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Donor Exciton Satellites in Cubic Silicon Carbide: Multiple Bound Excitons Revisited

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We report a new series of bound-exciton lines just below the associated luminescence of single excitons bound to the shallow donor N_C. The spectral position, Zeeman effect, and behavior under optical pumping indicate origin similar to a satellite series in Si, initially attributed to recombination within multiple bound-exciton complexes at neutral donors and acceptors. We find the multiple bound-exciton model consistent with the properties of these satellite lines both in SiC and in Si, in contrast with recent claims.

The near-gap low-temperature photoluminescence spectra of the best-available-quality cubic SiC (β-SiC) are dominated by a series of related sharp and moderately sharp lines. The highest-energy component is a single line lying ~10 meV below the exciton band gap E_{gx} due to the no-phonon (NP) recombination of an exciton bound to a shallow neutral donor, most probably N_C.[1] We refer to this line as the principal bound exciton (PBE) for this donor. The most significant of the related, lower-energy lines result from phonon-assisted transitions in which momentum-conserving phonons (MCP) predominate. In this Letter, we are concerned with a new series of lines, observed equally well as satellites of the NP and MCP lines, covering an energy range of ~30 meV below each of them.

The new satellites, $n=2\rightarrow 6(?)$ in Fig. 1(a), were most significant at high excitation intensities (Fig. 2), facilitated in our measurements by a short-focal-length lens for the laser exciting light and the relatively small penetration depth (~5 μm) of the ~360-nm light from a Coherent Radiation CR12 laser.[2] The crystals were cooled by direct immersion in liquid He, pumped below the λ point. Zeeman spectra [Fig. 1(a)] were obtained using a 10-MW Bitter magnet, operated in the Faraday configuration. Only the strongest satellite, $n=2$, has been reported previously; it is the B bound exciton of Hartman and Dean.[1] The Zeeman behavior is similar to a neutral acceptor-bound exciton. However, intercomparison of crystals showed that the B ($n=2$) exciton became relatively *weaker* with increasing compensation by such likely shallow acceptors as B or Al. Acceptor-bound excitons have yet to be recognized in cubic SiC.

These Zeeman properties in cubic SiC [Fig. 1(a)] are very similar to those given in a recent report for Si:P.[3] At low magnetic fields, the number of magnetic subcomponents of the satellites and the PBE are the same, although their relative intensities are very different, appearing to suggest "less thermalization in the transition excited states for increasing n."[3] This qualitative similarity in the Zeeman properties, independent of n, played a key role in the rejection of the multiple-bound-exciton (MBE) model.[3] Other inherent features of the MBE model, particularly the *increase* in exciton localization energy E_{BX} for each *additional* exciton bound, also seemed inplausible. We now show that these difficulties, as well as some previously disregarded apparent problems with the MBE model, can be resolved within the framework of this model.

One of us[4] has recently shown that in the absence of ground-state degeneracy, correlation effects play a strong role in the binding of electrons and holes in exciton complexes such as those in Fig. 1(b). When $m_e \sim m_h$, as in both Si and cubic SiC, the exciton localization energy E_{BX} is $\sim 0.44E_D$, where E_D is the donor binding ener-

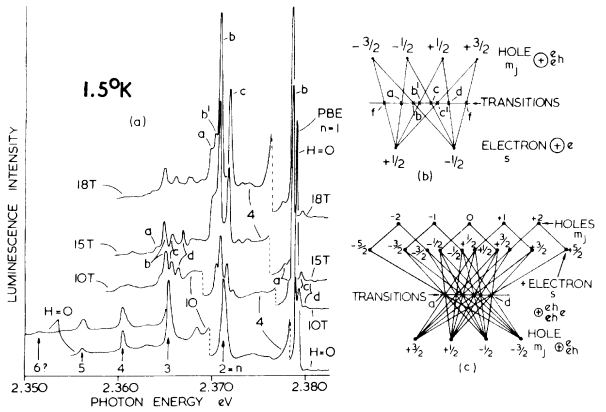

FIG. 1. (a) Sections of the low-temperature photoluminescence spectra of β-SiC:N recorded with the indicated magnetic fields. The donor principal bound exciton line PBE and the new series, index $n=2-6(?)$ are indicated. (b) Transition nomograph for the Zeeman spectrum of the PBE line, previously investigated (Ref. 1), between the neutral donor exciton and neutral donor states indicated to the right. Transitions f are forbidden and not seen in (a). Thermalization occurs between the hole magnetic substate populations. The diagram is based on a J-J coupling scheme. (c) Transition nomograph suggested for the $n=2$ ("satellite") line, involving transitions between the exciton states shown on the right-hand side. The electronic configurations correspond to Fig. 3. The final state has the magnetic characteristics of a single hole, just like the initial state of the PBE ($n=1$) luminescence transition. We assume negligible J-J splitting for the two holes with two electrons paired off in antisymmetric spin states. The magnetic subcomponents from the different possible total J states remain unresolved.

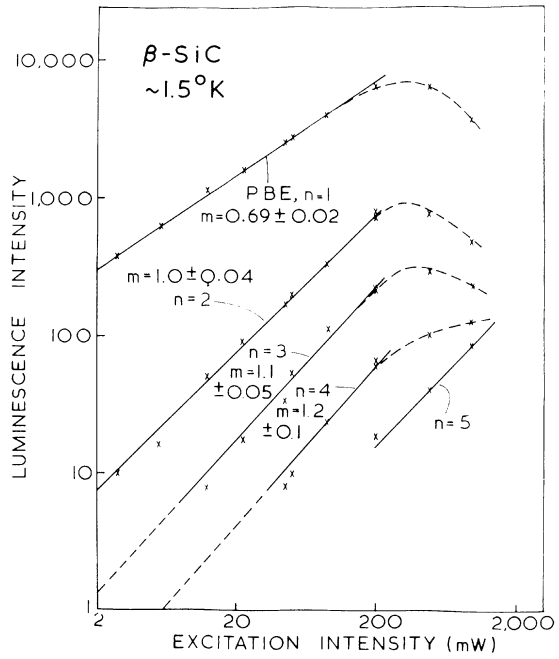

FIG. 2. The dependence of the intensity of the indicated exciton luminescence lines, labeled as in Fig. 1(a), on the intensity of the strongly focused 360-nm Ar^+ laser exciting light. The m values are the indices of empirical power-law relationships between the luminescence and excitation intensities.

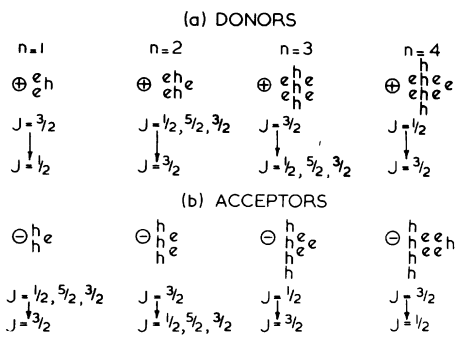

FIG. 3. Electronic configurations for multiple excitons bound (a) to neutral donors and (b) to neutral acceptors in a zinc-blende semiconductor where the electron and hole J values are $\frac{1}{2}$ and $\frac{5}{2}$, respectively. States with two holes contain possible zero-field splittings, relevant for the $n=2$ and $n=3$ transitions for the donors and the $n=1$ and $n=2$ transitions for the acceptors. The $J=\frac{5}{2}$ state may split further in the cubic field of the impurity core. These splittings are found to be negligible for the shallowest donors and acceptors seen in Si and cubic SiC. The index n indicates the number of excitons bound, as in Figs. 1 and 2. The assumption of $J=\frac{1}{2}$ for electrons presupposes a large valley-orbit splitting. If this assumption is removed, six line Zeeman spectra are still obtained if the electron spins are decoupled from the hole spins (Pashen-Back limit).

gy. This is a factor of 4 larger than experiment results for effective-mass donors or acceptors in Si and is at least twice that observed for cubic SiC.[5] Further calculations indicate[5] that this considerable predicted correlation contribution to binding is largely quenched by strong quantum fluctuations in the ground state of the single bound exciton which is highly degenerate. As the degenerate electron and hole states are filled through the addition of more excitons (Fig. 3), the quenching effect should be reduced and the binding increased towards the full value predicted for strong correlation when $m_e \sim m_h$. This prediction is in fair qualitative accord with the trend of E_{BX} with n in Fig. 1(a) and for Si[6,7] and Ge.[8]

The change in E_{BX} for $n>1$ in the donor series P → Sb → As and the acceptor series B → Al → Ga in Si[9] is insignificant compared with the well-established[10] shifts for the $n=1$ (PBE) components. Our measurements on cubic SiC show that, like

Si,[7] the relative strengths of the NP components for $n > 1$ *do not* increase very much with E_{BX}, quite unlike the behavior of the $n = 1$ (PBE) component[11] as E_{BX} is increased through a change in the donor or acceptor species. Finally, there is no experimental indication of the J-J splittings which might be anticipated from the electronic configurations of both donor and acceptor MBE satellites in Fig. 3, especially at larger n (larger E_{BX}). These properties all conspire to suggest relatively small wave-function overlap with the impurity core, despite the large E_{BX}. This can be understood by considering the effect of correlation. The increase of E_{BX} with n is due to an increase in the correlation energy between all mobile charges (electronic particles) with no particular reference to the static charge of the impurity core and therefore no significant increase in wave-function localization. In fact, in-out correlation reduces the probability of a given electronic particle being close to the impurity core, and the average overlap is further reduced with increase in the number of like-electronic particles in the complex. The reduced localization in the core region for $n > 1$ can also explain the increase we observe in the diamagnetic shift with n, surprising on the MBE model at first sight.

The absence of the known J-J splittings of the acceptor PBE in the acceptor satellites deserves special comment. This cannot be due to thermalization since Fig. 3(b) shows that this splitting occurs in the final state of the luminescence transition for $n = 2$, unlike the $n = 1$ (PBE) component. Sufficiently well-resolved acceptor MBE spectra have as yet been reported only for B, where the J-J splitting is negligible for the PBE.[9,12] An earlier report of a ~1-meV splitting[13] is invalid because of confusion with the then-unrecognized LO MCP component. The 1.3-meV J-J splitting for Al, and the still larger splitting for Ga,[13] must be present in the $n = 2$ acceptor luminescence satellite if the MBE model is correct, and should be seen when better-quality spectra become available.

No-phonon splittings due to J-J coupling are possible for all the donor MBE components in Fig. 3 in which the initial or final states contain two holes, unlike the well-investigated case of the PBE, $n = 1$ [Fig. 1(b)]. This criterion applies to the initial state of $n = 2$ and to the final state of $n = 3$ [Fig. 3(a)]. The above discussion suggests that the hole-hole splitting will be small, inasmuch as it depends upon overlap with the donor core. This overlap is small in any case for holes. Well-resolved luminescence spectra for P donors[6,7] and Li donors[7] in Si show no evidence of splittings, even when recorded at 5–10°K where thermalization is less. It seems unlikely that the splittings have been missed because they are extremely *large*. Therefore, we use in Fig. 1(c) the *Ansatz* of a *negligible* hole-hole (or electron-hole) splitting. It is assumed that the applied magnetic field decouples the electron and hole spins and that the electron and hole g values are unchanged between the transition initial and final states. This is very likely since $g_e \sim 2$ and g_h is relatively isotropic in cubic SiC[1] and in Si.[14]

The moderate resolution of available Zeeman spectra for Si[3] and cubic SiC even at high fields [Fig. 1(a)] does not justify a detailed analysis of the splittings. The important point is that the usual selection rules ($\Delta m_j = 0, \pm 1$) lead to *exactly* the same set of six magnetic subcomponent energies for the MBE two-exciton transition in Fig. 1(c) as shown for the single exciton PBE in Fig. 1(b). Small differences in line splittings and even in line ordering at very high fields [Fig. 1(a)] can be ascribed to small deviations from our assumption of constant g_h and to the increase of diamagnetism with n already mentioned. The π components ($\Delta m_j = 0$, Voigt configuration[3]) are just the inner pair b' and c both in Figs. 1(b) and 1(c).

An important feature of the MBE model as interpreted in Fig. 1 is the ready explanation that it offers for the striking n dependence in the degree of thermalization between magnetic subcomponents already mentioned. The magnetic behavior of the $n = 3$ line is described by the inverse of the nomograph in Fig. 1(c) according to Fig. 3(a). Then, the initial state of the luminescence transition has the magnetic character of a single hole, just like the $n = 1$ PBE line. The marked reduction in the degree of thermalization for $n = 3$ compared with $n = 1$ [Fig. 1(a)] follows directly from the nomographs. Transitions from the dominantly populated $m_j = -3/2$ magnetic substate contribute only to the strong component b for $n = 1$ [Fig. 1(b)], in contrast to $n = 3$ where they contribute across the whole energy spectrum of the magnetic subcomponents [Fig. 1(c), inverted]. The degree of thermalization of the $n = 2$ luminescence line is expected to fall somewhere between $n = 1$ and $n = 3$, in agreement with experiment, since Fig. 1(c) shows that in general the magnetic subcomponents for $n = 2$ receive contributions from more initial substates than for $n = 1$ [Fig. 1(b)]. However, subcomponent b remains strongest for $n = 2$ [Fig. 1(a)], whereas pure thermalization

would suggest that a should be strongest. Possibly, thermalization to the $m_j = -5/2$ magnetic substate is slow because the magnetic alignment of three particles is required and the influence of the weak spin-orbit coupling characteristic of conduction electrons must be considered. Account must also be taken of differences in the oscillator strengths of transitions from initial states of different parentage and the effect of the double contribution to the $|0,\pm\frac{1}{2}\rangle$ initial states in Fig. 1(c) ($|m_j,g_e\rangle$ representation), the pair from $J_h = 0$ being assumed degenerate with those shown from $J_h = 2$.

Far from discrediting the MBE model[6] we see that the Zeeman properties of the satellite lines provide substantial support for it, both in cubic SiC and Si. Generally, we find the MBE model to contain much less grave difficulties than any other model so far proposed, including a recent one in which the energy of a neutral donor-bound exciton is assumed to be appreciably lowered by interaction with a nearby polyexciton, with no significant coupling of the electron and hole spins between these two complexes.[15] Further theoretical study of the variation of binding energy with n in these MBE series is now urgently needed to complete our understanding. Unfortunately, this is a singularly difficult task.

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Failure of the Boltzmann Equation for Nonlinear Resistivity*

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The role of energy dependence of electronic parameters is given a more accurate formulation than previously. Explicit calculations for Nb show that the anomalous high-T resistivity cannot be explained in this way.

The usual Bloch-Grüneisen theory,[1] obtained by solving Boltzmann's transport equation, predicts an electrical resistivity $\rho = \rho_0 + \rho_{th}(T)$ where the residual resistivity ρ_0 is linear in defect density and the thermal sensitivity ρ_{th} is linear in phonon density and thus linear in temperature T for $T > \theta_D$. At sufficiently high temperatures, all metals deviate somewhat from a strict linear (in T) behavior. Often an explanation can be found in the details of electronic structure or thermal expansion, etc.[2] However, many metals[3,4] have a large negative deviation (ρ falls below the extrapolated linear law) which is not well understood. Among anomalous metals are virtually all d-band