Magneto-Optical Properties of the Dominant Bound Excitons in Undoped 6*H* SiC

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Undoped single crystals of 6*H* SiC often exhibit two series of luminescence lines, sharp at low temperature, in good quality strain-free crystals. A high-energy series, in the violet close to the energy gap, contains three prominent no-phonon lines P_0, R_0, S_0. We report the Zeeman splittings of these lines as functions of the magnetic field strength and its orientation relative to the crystalline c axis. These data indicate that the final state of the luminescence transitions contains a single electron bound to three distinct centers (donors) with lattice-site symmetry for the electron-attractive C sublattice, while the initial state contains an extra electron and a hole. The isotropic electron g value is close to 2, while the hole g value is 3.2 $\vec{H} \| \vec{c}$ and 0 for $\vec{H} \perp \vec{c}$. We thus confirm a model proposed by Choyke and Patrick for these lines, although we can provide no additional evidence for the reasonable supposition that the donor on the three crystallographically distinct C lattice sites in 6*H* SiC is N. A lower-energy series, in the blue, contains three no-phonon lines labeled A_0, B_0, C_0 by Hamilton, Choyke, and Patrick (HCP). The distinctive Zeeman splittings of these lines can be understood only if an L-S-coupling model is assumed for an exciton bound to a center containing no additional electronic particles. This is in contrast to the J-J coupling model used for the shallow P_0, R_0, S_0 lines, but such a difference is plausible for a semiconductor with an unusually small spin-orbit coupling like SiC. The detailed magneto-optical properties indicate that A_0 and particularly B_0 involve exciton decay at sites which do not possess the full lattice symmetry, most probably at axial (impurity-pair) defects. This finding, together with independent evidence of the properties of N donors in 6*H* SiC, particularly from electron-spin resonance, is inconsistent with the model of HCP that the A_0, B_0, C_0 lines involve the decay of excitons at *ionized* N donors. This conclusion supports a general theory for the stability of bound-exciton complexes, since the model of HCP was in strong violation of the predictions of this theory. In addition, we show that recent findings from the electronic Raman scattering of N donors in 6*H* SiC, together with a plausible upper-limit estimate of the effective-mass binding energy of donors, yield absolute values of donor binding energies E_D in much better agreement with values obtained from electrical transport than are the estimates from the HCP model for the A_0, B_0, C_0 lines. Further, the values of E_D obtained from the Raman data are consistent with the energy increments in the P_0, R_0, S_0 series, while those obtained from the analysis of HCP are not.

I. INTRODUCTION

The most frequently occurring hexagonal polytype of SiC is classified 6*H*. It has a crystallographic unit cell elongated along the c axis of length 3 times that of the simple "pure"-hexagonal polytype, labelled 2*H*. The low-temperature photoluminescence spectra of 6*H* SiC single crystals exhibit two prominent series of sharp lines. The high-energy series, starting close to the exciton band gap E_{gx} of this axial semiconductor, were first studied by Choyke and Patrick (CP).[1] They identified three no-phonon lines, P_0, R_0, S_0, lying 16–32 meV below E_{gx} and three associated, highly structured, vibronic sidebands. Choyke and Patrick noted that the properties of these spectra were generically similar to near-gap luminescence first observed in Si[2] and CdS,[3] where it had been established that the luminescence resulted from the decay of excitons bound to neutral donors and acceptors. Since N was known to be the dominant electrically active (donor) impurity, and the intensity of the P, R, S luminescence relative to intrinsic exciton luminescence increased with [N], CP concluded that the P, R, S lines were due to the decay of excitons at *neutral* N donors. *Three* no-phonon lines are possible because three crystallographically inequivalent sites are available to substitutional donors (and acceptors) in the 6*H* axial polytype of SiC. In a subsequent publication Hamilton, Choyke, and Patrick (HCP)[4] drew attention to a luminescence spectrum with three no-phonon lines A_0, B_0, C_0 spread over a much wider energy range (~75 meV) and displaced ~200 meV below E_{gx}. This spectrum had been discussed earlier by Choyke, Hamilton, and Patrick (CHP)[5] and Patrick[6] in terms of exciton decay at associated pairs of donors and acceptors (DA pairs), and was then designated the "Y-type spectrum." However, HCP advanced a new interpretation, in which A_0, B_0, C_0 were attributed to the decay of excitons at *ionized* N donors. Thus an intimate connection was claimed between the A, B, C and P, R, S line series. Later, this view of the bound-exciton chemistry of N donors in SiC was extended to many other polytypes. In some, such as cubic SiC,[7]

only the exciton–neutral-donor complex was seen. The magneto-optical properties of the single no-phonon line in cubic SiC have been recently determined, and support this interpretation.[8] In others, such as 33*R* SiC,[9] both types of spectrum have been reported.

The Westinghouse group have offered no microscopic or chemical proof of their model. A number of difficulties arise, all connected with the validity of their interpretation of the low-energy luminescence series. One problem is that, for realistic values of the electron-hole mass ratio m_e^*/m_h^* appropriate to N donors in 6*H* SiC, $m_e^*/m_h \gtrsim 1$, a simple dynamical theory of bound excitons[10] indicates that no bound state should exist for a hole at a neutral N donor. The temperature stability of the low-energy luminescence in 6*H* SiC shows that the least-tightly bound electronic particle for the A_0, B_0, C_0 excitons, the hole according to the HCP interpretation, must be bound by a rather large energy $\gtrsim 50$ meV.[4] It seems quite unrealistic to try to account for a hole binding energy of this order on the HCP model. The ionization energies of the three inequivalent N donors may be estimated on the HCP model. However, the resulting values are roughly twice as great as independent estimates from electrical-transport studies, including recent careful measurements on good quality, dilutely doped crystals.[11] In addition, the ratios of the HCP estimates of $(E_D)_N$ are in poor agreement with expectation from the P_0, R_0, S_0 lines when a simple application of Haynes's rule is made.

It is clear from the above that a reappraisal of these bound-exciton complexes in 6*H* SiC is timely. Experience with other semiconductors, such as CdS,[3] GaP,[12] and cubic SiC,[8] has shown that magneto-optical studies can provide invaluable evidence for the generic classification of bound-exciton transitions. The snag is that very high quality, dilutely doped single crystals exhibiting no-phonon linewidths $\lesssim 0.1$ meV, are required for a fully satisfactory study, since the magnetic splittings are small. The present paper reports the results of such a study, mostly made on 6*H* SiC single crystals generously provided by Knippenberg of the Philips Research Laboratories, Eindhoven. Two important conclusions emerge. The magnetic properties of the P_0, R_0, S_0 lines, described in Sec. III A, support the model of CP, as was so for the single no-phonon line observed close to E_{gx} in cubic SiC.[8] By contrast, although the Zeeman splittings of the A_0, B_0, C_0 lines (Sec. III B) are consistent with the decay of a tightly bound exciton at a center containing no additional electronic particles, as expected on the HCP model, the detailed behavior clearly demonstrates that lines B_0 and A_0 cannot arise from exciton recombination at a point defect. This conclusion seems sufficient to negate the model of HCP, removing at a stroke the interpretational difficulties which it entails. Our finding, together with recent work on GaAs mentioned below, removes the existing experimental evidence that ionized donors or acceptors may bind excitons *tightly*. Such bound-exciton complexes therefore seem of no consequence in the design of efficient light-emitting semiconductor diodes. We also conclude that the ionization energies of N donors in 6*H* SiC are ~100 meV, and note that excitation energies recently observed in electronic Raman scattering of the N donor (Sec. III C) give estimates of E_D much more consistent with the localization energies of the P_0, R_0, S_0 lines than are the energies of HCP. The magnetic studies also show that an L-S electron-hole spin-coupling model is required for the tightly bound A_0, B_0, C_0 excitons, a novel situation for bound excitons. The conventional J-J-coupling scheme[3] successfully describes the magnetic properties of the P_0, R_0, S_0 weakly bound excitons.

II. EXPERIMENTAL

A. Crystal Growth

As mentioned in Sec. I, the majority of the 6*H* SiC single crystals studies in detail were obtained from Philips Research Laboratores, Eindhoven. They were grown by Knippenberg's group in a special, small, modified Lely furnace, using induction heating and careful control of the gas ambient to obtain exceptional purity.[13] Crystals were grown at 2600 °C, and when undoped had $N_d - N_a$ in the 10^{16}–10^{17} cm^{-3} range, with mobilities of ~300 cm^{2}V^{-1}sec^{-1} at 300 °C.[11] Green-tinged deliberately N-doped crystals were also available with $N_d - N_a$ approaching 10^{18} cm^{-3}. These crystals were too heavily doped for useful Zeeman studies even of the tightly bound excitons, and showed predominantly blue-green DA pair luminescence at low temperatures. However, electronic Raman scattering was observed from the N donors in these crystals, but was not detectable in the water-white undoped crystals.

We also examined 6*H* SiC crystals supplied by Rosengreen of Stanford Research Institute, Palo Alto, Calif., and Shaffer of the Carborundum Co., Niagara Falls, N. Y. The nominally undoped, small, colorless plates from SRI showed mainly the P_0, R_0, S_0 luminescence lines, with very weak A_0, B_0, C_0. The CC crystals were mostly nominally undoped, colorless, and multifaceted, of chunky form. However, some exhibited relatively strong, sharp P_0, R_0, S_0 and A_0, B_0, C_0 luminescence lines, infrequently with negligible strain splitting. The magnetic splittings illustrated for these lines in this paper are primarily from data

on the Philips crystals. However, essentially identical splittings, allowing for small occasional effects of internal strain, were observed from some of the CC crystals.

B. Optical Measurements

The Zeeman spectra were recorded with the sample immersed in a bath of liquid helium, pumped below the λ point. The luminescence was excited by focused light at 3511 and 3638 Å from a model-52-uv Coherent Radiation Laboratories Ar^+ laser, usually operated at 30–40 mW power output. The spectra were recorded photographically, with a Jarrell-Ash 2-m focal-length spectrograph. Magnetic fields of up to 32 kG were available from a 12-in. Varian electromagnet, operated in the Voight configuration. The sample could be rotated about a vertical axis perpendicular to the magnetic field.

Preliminary studies of electronic Raman scattering[14] were made using a Spex 1400 double monochromator equipped with an S20 photocathode photomultiplier detector and a photon-counting recording system with a Hewlett-Packard multichannel analyzer.[15] The samples were cooled to ~15 °K in a stream of cold He gas and 90° scattering was observed.

III. RESULTS AND DISCUSSION

A. $P_0R_0S_0$ Lines: Excitons Bound to Neutral Donors

We observe three very sharp lines at the high-energy limit of the luminescence spectrum from the 6*H* SiC crystals we believe to contain low concentrations of N donors (Fig. 1). These lines are polarized predominantly $\vec{E} \perp \vec{c}$. We find the energies of these lines to be, respectively, 1.0, 0.6, and 0.9 meV *less* than lines P_0, R_0, S_0 of a series of very similar form reported by CP.[1] The average discrepancy might well be due to the use by CP of *air* calibration wavelengths with a conversion factor to energy appropriate to *vacuum* wavelengths. However, there seems to be no doubt that the lines in Fig. 1 are those discussed by CP. We observe a satellite spectrum very similar to that which CP attributed to the recombination of bound excitons with the emission of a variety of phonons which conserve momentum in the transition across the indirect gap in 6*H* SiC. These phonons have wave vectors lying nearly parallel to the *c* axis in the reduced zone.[1] The validity of the phonon assignments have received considerable support recently, from a comparison with phonon energies observed directly through Raman scattering.[16] Thus, there

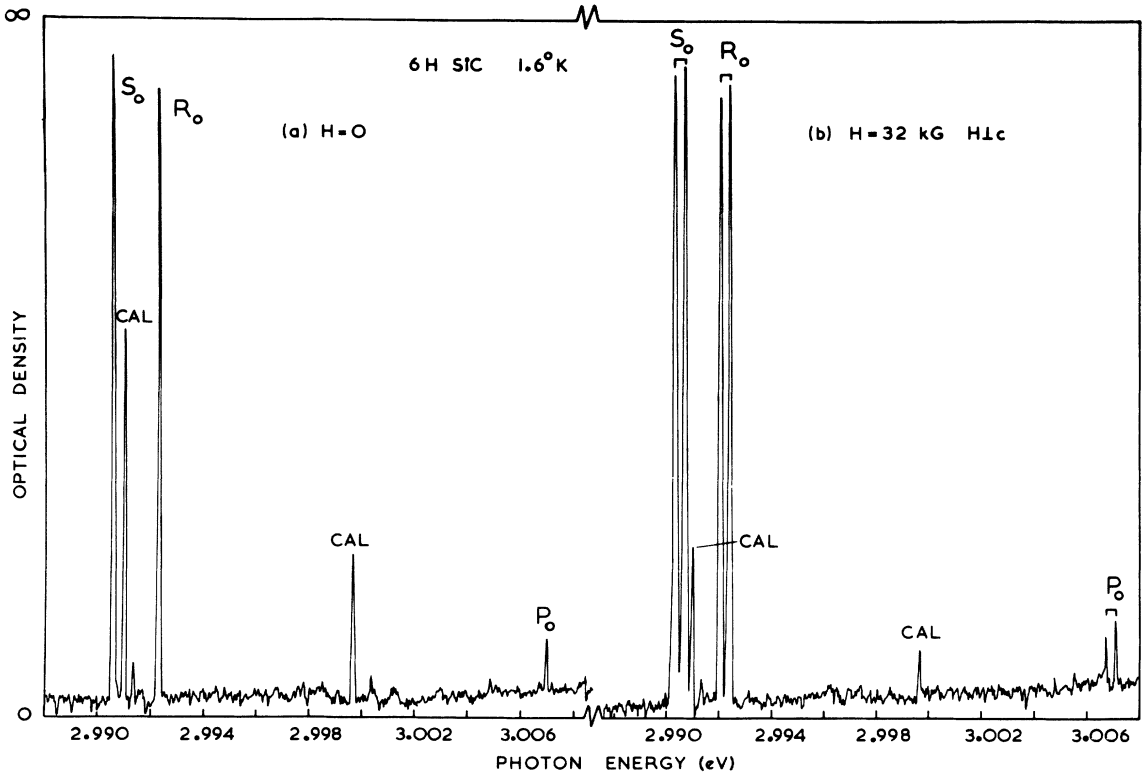

FIG. 1. Portions of the low-temperature photoluminescence of 6*H* SiC close to the exciton energy gap (3.024 eV), recorded photographically, (a) at zero magnetic field, (b) at $H = 32$ kG. For $\vec{H} \perp \vec{c}$ each of the three, prominent, shallow, no-phonon, bound-exciton lines P_0, R_0, S_0 splits into two. Lines marked CAL are from an Fe calibration lamp.

TABLE I. Energies of principal bound excitons in 6H SiC.

High-energy series			Low-energy series		
Line	Energy (eV)	Localization energy (meV)[d]	Line	Energy (eV)	Localization energy (meV)[d]
P_0	3.0070[a] 3.008[b]	17.0	A_0	2.8605[a] 2.862[e]	163.5
R_0	2.9924[a] 2.993[b] 2.9945[c]	31.6	B_0	2.8196[a] 2.821[e]	204.4
S_0	2.9906[a] 2.9915[b] 2.9928[c]	33.4	C_0	2.7856[a] 2.787[e]	238.4

[a]Values from present work at ~2 °K.
[b]Values from Ref. 1 at 6 °K, assuming $E_{gx}=3.024$ eV.
[c]Values from Ref. 17 at 86 °K.
[d]Calculated assuming $E_{gx}=3.024$ eV at 2 °K (Ref. 1).
[e]Values from Ref. 4 at 6 °K.

is no doubt that the lines in Fig. 1 are due to no-phonon transitions, although direct proof through the observation of these same lines in absorption was not obtained either by CP or in the present work.[17]

The general form of the luminescence spectrum suggests that the luminescence is due to the radiative decay of excitons bound to defects, a mechanism familiar in a variety of semiconductors.[2,3,12] Choyke and Patrick showed that the very small displacements of these lines below the free-exciton energy of 6*H* SiC (3.024 eV at liquid-He temperature) require exciton recombination at *neutral* centres. They implicated the N donor, although no *positive* proof was obtained. These three no-phonon lines cannot occur at a single centre. However, allowing for the greater susceptibility to luminescence quenching by tunneling for the much less tightly bound P_0 exciton, these three lines are present in a constant intensity ratio[18] over a wide variety of crystals. Recognizing this, CP suggested that they arise from recombination of excitons bound to neutral *N* donors uniformly distributed over the three crystallographically inequivalent sites[19] in the 6*H* lattice. Since the localization energies E_{Bx} of the R_0 and S_0 excitons are about equal and approximately twice the value of the P_0 exciton (Table I), CP concluded that the ionization energies E_D of the inequivalent N donors were ordered likewise. Patrick[20] speculated that the single site with relatively low E_D might be the (hexagonal) one which differs from the other two (cubic) sites in the configuration of its second-nearest neighbors, whereas the latter are indistinguishable until the third-nearest neighbors.

The theory of bound excitons in an axial polytype of SiC, such as 6*H*, is formally identical with that discussed by Thomas and Hopfield (TH)[3] for hexagonal CdS, provided that we make the ansatz that the spin-orbit coupling of the bound electrons and holes is small compared with the atomic spin-orbit coupling. This latter splitting is small in SiC, ~5 meV at the valence-band maximum at Γ according to CP and the recent absorption work of Gorban and Krokhmal.[17] We shall see that this ansatz fails for the much deeper A_0, B_0, C_0 luminescence lines discussed in Sec. III B. However, for the very weakly bound P_0, R_0, S_0 excitons, the ansatz should hold. We follow TH in describing these excitons with a *J*-*J* coupling scheme. The expected magnetic behavior of excitons bound to neutral donors [Fig. 2(a)] is directly distinguishable from that of excitons bound to neutral acceptors in CdS [Fig. 2(b)] only if it can be determined whether the magnetic *g* factor characteristic of the electron (hole) is in the initial or final state of the luminescence transition. Thomas and Hopfield have noted that the group-theoretical arguments leading to the forms in Fig. 2 are exact only for states of zero binding energy, and for energy bands at $\vec{k}=0$ in the wurtzite structure. The former assumption should be adequately fulfilled for the P_0, R_0, S_0 lines. The latter is true for the valence-band maxima in 6*H* SiC,[21] but the conduction-band minima lie near the zone boundary at π/c. However, we note that the complications due to the multivalley nature of the conduction band are removed by valley-orbit coupling for electrons bound to an attractive impurity core.[12] Experience with GaP[12] and cubic SiC[8] has shown that the simplified description of the electrons in terms of a Kramers-doublet state with an isotropic *g* value close to 2 is fully justified experimentally for donors on appropriate (electron attractive) lattice sites. This is as expected, since the symmetric A_1 valley-orbit state should then lie well below the other valley-orbit states. However, considerable additional complications normally arise for electrons bound to donors on electron-repulsive lattice sites[22] or for excitons bound to neutral acceptors on either type of lattice site in a binary semiconductor,[23] since the valley-orbit splittings should be then barely comparable with splittings due to the electron-hole *J*-*J* coupling. Thus, we may conclude that a simple magnetic behavior like Fig. 2 is possible only for excitons bound to neutral *donors* in axial semiconductors with multivalleyed conduction bands. The observation of such simple behavior in these materials therefore provides an additional distinction between different exciton complexes which does not exist for axial semiconductors with a direct band gap at $\vec{k}=0$. The *magnitude* of the electron *g* value is also critical for this distinction, as we shall see.

Figure 1(a) suggests that the zero-field spectrum of the P_0, R_0, S_0, excitons is simple; that is, there are no low-lying exciton states associated with higher valley-orbit states of the donors. Fig-

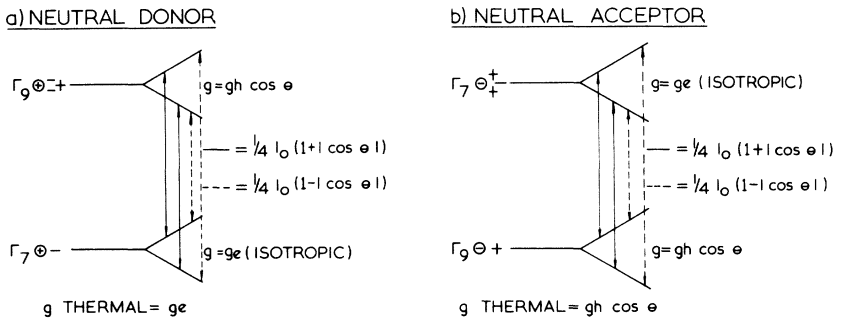

FIG. 2. Schematic representation of the energy states for the linear Zeeman effect of excitons bound to (a) neutral donors and (b) neutral acceptors. The holes are assumed to come from the Γ_7 valence band only, as in wurtzite CdS (Ref. 3), while the electron is isotropic and represented by a Γ_7 state. In reality, for a multivalleyed semiconductor like 6*H* SiC the electron should be much more complicated when bound to a repulsive core like the neutral acceptor.

ure 1(b) shows simple magnetic behavior for $\vec{H} \perp \vec{c}$, consistent with the simplified description of the associated electron states mentioned above. The magnetic splittings for $\vec{H} \parallel \vec{c}$, and as a function of the angle θ between $\vec{c}$ and $\vec{H}$ (Figs. 3 and 4) are also simple and like Fig. 2(a). The electron and hole g values obtained from the $\vec{H} \perp \vec{c}$ and $\vec{H} \parallel \vec{c}$ data in Figs. 3 and 4 are presented in Table II. As expected, g_e is close to 2,[24] whereas g_h is about 3.2 for $\vec{H} \parallel \vec{c}$. At intermediate angles, there are four magnetic subcomponents from each of P_0, R_0, S_0. Attempts to substantiate quantitatively the predicted

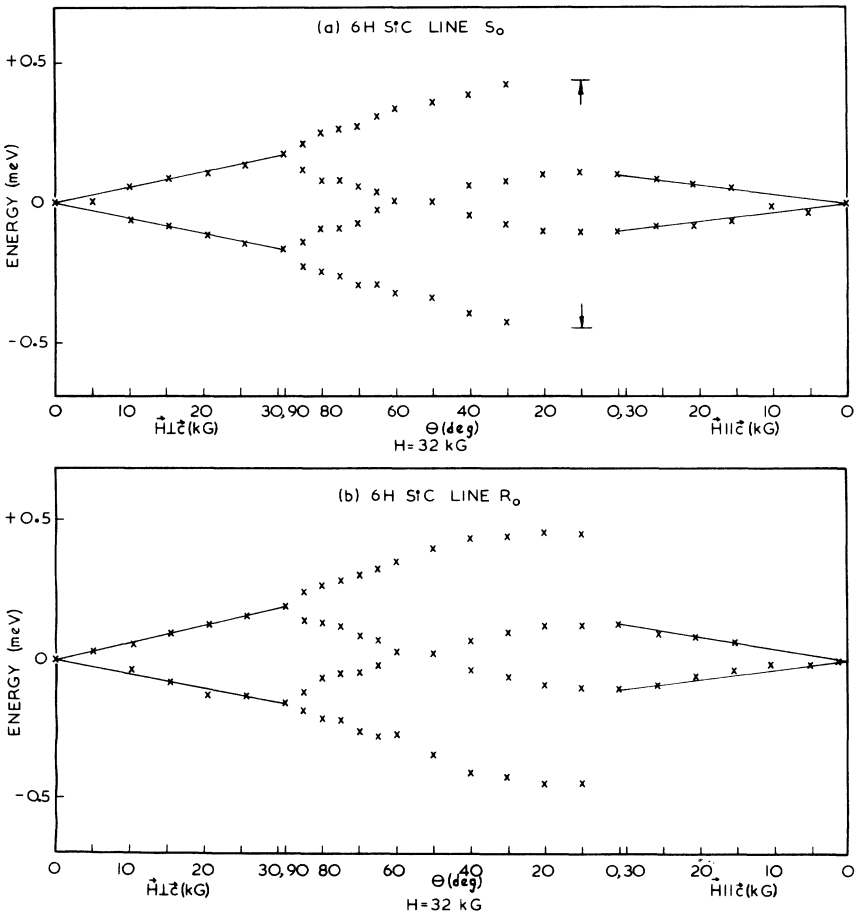

FIG. 3. Zeeman splittings of the principal, near-gap, bound-exciton, no-phonon lines (a) R_0 and (b) S_0 in 6*H* SiC as a function of H for $\vec{H} \perp \vec{c}$ and $\vec{H} \parallel \vec{c}$ and as a function of θ, the angle between H and c for $H = 32$ kG. The outermost pair of subcomponents becomes very weak near $\theta = 0°$.

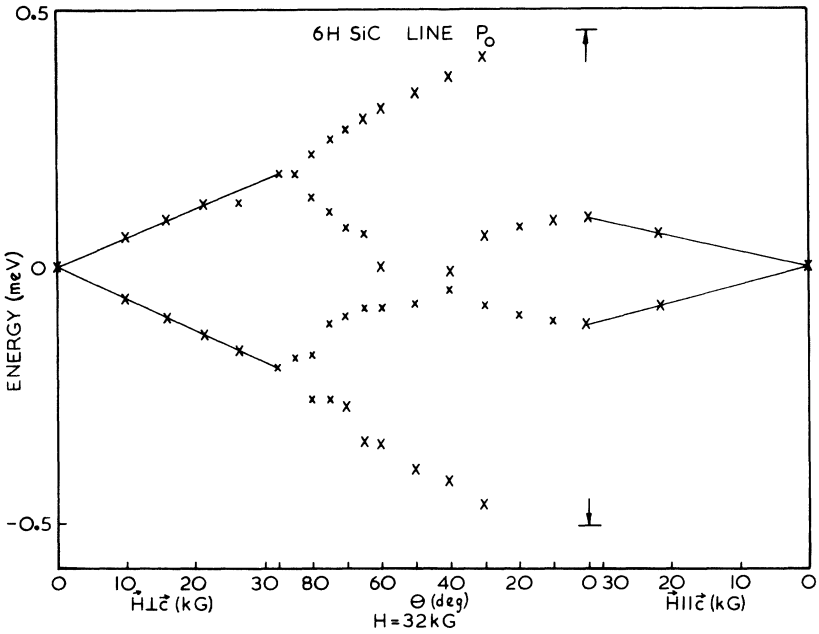

FIG. 4. Zeeman splitting of the principal near-gap bound-exciton line P_0 in 6*H* SiC, arranged as in Fig. 3.

relation $g = g_h \cos\theta$ are not very rewarding because of scatter in the data. Unfortunately, even the best available crystals of 6*H* SiC contained slight, inhomogeneous, internal strain. This strain introduced significant scatter into the angular-dependence data, since it was impossible to avoid displacements of the region of optical excitation across the surface of the samples during rotation in the magnetic field. However, Figs. 3 and 4 clearly show that g varies with this *type* of angular dependence. In addition, the intensity of the outer pair of magnetic subcomponents has an angular dependence in qualitative accord with the prediction in Fig. 2(a), becoming vanishingly weak for $\vec{H} \parallel \vec{c}$.

We conclude that the Zeeman data on the P_0, R_0, S_0 lines provide valuable support for the postulate of CP that they arise from the decay of excitons bound to neutral *donors*. Further, the form of Zeeman data shows that these donors have the site symmetry of the SiC lattice, and must lie on the electron-attractive lattice site. Like CP, we can make no chemical identifications of this donor directly from our experimental findings. However, we note with them that only one donor has been identified in 6*H* SiC, through electron-spin resonance.[19] In addition, it is well known that the electrical properties of various polytypes of SiC, including 6*H*, can be controlled by the addition of N_2 gas to the ambient from which the crystals are grown. The crystals become more strongly n type with the addition of the N_2 gas.[11] Spin resonance shows that the N donors substitute for C, and occupy the three crystallographically inequivalent sites with equal probability. Nitrogen is identified through the hyperfine structure appropriate to a nucleus with $I = 1$ (N^{14}). The strength and isotropic character of the hyperfine interaction shows that the antibonding electron on the N donor has S-like character, a requirement we have established for the donor observed in the optical spectra and one which is expected for a donor on the C sublattice in SiC.[25] We therefore conclude that it is very reasonable to identify N as the optically active donor in 6*H* SiC. The evidence for this association is in fact appreciably more satisfactory than in cubic SiC, where no well-authenticated, concordant information from electron-spin resonance has yet been obtained.[8]

TABLE II. Electron and hole g values from P_0, R_0, S_0 excitons.

Line	$\vec{H} \perp \vec{c}$, $g_{eff} = g_e$	$\vec{H} \parallel \vec{c}$, $g_{eff} = (g_h - g_e)$	$\vec{H} \parallel \vec{c}$, $g_{eff} = (g_h + g_e)$
P_0	2.0(9)	1.1(6), i.e., $g_h = 3.2(5)$	
R_0	1.9(5)	1.3(3), i.e., $g_h = 3.2(8)$	5.0(4), i.e., $g_h = 3.0(9)$
S_0	1.9(1)	1.1(4), i.e., $g_h = 3.0(5)$	

B. A_0, B_0, C_0 Lines: Excitons Bound to Ionized Centers

The blue-green luminescence from 6*H* SiC is often dominated by the sharp lines A_0, B_0, C_0 shown in Fig. 5, together with a complex sideband of strong phonon replicas at lower energy, not shown. These lines may be superimposed on a much more complicated, multiline, blue-green luminescence spectrum, undoubtedly arising from electron-hole recombinations at distant pairs of donors and acceptors.[26] However, it is clear that these two spectra are distinct. The sharp lines A_0, B_0, C_0 in Fig. 5

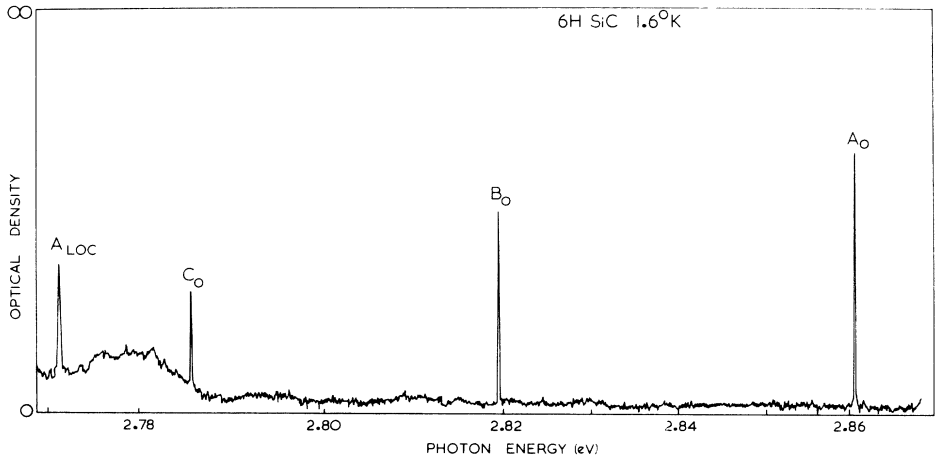

FIG. 5. Portion of the low-temperature photoluminescence of 6*H* SiC, recorded photographically, showing the prominent moderately deep bound-exciton no-phonon lines A_0, B_0, C_0. These lines exhibit strong structured phonon cooperation, but only the 90-meV phonon replica A_{LOC} is shown.

again have the form expected for the no-phonon decay of bound excitons. These lines are undoubtedly identical with the lines *A*, *B*, *C* reported by Hamilton, Choyke, and Patrick.[4] Once again we find small but significant systematic energy shifts to lower energy, about 1.5 meV in this case (Table I). These are the lines attributed to the recombination of excitons at ionized N donors by HCP. In addition, we have noticed that 6*H* SiC crystals can be found which exhibit either intense *A*, *B*, *C*, with essentially zero *P*, *R*, *S* luminescence or vice versa. The former situation perhaps may be understood by assuming complete quenching of the *P*, *R*, *S* luminescence through the tunneling dissociation of the weakly bound excitons. However, it is curious that this situation can obtain in crystals where the general doping level is sufficiently low to allow A_0, B_0, C_0 lines sharp enough for detailed Zeeman studies. Our complete failure to detect *A*, *B*, *C* lines from crystals in which the *P*, *R*, *S* lines are very strong is hard to understand on the HCP model, in which both sets of lines are attributed to transitions at isolated *N* donors. However, our comparative studies of a variety of crystals support the suggestion of HCP that the A_0, B_0, C_0 lines originate at *related* centers, since their *relative* intensities are nearly specimen independent.

As usual, Zeeman analysis of the A_0, B_0, C_0 lines (Figs. 6 and 7) provides a critical test of the model for the associated transition. Figures 6 and 7 contain much data (0 points) from the relatively weak satellites of the principal A_0, B_0, C_0 lines which will be discussed below. At first, we will consider only the data from the principal lines, indicated by *x* points. A striking general feature for A_0 and C_0 is the presence of simple symmetrical *three*-line magnetic spectra. Magnetic spectra of this form are characteristic of transitions between states containing even numbers of electronic particles with half-integral spin, and may be contrasted with the typical forms of Figs. 3 and 4 for systems containing odd numbers of particles. We shall see that B_0 also has the same generic type of magnetic spectrum, allowing for much larger perturbations of the zero-magnetic-field degeneracy by the local crystal field. The splittings of the outer magnetic subcomponents for all three lines correspond to a *g* value close to 4 (Table III), a second striking feature of these magnetic spectra. This *g* value is very difficult to explain on the usual *J*-*J* coupling scheme for electronic particles in an axial semiconductor (Sec. III A). At this point, it is relevant to note that the spin-orbit splitting Δ of the valence band of SiC (~ 5 meV[1,17]) is negligible compared with the localization energies of these bound excitons (~ 200 meV according to Table I). The electron-hole spin-spin splittings may be $\gtrsim \Delta$ for such tightly bound excitons. The ansatz used in Sec. III A then becomes inappropriate, and an *L*-*S*-coupling model is more realistic for the bound electronic particles. This situation is unusual in semiconductors; in fact we believe this to be the first instance in which *L*-*S* coupling has been used to describe bound excitons.

The *L*-*S*-coupling model is very simple (Fig. 8) if we assume that the initial state of the luminescence transition contains just two electronic particles, so the ground state contains none. We have included the effect of an additional simplifying assumption, justified by the fit to the experimental data, that the orbital degeneracy of the hole has been removed by strong coupling to the center such that the $c(z)$ polarized orbital predominates. The model then predicts the polarization of the magnetic subcomponents shown in Fig. 8(b). Then, the initial state splits in a magnetic field as shown. The final state remains unsplit. For a substitutional point defect in 6*H* SiC S_x and S_y must be degenerate,

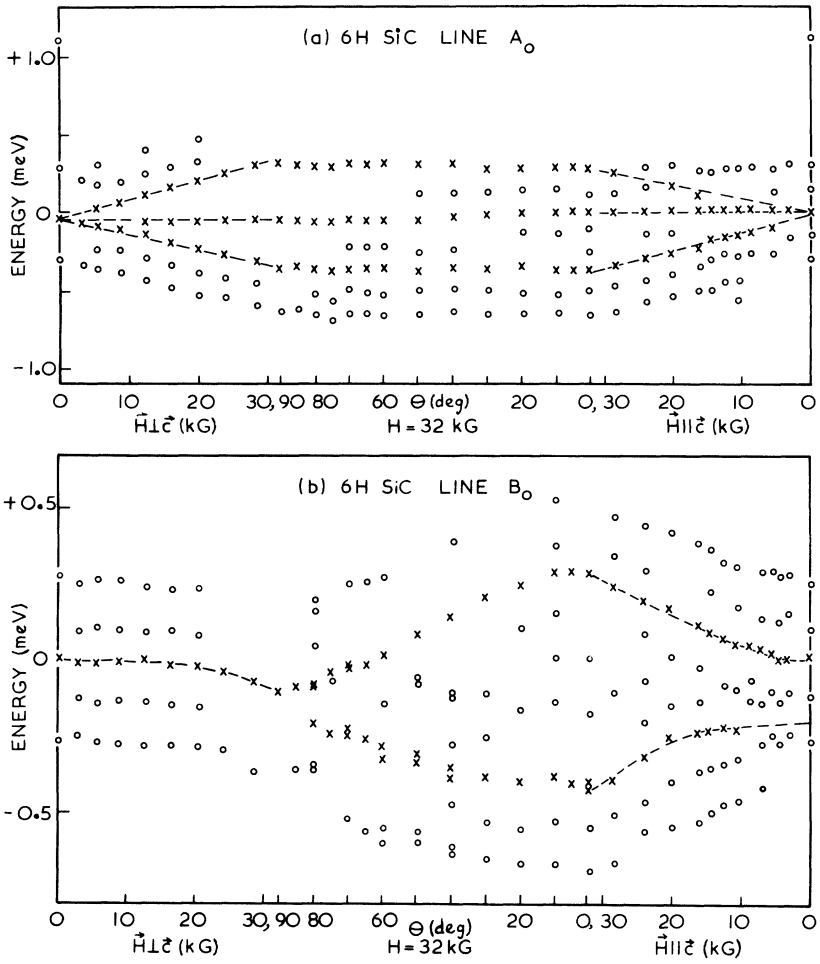

FIG. 6. Zeeman splittings of the bound-exciton no-phonon lines (a) A_0 and (b) B_0 in 6*H* SiC, arranged as in Fig. 3. Crosses are from the principal lines; the circles are from weak satellites discussed in the text. Outer subcomponents marked by *X* split with $g \sim 4$. Note the nonlinear splittings and shifts for B_0 at low *H*, also the splitting clearly deduced from the extrapolation to zero field of the $\vec{H}\parallel\vec{c}$ data.

but S_z could be split off by the crystal field. Figures 6 and 7 show that this splitting is negligible for the A_0 and C_0 lines. However, Fig. 6(b) shows that the crystal field effects are strong for line B_0, and S_z is not observed. More significantly, Fig. 6(b) also shows clearly for $\vec{H}\parallel\vec{c}$ a splitting

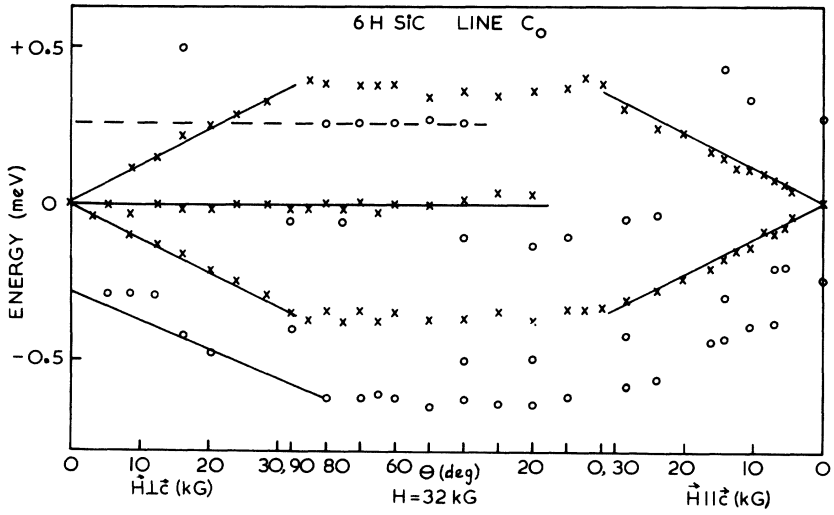

FIG. 7. Zeeman splitting of the bound-exciton no-phonon line C_0 in 6*H* SiC, arranged as in Figs. 3 and 6. The splittings are linear, unlike Fig. 6(b), and the polarization selection rules noted in Fig. 8(b) are obeyed.

TABLE III. g values from A_0, B_0, C_0 excitons.

Line	$(g)_{\vec{H}\perp\vec{c}}$	$(g)_{\vec{H}\parallel\vec{c}}$
A_0	3.7(3)	3.7(3)
B_0	0	3.9(0)
C_0	4.0(0)	4.0(0)

of ~0.2 meV between the two remaining components from B_0 extrapolated to zero magnetic field, the lower component becoming vanishingly weak at low field (below 10 kG) [Fig. 9(a)]. Evidently the two crystal-field-split states are mixed by the magnetic field, and split further, nonlinearly, at intermediate fields. Above $H=30$ kG, the magnetic splitting considerably exceeds this zero-field splitting, and the two magnetic subcomponents from B_0 behave very much like the outer components of A_0 and C_0, apart from their polarization, discussed below. The intensity ratio of these components reverses at high field and low temperatures [Fig. 9(b)] because of thermalization. The mixing of these two states is evidently forbidden for $\vec{H}\perp\vec{c}$. No nonthermalizing magnetic splittings were seen, so that final state is nonparamagnetic for all lines as required in Fig. 8(b).

The existence of the zero-field splitting of B_0 is important, since it proves that the B exciton is not bound to a point defect. In other respects, the magnetic behavior of the A_0, B_0, C_0 lines would be consistent with the model of HCP. However, if the B center is not a point defect, consistency with the N-donor interpretation requires the degeneracy of the N donor to be lowered by a static Jahn-Teller type of impurity-lattice deformation. This possibility has already been advanced by HCP in an attempt to account for small splittings of 1–2 meV observed in the no-phonon line patterns of the A and C excitons at high temperatures. However, static Jahn-Teller splittings *much* smaller than the energies $\hbar\omega$ of characteristic phonons in the sideband spectra of these excitons are hard to justify. On the other hand, a static Jahn-Teller splitting of magnitude $>\hbar\omega$ is both unlikely for a shallow donor in a covalent semiconductor and is also inconsistent with the findings for the P_0, R_0, S_0 lines in Sec. III A and with ESR for the N donor in 6H SiC.[19] We conclude, therefore, that the A, B, C lines cannot arise from exciton recombination at isolated N donors. We note that this clear cut finding removes at a stroke the various problems associated with this interpretation of HCP, outlined in Sec. I. The A, B, C lines may well *involve* N, possibly in an associated donor-acceptor-pair complex as originally discussed by CHP.[5] If so, this implies that acceptors exist in 6H SiC with ionization energies much larger than those quoted for B and Al.[27] The involvement of a deep acceptor is consistent with tight binding of the hole assumed in Fig. 8(b).

Further support for the model in Fig. 8(b) may be obtained from the experimental data. The probability P for the optical transition contains the term

$$P=|\vec{z}\times\vec{S}|^2, \tag{1}$$

where z is defined relative to the c axis for a point defect. Thus A_0 and C_0, for which the crystal-field effect of the axial defect is small, and B_0 at sufficiently high fields should exhibit the intensity and polarization selection rules shown in Fig. 8(b). The principal intensity effect is the absence of the central magnetic subcomponent, which transforms like z, for $\vec{H}\parallel\vec{c}$. Figures 6 and 7 show that this is true for line C_0, but not true for A_0, while the S_z component is not seen for B_0. The polarization selection rules predicted in Fig. 8(b) are also clearly obeyed for line C_0, both at zero field, where C_0 is strongly polarized $\vec{E}\perp\vec{c}$, and for the magnetic subcomponents. At zero field, B_0 is strongly polarized $\vec{E}\parallel\vec{c}$, which seems to imply that the axis of symmetry of the B center is perpendicular to c. The magnetic subcomponents from B_0 at large field are polarized $\vec{E}\parallel\vec{H}$. Line A_0 exhibits mixed polarization at zero field. In fact, close observation shows that A_0 is a nearly symmetrical close doublet at $H=0$, even in the best crystals,

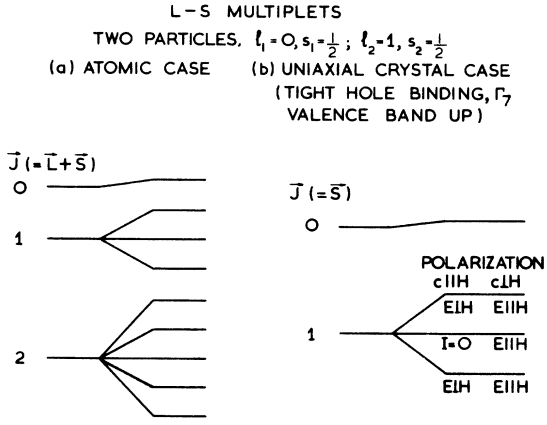

FIG. 8. Russell-Saunders (L–S) coupling between two electronic particles, one with $l=1$, $s=\frac{1}{2}$, the other with $l=0$, $s=\frac{1}{2}$. Part (a) shows the atomic case for the three neighboring states $^3P_0$, $^3P_1$, and $^3P_2$. The Landé g factor is $\frac{3}{2}$ for each of the magnetically degenerate states $^3P_1$ and $^3P_2$. A higher-lying state $^1P_1$, with $g=1$, is not shown. In part (b) the coupling scheme assumes $L=0$, due to tight binding of the hole in the uniaxial crystal. Then $g=2$ for the magnetically degenerate state with $J=1$. The polarization selection rules apply if the z ($\parallel c$ axis) Γ_7 valence band is locally uppermost.

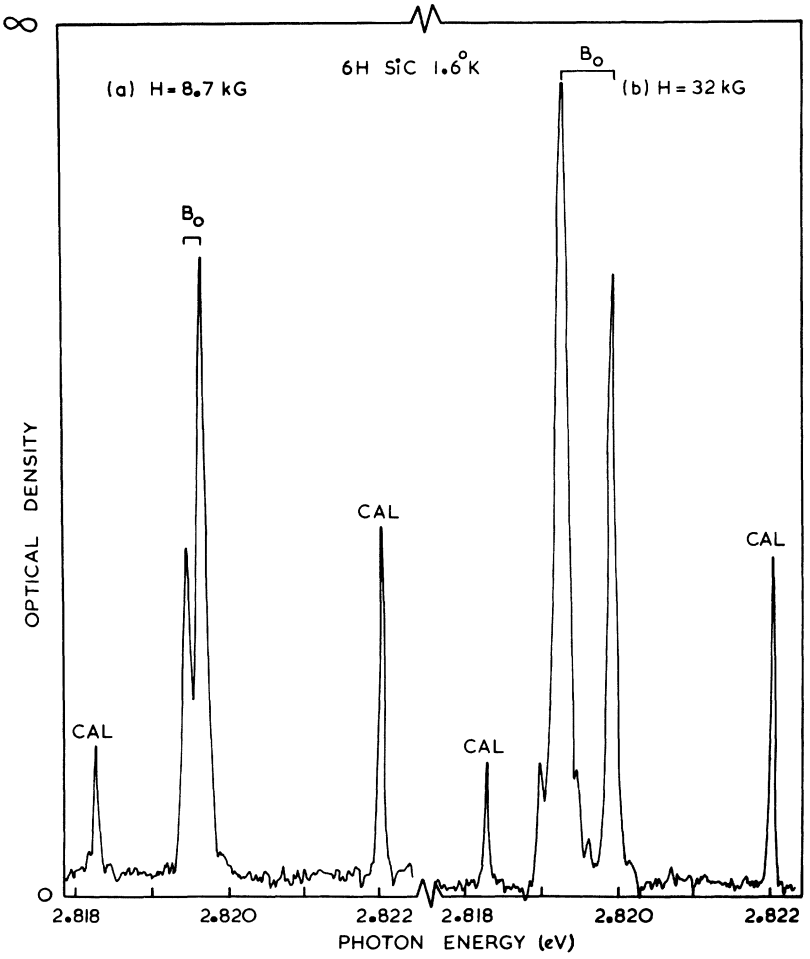

FIG. 9. Zeeman spectra of the moderately deep bound-exciton no-phonon line B_0, recorded photographically for (a) low and (b) high magnetic field. The lower-energy magnetic subcomponent becomes vanishingly weak at low H, although the splitting remains finite [Fig. 6(b)]. At larger H, the low-energy magnetic subcomponent becomes the stronger since the field-induced mixing is sufficiently great for thermalization to predominate. Some of the satellite lines discussed in the text can be seen in part (b). Lines marked CAL are from an Fe calibration lamp.

with a line separation of only ~0.03 meV. Such a small splitting can only be determined in our 6H SiC spectra through the use of a polarization analyzer, since it appears that the lower-energy component is strongly polarized $\vec{E} \parallel \vec{c}$, while the upper one is polarized $\vec{E} \perp \vec{c}$. At large field $\vec{H} \parallel \vec{c}$, the strong lower-energy component and (possibly) the weak higher-energy component shown by the x in Fig. 6(a) are strongly polarized $\vec{E} \perp \vec{H}$, like the components from C_0 in this orientation, while the central nonshifting component is polarized $\vec{E} \parallel \vec{H}$. These observations suggest that the central component is only seen from A_0 in $\vec{H} \parallel \vec{c}$ because of the presence of the "extra" subcomponent of A_0 polarized $\vec{E} \parallel \vec{c}$ at zero field, whilst the behavior of its sister subcomponent with and without a magnetic field is identical to that of C_0 and interpretable in terms of Fig. 8(b). These properties of line A_0 may well arise from perturbations from the x-y valence band, which will be significantly nearer for this most weakly bound of the A_0, B_0, C_0 excitons.

The nonlinear decrease in energy of line B_0 observed above 15 kG for $\vec{H} \perp \vec{c}$ must arise from a magnetic interaction with an initial state of higher energy, presumably S_g. However, no direct evidence of an excited state of B_0 has been obtained at zero magnetic field either by us or by HCP. Lines can be seen above A_0 and C_0, especially for temperatures $\gtrsim 5\,^\circ$K, corresponding to transitions from exciton states of higher energy. The energy spacing is least for the lowest-energy excited state of A_0, near +1.1 meV in Fig. 6(a), while C_0' lies ~2 meV above C_0. It is possible that some of these higher-energy states correspond to the $J=0$ state in Fig. 8(b). The 1.1-meV excited state *splits* in a magnetic field in a way too complex to clearly resolve. Two other excited states some 20 meV above A_0 have been identified by HCP in 77 °K spectra.

The magnetic fan diagrams in Figs. 6 and 7 are complicated by a remarkable series of weak satellite lines observed for each of the lines A_0, B_0, C_0 within an energy interval ~0.25 meV above and below the main line. The intensities of these lines are ~10% of the main lines, apparently sample

independent in the few crystals for which reliable measurements could be made. These satellites were not resolved by HCP. Their magnetic splittings ape those of the principal lines A_0, B_0, C_0 as far as they can be determined (Figs. 6 and 7). In particular, no differences could be detected between the magnetic behavior of the satellites and the principal lines as the magnetic field was rotated in the basal plane ($\vec{H} \perp \vec{c}$). This apparently removes the possibility that the satellite structure arises from small perturbations in the transition energy for (say) different positions of a donor around a nearest-neighbor acceptor on a DA-pair model in which the exciton is bound primarily to the acceptor. The displacements of these satellites from the principal line appear closely similar for all three systems, although the satellites are harder to see from the relatively weak C_0 line. The data on the B_0 line for $\vec{H} \perp \vec{c}$ in Fig. 6(b) clearly shows the inner pair to be asymmetrically disposed around B_0, although the outer pair are essentially symmetrical. The intensities are essentially symmetrical within the pairs, although the lower-energy member of the outer pair appears slightly, but distinctly, stronger than the other three satellites. An obvious possibility is that the satellites arise from isotope shifts of the no-phonon line. However, we have not been able to find a satisfactory interpretation in terms of isotope shifts for plausible impurities, even allowing for possible effects of the natural isotopes of the host atoms.

C. Electronic Raman Scattering from Donors

Colwell and Klein (CK)[28] have recently observed extra Raman scattering of Ar^+ laser light in N-doped 6*H* SiC which they interpret in terms of electronic excitations of the N donor. Three transitions of E_2 symmetry occur (Table IV) in addition to the phonon scattering,[16] each one apparently connected with one of the three inequivalent N donors in 6*H* SiC. We have confirmed the presence of these components in our green-tinged N-doped ($N_d - N_a \sim 10^{18}$ cm^{-3}) crystals in Raman scattering of the blue line of a He-Cd laser and the 6328-Å light of a He-Ne laser.[14] This scattering is not detectable in the water-white crystals we used for the Zeeman experiments, which contain $\lesssim 10^{17}$ neutral N donors. We observed that the extra components are strongly quenched above ~150 °K, unlike the phonon scattering, presumably because of thermal ionization of the N donors. Like CK, we believe that the electronic scattering components correspond to electronic excitations between the symmetric-donor ground state and an excited valley-orbit state of appropriate symmetry, analogous to the $1s(A_1) \rightarrow 1s(E)$ donor excitations observed in Si[29] and GaP.[30]

Enough information is now available to allow a rough estimate of $(E_D)_{EM}$ for 6*H* SiC, where the subscript EM denotes the value of donor ionization energy obtained from simple effective-mass theory. Although there is evidence from fine structure in momentum conserving phonon replicas of P_0, R_0, S_0 to suggest that the conduction-band minima in 6*H* SiC do not lie precisely on the principal symmetry axis,[1,20] the room-temperature Hall effect is essentially isotropic.[31] The most straightforward interpretation of this isotropy is that the constant-energy surfaces of the conduction-band relevant to these Hall measurements are ellipsoids of revolution about the *c* axis.[32] Assuming this, there are only two independent components of the effective-mass tensor. The transverse effective mass m_t^* can be determined from Faraday rotation, and Ellis and Moss[31] estimate $m_t^* = (0.25 \pm 0.02)m_0$, where m_0 is the free-electron mass. In terms of this model, the longitudinal effective mass m_l^* may be obtained, knowing m_t^*, directly from measurements of the crystalline anisotropy of the free-carrier absorption measured both at low and high frequencies.[33] Ellis and Moss[33] find $m_l^* = (1.5 \pm 0.2)m_0$ for 6*H* SiC. Once the mass-anisotropy parameter $\gamma = m_t^*/m_l^*$ is known, $(E_D)_{EM}$ can be determined using the Kohn-Luttinger procedure for donor states associated with prolate-spheroid conduction-band extrema, as recently discussed and refined by Falkner for shallow donors in Si and Ge.[34] With $\gamma = \frac{1}{6}$ and a static dielectric constant of 10.2,[35] Faulkner's calculations for the 1*s* donor state give $(E_D)_{EM} \sim 55$ meV for 6*H* SiC. The precision of this estimate is hard to judge in view of the difficulty of the experimental measurements made by Ellis and Moss, which determine the validity of the simple model upon which these calculations are based. However, it seems very probable that $(E_D)_{EM}$ lies within the range 45–65 meV. Table IV contains a list of donor energies obtained by adding the electronic-Raman-scattering energies to the upper end of this range for $(E_D)_{EM}$, with the additional assumption that the excited states of the Raman transitions lie ~15 meV *below* the effective-mass donor ground state. In view of the above discussion, and the evidence from electronic Raman scattering and energy level location for donors in other multivalleyed semiconductors, Si and GaP, it seems very likely that these estimates of E_D

TABLE IV. Electronic Raman scattering of N donors in 6*H* SiC and donor ionization energies.

Donor site	Raman shift[a] (meV)	Donor energy[b] (meV)
1	13.0	93
2	60.3	140.3
3	62.6	142.6

[a]References 14 and 28. [b]Assuming $(E_D)_{EM} = 65$ meV.

are upper limits. However, it should be noted that the shallowest donor in Table IV has E_D essentially identical with the value obtained from the recent detailed electrical transport studies of Hagen and Kapteyns[11] for $N_d - N_a \sim 5\times10^{16}$ cm^{-3}, a seemingly plausible limiting situation.

The increments in E_{BX} for the P_0, R_0, S_0 bound-exciton lines (Table I) are much more nearly proportional to those in E_D from Table IV than to the increments in E_D obtained from the HCP analysis of the A_0, B_0, C_0 lines, which are nearly evenly spaced in energy. Simple perturbation theory applied to exciton binding at neutral donors indicates that ΔE_{BX} should be proportional to ΔE_D for relatively shallow donors such as those in 6*H* SiC, even though E_{BX} need not be proportional to E_D.[23] The data in Tables I and IV imply that $E_{BX} \sim 8$ meV for an effective-mass donor in 6*H* SiC if $(E_D)_{EM} \sim 65$ meV. This corresponds to $m_e^*/m_h^* = 0.65$,[10] a realistic value for the shallow P_0, R_0, S_0 excitons.

IV. CONCLUSIONS

We have confirmed from Zeeman analysis the assignment of CP that the three-exciton series *P*, *R*, *S* with no-phonon energies within ~30 meV of the exciton energy gap of 6*H* Sic involves the decay of excitons bound to point-defect centers containing one extra electron in a symmetrical valley-orbit state. The electron *g* value is close to 2, and isotropic. The hole *g* value is about 3.2 for $\vec{H} \parallel \vec{c}$, and has the expected anistropic form, varying roughly as $\cos\theta$. The forms of these magnetic splittings are very similar to those observed in the wurtzite *direct*-gap semiconductor CdS.[3] In particular, the *J*-*J* coupling model, developed for CdS, is appropriate for these weakly bound excitons in 6*H* SiC. However, the absence of extra complexity due to valley-orbit degeneracy, possible for excitons bound to neutral acceptors in *indirect*-gap axial semiconductors, allows us to rule out this recombination process. Such distinctions can only be made through careful observation of the thermalization behavior of magnetic subcompoents for direct-gap axial semiconductors like CdS. Presumably three related series appear because donors in 6*H* SiC occur on three crystallographically inequivalent sites. We conclude, with CP, that the donor energy is appreciably lower for one of the three sites. The most likely donor is N. It substitutes on C lattice sites, as required. There is no evidence for static Jahn-Teller distortions from the Zeeman data, or from ESR of the N donor.[19]

The magnetic splittings of the A_0, B_0, C_0 luminescence no-phonon lines reported by HCP have also been studied. These three no-phonon lines are ~200 meV below E_{gx}, but cover a rather wide energy range ~75 meV. The interpretation proposed by HCP is much more problematical than that for the P_0, R_0, S_0 lines. The notion that excitons could exhibit such a large binding energy at ionized donors in a semiconductor in which the relevant electron-hole mass ratio is of order unity is in conflict with the general dynamical theory of exciton binding.

In addition, the ionization energies of the N donors estimated from the optical spectra using the model of HCP are ~ *twice* the largest ever reported from electrical transport studies of 6*H* SiC crystals, even in crystals of the quality used in the present work[11] with $N_D - N_A \lesssim 10^{17}$ cm^{-3}. The optical estimates of HCP are much larger than expected if the effective mass binding energy of donors in 6*H* SiC is simply augmented by the excitation energies observed in electronic Raman scattering by donors in moderately heavily N-doped crystals.[28] This procedure gives a fairly close account of the actual energies of donors in Si[29] and GaP.[30] Indeed, the sequence of donor ionization energies thereby obtained from the Raman data is in much better accord with that from the P_0, R_0, S_0 lines, deduced simply according to Haynes's rule, unlike the corresponding sequence obtained from the HCP model for the A_0, B_0, C_0 bound-exciton lines.

The Zeeman behavior of the A_0, B_0, C_0 lines is consistent with the decay of excitons bound by such large energies that the electron-hole spin-spin splittings exceed the spin-orbit splitting of the valence band of SiC. Then, an *L*-*S* electron-hole coupling is appropriate. The magnetic splittings of the A_0, B_0, C_0 luminescence lines indicate that the initial states are derived from the $S=1$ spin state of the bound exciton, while the final states contain no free spin. The component S_z may be split off by the axial field of 6*H* SiC. This splitting is large for B_0, but negligible for A_0 and C_0. The line polarizations for C_0 are in accord with the predictions made from this model, using a simple appropriate form for the optical matrix element for the transition. Thus far, the magnetic behavior is consistent with the HCP interpretation of these lines. However, the energy fan diagram and the relative intensities of the two magnetic subcomponents from B_0 clearly show an additional splitting of ~0.2 meV at zero magnetic field. The existence of this splitting proves that the B_0 exciton is not bound to a point defect. This is strong evidence against the HCP model, since it is clear from the behavior of the P_0, R_0, S_0 lines and from electron-spin resonance that the N donor does not exhibit a static Jahn-Teller distortion in any of the three inequivalent lattice sites.

Therefore, there is no reason to look for special causes for alleged deviations of the behavior of 6*H* SiC from expectation according to general ideas which have accounted well for the properties of

bound-exciton complexes in other semiconductors. The present work shows that there is no hard experimental evidence for these deviations.

We do not have a clear assignment for the A_0, B_0, C_0 excitons. A minimal necessary elaboration beyond a point defect model for these related centers would involve the assumption of a pair of defects on nearest-neighbor lattice sites. The binding of an exciton to such a pair can be most readily understood if the pair is neutral, for example a DA pair. If we preserve the suggestion of HCP that the splittings of A_0, B_0, C_0, like those of P_0, R_0, S_0, arise from the inequivalence of donor sites, then we must assume that the exciton is bound mainly through interaction with the electron. However, nitrogen is not deep enough to form such states with a shallow acceptor.[27] Thus, the disparity between the energy sequence of A_0, B_0, C_0 and either P_0, R_0, S_0 or the sequence of N-donor levels obtained from a simple interpretation of the Raman spectra, requires no special interpretation. Since relatively deep acceptors have been reported in 6*H* SiC,it may be more plausible to assume exciton binding via the hole and to ascribe the energy displacements to differences in the binding energies of an *acceptor* within the crystallographically inequivalent lattice sites. Fine structure has been observed comprising two pairs of weak satellite lines displaced on either side of the principal lines by approximately constant energies for A_0, B_0, and C_0. We feel that an interpretation of these satellites is probably critical to the assignment of these defect centers, but we have not been able to develop a satisfactory model.

Our conclusion that the relatively deep A_0, B_0, C_0 lines cannot arise from the recombination of excitons at simple ionized N donors has significant consequences for the choice of luminescence activators for efficient light-emitting semiconductor diodes. Were it possible to produce a tightly bound-exciton state of this simple form, exhibiting luminescence with moderately small thermal quenching because of the relatively large binding energies of both electronic particles, such centers would be very attractive as luminescence activators. The absence of Auger recombinations for this type of transition would be a very significant advantage for efficient luminescence in an indirect-gap semiconductor like SiC.[36] However, the conclusions of this paper lend strong support to the theoretical views of Hopfield,[10] that such bound exciton complexes are stable only under conditions which automatically yield a very small localization energy for the exciton at the ionized center. The luminescence of excitons bound to ionized donors has been positively identified in a number of II-VI compounds where the requisite condition of electron-hole mass ratio obtains, particularly in CdS.[37] The resulting so-called I_3 no-phonon lines are never dominant, even at 1.6 °C, and quench rapidly with increasing temperature, so being of no interest for devices operating at 300 °K. The only report of an exciton complex which grossly violates the stability theory of Hopfield, besides the HCP work on 6*H* SiC, involves luminescence alleged due to the recombination of excitons bound to ionized *acceptors* in GaAs. This identification has aroused considerable contention.[38,39] The present consensus seems to be that the experimentally reliable evidence for the relevant luminescence components arises from the simultaneous presence of two acceptors with slightly different ionization energies in many crystals of refined GaAs, the "extra" luminescence line then simply arising from donor-acceptor pair recombinations involving the shallower acceptor.[40] Thus, there is at present no experimental reason to question the general guide to bound-exciton stability offered by Hopfield.[10] This shows that exciton recombination at ionized donors or acceptors will never be a dominant recombination process, probably not even at liquid-helium temperature; but certainly not at room temperature.

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