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LETTER TO THE EDITOR

Higher resolution studies of shallow bound exciton luminescence in diamond

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Abstract. Luminescence produced by the decay of excitons bound to neutral boron acceptors in diamond is reported at higher resolution than hitherto. The line-widths of the phonon-assisted processes are consistent with the electron and hole of the bound exciton having a spatial localization within an effective Bohr radius of about 0.85 nm. New fine structure is reported in the no-phonon components of the luminescence, caused by splittings in both the ground and excited states of the localized particles.

The general description of the intrinsic, near-band-gap luminescence from diamond is well known. Diamond is an indirect gap semiconductor, with the minimum of the conduction band about 0.76 of the distance, in wave-vector space, to the (001) zone boundaries (Clark *et al* 1964, Dean *et al* 1965). Luminescence from free excitons involves wavevector-conserving phonons of energy 87 ± 2 meV (transverse acoustic modes), 141 ± 1 meV (transverse optic) and 163 ± 1 meV (longitudinal optic). Excitons can also be captured by substitutional boron acceptors. The localized excitons can then decay without the emission of phonons, but the TA, TO and LO phonon-assisted features still dominate in the spectra (see figure 1).

More recently, considerable control has been achieved over the growth of synthetic diamond and it has become worthwhile to revisit the near-band-gap luminescence. For example, the control of growth has been exploited to measure the change in near-band-gap luminescence in ^{13}C diamond compared to ^{12}C diamond (Collins *et al* 1990). New structure has been resolved in the free exciton luminescence (Sharp and Collins 1996). The lifetime of the free excitons has been investigated (Sharp and Collins 1996, Takiyama *et al* 1996) and free-exciton lifetimes τ_{fe} of up to 85 ns have been observed. The temperature dependence of τ_{fe} suggests that, in pure diamond, the lifetime could be about 250 ns (Takiyama *et al* 1996).

For this letter, diamond synthesized at high temperature and high pressure has been studied using cathodoluminescence generated by an electron beam of typically 40 keV and $\approx 10 \mu\text{A}$, focused on a circle of diameter $\approx 300 \mu\text{m}$. The samples were cooled using a helium flow cryostat, with the temperature being measured from the lineshape of the free exciton luminescence as described below. The luminescence was analysed using a Spex monochromator fitted with a Hamamatsu R1657 photomultiplier. The boron concentrations of the samples were of the order of 10^{17} cm^{-3} , using the calibration of Kawarada *et al* (1993).

In strain-free diamond the lineshape of free exciton luminescence is expected to be a Maxwell–Boltzmann curve, with an intensity $I(E)$ at photon energy E given by

$$I(E) \propto \sqrt{E - E_t^i} \exp[-(E - E_t^i)/kT] \quad (1)$$

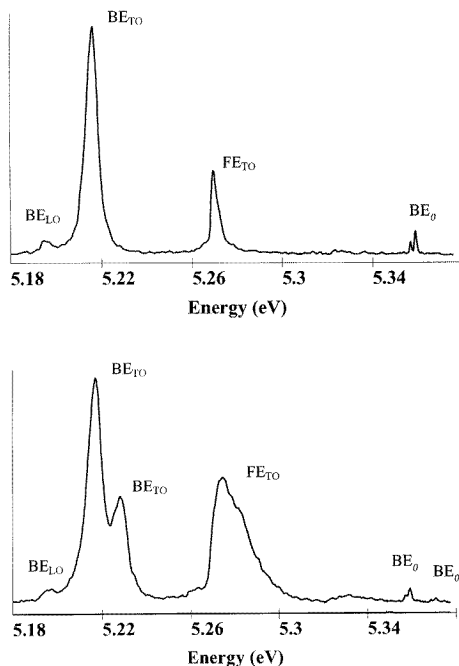


Figure 1. Cathodoluminescence at 20 ± 2 K (top) and 80 K (bottom) from a synthetic diamond. At 20 K the no-phonon luminescence of Dean *et al* (1965) is observed as a doublet (feature BE_0). Phonon assisted peaks are labelled by their mode type and by BE for the bound excitons and FE for the free excitons. The no-phonon lines were previously reported as a thermalizing doublet at the positions BE_0 and BE'_0 .

where E_t^i is the threshold energy of the transition involving the i th wavevector-conserving phonon emitted in the luminescence transition. For a free exciton, the phonon has a wavevector which is precisely equal to the wavevector of the minimum of the conduction band. The square-root term in equation (1) represents the density of exciton states, and the exponential term is the Boltzmann probability distribution. In practice, the spectrum is broadened by strains in the crystal and by the finite spectral resolution. We have fitted the experimental lineshapes by convoluting equation (1) with a Gaussian lineshape. The temperatures quoted for the data have been derived from the fits and thus correspond to the temperatures of those parts of the samples which were producing the luminescence.

Excitons bound to the boron acceptors have no kinetic energy, and so might be expected to produce sharper transitions than free excitons. Figure 1 shows that in fact the TO phonon-assisted bound exciton feature at a temperature of 20 ± 2 K is wider than the corresponding free exciton feature. The strain broadening and the finite spectral resolution are given by the widths of the no-phonon components of the luminescence. For the sample used for figure 1, at 20 K the widths of the no-phonon lines are only ≈ 1 meV, and an additional broadening of ≈ 4.3 meV is required to reproduce the measured width of the TO peak. Similar values have been observed in other synthetic diamonds, both in ^{13}C and in ^{12}C diamonds, at low temperature. Analogous effects are known for bound excitons in silicon (Thewalt *et al* 1976) and have been ascribed to the localization of the exciton. The wavevector K of the phonon emitted is not uniquely defined as a result of its localization in real space. Since the energy of the phonon varies with its wavevector, a spread in the phonon energy

is produced. The conduction band has its minimum energy at a wavevector along the (001) directions, and for this situation Thewalt *et al* (1976) have shown that the gradient of the phonon dispersion curve for K perpendicular to [001] is zero. Consequently the spread in energy of the phonons is given, to first order, by the gradient only along the [001] direction. From the measured dispersion curves for diamond (Warren *et al* 1967) the gradient $dE/dK \approx 3.9 \times 10^{-9}$ meV m for the TO phonon. To obtain an extra linewidth of 4.3 meV requires a spread in K of $\Delta K = 1.1 \times 10^9$ m⁻¹ for the electron and hole. We note that the Fourier transform of the hydrogenic 1s state $\psi(r)$ with Bohr radius r_o , $\psi(r) = \sqrt{1/\pi r_o^3} \exp(-r/r_o)$, is $F(k) = (2r_o)^{3/2} / \pi (1 + r_o^2 k^2)^2$, which has a full-width at half height of $2\sqrt{\sqrt{2} - 1}/r_o$. Consequently the spread in ΔK corresponds to spatial localization with an effective Bohr radius of $r_o = 0.85$ nm. Although only five times the nearest neighbour distance in diamond, this value is consistent with the effective-mass value of the Bohr radius for one hole bound to the boron acceptor of $r_b \approx 0.4$ nm. In silicon a similar ratio is also obtained for r_o/r_b (Thewalt *et al* 1976).

The compact size of the bound exciton allows interactions between the two holes and the electron trapped on the neutral acceptor. Figure 2 shows the no-phonon lines. Previously only two lines were resolved, at 5.356 and 5.368 eV respectively. They were ascribed to transitions involving recombination of the electron with a hole in a state derived, respectively, from the Γ_8 valence band maximum and the Γ_7 maximum (Dean *et al* 1965). The higher energy group of lines labelled BE'_o on figure 2 weakens relative to the BE_o set on lowering the temperature, consistent with the splitting occurring in the initial states of the bound exciton. Figure 2 shows that the lower energy line BE_o can be resolved into a triplet with possibly a fourth line also present, and the higher energy line BE'_o is a clearly resolved quadruplet. The lowest energy pair of lines, a and b on figure 2, are separated by $E_{ab} = 2.0 \pm 0.2$ meV, and do not thermalise with changing temperature but maintain a constant ratio of $r = 1 : 2.5$. The lack of thermalization suggests that the energy splitting of a and b occurs in the ground state of the transition. The higher energy quadruplet consists of two pairs of lines, a', b' and c', d', with each pair separated within experimental error by E_{ab} . The equal separations imply that the doublet natures of a' and b', and of c' and d' also arise from the ground state splitting. Consistent with this assignment, within experimental uncertainties the intensity ratio of a' and b' is independent of temperature. There are seven clearly observed components in figure 2, but the ground state splitting would suggest that component d should also have a weaker lower energy partner. A better fit to the observed spectrum is obtained if we assume that there is a component c, 2 meV below d. The total fit in figure 2 therefore implies that there are two ground states and four excited states involved in the transitions.

The ground state of the neutral acceptor has one hole, in a state derived from the Γ_8 valence band. The hole is therefore expected to be in a four-fold degenerate state. However, in silicon it has been shown spectroscopically that the bound Γ_8 is split, with splittings of 0.01 to 0.02 meV for the ground states of Al, Ga and In (Karasyuk *et al* 1994). The origin of the splitting is not known, although an off-centre acceptor atom could cause it. Luminescence transitions are allowed to both split states, with similar intensities in the case of Si:Al (Karasyuk *et al* 1994). The results are qualitatively similar here, although the magnitude of the splitting is two orders of magnitude larger. However, the binding energy E_b of the exciton to the acceptor in diamond is significantly larger than for Si. Excitons are bound to Si:B by about 3.8 meV while for C:B $E_b = 53$ meV. Expressed in terms of the localization distances derived from the phonon uncertainties, $r_o = 0.85$ nm for C:B, and 4.4 nm for Si:B (Thewalt *et al* 1976).

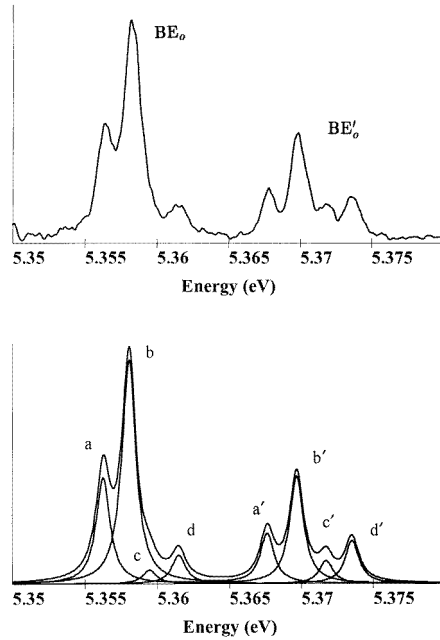


Figure 2. Top: BE_o and BE'_o no-phonon lines measured at 100 K from the same synthetic diamond as in figure 1. A fit to the measured spectrum is shown (bottom). Components a, b and d were previously reported as the lower energy no-phonon line, and a' , b' , c' and d' were previously reported as the higher energy line. Line c is the assumed lower energy partner of d.

The origin of the four excited state components is not clear at present. The bound exciton state consists of a two holes and one electron. Assuming tetrahedral symmetry, which we have seen may not be accurate for the ground state, the lowest energy hole states are expected to derive from the two indistinguishable holes occupying Γ_8 states. After deleting states which violate the Pauli exclusion principle, these states transform as $\Gamma_8 \times \Gamma_8 = \Gamma_1 + \Gamma_3 + \Gamma_5$. However, in pure diamond the Γ_8 and Γ_7 valence band states, corresponding to the $j = \pm\frac{3}{2}$ and $j = \pm\frac{1}{2}$ valence bands, are separated by only 7 ± 2 meV (Dean *et al* 1965) and so the Γ_7 valence band must be considered in the bound exciton states. Promotion of one hole to the Γ_7 state results in states $\Gamma_7 \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$, and excitation of both holes to the Γ_7 states gives a Γ_1 level. The electron is located at the conduction band minimum along K parallel to $\langle 001 \rangle$ and so there are six equivalent minima which transform in T_d symmetry as the valley-orbit split states $\Gamma_1 + \Gamma_3 + \Gamma_5$, and for each state the electron spin of $\pm\frac{1}{2}$ (transforming as Γ_6) must also be taken into account. All these basis states need to be combined to generate the observed states. The strengths of the hole-hole interaction, the valley-orbit electron splitting and the hole-electron interactions are not known at present. If one coupling dominates the others then a simple description is possible, as for Si:Al where the hole-hole interaction produces the major splittings and the other interactions add fine structure to those splittings. If the couplings are comparable, as for Si:B, the basis states are strongly mixed, and no simple description is possible (Karasyuk *et al* 1992). The relatively large localization of the bound exciton at the C:B acceptor could also produce Jahn-Teller coupling which is sufficiently strong to affect the ordering of the levels (Ham and Leung 1993). To determine the strength of the interactions requires application of external

perturbations: for example, a large $\langle 111 \rangle$ uniaxial compressive stress will generate a low energy triplet whose separations give the valley-orbit splittings immediately (Karasyuk and Pokrovskii 1983). These measurements remain to be carried out.

We have demonstrated that in high quality synthetic diamond at low temperatures it is possible to resolve multiplet structure in the luminescence from excitons bound to boron acceptors. Part of the structure is consistent with a splitting in the ground state of the neutral acceptor, and may be analogous to the splittings recently reported in Si. Part of the structure is produced by splitting of the exciton states; there are ample mechanisms available. We have drawn attention to the localization of the exciton, within a 'Bohr radius' of 0.85 nm, as derived from the phonon uncertainty, which allows strong interaction amongst the bound particles and between them and the lattice. The details of this system remain to be mapped out.

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