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Intrinsic radiative lifetimes of donor-acceptor pair excitations in diamond

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The intrinsic decay dynamics of pair excitations involving a deep donor and a shallow acceptor in chemical-vapor-deposited diamond is studied by time-resolved photoluminescence. Appropriate excitation conditions result in a distinctive decay behavior of individual donor-acceptor pair excitations, with extremely short radiative decay times in the picosecond-to-nanosecond regime.

Since the pioneering work by Hopfield, Thomas, and Gershenzon[1] on pair spectra in GaP, the radiative recombination of an electron trapped to a donor with a hole trapped to an acceptor has become a topic of considerable, both fundamental and technological, interest. Donor-acceptor pair spectra typically consist of a variety (10–100) of different luminescence lines. Each line is associated with a specific donor-acceptor distance r_m. This distance can only assume discrete values, indexed by the shell number m, if acceptor and donor are located at substitutional lattice sites.[2] The spectral position $\hbar\omega_m$ of each line is given by[3]

$$\hbar\omega_m = E_g - E_A - E_D - E_{\text{coul}} + E_{\text{int}} , \tag{1}$$

where $E_{\text{coul}} = -e^2/\epsilon r_m$ is the Coulomb energy between the ionized donor and acceptor, with e denoting the electronic charge and ϵ the dielectric constant. E_g is the band-gap energy, E_A and E_D the acceptor and donor binding energies, respectively. The energy E_{int} can be expressed as an overlap integral containing the electron-hole and carrier-impurity Coulomb interactions.

Donor-acceptor pair recombination (DAPR) has been observed in a variety of semiconductors, including Si, SiC, GaAs, GaN, InP, CdS, and ZnS.[4] DAPR in diamond has been proposed[5] in order to explain the broad luminescence band ("A" band) observed in the range of 2.0–3.5 eV. This interpretation has been discussed controversially in the past few years,[6,7] in which controlled growth of diamond has become possible by plasma-assisted chemical-vapor deposition.

Very recently, a series of sharp, spectrally isolated luminescence lines has been observed in diamond and identified as being due to donor-acceptor pair excitations. The DAPR spectra have been attributed to boron, forming a shallow acceptor with $E_A = 0.37$ eV, and to a deep donor with $E_D = 3.20$ eV.[8,9] Due to these large binding energies, the line system has the unique property that luminescence of very close donor-acceptor pairs (down to $m = 1$) can be observed.

The dynamical behavior of these extrinsic recombination processes should also depend on the distance between the donor and the acceptor. However, observed decay times are mostly dominated by population transfer within the ensemble of impurities[4] or by transfer processes between different kinds of impurities.[10] Recombination times then depend on the occupation probability in the former case and on transfer times in the latter. This usually leads to a nonexponential decay behavior and to very slow DAPR components from the μs regime up to several seconds.[11] Long luminescent lifetimes have also been found in previous studies in diamond.[5,7] A number of faster luminescing defect centers have been reported in the literature, with lifetimes in the range of 10^{-8}–10^{-7} s.[12]

The *intrinsic* DAPR lifetime, i.e., the radiative decay time of an excited, isolated donor-acceptor pair, should be much shorter, provided that the donor-acceptor spacing is not too large. To our knowledge, intrinsic lifetimes of individual DAPR transitions have not been reported in the literature for *any* DAPR system.

In this paper, we present an experimental and theoretical investigation of intrinsic radiative lifetimes of DAPR lines in diamond. These lifetimes are strikingly different from the decay times of the surrounding background luminescence. The observed lifetimes are very short (in the ps-to-ns regime) and show a pronounced dependence on the donor-acceptor spacing. Both observations are in excellent agreement with a theoretical calculation and reproduce the qualitative expectation predicted by Thomas, Hopfield, and Augustyniak.[11]

The sample under study is a nominally undoped homoepitaxial diamond film prepared by microwave plasma-assisted chemical-vapor deposition.[13] The 155-μm-thick film was grown on a polished 100 natural diamond plate, placed on a boron-doped silicon substrate, which was removed after diamond growth. Electron-spin-resonance measurements indicate the presence of isolated neutral nitrogen at a concentration of 2×10^{18} cm^{-3}.[14] As described previously,[8,14] the cathodoluminescence of the sample is dominated by four DAPR lines associated with the pairs in shells number $m = 1$, 4, 8, and 16. The corresponding radiative transitions are located at 2.67, 2.505, 2.330, and 2.205 eV, respectively.[9]

In our experiments, the photoluminescence (PL) was excited by the second or the fourth harmonic of the radiation of a mode-locked titanium-sapphire laser, with a pulse width of about 3 ps (< 1-nm spectral width) and a repetition rate of 76 MHz. The PL was measured using a synchroscan streak camera. The experiments were performed with an overall time resolution of about 20 ps and a spectral resolution of 0.5 nm. The time-averaged incident power density was 10 W cm^{-2}. No spectral or dynamical changes were observed on changing the excitation power within one order of magnitude. The spectral shape of the time-integrated PL did not differ

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significantly from previous luminescence measurements[14] performed under continuous excitation.

Figure 1(a) shows a series of time-resolved PL spectra in the vicinity of the $m=4$ DAPR line, obtained at an excitation energy of 2.725 eV. The spectra consist of the narrow zero-phonon DAPR line observed at 2.504 eV and a broad background luminescence. The background PL is partially due to vibronic sidebands of higher-energy transitions. The broad structures centered at 2.455 and 2.51 eV in Fig. 1, e.g., arise from the phonon replica of the No. 1 line. The time dependence of the DAPR intensity differs strongly from the background PL. While the background PL has a lifetime of about 2.7 ns, the $m=4$ DAPR decays with a time constant of 250±60 ps. In contrast, we observe a two-component decay of the $m=4$ DAPR line when exciting at 5.904 eV, which is above the diamond band gap. As shown by the PL transients in Fig. 1(b), the fast decay time is again ≈250 ps, while the slow component corresponds to the decay time of the background PL. As an explanation, we attribute the two-component DAPR dynamics to the radiative decay of *directly generated* donor-acceptor pair excitations, giving rise to the fast recombination time, and to capture and/or relaxation processes of photoexcited carriers occurring on a longer timescale.

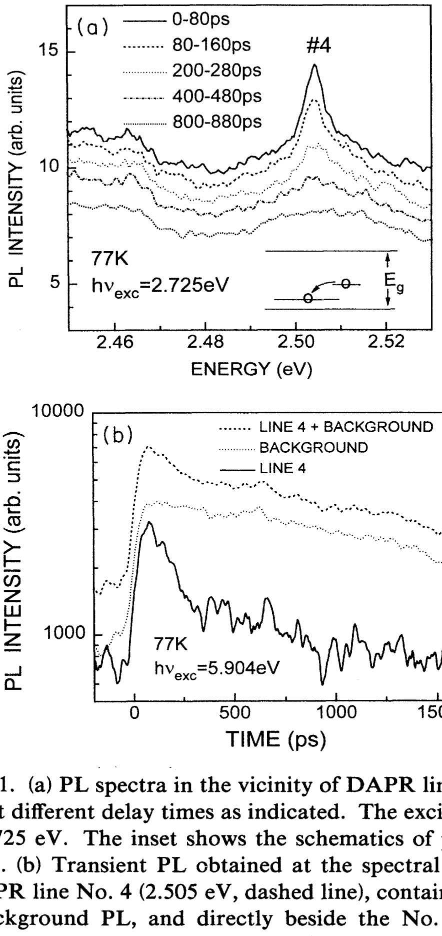

FIG. 1. (a) PL spectra in the vicinity of DAPR line No. 4 obtained at different delay times as indicated. The excitation energy is 2.725 eV. The inset shows the schematics of pair recombination. (b) Transient PL obtained at the spectral position of the DAPR line No. 4 (2.505 eV, dashed line), containing DAPR plus background PL, and directly beside the No. 4 emission (2.514 eV, dotted line), containing only the background. The No. 4 emission (full line) corresponds to the difference. The excitation energy is 5.904 eV.

For the $m=8$ DAPR line, a similar behavior is observed. Some representative PL transients are shown in Fig. 2. Here the DAPR intensity has been obtained by subtracting the nonresonant background, as obtained in the vicinity of the DAPR wavelength, from the PL intensity at the spectral position of the DAPR. We deduce from these data a radiative lifetime of 750±35 ps for the $m=8$ DAPR and about 1.7 ns for the background PL. The $m=8$ DAPR does not contain an additional slow component under 5.904-eV excitation, which is in contrast to the behavior of the $m=4$ line. We note that the background PL in Fig. 2 contains additional components with much longer lifetimes, which cannot be measured with the present setup. At smaller excitation energies, the $m=8$ DAPR shows the same dynamical behavior as for 5.904-eV excitation, with a reduced DAPR intensity relative to the background.

We have also investigated the $m=1$ and $m=16$ DAPR dynamics. The $m=1$ emission shows essentially the same dynamical behavior as the background PL, in a similar way as the long-lived component of the $m=4$ DAPR at 5.904-eV excitation discussed above. Apparently, direct excitation of a considerable number of $m=1$ pairs was not possible under the conditions used in our experiments. Therefore, the intrinsic $m=1$ DAPR lifetime is masked by the relaxation dynamics. In contrast, the observed decay of the $m=16$ DAPR is significantly slower than the background PL, which enables us to determine a time constant of the order of 4 ns for the $m=16$ emission.

Direct excitation of donor-acceptor pairs occurs also at nonresonant laser energies due to the strong vibronic coupling of these excitations to the diamond lattice. This excitation mechanism has been confirmed by additional experiments (not presented here), where we observed a considerable enhancement of the DAPR intensity for excitation energies resonant with the anti-Stokes shifted phonon sidebands. Such an excitation mechanism has also been observed previously in GaP.[15]

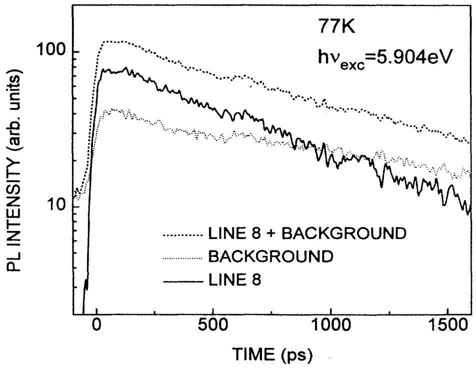

FIG. 2. Transient PL obtained at the spectral position of the DAPR line No. 8 (2.330 eV, dashed line), and directly beside the No. 8 emission (2.337 eV, dotted line), containing only the background. The No. 8 emission (full line) corresponds to the difference. The excitation energy is 5.904 eV.

In order to understand DAPR decay times theoretically, we note that the intrinsic radiative lifetime $\tau_{D\text{-}A}$ for donor-acceptor recombination can be written as[16]

$$\frac{1}{\tau_{D\text{-}A}}=\frac{4ne^2\omega}{m_0^2c^3\hbar}|\mathbf{p}_{AD}|^2\ , \tag{2}$$

where n is the index of refraction, m_0 the free-electron mass, c the speed of light, and ω the optical frequency. $\mathbf{p}_{AD}=\langle\psi_A|\mathbf{P}|\psi_D\rangle$ is the momentum matrix element of the momentum operator $\mathbf{P}$.

While Eq. (2) is generally valid, a realistic determination of $\mathbf{p}_{AD}$ for deep impurities is beyond the scope of this paper. We, therefore, restrict our analysis to the envelope approximation. Although this approach is not a good approximation for deep impurity states, it should still give us a crude impression of typical $\tau_{D\text{-}A}$ values. For the (shallow) acceptor-bound hole with the effective mass m_h, we use the wave function

$$\Psi_A(\mathbf{r})=\frac{1}{\sqrt{\pi a_A^3}}\exp\left[\frac{-|\mathbf{r}-\mathbf{r}_A|}{a_A}\right]u_{v0}(\mathbf{r})\ . \tag{3}$$

Here $\mathbf{r}_A$ denotes the position of the acceptor, $u_{v0}(\mathbf{r})$ the core wave function at zero momentum, and $a_A=\hbar^2/\sqrt{2m_hE_A}$ the Bohr radius with binding energy E_A. A similar wave function Ψ_D is used for the donor-bound state at $\mathbf{r}_D$ with binding energy E_D and radius a_D. For a particular donor-acceptor spacing $d=|\mathbf{r}_D-\mathbf{r}_A|$, we thus obtain the matrix element

$$\begin{aligned}\mathbf{p}_{AD}=\mathbf{p}_{cv}&\frac{8(a_Aa_D)^{3/2}}{(a_A^2-a_D^2)^2}\\ &\times\left[a_A\exp\left[-\frac{d}{a_A}\right]+a_D\exp\left[-\frac{d}{a_D}\right]\right.\\ &\left.\quad+4\frac{\exp(-d/a_A)-\exp(-d/a_D)}{d(a_A^{-2}-a_D^{-2})}\right]\ .\end{aligned} \tag{4}$$

Equation (4) has the limiting cases $\mathbf{p}_{AD}=\mathbf{p}_{cv}(1+d/a_A+d^2/3a_A^2)\exp(-d/a_A)$ for $a_D\rightarrow a_A$, and $\mathbf{p}_{AD}=8\mathbf{p}_{cv}(a_Aa_D)^{3/2}(a_A+a_D)^{-3}$ for $d\rightarrow 0$. For large donor-acceptor spacings, i.e., $d\gg a_A\gg a_D$, $|\mathbf{p}_{AD}|$ varies as $\exp(-d/a_A)$, which has been predicted previously by Thomas, Hopfield, and Augustyniak.[11]

The momentum matrix element $\mathbf{p}_{cv}=\langle u_{v0}|\mathbf{P}|u_{c0}\rangle$ is obtained from the relation[17] $|\mathbf{p}_{cv}|^2/m\approx E_g$, with the implicit assumption that the donor-bound state is related to the Γ-point minimum. (In reality, deep impurity states are related to essentially the whole Brillouin zone.) Assuming an effective hole mass of $m_h=0.7m_0$,[18] the 0.37-eV binding energy of the shallow acceptor (boron) yields $a_A=0.4$ nm. Note that this also corresponds to the onset value at which the correlation energy E_{int} influences the transition energy of the DAPR significantly.[8,14]

Figure 3 shows radiative DAPR lifetimes resulting from Eqs. (2)–(4) for some tentative a_D values, namely 0.4 nm (the size of a shallow donor state with $m_e=0.7m_0$), 0.13 nm (resulting in a Coulomb energy $e^2/\epsilon a_D$ of 3.2 eV), and 0.77 nm (half the C-C bond length). We also included for comparison the lifetimes observed in our experiments. The qualitative agreement between the measured and calculated values should not be overestimated since the theoretical approximations are not quite justified in the case of a deep donor. A precise quantitative theory will require a quasi-first-principle calculation of $\mathbf{p}_{AD}$.[19]

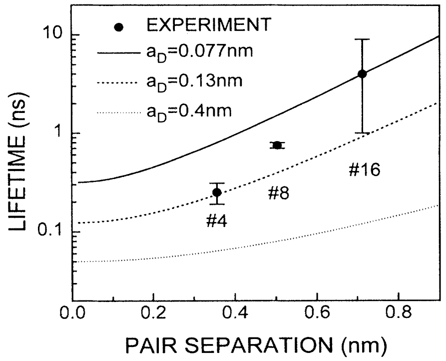

FIG. 3. Radiative lifetime vs donor-acceptor pair separation, showing the experimental values for $m=4$, 8, and 16 DAPR (full circles) and the theoretical prediction for $a_A=0.4$ nm and $a_D=0.077$ nm (full line), $a_D=0.13$ nm (dashed), and $a_D=0.4$ nm (dotted).

The *variation* of $\tau_{D\text{-}A}$ with pair separation, however, only depends on the spatial extension of the donor state since the acceptor is shallow in character. This relative dependence is, therefore, well described within our theory, and agrees reasonably well with the experiment. This observation further supports our conclusion that the observed DAPR decay times are indeed radiative lifetimes. We note that the present results also confirm the previous[8,14] assignment of the PL transitions as being due to DAPR.

The extrapolated limiting value $\tau_{D\text{-}A}|_{d=0}$ (zero pair separation in Fig. 3) observed in the experiment is of the order of 10^{-10} s. This is much shorter than limiting values for other DAPR systems, for which values in the range of 10^{-5}–10^{-8} s are quoted (see Table 5 in Ref. 4). This behavior is attributed to the fact that the relatively large binding energy of shallow acceptors in diamond (0.37 eV), combined with the small Bohr radius, suppresses interimpurity transfer of holes by impurity-band conduction or hopping at moderate acceptor concentrations. Therefore, DAPR contains a component that only involves *individual,* excited pairs, resulting in a short lifetime. Slow components can only exist if DAPR is delayed by carrier capture processes, as observed under appropriate excitation conditions [see Fig. 1(b)]. In previous DAPR systems, the decay rate is usually proportional to the majority concentration of the (shallow) impurities.[4,11]

In conclusion, we have investigated the recombination dynamics of donor-acceptor pair excitations in diamond. The DAPR emission exhibits very fast components in the range of $10^{-9}-10^{-10}$ s, much shorter than in any other DAPR system studied previously. This decay behavior is attributed to the *intrinsic radiative decay* of directly excited donor-acceptor pairs. Direct excitation at nonresonant energies is made possible by the strong vibronic coupling of the pair excitations with the diamond lattice. The observed decay times are in agreement with a theoretical estimation of intrinsic DAPR lifetimes. In contrast to many other DAPR systems, these transitions involve *individual pairs,* thus providing an efficient radiative channel, and a low-dimensional model system with interesting optical properties.

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[1] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Lett. **10**, 162 (1963).

[2] In the diamond lattice, we have $r_m = r_b\sqrt{\frac{4}{3}(m-x)}$, where $r_b = 0.1545$ nm is the bond length, and $x = 0.25$ for odd and $x = 0$ for even shell numbers $m \geq 1$.

[3] F. Williams, J. Phys. Chem. Solids **12**, 265 (1960); Phys. Status Solidi **25**, 493 (1968).

[4] P. J. Dean, in *Progress in Solid State Chemistry,* edited by J. O. McCaldin and G. Somorjai (Pergamon, Oxford, 1973), Vol. 8, p. 1.

[5] P. J. Dean, Phys. Rev. **139**, A588 (1965).

[6] J. Ruan, K. Kobashi, and W. J. Choyke, Appl. Phys. Lett. **60**, 3138 (1992).

[7] J. A. Freitas, P. B. Klein, and A. T. Collins, Appl. Phys. Lett. **64**, 2136 (1994).

[8] B. Dischler, W. Rothemund, C. Wild, R. Locher, H. Biebl, and P. Koidl, Phys. Rev. B **49**, 1685 (1994).

[9] The 3.2-eV donor level participation in DAPR is possibly related to nitrogen. Isolated substitutional nitrogen induces an absorption band at 3.3 eV [J. Koppitz, O. F. Schirmer, and M. Seal, J. Phys. C **19**, 1123 (1986)] and a photoconductivity peak at 3.2 eV [R. G. Farrer, Solid State Commun. **9**, 685 (1969)]. However, it is still controversial to associate this energy with the binding energy of nitrogen, since the photoconduction threshold observed by Farrer is at 1.7 eV. It is not the aim of this paper to settle this question.

[10] A. M. Frens *et al.*, Phys. Rev. Lett. **72**, 2939 (1994).

[11] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).

[12] E. Pereira, in *Properties and Growth of Diamond,* edited by G. Davies (Short Run, Exeter, UK, 1994), p. 228.

[13] C. Wild, W. Müller-Sebert, T. Eckermann, and P. Koidl, *Applications of Diamond Films and Related Materials,* Materials Science Monographs Vol. 73 (Elsevier, Amsterdam, 1991), p. 197.

[14] B. Dischler, W. Rothemund, K. Maier, C. Wild, H. Biebl, and P. Koidl, Diamond Relat. Mater. **3**, 825 (1994).

[15] W. Senske and R. A. Street, Phys. Rev. B **20**, 3267 (1979).

[16] W. P. Dumke, Phys. Rev. **132**, 1998 (1963).

[17] B. K. Ridley, *Quantum Processes in Semiconductors,* 2nd ed. (Clarendon, Oxford, 1988), Chap. 5.

[18] A. Mainwood, in *Properties and Growth of Diamond* (Ref. 12), p. 3.

[19] P. R. Briddon, and R. Jones, Physica B **185**, 179 (1993).