Revised Fine Splitting of Excitons in Diamond

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We study low-strain synthetic high pressure, high temperature diamonds by cathodoluminescence and observe novel fine structure in the free exciton and the boron-bound exciton emission. The basic spectral structure is a doublet with $\Delta E \approx 11$ meV *common to both exciton spectra*. This resolves the previously found inequivalence of free exciton ($\approx$7 meV) and bound exciton ($\approx$12 meV) fine splitting. It is argued that for a spin-orbit interaction Δ_0 much smaller than the excitonic binding ($E_X \approx 80$ meV) and the excitonic localization ($E_{\mathrm{loc}} \approx 51$ meV) at the boron acceptor, the orbital momentum and the spin of the particles constituting the electron-hole pair are recoupled to form spin singlet and triplet exciton states as the elementary excitations.

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Diamond has an indirect band structure similar to silicon, with six equivalent conduction band minima located on the [100] axes at $0.76k_{\mathrm{max}}$. Quantitatively, however, diamond is different from all standard cubic semiconductors including silicon in that the valence band spin-orbit interaction Δ_0 at $k = 0$ is very much smaller than the excitonic interactions important in optical experiments. The latter are the exciton binding energy $E_X = 80$ meV and the localization energy $E_{\mathrm{loc}} = 51$ meV of excitons to the acceptor boron in p-type semiconducting diamonds [1]. (Substitutional boron is the only shallow impurity in diamond with an ionization energy $E_i = 370$ meV [2].) The spin-orbit splitting between the fourfold degenerate Γ_8^+ band and the twofold Γ_7^+ band amounts to $\Delta_0 = 6$ meV experimentally [3] or to $\Delta_0 = 13$ meV theoretically in linear muffin-tin orbital and $k \cdot p$ calculations [4]. In all other standard cubic semiconductors this ordering of the interaction energies is inverse, yielding $\Delta_0 \gg E_X$ and E_{loc}. In silicon, e.g., $\Delta_0 = 44$ meV [5], $E_X = 14.7$ meV [6] and $E_{\mathrm{loc}} \approx 0.1E_i$ according to Haynes' rule [7], with E_i ranging from $\approx$45 meV for the shallow donor phosphorus and the shallow acceptor boron up to $\approx$155 meV for the relatively deep acceptor indium [7].

It is the purpose of this Letter to present optical data relevant to this unique situation in diamond. We first show that a long-standing discrepancy between fine structure of free excitons (FEs) and boron-bound excitons (BEs) in the literature is actually not existent. Instead, a main fine splitting of $\approx$11 meV is common to the FEs and BEs which cannot be ascribed to the spin-orbit splitting of the holes as is the present standard explanation. Second, in an attempt to solve the resulting dilemma we discuss a novel coupling scheme for electrons and holes into spin singlet and spin triplet excitons.

Our cathodoluminescence study was performed on low-strain high pressure–high temperature synthetic bulk diamonds which were produced as described in the literature [8]. Low concentrations of boron acceptors are inadvertently present, yet high enough for the observation of boron-BE luminescence even in the no-phonon transition which is significantly narrower—but also much weaker—than the TO-phonon assisted replica. High-resolution detection of all BE and FE near-gap transitions was possible after optimization of the optical equipment. We have used an electron gun at (typically 6 keV) acceleration energy to excite the cathodoluminescence while the crystals are kept at low temperature, and a 1 m grating monochromator with a UV-enhanced CCD camera [9]. The setup allowed detection of the spectra with a signal-to-noise ratio $>$100 (e.g., the original spectra in Fig. 1 are not smoothed except for removing single spikes). The derivative spectra shown in Fig. 1 were numerically calculated after smoothing the original spectra over an energy range $<$1 meV. Their typical structure is independent of smoothing.

The present understanding of FE and boron-BE optical spectra in diamond is as follows: The FE spectrum consists of a doublet split apart by $\approx$7 meV from peak to peak, with the higher-energy component being thermally activated [1]. The doublet structure has been associated with electron transitions to the fourfold Γ_8^+ and the twofold Γ_7^+ valence band states, respectively, in the radiative decay of the FE [1]. This was taken as a confirmation of the Γ_8^+/Γ_7^+ spin-orbit splitting $\Delta_0 = 6$ meV originally obtained from cyclotron resonance measurements of holes under tunable light excitation [3]. The BE spectrum also consists of a thermalizing doublet, however, split apart by $\approx$12 meV [1]. This doublet was ascribed to the decay of BEs, incorporating either two Γ_8 holes or one Γ_8 and one Γ_7 hole, respectively, the energy difference being due to the spin-orbit interaction Δ_0 together with a weakened excitonic binding in the case of the inequivalent holes [1]. Infrared excitation spectra of holes at boron acceptors showed [10,11] that the ground state of the bound hole is

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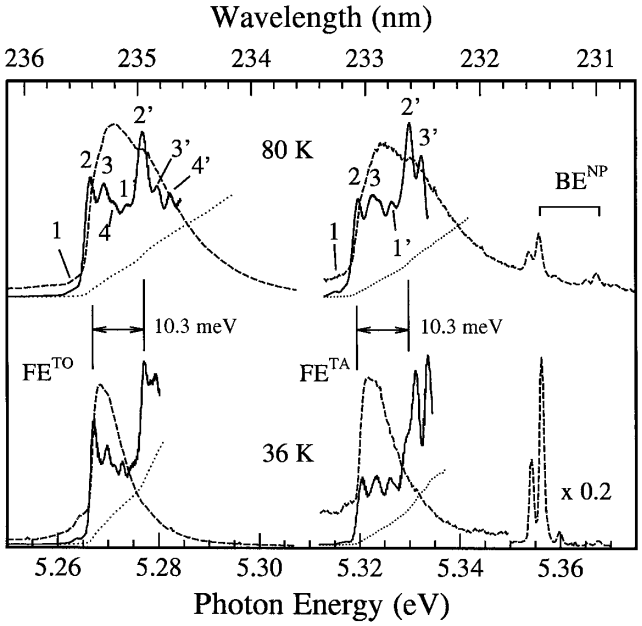

FIG. 1. Portion of near-band-edge spectra of diamond showing BE and FE recombination lines: Measured cathodoluminescence intensity spectra $I(h\nu)$ (dashed lines), calculated absorption curves $\alpha(h\nu) \sim I(h\nu)\exp(h\nu/kT)$ (dotted lines), and calculated derivative spectra $d\alpha(h\nu)/d(h\nu)$ (solid lines).

split by 2.1 meV, and these two states were assigned to Γ_8 (lower energy) and Γ_7 (higher energy) by uniaxial-stress measurements [10,12]. Recent Raman and infrared absorption measurements including magnetospectroscopy [13,14] confirm this interpretation demonstrating conclusively that the spin-orbit interaction of holes at boron acceptors is only $\Delta_B = 2.1$ meV. Finally, full-zone $k \cdot p$ band structure calculations, using a Slater-Koster attractive potential have been performed recently to show that the spin-orbit splitting $\Delta_0 = 13$ meV, calculated *ab initio* for the Γ_8^+ valence band [4], is reduced to $\Delta_{\text{exc}} \approx 8.6$ meV for the FE and to $\Delta_B \approx 3.9$ meV for boron-bound holes [15]. Basically, these calculations seem to model the experimental trends.

Our measurement gives evidence that the simple doublet splitting ($\approx$7 meV) of the FEs does not hold changing radically the experimental situation. Figure 1 shows the near-band-edge portion of the luminescence spectrum exhibiting at high photon energy the no-phonon (NP) doublet of the boron-bound exciton (BE^{NP}) followed at lower photon energy by the FE emission accompanied by wave-vector-conserving TA- and TO-lattice phonons with $\hbar\Omega(\text{TA}) = 87$ meV and $\hbar\Omega(\text{TO}) = 141$ meV [1]. In the spectra measured at the higher temperature (80 K), there are in both phonon replicas the two FE components visible mentioned earlier which are split by $\approx$7 meV peak-to-peak. However, a totally different structure is clearly discernible upon more sophisticated analysis. In Fig. 1, a weak extra component labeled 1 is directly observable on the low-energy side. This structure was also observed independently in low-temperature ($T = 18$ K) CL measurements where it develops into a relatively much stronger, nearly resolved component [16]. We demonstrate by the following procedure the full structure contained in the FE spectra. Since the FE emission is given by the absorption constant $\alpha(h\nu)$ times the Boltzmann tail $\exp(-h\nu/\text{kT})$ we first multiply the measured spectra by $\exp(h\nu/\text{kT})$ to obtain $\alpha(h\nu)$ which is directly proportional to the FE density of states assuming a constant transition matrix element. Second, we compute numerically the first derivative of $\alpha(h\nu)$ to better identify subtle features in $\alpha(h\nu)$. The results in Fig. 1 demonstrate that for low and high temperatures the *same* fine structure emerges in *both* phonon satellites of the FE. This gives us confidence that the fine structure is real and electronic in nature, being independent of the accompanying phonons. The fine structure is observed in several specimens, and it is independent of their isotopic compositions. In each phonon replica there are two identical groups of lines exhibiting a main splitting of $\Delta E = 10.3$ meV which has not been recognized before. Any indication of a 6 or 7 meV splitting is now absent which could be associated with the experimental value of Δ_0. Each group of this basic doublet structure shows the same substructure composed of at least three peaks (possibly even four peaks) labeled $1, 2, 3, 4$ or $1', 2', 3', 4'$, respectively, in Fig. 1. The positions of the lines are listed in Table I.

TABLE I. Photon energies of FE components at 80 K.

TO-phonon replica				TA-phonon replica			
No.	$h\nu$ (eV)	No.	$h\nu$ (eV)	No.	$h\nu$ (eV)	No.	$h\nu$ (eV)
1	5.2629	$1'$	5.2737	1	5.3151	$1'$	5.3264
2	5.2665	$2'$	5.2768	2	5.3197	$2'$	5.3300
3	5.2693	$3'$	5.2798	3	5.3227	$3'$	5.3324
(4)	5.271	$(4')$	5.282	(4)	⋯	$(4')$	⋯

Next we discuss our BE spectra. The doublet NP transition of the BE in Fig. 1 is shown in detail in Fig. 2 as recently reported [17]. Like the FE, there are two identical groups of lines forming a main doublet structure with a spacing of 11.4 meV. This is the more precise value of the above cited $\approx$12 meV BE line splitting [1]. In addition, there is a novel fourfold substructure identically observed in each of the two groups which we label $(a, \ldots, d)$ or $(a', \ldots, d')$, respectively. Computer fits to the spectra (Fig. 2) using Gaussian broadened line shapes (FWHM = 1.0 meV at 36 K and 1.4 meV at 80 K, equal to the experimental linewidths) firmly establish the existence of all four components. The line positions are listed in Table II. At varying temperatures the components c and d are simultaneously thermally activated leaving the components a and b in a constant intensity ratio. From this behavior, we derive the level scheme shown in the inset of Fig. 2 which applies to either of the two doublet groups separated by 11.4 meV. The transitions terminate on two final acceptor states spaced by 2 meV. This is evidently the split ground state of the isolated neutral boron acceptor

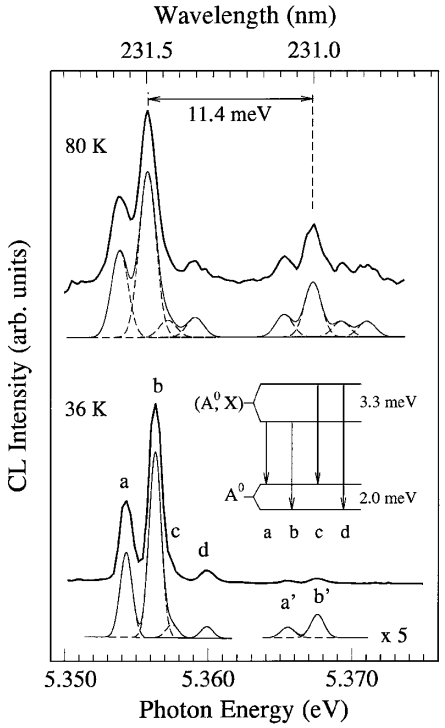

FIG. 2. Fine structure of the no-phonon BE recombination spectra showing original spectra and computer fits with Gaussian broadened lines (FWHM = 1.4 meV) to the components, and recombination level scheme.

(A^0), and our splitting of 2 meV is in excellent agreement with the recent Raman data ($\Delta_B = 2.07$ meV for natural diamonds and 2.01 meV for ^{13}C) [13] and the former infrared data ($\Delta_B = 2.1$ meV) [10,11] on the boron acceptor.

As shown, the main feature in the FE and BE spectra is the splitting of ≈11 meV (FE: 10.3 meV, BE: 11.4 meV). We believe this is not accidental but due to the same interaction in both excitonic complexes. For the FE, the observed splitting is between the value $\Delta_0 = 13$ meV calculated *ab initio* for the Γ_8^+ hole [4] and the value $\Delta_{\text{exc}} \approx 8.6$ meV calculated for the free exciton [15]. Hence, with improved computational accuracy it appears possible to associate the observed FE splitting with Δ_{exc}. However, this is very unlikely for the BE with its two strongly localized holes. Instead—as also stated in Ref. [15]—it is more probable that other effects or interactions have to be invoked for the BE.

To solve this apparent dilemma we note that if the ≈11 meV splitting has the same generic origin for FEs and BEs it must be due to the coupling of electrons and holes. This prompts us to discuss a novel coupling scheme of electrons and holes into excitons applying specifically to diamond. The concept is natural in taking into account the ordering of the relevant interactions in diamond, i.e., the spin-orbit coupling $\Delta_0 = 6$ or 13 meV [3,4], the electron-hole binding energy into excitons, $E_X = 80$ meV, and an additional exciton localization at boron acceptors, $E_{\text{loc}} = 51$ meV. We suggest that the weak spin-orbit coupling of free holes in the band structure is broken up when they interact much more strongly with electrons to form excitonic complexes. In terms of atomic physics, the concept leaves the case of jj coupling in favor of LS coupling as it applies to light many-electron atoms [18]. In diamond, we assume that the p-like hole orbital first couples to the s-like electron to form a P orbital term for the FE. Coupling of the electron and hole spins leads to a spin singlet $^1P_1$ and spin triplet $^3P_{0,1,2}$ with the singlet lower in energy for our case of the electrostatic interaction of oppositely charged particles. The intercombination rule forbids transitions from the triplet into the vacuum ground state, $^1S_0$. However, a nonzero spin-orbit interaction splits the degenerate manifold of the $J = 0, 1, 2$ states of total-angular momentum and lifts the intercombination rule rendering the transition $^3P_1$ to the ground state $^1S_0$ allowed depending on the magnitude of the interaction. For the present model it has to be assumed that the triplet splitting is smaller than the observed half-widths of the derivative spectra in Fig. 1, ≈2 meV. For an "allowed" splitting of this size the optical matrix for the triplet transition should be rather large as it depends critically on this switching on of the spin-orbit coupling.

Calculation of the spin singlet-triplet splitting is beyond the scope of the present experimental paper and principally difficult to perform for the BE since the effective potentials are not known in this four-particle complex. However, a rough estimate suggests that a singlet-triplet splitting of order 11 meV as required by the experimental data is reasonable. The He atom is taken for comparison and scaled to the diamond exciton case. For ($1s\,np$) electron configurations, He represents a system similar to the exciton as the outer p electron has vanishing probability density at the nucleus site and therefore "sees" only one positive charge resulting from the inner $1s$ electron and the doubly charged nucleus. Experimental singlet-triplet splitting energies of the P terms of He from Ref. [18] are $^{1,3}\Delta E = 253.8$ meV ($n = 2$), 79.9 meV ($n = 3$), 34.2 meV ($n = 4$), and 17.6 meV ($n = 5$), n being the principal quantum number. The corresponding ionization energies from the ^3P terms to the series limit are [18] $\varepsilon_i = 3.62$ eV ($n = 2$), 1.58 eV ($n = 3$), 0.88 eV ($n = 4$), and 0.56 eV ($n = 5$). We scale the He singlet-triplet energy differences normalized to their ionization energies with the experimental FE binding energy in diamond of 80 meV to obtain 5.6 meV ($n = 2$), 4.0 meV ($n = 3$), 3.1 meV ($n = 4$), and 2.5 meV ($n = 5$). Empirically, these values times n yield an almost constant value of ≈12 meV. We use this to extrapolate

TABLE II. Photon energies of BE^{NP} components at 80 K.

No.	$h\nu$ (eV)	No.	$h\nu$ (eV)
a	5.3538	a'	5.3652
b	5.3558	b'	5.3672
c	5.3572	c'	5.3692
d	5.3591	d'	5.3710

to our exciton case, representing $n = 1$ (for He, there are no P terms in the ground state), and obtain $\approx$12 meV singlet-triplet splitting for diamond excitons.

This agreement may be fortuitous. Other arguments are needed to support the present spin singlet-triplet hypothesis. Serrano *et al.* [15] have calculated a strong reduction of the spin-orbit splitting Δ_0 from the free hole value Δ_0 (13 meV theoretically) via the exciton value ($\Delta_{\mathrm{exc}} \approx 8.6$ meV) to $\Delta_B \approx 3.9$ meV for the boron-bound hole. We, on the other hand, following experiment, have to explain why the singlet-triplet splitting would *not* strongly depend on the binding of the hole. Without being able to give numbers we note that the strength of the spin-orbit interaction is given by $(1/r)\,\mathrm{grad}V(r) \cdot \vec{l}\vec{s}$, $V(r)$ being the potential in which the interacting orbital ($\vec{l}$) and spin ($\vec{s}$) wave function move. For a Coulomb-like potential this term would scale as $1/r^3$. The singlet-triplet splitting in contrast is in zero order approximation given by a "resonance interaction" expressed by the exchange integral $\langle s(1)p(2)|V(r_{12})|s(2)p(1)\rangle$ where s and p refer to the orbital wave functions of the electron and the hole, and the Coulomb-like interaction operator enters directly which should lead to a much weaker dependence on the hole binding energy. Physically, this splitting is due to the antisymmetric behavior of the total wave function, the ^1P state being associated with a symmetric orbital and an antisymmetric spin function, and vice versa for the ^3P states.

Apart from the FE and BE lines which show the $\approx$11 meV splitting as demonstrated above there are two other near-band-edge luminescence lines being split in a strikingly similar way. The N9 spectrum exhibits two strong lines at 5.254 and 5.263 eV split apart by $\approx$9 meV [19]. This splitting was suggested to be due to spin-orbit interaction of the hole state of a bound exciton [1]. Another yet unidentified near-band-edge spectrum consists of two main lines at 5.16 and 5.17 eV [19] which we similarly often observe in boron implanted and annealed natural type IIa diamonds as well as in some virgin natural type IIa diamonds. All these spectra show very similar splittings which could be ascribed to the singlet-triplet interaction under discussion. In contrast, optical defect spectra at significantly lower photon energies (i.e., strong electron-hole localization) would not show doublet transitions due to this singlet-triplet interaction. In that case the orbital momentum of the hole would be quenched, as is well known from optical defect studies in silicon [20], yielding *pure* spin singlet-triplet states rendering the radiative triplet decay strictly forbidden.

The origin of the components $(1, \ldots, 4)$ or $(1', \ldots, 4')$ in the FE spectra and the finer structure in the BE spectra could arise from various effects, such as the lifting of the residual electronic degeneracies, valley-orbit scattering, or effective mass reversal. An interpretation can be made only after the nature of the main splitting has definitely been established.

To summarize, we have demonstrated a rich fine structure of the FE, with a main doublet splitting of 10.3 meV inconsistent with the standard quotation of a $\approx$7 meV splitting. The new data establish an equivalence between FE and BE splittings. Taken in conjunction with the dominance of the excitonic binding energies over the spin-orbit interaction this equivalence leads us to discuss spin singlet and triplet excitons as the elementary electronic excitations in diamond.

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