3. Lines of the D_3 spectrum are shaded and identified. LA and LOC(1) are not resolved in this figure. The origin of the added *phonon* energy scale is placed at D_3^0 and the gap in the scale is the gap between acoustic and optic branches. D_{4F}^0 and D_{5F}^0 are spin-forbidden lines of the axial centers.

convenient but not quite accurate terminology of transverse (T) and longitudinal (L).[18]

In addition to the D_1, D_2, and D_3 spectra we observe the weak lines D_{4F}^0 and D_{5F}^0 but we have not found any associated phonon lines, perhaps because of their weakness. At higher temperatures nearby lines D_4^0 and D_5^0 give rise to strong spectra. Thus, we identify D_{4F}^0 and D_{5F}^0 as no-phonon lines of the spin-forbidden ground states of two of the axial centers. We therefore attribute the D_1, D_2, and D_3 spectra to the three nonaxial centers.

The 1.3 °K luminescence spectrum of an H-implanted sample was given in Ref. 1. It extended far enough to include the lines due to the CH bond-stretching modes, and it showed the CD bond-stretching modes as an insert. These large CH and CD mode energies and their ratios were tabulated there. Other differences between the spectra of H- and D-implanted samples are much smaller. For example, the H and D differences in exciton binding energies E_B are only 1–2 meV. This information is summarized in the schematic of Fig. 2, which shows all the observed no-phonon lines (superscript zero), including the axial and thermally excited lines to be discussed later.

For convenience in labeling, the lines in Fig. 2 are separated into nonaxial (NA) and axial (A) sets, but the same energy scales apply to both sets. In all cases there is a small energy displacement between an upward pointing H line and the corresponding downward pointing D line. The presence of the H_{5T}^0 line without a corresponding D_{5T}^0 line is due to the fact that a 26 °K measurement was made on an H-implanted sample but not on a D-implanted sample. The E_B scale at the top of Fig. 2 enables one to read the binding energy of the exciton at each center, for the value of E_B is the displacement in energy of a no-phonon line from the exciton energy gap ($E_{Gx} = 3.024$ eV).

Other differences between H and D spectra are observed in the two localized modes called LOC(1) and LOC(2), whose energies are listed in Table I. The 81-meV gap mode in the H spectrum becomes a 76.9-meV resonant mode in the D spectrum. The label LOC(1) is retained to facilitate comparison with the corresponding line of the H spectrum, but the line so marked is actually a *resonant* mode in D-implanted samples, overlapping the LA line. The LA and LOC(1) modes are not resolved in Fig. 1, but they were later resolved by the use of a polarized light, as described in Sec. IV.

IV. DISCUSSION OF 1.3 °K RESULTS

A. Polarization

The spectra shown here and in Ref. 1 were recorded with unpolarized light. However, we have made detailed polarization analyses of the spectra and we shall summarize the results. We find one

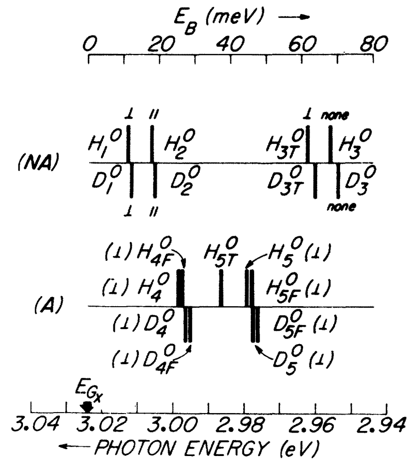

FIG. 2. Schematic drawing showing energies of all no-phonon lines observed in H- and D-implanted samples of 6*H* SiC. H lines are drawn upward and D lines downward. Lines of nonaxial (NA) and axial (A) centers are separated for convenience in labeling, but the photon energy scale applies to both sets. The exciton binding energies E_B may be read from the upper scale, whose origin coincides with the value 3.024 eV (E_{Gx}) on the lower scale. The dominant polarization of a line $\vec{E} \perp \hat{c}$, $\vec{E} \parallel \hat{c}$, or none, is indicated except where no polarization measurement was made.

TABLE I. Comparison of H_1 and D_1 exciton binding energies (E_B) and localized phonon energies. The ratio H_1/D_1 is a measure of the H or D involvement in the vibrational mode.

	E_B (meV)	Stretch[a] (meV)	LOC(1) (meV)	LOC(2) (meV)
H_1	10.3	370.4	81.0	89.7
D_1	11.1	274.5	76.9	89.2
H_1/D_1		1.35	1.05	1.006

[a] Reference 1.

result for MC phonon lines and a very different result for all other lines.

1. MC Phonon Lines

Because the 6*H* SiC energy gap is indirect, light emission by a *free* exciton requires the simultaneous emission (or absorption) of an MC phonon. If the exciton is *loosely* bound to an impurity, as it is to the CH bond or to the donor N, MC phonons will continue to dominate the spectrum. The energies of MC phonons and the polarizations of the phonon lines are determined by the band structure and therefore do not depend on the impurity, nor on which of the three inequivalent sites the impurity occupies. The energies and the polarizations of the MC phonons have already been given for the N donor luminescence centers in Ref. 3. We find the same energies and polarizations for the MC phonons in all the H and D spectra. Most of the phonons listed in Ref. 3 have been found in one or more of the H_1, H_2, or H_3 spectra (and also in the D spectra). It is difficult to resolve all the weak lines because of the overlapping of the various spectra, but polarization measurements help to resolve many close lines.

2. Other Phonon Lines

The polarization of the no-phonon spectral lines and of those due to localized modes is found to depend on the *site* of the bound exciton. The MC phonon results of the preceding paragraph indicate that the effective-mass approximation is fairly good for the bound excitons as a whole. The different results for no-phonon and localized-mode lines indicate the failure of that approximation close to the luminescence center, for it is the wave function in this region that makes the greatest contribution to exciton recombination *without* MC phonon emission. Such transitions are made possible because the local perturbation mixes in additional wave-function components with different values of crystal momentum, resulting in an overlap of hole and electron momenta.

The polarization of a no-phonon or localized-mode line depends on the effective *local* band structure, which can be different at each of the three inequivalent sites. The axial crystal field is not required by the crystal symmetry to be the same at each of the three sites, and this field determines the *local* crystal-field splitting of the valence bands. Certain deep luminescence centers previously reported[19,20] for 6*H* SiC were found to have very different polarizations for their three no-phonon lines, and the results were interpreted in terms of the different "hole percentages" in the three different bound excitons.[21]

The polarization results for the no-phonon lines are indicated in Fig. 2. Although the predominant polarization is $\vec{E}\perp\hat{c}$, the lines H_2^0 and D_2^0 are strongly polarized $\vec{E}\parallel\hat{c}$. The strong localized mode at 81 meV in H-implanted samples has the opposite polarization, predominantly $\vec{E}\parallel\hat{c}$, but $\vec{E}\perp\hat{c}$ in the H_2 spectrum. To find the corresponding line LOC(1) in D-implanted samples we therefore looked for a line with the same characteristic polarization, and we found it at 76.9 meV. Actually, the 81-meV gap mode in H-implanted samples becomes a resonant mode in D-implanted samples, for it overlaps the 76.3-meV LA line. Figure 3 shows a portion of the D_2 spectrum as measured on a high-resolution spectrometer with photomultiplier detector. The extra component at 76.9 meV is polarized $\vec{E}\perp\hat{c}$, like the 81-meV phonon line of the H_2 spectrum, and this polarization of LOC(1) is observed only in the H_2 and D_2 spectra. On the

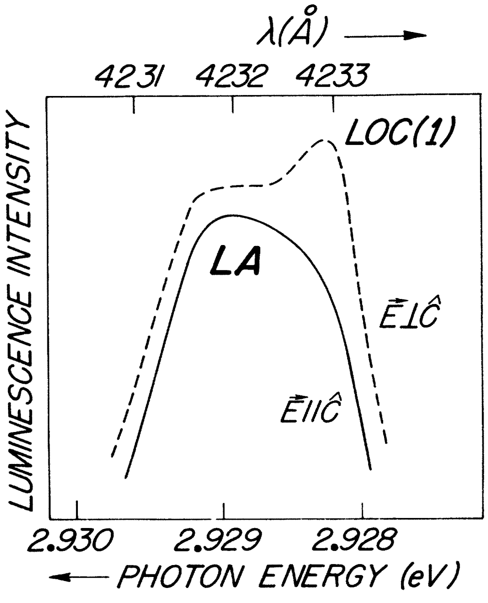

FIG. 3. High-resolution polarized spectrum of the LA and LOC(1) lines of the D_2 spectrum at 1.3 °K. The LA line is known to have only very weak polarization, but the 76.9-meV LOC(1) line is strongly polarized $\vec{E}\perp\hat{c}$ like the corresponding 81-meV line of the H_2 spectrum.

TABLE II. Properties of the three kinds of vibrational modes and correlation with their localization on the H or D center.

Localization site	Size (Å)	Vibrational modes	Effect of substituting D for H	Polarization site dependent
CH or CD bond	1.12	Internal	Large	Yes
Si vacancy	3	Localized	Small	Yes
Extended	>3	MC	None	No

other hand, the polarization of the MC 76.3-meV line (LA) is the same in all three H and three D spectra.

B. Localized Modes

Unlike the MC phonons that are characteristic of the lattice, the localized modes[22] are characteristic of the lattice *defect*, and their observation can be used to suggest or confirm a model of the luminescence center. The localized modes found in H- and D-implanted samples are listed for the H_1 and D_1 centers in Table I. The very large bond-stretching mode energies are close to those found for CH and CD bonds in organic molecules,[23] and indicate that the H or D atom is well isolated from the lattice except for the bond to the C atom. In molecular crystals such modes have been called "internal" modes.[24] The CH or CD bond also brings in a doubly-degenerate bond-bending mode,[23] but we have not been able to find it in our spectra. Apparently, the ratio of bond-stretching to bond-bending excitations during exciton recombination is at least ten in the 1.3 °K luminescence.

The Si vacancy is a major lattice perturbation that introduces many localized modes. These are modified by the presence of the H or D atom, and two such modes are observed in the H and D spectra. The extent to which the H or D atom is involved in these vibrations is indicated by the extent of the reduction of the phonon energy on substituting the heavier D for the H atom. In the case of LOC(2) this reduction is just slightly larger than the accuracy of our measurement. Thus, two categories of localized modes are present, the degree of localization being associated with the two size scales of the model, the 1.12-Å CH or CD bond length, and the approximately 3 Å of the Si vacancy. The MC modes are associated with the perfect lattice, i.e., with a third scale of size >3 Å. These results are summarized in Table II.

C. Comparison with N Spectra

The H and D spectra are similar in some respects to those of the donor N.[3] Because both kinds of centers have relatively small values of exciton binding energies E_B, their spectra (a) fall in the same photon energy range, (b) are observable only at low temperatures (< 45 °K), and (c) have strong and similar momentum-conserving phonon lines. However, the H and D spectra are very different from the N spectra in localized modes, efficiency, and dependence of certain intensity ratios on the three inequivalent sites. These differences can be explained qualitatively in terms of the magnitude of the lattice perturbation, the Auger effect, and the electrical charge of the center. Some of the data to be discussed are collected in Table III.

The localized modes of the H and D spectra have been correlated (Sec. IV B) with the structure of the luminescence center, which is a major perturbation of the lattice. By contrast, the donor N is not very different from the substituted C atom in mass and size. It is therefore not surprising that no localized modes have been detected in its spectrum.

The luminescence efficiency of an exciton bound to a neutral donor or acceptor in an indirect gap semiconductor is always poor, for there are three loosely bound particles present (electrons plus holes) and a recombining electron and hole can give the available energy to the third particle in an Auger process. This explains the weakness of the N spectrum. Table III shows that N_1, the center with the smallest E_B, is much more efficient than N_2 or N_3. It seems likely that this is also due to the Auger effect, for Auger recombination is faster[4] in more compact centers (i.e., with larger E_B). The H or D center appears to be at least 100 times as efficient as N, and its efficiency has only a weak dependence on E_B, presumably because it does not contain a loosely bound third particle and is therefore free of Auger recombination.

A rough measurement[25] gave 200 μsec as the decay time of the luminescence of H_3^0. The measured lifetime and the radiative lifetime are expected to be the same in the absence of Auger recombination. We have no comparable measurement for the donor N, but we expect a radiative lifetime of the same magnitude as that of H, with the actual lifetime

TABLE III. Comparison of H and N exciton binding energies E_B, luminescence intensities (rough), ratio of no-phonon to LA phonon line intensities (approximate), and excitation energies of thermally excited states. The latter were not observed (N.O.) for the shallow centers. In Ref. 3 the N centers were called *P*, *Q*, and *R* as indicated in the first column.

Center	E_B (meV)	Intensity (relative to N_1)	I^0/I^{LA}	Thermally excited state (meV)
$N_1(P)$	16	1	0.1	N.O.
$N_2(Q)$	31	0.2	5	4.8
$N_3(R)$	32	0.2	5	4.8
H_1	10	100	1	N.O.
H_2	17	100	1	N.O.
H_3	67	300	1	6.5

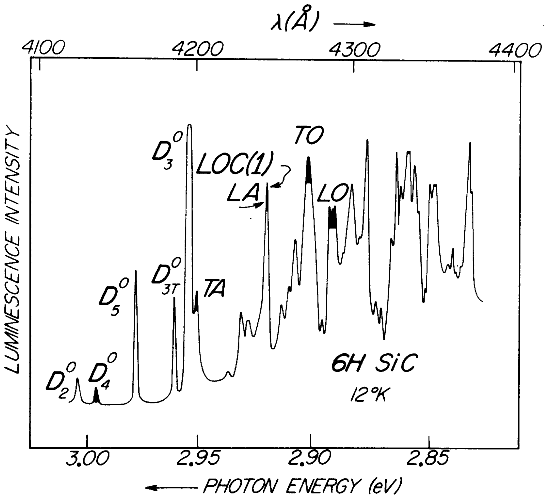

FIG. 4. Photoluminescence spectrum of D-implanted 6*H* SiC at 12 °K. Three spectra not observed at 1.3 °K are now present because of thermal excitation. D_4^0 and D_5^0 are the spin-allowed no-phonon lines of two axial centers. The strong D_4 spectrum is shaded and identified.

drastically shortened by the Auger effect. As an example, we note that for acceptors in GaP[26] the *calculated* radiative lifetime is approximately 50 μsec, but the measured lifetimes, determined largely by Auger recombination, range from 14 to 300 nsec.

The long radiative lifetime is, for the most part, a consequence of the fact that the transition is indirect, and for H and D spectra the predominance of MC phonons shows that the exciton binding does not shorten the lifetime appreciably through direct (non-MC) transitions. Using Eq. (3) of Cuthbert and Thomas,[27] we find that the 200-μsec decay time implies an oscillator strength of 1.5×10^{-5}. A thermally excited state H_{3T} with a larger oscillator strength is discussed in Sec. VI.

We now consider the third difference stated above, the site dependence of the ratio I^0/I^{MC}, which is negligible in the H or D spectrum but very strong in the N spectrum. In Table III we list the ratio I^0/I^{LA}, which is essentially a constant multiple of I^0/I^{MC}, for the relative strengths of the various MC spectral lines are nearly the same for all six centers. In the spectrum of an exciton bound to a neutral donor in an indirect gap semiconductor, the relative intensity of the no-phonon line increases with the localization of the two planetary electrons. The binding energy E_B also increases with localization, for the increased electron density near the donor ion is subject to a Coulomb force. Table III shows that the ratio I^0/I^{MC} increases with increasing E_B for the N centers, and a similar result has been noted for a series of acceptors in GaP.[26]

For a neutral center, however, increased localization of an electron or hole does not necessarily lead to stronger binding. A well-known example is the binding of an electron to the isoelectronic N in GaP.[28] The binding energy is only about 8 meV,[29] although the electron is strongly localized by a short-range potential. In this respect the neutral H or D center is somewhat like N in GaP. As Table III shows, the ratio I^0/I^{MC} is approximately independent of the center, although E_B varies from 10 to 67 meV. Thus, the localization of the electron and/or hole that induces the no-phonon line intensity in H or D centers appears to be nearly independent of the site, and uncorrelated with E_B. We know very little about the nature of the potential that binds the exciton, nor how it varies from one site to another. We therefore shall not speculate about the reason for the strong site dependence of E_B.

Finally, we note that the observation of two of the effects discussed here depends on the presence of the three inequivalent lattice sites. This is one property of 6*H* SiC that makes it a good material in which to study defects.

V. EXPERIMENTAL RESULTS ABOVE 1.3 °K

The spectrum of a D-implanted sample at about 12 °K is shown in Fig. 4.[30] A comparison with the 1.3 °K spectrum in Fig. 1 shows many changes. At 12 °K the spectrum of the shallow D_1 center has been thermally quenched, and the D_2 spectrum is weak. The spectrum of the deep D_3 center remains strong, and a thermally excited state of this center gives rise to the D_{3T} spectrum. The forbidden D_{4F}^0 and D_{5F}^0 of the axial centers have been replaced by the allowed D_4^0 and D_5^0, both displaced 1.4 meV to higher energies. In H-implanted samples very similar changes occur when the temperature is raised from 1.3 to 12 °K.

The axial-center no-phonon lines D_4^0 and D_5^0 are weak but they have strong phonon-emission lines associated with them. All the resolved lines of the D_4 spectrum are identified and shaded in Fig. 4. They are all MC lines except LOC(1) which merges with LA in D-implanted samples. The 81-meV LOC(1) is a strong line in the H_4 and H_5 axial-center spectra of H-implanted samples, as it was in the nonaxial H_1, H_2, and H_3. Neither LOC(2) nor the 120-meV LO (Γ) line have been resolved in the *axial* spectra in either D- or H-implanted specimens. Perhaps LOC(2) is not resolved because it overlaps other spectral lines. The 120-meV line also falls in a region where it overlaps other spectra, but it probably is weak like the no-phonon line.

The CH and CD bond-stretching modes have not been observed in the spectra of the axial centers. Thus, an important piece of evidence for the model

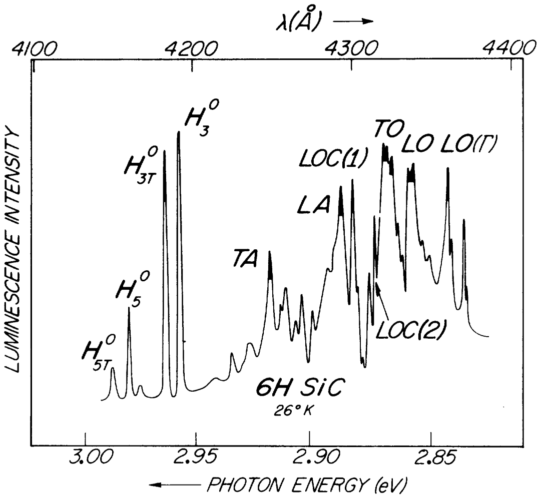

FIG. 5. Photoluminescence spectrum of H-implanted 6*H* SiC at 26 °K. Spectra remaining at this temperature are due to the H_3 and H_5 centers because of their large exciton binding energies. Both have thermally excited states, one of which gives rise to the strong H_{3T} spectrum that is shaded and identified.

of the luminescence center is missing, and we have to rely on the annealing evidence and the predictions of the model itself to identify these centers. Our model suggests that H_{5F}^0 is a spin-forbidden line. Between 1.3 and 4 °K both H_5^0 and H_{5F}^0 could be seen in the spectra of H-implanted samples, and their relative intensities were measured at six temperatures. The ratio of intensities was fitted by the expression

$$H_5^0/H_{5F}^0 = 1000\, e^{-15.5/T} \quad . \qquad (1)$$

The activation energy of 15.5 °K is approximately equal to 1.4 meV, the measured separation of the two lines, and the preexponential factor of 1000 shows that H_{5F}^0 is strongly forbidden. The ratio of oscillator strengths is probably more than 1000, for the phonon lines of the H_5 spectrum are strong, whereas the phonon lines of H_{5F} have not yet been identified because they are lost in the background of the competing spectra. A comparable result is found in D-implanted samples.

The thermally excited D_{3T} spectrum in Fig. 4 is a fairly accurate replica of the D_3 spectrum, but again we do *not* see the CD bond-stretching phonon line that is strong in the D_3 spectrum, and the no-phonon and 120-meV lines are relatively weak compared with the MC phonon lines. A general observation is that the ratio of localized mode to MC phonon intensities is reduced in all thermally-excited spectra, suggesting that there is a smaller wave-function density at the luminescence center. This may account for our failure to observe the CH and CD bond-stretching phonon lines in any spectra other than the previously reported three H and three D ground-state spectra of the nonaxial centers.

The displacement of D_{3T} from D_3 is 6.5 meV, somewhat larger than the 4.8 meV observed for thermally excited states in the N spectra.[3] Because N substituting for C does not perturb the lattice much, it seems probable that the higher state is that of an exciton with the hole taken from the second valence band, and that the 4.8 meV is, in first approximation, the spin-orbit splitting of the valence bands.[31] A similar origin may be suggested for the 6.5-meV excited state of D_3, but the D center is a major lattice disturbance and can therefore perturb the hole wave function at the center, leading to a different local separation of the valence bands. This explanation is consistent with the fact, shown in Sec. VI, that the thermal excitation energy is site dependent in the H and D spectra, but not in the N spectra.

VI. EXPERIMENTAL RESULTS AT 26 °K

The spectrum of an H-implanted sample at 26 °K is shown in Fig. 5. The 26 °K spectrum of a D-implanted sample would be very similar except for the absence of the 81-meV LOC(1) line. The H and D discrepancies in E_B and in thermally excited states are so small that the development of the H spectrum with temperature is not significantly different from that of the D spectrum.

At 26 °K the spectrum of the deep H_3 center is the only one remaining of the three observed at 1.3 °K. The H_{3T} ahd H_5 spectra are the counterparts of the D_{3T} and D_5 spectra shown in the 12 °K spectrum of Fig. 4. The fourth spectrum, seen for the first time here, is H_{5T}, due to a thermally excited state of H_5. The displacement of H_{5T}^0 from H_5^0 is 7.4 meV, significantly greater than the 6.5-meV displacement of H_{3T}^0 from H_3^0. Thus, the thermal excitation energy is site dependent, unlike the 4.8-meV excitation energy of the N luminescence centers. Only H_3 and H_5 thermally excited states can be observed before quenching. The H_3 center is nonaxial and the H_5 center is axial. Whether they correspond to the same or to different Si vacancy sites we cannot say, for we have no way of matching axial and nonaxial spectra, or of identifying their Si vacancy sites.

The phonon lines of H_{3T} are the most prominent lines in Fig. 5, and they are shaded and identified by the usual symbols. Although H_{3T}^0 is less intense than H_3^0, its phonon lines are two or three times as strong. We have measured the intensity ratios H_{3T}^0/H_3^0 at several temperatures and have fitted them to the expression

$$H_{3T}^0/H_3^0 = 18\, e^{-75/T} \quad , \qquad (2)$$

where the activation energy 75 °K corresponds to the line separation of 6.5 meV. If the ratios of

TABLE IV. Summary of nonaxial (NA) centers in D-implanted SiC polytypes. The exciton binding energies (E_B) increase with exciton energy gaps (E_{Gx}). Thus, missing spectra in 3*C* and 15*R* polytypes may be due to vanishing E_B.

Polytype	E_{Gx} (eV)	Sites	Observed NA centers	E_B (meV)
3*C*	2.390	1	0	
15*R*	2.986	5	2	5, 45
6*H*	3.024	3	3	11, 18, 69
4*H*	3.265	2	2	112, 129

the complete spectra were plotted in this way, the preexponential factor would be about 50. Thus, the thermally excited state may have an oscillator strength 50 times the 1.5×10^{-5} that was estimated for the ground state in Sec. IV C.

VII. H AND D LUMINESCENCE CENTERS IN OTHER SiC POLYTYPES

The case of the missing axial spectrum will now be considered. It seems likely that three axial centers are formed, but that one of them is unable to capture and bind excitons. It is instructive to look at the situation in other SiC polytypes, four of which have now been implanted with H and D ions. The results show a correlation between exciton binding energy E_B and exciton energy gap E_{Gx}. Some of the data are collected in Table IV, which shows the values of E_B for the *nonaxial* centers, the number of which should equal the number of inequivalent sites. The expected number is found in the large-energy-gap polytype 4*H*,[32] and the values of E_B are very large. On the other hand, no luminescence center is observed in the small-energy-gap polytype 3*C* (cubic), and the probable explanation is that E_B vanishes, so that excitons cannot be captured, for it is likely that the center itself is formed in this polytype as it is in the others.

Now let us consider 6*H* and 15*R*, the polytypes with intermediate values of E_{Gx}. Here the range of E_B over inequivalent sites is greater than some of the E_B values. Thus, one might expect that excitons can be bound at some sites but not at others. This would account for our observation of only two nonaxial luminescence centers in 15*R* SiC instead of the possible five.[33] The number of *axial* centers observed in these polytypes is one in 15*R* and two in 6*H*. Therefore, of the total number of centers, both axial and nonaxial, three of ten have been observed in 15*R* and five of six in 6*H*. The slightly smaller E_{Gx} of 15*R* is a possible reason for the observation of the smaller proportion of centers.

VIII. SUMMARY

Proton bombardment of 6*H* SiC displaces Si (and C) atoms and introduces H atoms that diffuse to Si vacancies during annealing. There an H atom attaches itself to the broken bond of a C atom to form a luminescent center that is very efficient below 30 °K. The 200-μsec decay time of an H center indicates that it has a small oscillator strength, but high luminescence efficiency is nevertheless possible because of the absence of radiationless Auger recombination, the decay time being the *radiative* lifetime. Six different centers are expected on our model, for axial and nonaxial centers are formed at each of three inequivalent Si vacancy sites. Five have been observed, the missing sixth spectrum being explained by the failure of one center to bind an exciton.

The spectra of the three nonaxial centers are observed at 1.3 °K, but those of two axial centers require higher temperatures, for the axial center has high symmetry that leads to a spin-forbidden ground state. Still other thermally excited spectra are found at 26 °K. Each spectrum has both momentum-conserving and localized-phonon lines. The 370-meV CH bond-stretching mode is observed, and its energy changes the expected amount on substitution of D for H. The CH bond-bending mode has not been found. Other localized modes are associated with the Si vacancy. Their energies change much less on D substitution, indicating that the H or D atom plays only a small role in such modes. Momentum-conserving phonons are unaffected by substitution of D for H, and are identical with those previously reported for N luminescence centers.

The polarization of the spectral lines is site dependent for the no-phonon and localized-mode lines, but not for momentum-conserving lines. This is interpreted in terms of the validity of an effective-mass approximation. Exciton binding energies E_B vary considerably with site but do not correlate with the relative strength of the no-phonon line. This behavior contrasts with that of the N centers, but is consistent with the lack of a Coulomb interaction. E_B also varies with polytype and correlates with the energy gap. For this reason no H or D luminescence is found in the small-gap 3*C* polytype.

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Heat-Pulse Propagation in Dielectric Solids[*]

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The usual phonon Boltzmann equation is solved by using two mean relaxation times, τ_N for normal and τ_R for resistive processes. For a Debye solid with three polarizations, an explicit expression for the Fourier transform of the local temperature in a heat-pulse experiment is calculated. It describes hydrodynamic phenomena for $\Omega\tau < 1$, such as second sound and diffusive heat conduction, and heat transport by ballistic phonons for $\Omega\tau > 1$. In the intermediate regime, $\Omega\tau \approx 1$, we find the following results: a second-sound wave with wave vector $\vec{Q}$ can only propagate if $Q\tau_N$ and $Q\tau_R$ are smaller than certain critical values, $(Q\tau_N)_c$ and $(Q\tau_R)_c$, i.e., for $T \geq T_c$, assuming the usual monotonic T dependence of τ_N and τ_R. The velocity C_2 of second sound strongly depends on these relaxation times. Its maximum value, occurring at $T = T_c$, is the larger the smaller the ratio $(\tau_N)_c/(\tau_R)_c$. Then C_2 decreases with rising T and finally goes to zero for $\Omega\tau_R \lesssim 1$.

I. INTRODUCTION

In a solid the condition for second sound to be observable is the well-known frequency window

$$\bar{\Omega}\bar{\tau}_N \ll 1 \ll \bar{\Omega}\bar{\tau}_R , \tag{1.1}$$

where $\bar{\Omega}$ is the frequency of the second-sound oscillation, and $\bar{\tau}_N$ and $\bar{\tau}_R$ are mean relaxation times for momentum-conserving (normal) and momentum-destroying (resistive) phonon scattering processes. The crucial part of (1.1) is the second inequality which requires a very pure crystal with high values of the thermal conductivity near its maximum. Up to now second sound has been detected in solid ^{4}He,[1,2] solid ^{3}He,[3,4] NaF,[5-8] and in Bi.[9] In all these experiments essentially the same technique was used: A heat pulse is generated at one end of the crystal at $t=0$ and the deviation of the local