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Bound Excitons and Donor-Acceptor Pairs in Natural and Synthetic Diamond

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Recent studies on x-ray and electron-excited luminescence (cathodoluminescence) in natural and synthetic diamond provide evidence that the previously reported band-*A* luminescence is due to the radiative recombination across the indirect energy gap of electrons and holes separately trapped at donor and acceptor centers. Analysis of the temperature dependence of the luminescence from unirradiated natural specimens suggests that the principal acceptor is that responsible for the semiconductivity of type-IIb specimens. The donor and acceptor centers are, respectively, identified with isolated substitutional nitrogen and aluminum. Radiative recombinations apparently occur at both highly associated and diffuse pairs in natural diamond. Diffuse pair transitions predominate for typical General Electric, South African, and Swedish synthetic specimens. A band-*R* luminescence, produced in the cathodoluminescence spectrum of type-I diamonds by electron-irradiation damage, is tentatively identified in part with relatively close pair recombinations between *GR*1 (vacancy?) donor centers and *ND*1 (impurity+interstitial?) acceptor centers. A new Mössbauer-type fluorescence system with zero-phonon line at 1.40 eV, which is prominent in the cathodoluminescence spectra of nitrogen-doped synthetic diamond, is identified with the annihilation of indirect gap excitons tightly bound to ionized isolated nitrogen donors. The well-known *N*3 (3.0 eV) and *N*9 (5.26 eV) absorption-luminescence systems of natural diamond are identified with the creation or annihilation of excitons bound to ionized or neutral nitrogen donors which are modified by the presence of an ionized aluminum acceptor center in an adjacent substitutional lattice site.

I. INTRODUCTION

THE extrinsic luminescence of natural diamond has received a considerable amount of attention, particularly during the last twenty years.[1–4] Recent studies have shown that natural diamonds generally exhibit "visible" luminescence under "edge" ultraviolet excitation (most efficiently for exciting quantum energies $\gtrsim 5.15$ eV). The same type of luminescence (emission quantum energies 1.5–3.8 eV) is also efficiently excited in diamond by electrons of energy $\sim 10^4$ eV,[5] β and particularly α particles of energy $\gtrsim 1$ MeV[5,6] and x rays of energy $\gtrsim 10^4$ eV.[3] This so-called "band-*A*" luminescence has also been detected in synthetic diamond[7] and is often very intense for these specimens. [Synthesized at General Electric Research Laboratory (G.E.), Schenectady, New York.]

The properties of the "band-*A*" luminescence have recently[8] been contrasted in detail with those of other visible luminescence bands, such as the bands with principal (zero-phonon) lines at 4149 Å (2.989 eV), 4962 Å (2.499 eV), and 5035 Å (2.462 eV), classified as *N*3, *H*4, and *H*3.[9,10] Attention was mainly concentrated on the *N*3, *H*4, and *H*3 bands in the earlier work, and these bands are most efficiently excited by relatively low-energy ultraviolet quanta ($\lesssim 3.5$ eV). The centers responsible for the *N*3, *H*3, and *H*4 emission bands have remained unidentified, although it has been shown from the polarization properties of the *N*3 and *H*3 luminescence that the electronic axes of the centers are, respectively, $\langle 111 \rangle$ and $\langle 110 \rangle$.[11,12] The *H*3 center, which can be introduced in type-I diamonds by radiation damage and annealing treatment, is thought to involve a double defect,[11] but this is not necessarily true for the *N*3 center. The emission spectra of these centers are of the Mössbauer type.[13] In contrast with such centers in the alkali halides[14] the relevant phonon energies deviate considerably from those of the density-of-states maxima of the vibrational spectrum of the pure diamond lattice.[15]

The object of the present paper is to show that the known properties of the band-*A* diamond luminescence (emission spectrum, temperature dependence of intensity, and luminescence decay time and the dependence of the emission spectrum upon the mode of excitation) are consistent with electron-hole recombinations at donor-acceptor pairs. The results of recent experimental measurement, mainly of the emission spectrum and decay time of x-ray-excited band-*A* luminescence, which were explicitly designed to test this identification are shown to be consistent with it. The emission spectra and luminescence decay times suggest that a significant proportion of the donors and acceptors are spatially associated (in close pairs) in most natural diamonds,

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[1] P. G. Nayar, Proc. Indian Acad. Sci. **A15**, 293 (1942).

[2] H. B. Dyer and I. G. Matthews, Proc. Roy. Soc. (London) **A243**, 320 (1957).

[3] I. G. Matthews, Proc. Phys. Soc. (London) **72**, 1074 (1958).

[4] P. J. Dean and J. C. Male, Proc. Roy. Soc. (London) **A277**, 330 (1964).

[5] P. J. Dean, P. J. Kennedy, and J. E. Ralph, Proc. Phys. Soc. (London) **76**, 670 (1960).

[6] P. J. Dean and J. C. Male, J. Phys. Chem. Solids **25**, 311 (1964).

[7] J. C. Male, Ph.D. thesis, London, 1962 (unpublished).

[8] P. J. Dean and J. C. Male, J. Phys. Chem. Solids **25**, 1369 (1964).

[9] C. D. Clark, R. W. Ditchburn, and H. B. Dyer, Proc. Roy. Soc. (London) **A234**, 363 (1956).

[10] C. D. Clark, R. W. Ditchburn, and H. B. Dyer, Proc. Roy. Soc. (London) **A237**, 75 (1956).

[11] R. J. Elliott, I. G. Matthews, and E. W. J. Mitchell, Phil. Mag. **3**, 360 (1958).

[12] C. D. Clark, G. W. Maycroft, and E. W. J. Mitchell, J. Appl. Phys. Suppl. **33**, 378 (1962).

[13] D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolf, Phys. Rev. Letters **11**, 275 (1963).

[14] C. B. Pierce, Phys. Rev. **135**, A83 (1964).

[15] J. R. Hardy and S. D. Smith, Phil. Mag. **6**, 1163 (1961).

whereas in synthetic diamond the spectra suggest that the distribution of donors and acceptors generally possess much less mutual correlation. This distinction probably arises from the wide difference likely between the growth conditions of natural and synthetic diamonds, and is consistent with the relatively fast growth of synthetic specimens. Natural and synthetic (aluminum-doped) semiconducting specimens show spectral evidence of both types of donor-acceptor distributions.

The spectral position of a newly discovered Mössbauer-type emission spectrum, which has been found to be particularly strong in the cathodoluminescence spectra of nitrogen-doped G.E. synthetic diamond, suggests that it arises from the annihilation of indirect gap excitons deeply bound to the ionized donor centers which are involved in the pair spectrum. These donor centers have been detected in natural[40] and synthetic[22] diamond by electron-spin-resonance measurements. Analysis of the luminescence and thermoluminescence of natural semiconducting diamonds shows that the acceptor center from the band-*A* pair spectrum is identical with the shallow acceptor center observed electrically and in the infrared absorption spectrum.[16] Using activation analysis techniques, this center has been identified with isolated substitutional aluminum.[17]

The luminescence properties of type-I specimens which have been irradiated by fast electrons (energy ~0.5 MeV) are briefly reviewed and possible pair recombinations are identified which involve donor and acceptor centers introduced by the radiation damage.[18] Additional structure is tentatively associated with bound indirect gap exciton transitions at these ionized donor and acceptor centers. Identifications arising from the present work are summarized in Sec. IV, Table II.

II. RESULTS

A. Photoluminescence Spectra

Much of the relevant experimental information has already been published.[4–6,8] The previously reported band-*A* photoluminescence spectra were obtained using an $f/4$ double-passed monochromator fitted with an EM1 type 9558 red-sensitive glass-window photomultiplier, cooled to 80°K. The sharp structure observed near the high-energy limit of the emission band was more prominent for excitation energies below the *N*9-system doublet at 5.26 eV (Fig. 1). Curve A shows evidence of phonon structure below ~3.0 eV. The phonon energy given from the separation of the broad peaks is 0.16±0.01 eV.

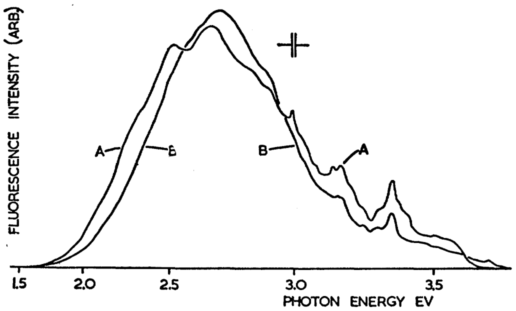

FIG. 1. Band-*A* photoluminescence spectra of specimen *DS*21 (*N*3 fluorescent), 80°K. Curve A—4.9-eV excitation. Curve B—5.3-eV excitation.

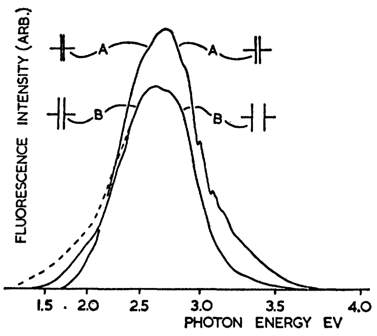

FIG. 2. X-ray-excited band-*A* luminescence spectra from specimen *DS*21, 80°K. X-ray tube voltage 45 kV. Curve A—x-ray tube current 45 mA. Curve B—x-ray tube current 2 mA. (At 45 mA x-ray flux ~10^5 R/h.)

B. X-Ray–Excited Luminescence Spectra

1. *Nonsemiconducting Specimens*

A photographic-plate spectrograph was employed in the most extensive previous investigation of x-ray–excited luminescence in diamond.[3] Typical emission spectra obtained in the present work, using photoelectric recording with an EM1 type 9558Q quartz-window photomultiplier, are shown in Fig. 2. The spectrum recorded under the highest available x-ray flux (curve A) is clearly displaced to the high-energy side of the spectrum excited by a low x-ray flux (by ~0.1 eV for the high-energy threshold and at the peak intensity near 2.7 eV). The detailed dependence of the energy at which the peak intensity of the spectrum occurs on the magnitude of the x-ray flux is shown in Fig. 3 for two

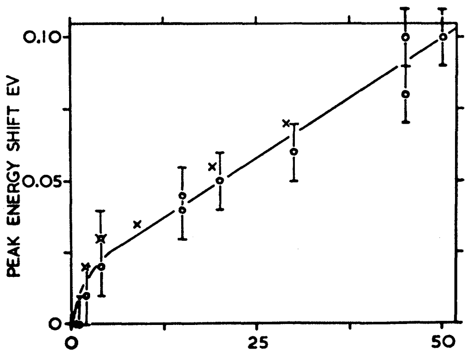

FIG. 3. Dependence of quantum energy of intensity peak of x-ray–excited band-*A* luminescence spectrum on intensity of x-ray beam (tube current). ○—points, specimen *DS*21; ×—points, specimen *SL*78; 80°K. Ordinate zero = 2.640 eV for *DS*21; 2.605 eV for *SL*78.

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[16] I. G. Austin and R. Wolfe, Proc. Phys. Soc. (London) **B69**, 329 (1956).

[17] E. C. Lightowlers, Ph.D. thesis, London, 1964 (unpublished).

[18] H. B. Dyer and L. du Preez (private communication).

specimens. Curve A of Fig. 2 shows weak evidence of the *N*3 main line at 3.00 eV and the first associated phonon-emission band at ~2.90 eV, and also sharp structure at 3.15 eV. The latter line is coincident in position with the sharp line, which is enhanced by radiation damage, reported by Ralph in cathodoluminescence spectra,[19] and recently found to occur in irradiated type-I diamond as the zero-phonon line of an absorption system which is independent of the *N*3 system.[18] This structure is weakly superimposed upon the band-*A* emission in Fig. 2 and was only shown by specimens which fluoresced strongly under 3.4-eV excitation. Although emission in Fig. 2 is observed over roughly the same energy range as in Fig. 1, there is no trace of the structure shown in Fig. 1 between 3.0 and 3.5 eV. This is consistent with the observation that the visibility of this structure in the photoluminescence spectra becomes less as the quantum energy of the exciting radiation increases towards the threshold of strong intrinsic absorption, and also with the absence of this structure in the cathodoluminescence of α-particle–excited luminescence spectra.[5]

The photoelectrically recorded spectra show no trace of the broad minimum at 2.5 eV reported by Matthews for the x-ray fluorescence spectra of unirradiated type-I and type-IIa specimens.[3] This feature and the rapid attenuation of the spectra at energies $\gtrsim 3.0$ eV are artifacts of the energy-sensitivity curves of the photographic plates. The same effect occurs in previously published α-particle–excited and cathodoluminescence spectra.[5] Uncorrected photoelectric spectra are shown in Fig. 4. At photon energies $\lesssim 2.5$ eV the luminescence emission spectra of irradiated and annealed type-I diamonds are genuinely enhanced relative to the spectra from unirradiated specimens even for α-particle excitation (compare curves A and C of Fig. 4). This effect augments the energy sensitivity artifact in photographically recorded spectra.[3,5,19]

The spectra of Fig. 4 are severely attenuated on the low-energy side by the response curve of the photomultiplier (EM1 type 9502S) and on the high-energy side by absorption in the dense-flint prism. In spite of this, comparison of curves A and B again shows that the intensity distribution of the emission is shifted towards high energies under high (α-particle) excitation densities relative to much lower (β-particle) densities. The low-energy tails of all of the photoelectrically recorded spectra suffer some attenuation by the response curve of the detector, although the magnitude of the effect is small for the red-sensitive photomultiplier (estimated by the dotted line in Figs. 2, 5, 7, and 9). Recent measurements of the band-*A* spectrum from synthetic diamond using a PbS detector confirm that the low-energy limit of the main cathodoluminescence emission band lies near 1.4 eV. A very weak featureless tail extends to ~0.65 eV after a pronounced point of inflexion near 1.4 eV.

2. *Semiconducting Specimens*

The emission spectra of four semiconducting specimens were recorded. These spectra are distinguished at 80°K by the presence of *two* broad bands whose peaks occur at ~2.2 and 2.8 eV. The relative intensities of the 2.2- and 2.8-eV bands appear to be roughly related to the percentage of un-ionized acceptors in the specimen (Fig. 5), and the peak of the 2.2-eV band moves to higher energies as it increases in strength relative to the 2.8-eV band. The 2.8-eV band is considerably narrower (half-width 0.35 eV) than the single band observed in nonsemiconducting natural specimens (0.75 eV). The oscillatory structure characteristic of phonon-assisted transitions is generally more evident in these spectra, and sometimes appears on both bands (Fig. 5, curve A). Figure 6 shows that similar oscillatory structure may

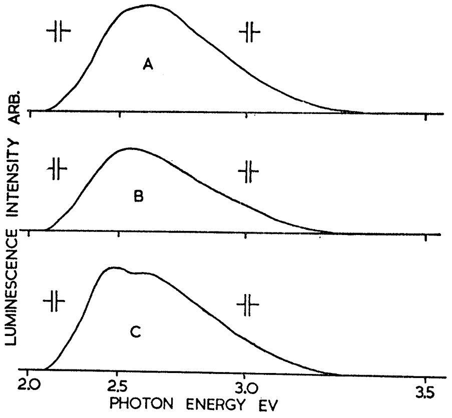

FIG. 4. Charged-particle–excited band-*A* emission spectra, 295°K. Curve A—specimen *S*5 (type I) excited by 5-MeV α particles; peak intensity 2.510 eV. Curve B—specimen *S*5 excited by 2-MeV β particles; peak intensity 2.505 eV. Curve C—specimen Co7 (type IIa, irradiated by 13-MeV electrons—dose ~10^{18} electrons/cm^2, and annealed) excited by 5-MeV α particles; peak intensities 2.510, 2.470 eV.

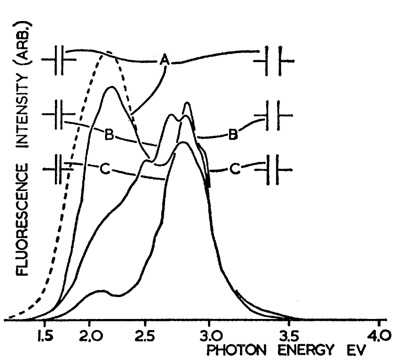

FIG. 5. X-ray–excited band-*A* luminescence spectra from semiconducting diamond, 80°K. X-ray tube voltage 45-kV, current ~30 mA. Curve A—specimen *A*100 ($N_A-N_D=2.6\times10^{16}$ cm^{-3}). Curve B—specimen *E*4 ($N_A-N_D=0.66\cdot10^{16}$ cm^{-3}). Curve C—specimen *CS*1 ($N_A-N_D=1.5\times10^{16}$ cm^{-3}). N_A-N_D = concentration of uncompensated acceptors.

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[19] J. E. Ralph, Proc. Phys. Soc. (London) **76**, 688 (1960).

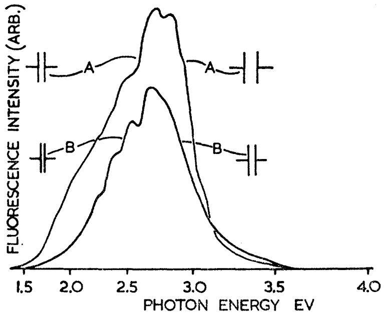

FIG. 6. X-ray-excited band-*A* luminescence spectra from diamond, 80°K. X-ray tube voltage 45 kV. Curve A—specimen *E*4 (type IIb), x-ray tube current 45 mA. Curve B—specimen *DS*21 (type I), x-ray tube current 4 mA.

also be observed for nonsemiconducting specimens under low densities of excitation. The phonon energy deduced from the spacing between emission maxima is 0.16±0.01 eV. This structure appears to be similar to, but not quite identical with, some of the structure found by Matthews.[3] The spectral resolution of Figs. 5, 6, and 7 was not sufficient to enable bands separated by <0.05 eV to be adequately resolved.

The intensity ratio of the 2.8- and 2.2-eV bands increased with increase in the magnitude of the x-ray flux (Figs. 7 and 8). Increase of temperature between 80 and 200°K caused the two emission bands to move to lower energies by $\sim 0.05 \rightarrow 0.1$ eV, without significant change in their relative intensity (Fig. 9). A radical change in the intensity distribution within the spectrum occurred between 200 and 295°K, however. The peak intensity of the 295°K spectrum is at 2.55 eV, and the high-energy band observed at lower temperatures now appears as a weak shoulder at $\sim$2.7 eV. The total emission intensities at 80 and 295°K were in the ratio of $\sim$2.1.

C. Rise and Decay Time of the X-Ray-Excited Luminescence

The mean decay time of band-*A* photoluminescence excited in the intrinsic absorption bands at 80°K has been reported to be 10 msec for emission quanta $\sim 1.8\ \mathrm{eV} \lesssim h\nu \lesssim 3.1$ eV.[8] It was also known qualitatively that uncompensated acceptor centers influence the decay time of the edge-excited luminescence in diamond.[4] In view of the inter-relationship of the emission energy and the decay time expected for luminescence from donor-acceptor pairs (Sec. IIIB1) it was useful to obtain detailed decay time measurements.

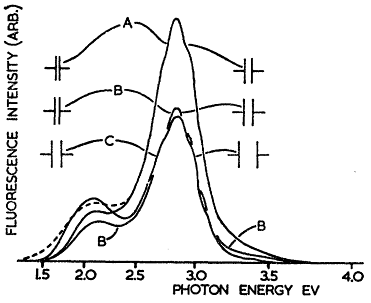

FIG. 7. X-ray-excited band-*A* luminescence spectra from semiconducting diamond, *CS*2, 80°K—variation of emission spectrum with x-ray beam intensity (tube current). X-ray tube voltage 45 kV. Curve A—x-ray tube current 30 mA. Curve B—x-ray tube current 10 mA. Curve C—x-ray tube current 3 mA.

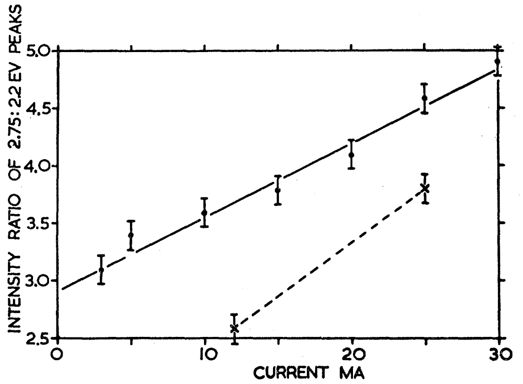

FIG. 8. Intensity ratio of peak heights in the x-ray-excited band-*A* luminescence spectra of semiconducting diamond as a function of the x-ray beam intensity (tube current). ● points—specimen *CS*2, 80°K. ✕ points—specimen *CS*2, 200°K.

The x-ray beam was periodically interrupted by a segmented wheel before striking the specimen, and the resulting pulsed luminescence, after passage through one of three different optical filters, was detected by an EM1 type 6256B photomultiplier. The photomultiplier output signal was displayed on a Tektronix type 545 oscilloscope. Rise and decay times $\tau > 0.5$ msec could be measured. Wratten filters 15, 47B, and 18A were used to divide the spectrum into three energy intervals: $2.0 \rightarrow 2.4$ eV, $2.4 \rightarrow 3.3$ eV, and 3.1 to 4.2 eV (spectral regions A, B, and C). Measurements were made on semiconducting specimens (type IIb) and on type IIa, intermediate type and type I[20] nonsemiconducting specimens at 80, 200, and 295°K.

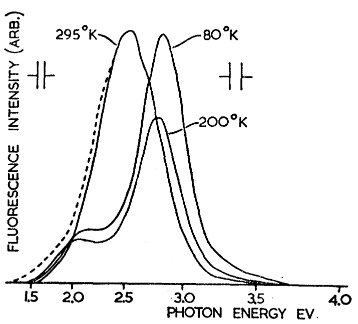

FIG. 9. X-ray-excited band-*A* luminescence spectra from semiconducting diamond—variation of emission spectrum with temperature. X-ray tube voltage 45 kV, tube current 25 mA.

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[20] The classification of natural diamond with respect to absorption spectra is discussed in Refs. 9 and 42.

1. *Nonsemiconducting Specimens*

The rise and decay times for high x-ray fluxes were complex in general with usually at least two clearly differentiated components present, typically of $\tau<1$ msec and $\tau\gtrsim 50$ msec duration (the "fast" and "slow" components). The decay times will be quoted as the time taken for the intensity to drop to e^{-1} of the initial value, although the shape of the decay curves was generally nonexponential. The slow components, which were reliably recorded, exhibited a slower than exponential decay time. Measurements at low x-ray flux showed a larger fraction of slow decay component than at high flux and usually tended to equalize the rise and decay times. At high x-ray fluxes the proportion of fast component was much larger in the rise time than in the decay time. This suggested that the recombination statistics are not monomolecular in agreement with expectation from the interpretation of the band-*A* emission (Sec. IIIB). The slow component decay time decreased with increase of temperature, particularly between 80 and 200°K, and at 295°K the decay curves were more nearly exponential.

For the type-IIa specimen there was a strong correlation between the spectral region of the emission and the magnitude of the decay time. The proportion of the slow component and the magnitudes of the fast and slow decay times all decreased in going from spectral region A through B to region C. The slow component predominated in region A and was entirely absent in region C. A similar trend was observed for the intermediate and type-I specimens, although a significant fraction of slow component was observed in region C and of the fast component in region A. The magnitude of the slow-component decay times in regions A and B were very similar.

2. *Semiconducting Specimens*

Four specimens were studied. Except for one (*E*4) the recombination kinetics were distinguished from those of nonsemiconducting specimens by the presence of a significant very slow decay component at temperatures $\gtrsim 250$°K. The decay time decreased rapidly with increase in temperature and at 295°K was ~ 10 sec. Similar effects have been reported in the photoluminescence of type-IIb diamond,[4,21] and are due to the thermal liberation of holes from the uncompensated acceptor centers. The exceptional specimen had a very low density of uncompensated acceptors, since it had been irradiated by fast neutrons and annealed. Figure 5, curve B shows that the 2.2-eV peak was very weak for this specimen. The very slow component was absent in spectral region C and relatively strongest in spectral region A.

At 80°K fast ($\tau<1$ msec) and slow ($\tau\gtrsim 1$ sec) components were present even in region C, although the slow component was again most prominent in region A. Between 295 and 80°K the luminescence from specimen *CS*2 increased by 0.8×, 2.3×, and 4.5× in regions A, B, and C, with an initial decrease to 0.5× at $\lesssim 250$°K for regions A and B. For specimen *E*4 the corresponding increase was 2× and 2.5× for regions A and B. Figures 5 and 6 show that for this specimen region A is dominated by emission having the characteristics of transitions within region B, but shifted into region A by multiple phonon emission.

D. Cathodoluminescence Spectra of Natural and Synthetic Diamond

1. *Comparison of the Band-A Spectra*

Typical band-*A* cathodoluminescence spectra of natural type-IIa and type-IIb and synthetic diamond are shown in Fig. 10. The broad spectrum from the type-IIa specimen is consistent with the x-ray–excited spectra from similar specimens, although the peak is shifted from ~ 2.8 eV to nearly 3.1 eV and the high-energy tail extends to nearly 4 eV. The spectra obtained from a few specimens under the highest available densities of excitation show appreciable band-*A* luminescence at energies above 4 eV.

The natural semiconducting specimen exhibited a narrower luminescence peak at 2.8 eV. This is similar to the higher energy peak observed under x-ray excitation (Figs. 5 and 7), but there is no trace of the 2.2-eV peak also present for the lower density x-ray excitation. The sharp line at 2.53 eV is often present in the cathodoluminescence spectra of type-IIb specimens and would not have been detected in the x-ray–excited luminescence spectra because of the considerably poorer resolution attainable in these spectra.

The cathodoluminescence spectrum of the G.E. synthetic diamond shown in Fig. 10 is typical of those obtained from G.E., Swedish (ASEA), and Irish (Industrial Distributors) synthetic diamond, except that the

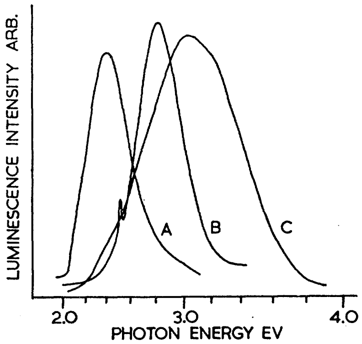

FIG. 10. Band-*A* cathodoluminescence spectra from diamond, $\sim$100°K. Curve A—specimen *C*2 (G.E. synthetic) 60 kV, 5-μA electron beam. Curve B—specimen *CS*2 (type IIb) 30 kV, 20-μA electron beam. Curve C—specimen *K*82 (intermediate type) 50 kV, 45-μA electron beam. Electron beam focused onto area $\sim$0.5-mm diam.

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[21] J. F. H. Custers, Physica 18, 489 (1952).

spectra of the Irish specimens are dominated by very strong $H3$ system emission which has a characteristic Mössbauer-type spectrum (Sec. I). The 2.14-eV emission system[19] was also present. No emission close to the intrinsic absorption edge of diamond[47] was observed for specimens showing the $H3$ visible system. The featureless spectrum shown in Fig. 10, curve A has a peak at $\sim$2.4 eV and is similar to the low-energy peak of the x-ray–excited spectra of natural IIb specimens (Fig. 7). The whole low-energy side of the spectrum is attenuated by the energy-sensitivity function of the EM1 6256B photomultiplier detector. Measurements with a PbS photoconductive detector have shown that the low-energy threshold of the band-A cathodoluminescence spectrum of synthetic diamond is at $\sim$1.4 eV and the peak energy is $\sim$2.1 eV.

The spectral differences between the band-A luminescence natural and synthetic specimens are clearly visible to the eye, since the majority of natural specimens luminesce a deep blue color, whereas the synthetic specimens all exhibit an intense green luminescence under electron-beam stimulation. However, type-I natural diamonds which have suffered heavy electron or neutron radiation damage and which have been subsequently annealed at $\gtrsim$500°C can also show intense green cathodoluminescence due to the induced $H3$ or $H4$ system. Natural and synthetic specimens can be clearly distinguished by their cathodoluminescence spectra only if the synthetic specimens produce a spectrum like that shown in Fig. 10, curve A rather than the $H3$ spectrum. We have never observed a spectrum like Fig. 10, curve A from a natural specimen.

Similar but less pronounced differences have been observed between the edge-excited photoluminescence spectra of natural and synthetic diamond.[7] The interpretation of these measurements is complicated by the interference due to the spectral sensitivity of the photographic plate (Sec. IIB1), and the luminescence was weak and difficult to record. It was not possible to obtain x-ray–excited luminescence spectra from synthetic specimens because of the very small size of these crystals (usually $\ll$0.5 mm^3).

2. *New Mössbauer-Type Spectrum*

The cathodoluminescence spectra of synthetic specimens has recently been studied in the energy range 0.5 eV$\lesssim h\nu \lesssim$3 eV using a PbS photodetector. A new Mössbauer-type emission system was discovered with the principal, zero-phonon line at 1.40 eV. The new emission spectrum is compared with the well-known $N3$ emission spectrum in Fig. 11. D_0 denotes the zero-phonon lines and D_1 and D_8 denote fine structure in the phonon-assisted wings of the spectra. The presence of this structure indicates that certain phonons interact particularly strongly with the electronic transitions. The subsidiary peaks in Fig. 11 suggest that phonons of energy $\sim$70 and $\sim$90 meV are significant in the 1.40-eV transition. The $N3$ transition is apparently strongly coupled to phonons of $\sim$80 meV (D_2, D_4, etc.) and weakly coupled to phonons of energy $\sim$40 meV (D_1 and D_3, etc.). The H_3, H_4, $GR1$[9,10] and 2.14 eV (5755 Å)[19] Mössbauer-type spectra all show evidence of strong interaction with phonons of energy $\sim$40 meV. The intensity ratio of the phonon-assisted to the zero-phonon spectral regions is $\sim$50:1 for the $N3$ system, but only $\sim$5:1 for the 1.40-eV system.

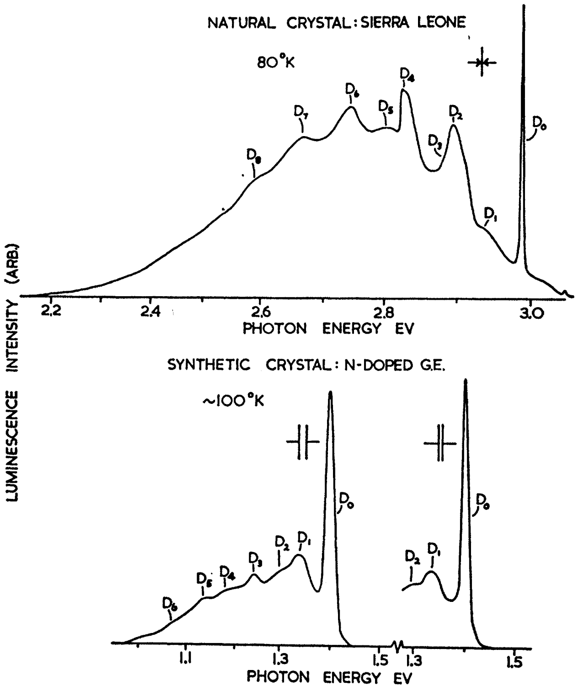

FIG. 11. *Upper spectrum:* $N3$ photoluminescence spectrum from a natural diamond. Transition D_0 is zero-phonon, $D_1 \rightarrow D_8$ are discussed in the text. *Lower spectra:* 1.40-eV cathodoluminescence system exhibited by a nitrogen-doped G.E. synthetic diamond. The second (right-hand) spectrum shows the natural width of the zero-phonon line D_0 and was recorded with a relatively poor signal/noise ratio.

The 1.40-eV emission spectrum was especially prominent in spectra from G.E. nickel-catalyst synthetic diamond which had been doped with nitrogen ($\sim$60 mesh golden-yellow octahedra). Similar specimens have been found to contain $\sim$0.05% of nitrogen, much of it in the electron-spin-resonance-active isolated substitutional form.[22] We hope soon to extend these near-infrared luminescence measurements to natural specimens (Sec. III D 2).

III. DISCUSSION

A. Notation

Photoabsorption and photoluminescence of excitons bound to neutral and/or ionized donors and acceptors

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[22] C. M. Huggins and P. Cannon, Nature **194**, 829 (1962).

TABLE I. Notation for exciton-impurity complexes.

Symbol	Identity
e or h	Free electron or hole
x	Free exciton (binding energy E_x)
①D or ①A	Ionized donor or acceptor (binding energies E_D and E_A)
②D or ②A	Neutral donor or acceptor
③D or ③A	Exciton bound to ionized donor or acceptor
④D or ④A	Exciton bound to neutral donor or acceptor
②DA_n	Ionized donor-acceptor pair
④DA_n	Exciton bound to ionized donor-acceptor pair, i.e., a neutral donor-acceptor pair. $n=1,2$—r denotes pair separation (nearest neighbor, second nearest neighbor, etc.) for substitutional donor and acceptor.

have been reported for a number of materials.[23–25] We adopt a notation for these electronic centers consistent with that used by Hamilton, Choyke, and Patrick[25] but extended (Table I) to cope with excitation complexes bound to double-lattice-site centers (donor-acceptor pairs). Photoluminescence due to recombinations at DA pairs has been detected in GaP[26] (indirect gap). In this material structure has not been detected for pair separations less than ~10 Å, essentially because of the large extent of the ground-state wave functions of the relevant effective-mass-like donors and acceptors. Edge photoluminescence has been attributed to nearest-neighbor DA pairs in ZnS[27] and in SiC,[28] although one of the two spectral modifications thus identified in SiC has since been attributed to a ③D complex involving nitrogen donors. Fine structure due to luminescence of highly associated ④DA_n centers ($n=1$ to 5) has recently been observed in fluorite.[29]

B. Identification of Band-*A* Emission with *DA* Pair Recombinations

The energy available for luminescence when an electron on a neutral donor recombines directly with a hole on a neutral acceptor (transition ④$DA_n \rightarrow$ ②DA_n) is[26]

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{\epsilon r} - \frac{e}{\epsilon}\frac{a^5}{r^6}, \tag{1}$$

where E_g is the energy gap, e is the electronic charge, ϵ is the static dielectric constant, a is an adjustable parameter in the polarization term, and r is the distance between the donor and acceptor. Neglecting the polarization term, this formula is essentially derived using the simplest assumptions of the effective-mass theory of impurity states. More complicated expressions involving the detailed wave function of the impurity centers are necessary to properly describe the energy states of an exciton bound to a nearest-neighbor pair,[30] although the simple formula without the polarization term holds surprisingly well for transition at pairs with $n=2$ to 5 in fluorite.[29] We regard the energy difference $h\nu - [E_g - (E_A + E_D)]$ as an experimentally determined parameter $f(r)$ for excitons bound to ②DA_1 pairs in Sec. III D 2.

The individual pair lines have not yet been classified in the band-A emission spectrum of diamond. It is likely that the structure resolved at ~3.15 and ~3.4 eV in Fig. 1 arises from transitions of more complicated centers than ④DA_n, for example those involving more than one nitrogen atom (see Sec. III F for the 3.15-eV transition). Poorly resolved line structure has recently been seen between ~2.5 and ~3 eV in the cathodoluminescence spectra of aluminum-doped G.E. synthetic diamond, and probably represents discrete pair recombinations. The $N3$ system zero-phonon line (3.0 eV) apparently represents pair transitions at the ②DA_1 center (Sec. III D 2). The long high-energy tail of the band-A emission spectrum of natural diamonds under high excitation densities (Fig. 10) probably contains DA emission involving the 'modified' nitrogen donor also discussed in Sec. III D 2.

The lack of resolved structure for all but the closest pairs appears to be a consequence of the participation of deep donors and acceptors in the recombination process.[30] Comparison of diamond and GaP, using an overlap expression given by Shaffer and Williams[30] and the value of E_A for aluminum acceptors in diamond (0.36 eV), since for diamond the overlap will be mainly determined by the relatively weakly bound acceptor center, predicts that pair lines might be seen out to $n=12$ or 13. The estimated separation of adjacent lines is then only ~6 meV, since pair lines from both type-I and type-II spectra[26] should be present together in the spectra from an elemental semiconductor like diamond which has inversion symmetry. Such fine structure could not be experimentally resolved at present and might even be inherently unresolvable owing to the lack of perfection of the specimens (strain-broadening effects, etc.) or to broadening effects due to the simultaneous interaction of more than two impurity centers. This latter factor may be relatively more important when significant association occurs in the DA pairing.

The identification of the band-A luminescence with recombinations at DA pairs must therefore be tested by other means. The evidence for the identification is reviewed in subsections (1) and (2).

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[23] J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).

[24] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[25] D. R. Hamilton, W. J. Choyke, and L. Patrick, Phys. Rev. **131**, 127 (1963).

[26] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

[27] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956).

[28] W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. **117**, 1430 (1960).

[29] J. R. O'Conner, Appl. Phys. Letters **4**, 126 (1964).

[30] J. Shaffer and F. E. Williams, *Proceedings of the International Conference on Semiconductor Physics* (Dunod Cie., Paris, 1964), p. 811.

1. *Dependence of Emission Spectrum and Decay Time on Excitation Density*

It has been shown in Sec. IIB that the emission spectrum moves to higher energies with increasing excitation density. This is a characteristic pair spectrum effect and is due to the increasing saturation of the recombinations at diffuse pairs relative to those at close pairs. The electron and hole bound to a diffuse pair have a small wave function overlap and therefore a relatively long lifetime against radiative recombination. Equation (1) shows that the pairs with large internal separations are responsible for the low-energy tail of the emission band. The exact position of the peak intensity therefore depends upon the distribution of available pairs as a function of the internal separation r, on the transition probability of a pair of given r, and on the density of the primary excitation. Figure 10 shows band-A emission spectra obtained with electron-beam excitation (50-keV electrons, 30-μA beam current focused onto an area $\sim$0.5 mm diameter). The energy of the peak intensity of the spectrum (curve C) from the intermediate-type natural diamond $K82$ is about 0.5 eV higher than its position under excitation by the lowest useful x-ray flux. The excitation density is $\sim 10^9\times$ greater for the cathodoluminescence spectrum.

The results of the decay time measurements reported in Sec. IIC are also consistent with the behavior expected for DA pair spectra, provided that allowance is made for the effects of the phonon-assisted pair recombinations mentioned in Secs. IIB, IIC, and IIIB. These phonon effects are difficult to resolve in diamond, since the width of the spectrum of zero-phonon transitions is about ten times larger than the energy of the optical phonons which can assist the transitions (the maximum possible value of $e^2/\epsilon r$ is 1.64 eV, the actual overlap energy for the ④DA_1 state may well be appreciably larger than this and is $\sim$1.8 eV according to Sec. IIID2). The resolved phonon structure appears to be due to phonon-assisted recombinations at close pairs, as would be anticipated (Sec. III D). These spectral features do not overlap appreciably in GaP.[26]

At 80°K the observed decay time varies between <0.5 msec at $h\nu\gtrsim 3.2$ eV to >100 msec for $h\nu\lesssim 2.3$ eV. The exact values are dependent upon the particular type of specimen studied, as would be expected from the spectral variations shown in Fig. 10, and also to a smaller extent upon the particular specimen of a given type. More measurements will have to be made before a precise analysis of the decay times is warranted. $h\nu\sim 3.0$ eV corresponds to pairs with $n=1$ (Sec. IIID2), whereas $h\nu\sim 2.1$ eV (the corrected value of the low-energy emission peak) corresponds to pairs with $n\sim 5$, according to Eq. (1). For such close pairs in diamond, the value of $h\nu-[E_g-(E_A+E_D)]$ will be considerably larger than $e^2/\epsilon r$, since the effective value of ϵ will become much less than the low-frequency dielectric constant and this effect will outweigh the opposite effect of the polarization term in Eq. (1). Thus large values of $h\nu-[E_g-(E_A+E_D)]$ will be obtained for pairs with low n. The discrepancy between this quantity and $e^2/\epsilon r$ may be expected to increase very rapidly as n decreases below $\sim$5 (i.e., r decreases below $\sim$4 Å). This discrepancy with the effective mass formula [Eq. (1)] is of similar origin to that observed in the values of E_D or E_A for tightly bound donor and acceptor centers. The values of n quoted above will tend to be low, therefore.

Appreciable emission has been observed within 0.2 eV of the 1.4-eV low-energy threshold (Sec. IID1). The spectrum should be accurately described by Eq. (1) in this region, since if $e^2/\epsilon r \doteq 0.2$ eV, $r\sim 12.5$ Å and we are dealing with transitions at pairs with $n\sim 50$. The radiation is predicted to have a very long decay time for such diffuse pairs, but decay times have not yet been measured for $h\nu<2.0$ eV.

2. *Temperature Dependence of Emission Intensity and Decay Time*

Provided that the temperature is sufficiently low so that the donors and acceptors remain thermally un-ionized over the average decay time of the pair spectrum, changes of temperature will have little effect either on the over-all luminescence intensity or the decay time. If a given donor or acceptor can be thermally ionized before pair recombination occurs, then the integrated intensity of the luminescence may be reduced since the mobile carrier may be retrapped at a nonradiative recombination center. The average decay time of the emission will also be reduced as usual for any center which can be phenomenologically described by a configurational coordinate model with a thermally activated radiationless de-excitation process for the excited state.[31] The band-A luminescence has already been described in this way[8] and it has been found that the activation energy for the thermal process is 0.36±0.02 eV. This is an average value for photon energies between 1.8 and 3.1 eV and within the accuracy of the data is identical with the thermal and optical activation energy of the acceptors in semiconducting diamond.[32]

Semiconducting diamonds are distinguished by containing a significant concentration of uncompensated acceptors, but analysis of the Hall effect shows that at least 10% of the total acceptor concentration generally remains compensated by donors. We can therefore divide the acceptor population into two classes; namely, those which are spatially near to donor centers and are compensated by them in the unexcited crystal at low-temperature (class A), and the class-B centers which are relatively remote from the donors and are neutral in the unexcited crystal at low temperature (below

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[31] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).

[32] A. Halperin and J. Nahum, J. Phys. Chem. Solids **18**, 297 (1961).

~200°K according to the Hall data). It is proposed that the 2.8-eV luminescence peak shown in Figs. 5, 7, and 9 is due to recombinations involving class-A acceptors, while the 2.1-eV peak is due to class-B acceptors. As the temperature is increased, particularly above 200°K, the holes can be thermally liberated from the class-B acceptors well before radiative recombination with an electron at a relatively remote neutral donor can occur. It is then more probable that luminescence will be observed when the hole is retrapped at an acceptor belonging to a relatively close pair, since the radiative decay time is comparatively short. At these temperatures very close pairs are not favored because the value of E_A is significantly reduced by the donor-acceptor overlap [Eq. (1)] and the probability of thermal rerelease of the holes is relatively large. This accounts for the intermediate position[33] of the peak intensity at 295°K (Fig. 9).

From the comments given in Sec. IIIB1 it follows that the 2.8- and 2.1-eV emission peaks correspond to transitions at pairs with $n \gtrsim 1$ and $n \gtrsim 4$. Thus both peaks correspond to transitions at relatively closely associated pairs. The minimum near 2.4 eV in the low-temperature spectra (Fig. 7) corresponds to $n \gtrsim 2$. The experimental results therefore suggest that the 2.8-eV band corresponds to transitions at nearest-neighbor pairs, which can be resolved from those at more diffuse pairs ($h\nu \lesssim 2.4$ eV) only in type-IIb diamonds. The donor-acceptor pair properties of type-IIb diamonds are therefore much simpler than those of nonsemiconducting diamond, and are apparently largely determined by a single donor and acceptor center. The high-energy tail of the 2.8-eV emission band at 80°K (Fig. 9) suggests that the radiative transition occurs before the hole reaches the ground state of the pair acceptor center.

The much broader band-*A* emission band observed for natural nonsemiconducting diamond suggests the presence of associated *D-D-A* and more complex structures. These complexes are very likely to form, particularly when there is an excess of donor centers, in view of the properties of nitrogen in type-I diamond.[34]

It is possible that the additional low values of E_A, particularly that at 0.21 eV, reported by Halperin[35] may be due to the effect of *DA* overlap. Usually the optical characteristics of ④DA_1 centers (Sec. IIID2) are very weak in semiconducting diamond, but in a given specimen sufficient ④DA_1 centers may be present to account for the magnitude of the weak 140°K (0.21-eV) thermoluminescence peak.[36] The effect of the decrease in the value of E_A for the close pairs can also be seen in the band-*A* spectra of nonsemiconducting diamond. For example, Fig. 6 of Ref. 5 shows quite clearly the increasing relative attenuation of the high-energy tail of the cathodoluminescence spectrum with increase in temperature from 90 to >400°K. A similar effect has been noted for x-ray–stimulated band-*A* luminescence. The value of E_D is so large (Sec. IIIC) that the electrons remain bound to the donors at all available temperatures until radiative pair recombination occurs.

The temperature dependence of the spectra shown in Fig. 9, the role of acceptor centers in the thermoluminescence of semiconducting diamond, and the presence of the long decay component in the band-*A* luminescence edge excitation spectra of type-IIb specimens can therefore all be accounted for on the pair spectra model. The fact that radiative electron-hole recombinations are apparently possible both at close pairs and at diffuse pairs in diamond may be due to the chance coincidence that one pair impurity center has a strongly localized electronic ground state, whereas the other pair center is quasieffective-mass-like.[26,30] It appears probable that the donor centers deduced from the Hall-effect measurements on natural semiconducting specimens are those which take part in the pair spectra. Those donors are likely to be due to impurities since the additional donors introduced by threshold electron radiation damage[8,37] do not promote similar radiative recombinations in type-IIb specimens.

The proposed identification of the two peaks in the x-ray–induced luminescence spectra of natural type-IIb diamonds is supported by recent cathodoluminescence experiments. Cathodoluminescence spectra from natural type-IIb specimens contain only the high-energy peak (e.g., Fig. 10, curve B) presumably because the excitation density due to the electron beam is $\sim 10^8$ times higher than under the x-ray excitation conditions employed for Fig. 7. The 100°K spectra from aluminum-doped G.E. synthetic diamond showed both peaks, however, indicating on the above interpretation that the density of ionized (compensated) aluminum acceptor centers is much higher than in the natural IIb specimens. Activation analysis suggests that the aluminum concentration of these specimens is in fact $\sim 1000\times$ larger than for the natural specimens. It was found that a ~twenty-fold increase in the electron-beam current (at constant accelerating voltage) caused the intensity ratio of the 2.83- to 2.38-eV peaks to increase from 0.42:1 to 2.8:1. The peak energies also shifted slightly to higher energy with increase in the beam current. This large change in the peak intensity ratio is consistent with the conclusion that both are due to transitions at relatively close pairs (Sec. IIIB1).

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[33] The room-temperature electroluminescence spectra and the emission spectrum of the 240°K thermoluminescence peak also exhibit maxima near 2.6 eV (Ref. 32).

[34] T. Evans and C. Phaal, Proc. Roy. Soc. (London) **A270**, 538 (1962).

[35] J. Nahum and A. Halperin, J. Phys. Chem. Solids **24**, 823 (1963).

[36] In confirmation of this hypothesis, analysis of the temperature dependence of the mean decay times of the 2.8- and 2.1-eV bands (for $h\nu \gtrsim 2.0$ eV) between 275 and ~400°K yielded thermal activation energies for the radiationless de-excitation process of ~0.2 and ~0.35 eV, respectively.

[37] C. D. Clark, P. J. Kemmy, and E. W. J. Mitchell, Discussions Faraday Soc. **31**, 96 (1961).

C. Identification of the Donor Center

Equation (1) shows that if the point in the spectrum where $e^2/\epsilon r \rightarrow 0$ can be identified, then the value of E_A+E_D can be calculated, if E_g is known. The lowest value of E_g in diamond corresponds to indirect transitions[38] and it is this gap which should be used in Eq. (1), at least for recombinations at pairs of large separation.[26] The absence of absorption features corresponding to the band-A emission spectrum is consistent with the fact that the luminescence transitions are indirect. E_g is 5.48 eV at 80°K.[38] By analogy with GaP,[26] the value of $E_g-(E_A+E_D)$ is expected to lie close to the low-energy tail of the emission band, allowing for phonon-assisted transitions. Figures 1, 2, 5, 6, 7, and 9 show that $E_g-(E_A+E_D)$ is therefore probably close to 1.4 eV. Taking $E_A=0.36$ eV, we therefore obtain

$$E_D=5.48-0.36-1.4=3.9 \text{ eV}.^{39} \qquad (2)$$

This represents an extremely localized (noneffective-mass) center. No effective-mass-like donor centers have ever been detected in natural or synthetic diamond. This large activation energy is consistent with the very localized nitrogen donor center located by electron-spin resonance.[40] Since it is known that nitrogen is a sufficiently important impurity in diamond to account for the persistence of the band-A emission, it is tempting to identify the pair spectrum donor with isolated substitutional nitrogen. (See Sec. III D.)

Activation-analysis studies[41] have shown that both aluminum and nitrogen are always present in concentrations sufficient to account for the intensity of the band-A emission ($\sim$1 ppm). The bulk of the very large nitrogen concentration found in type-I diamonds[42] does not take part in the pair spectra since these nitrogens are associated together on $\langle 100\rangle$ planes[34] and produce nonradiative defects. It would be expected that a large concentration of isolated (or DA-paired) nitrogen will generally be found together with the large over-all concentration of nitrogen in strongly type-I specimens, and this is consistent with the experimental result that band-A emission is usually strong in these specimens. Intermediate-type natural specimens also show strong band-A emission and apparently have appreciable concentrations ($\gtrsim$10 ppm) of close pairs (Sec. III D) but few nitrogen platelets.

The presence of appreciable concentrations of close DA pairs in natural, but not in synthetic diamond (Sec. IIIE), is consistent with the fact that associated nitrogen structures ($\langle 100\rangle$ platelets) are a common property of natural diamond but have not yet been demonstrated as a prominent feature of synthetic diamond.[43,44]

D. Bound Excitons and Pair Spectra in Diamond

1. *The 1.40-eV Emission System*

The properties of the 1.40-eV emission system, discussed in Sec. II D 2, suggest that it may be connected with the isolated nitrogen donor center. The zero-phonon line might correspond to an electronic transition between two localized states of the center, but the low transition energy compared with the value of E_D obtained from Eq. (2) makes this appear unlikely. The 1.40-eV line is too sharp (half-width $\lesssim$10 meV) to be accounted for by electron transitions from the valence-band states to the donor ground-state level. Analogy with the properties of sharp electronic spectra in other materials (e.g., ZnTe),[45] and the spectral position of the zero-phonon line suggests an association with an indirect exciton tightly bound to the *ionized* nitrogen donor. The donors in the nitrogen-doped synthetic specimens may be mainly neutral in the unexcited specimen, but the intense electron-beam excitation is likely to produce a high concentration of ionized donors. The nitrogen-doped specimens did not luminesce appreciably under 3.4-eV excitation which cannot produce the transition ②$D \rightarrow$ ①D. The transition energy $h\nu$ is then

$$h=E_g-E_D+\Delta=1.58-\Delta \text{ eV}, \qquad (3)$$

where Δ represents the binding energy of the hole to the neutral donor ($\ll E_D$).[46] The way in which the value of E_D used in Eq. (3) is calculated [Eq. (2)] suggests that it may have been slightly underestimated, not overestimated. Thus the value of Δ given by direct comparison of Eq. (3) with experiment (0.18 eV) may be appreciably overestimated. However, a value of $\Delta \lesssim E_D/20$ appears to be plausible in view of the comments of Sec. III D 2 concerning the binding energy of holes at neutral donor centers. It is probable that ③D luminescence from these deep donors is seen under band-gap excitation because of an indirect process in which the DA pair luminescence is absorbed at the ①D donor centers. Similar effects have been observed for the $N3$ system in natural diamond,[5] but the effects are there complicated by the overlap of the two *emission* spectra.

The intrinsic and extrinsic components of the edge-recombination radiation spectrum[47] were not detectable when the 1.40-eV emission system was strongly present. The band-A spectrum was very strong, however, and its spectral position and strength (Secs. III B 1 and

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[38] C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) **A277**, 312 (1964).

[39] This deep donor level may be responsible for the $\sim$1.5-eV hole trapping level which is an important feature of type-I diamond, but is also present for type-IIa specimens. (See Ref. 35.)

[40] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).

[41] E. C. Lightowlers (private communication).

[42] W. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).

[43] J. J. Charette, J. Chem. Phys. **37**, 3014 (1962).

[44] H. O. A. Meyer and H. J. Milledge, Nature **199**, 167 (1963).

[45] R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters **8**, 391 (1962).

[46] M. A. Lampert, Phys. Rev. Letters **1**, 450 (1958).

[47] P. J. Dean and I. H. Jones, Phys. Rev. **133**, A1698 (1964).

IIIE) suggest that diffuse donor-acceptor pair transitions account for a large fraction of the electron-hole recombinations. These facts suggest that isolated nitrogen donors play an important part in the electronic properties of synthetic diamond as they do also in synthetic cubic silicon carbide.[48] Although nitrogen is apparently present even in pure silicon[49] it is not normally detected in the electrical and optical measurements. In diamond, nitrogen is also very active in the associated ⟨100⟩ platelet configuration. These platelets promote strong optical absorption[42] and also act as efficient radiationless recombination centers.[6,47]

2. *The N3 Absorption-Emission System*

The strength of the $N3$ system was thought to correlate with that of the $N9$ edge absorption and luminescence excitation spectrum.[50] The group-B infrared lines identified by Sutherland[51] were also thought to correlate in magnitude with the $N3$ system. Recent work has shown that the $N9$ system may be strongly present in the absence of the $N3$ system,[8] however. The tentative model of the $N9$ system, proposed by the present author,[52] identified it with transitions at a nearest-neighbor substitutional donor-acceptor pair. It was recognized that such a center should provide, even in the electronic ground state, efficient coupling between electromagnetic radiation and the lattice. Single-phonon infrared absorption, normally forbidden in diamond,[53] should therefore be activated. Independent experiments by Holland[54] have recently shown that there is a connection between the strength of the group-B infrared and the $N9$ absorption systems (correlation coefficient 0.94 for 10 specimens), but the coefficient was reduced to 0.89 when data from 4 crystals containing relatively large concentrations of platelet (associated) nitrogen were included. For 20 crystals containing $<5\times10^{18}$ cm^{-3} platelet nitrogen atoms, the correlation coefficient between the $N3$ system and the B infrared bands was 0.28, whereas for 19 specimens containing $>5\times10^{18}$ cm^{-3} platelet nitrogen atoms, the same coefficient was 0.95.

The $N3$ zero-phonon transition energy (3.0 eV) is close to the value expected for transitions at DA_1 states in the band-A spectrum (Sec. III B 1). This transition may be alternatively thought of in terms of the annihilation of an exciton bound to an ionized modified nitrogen ②DA_1 donor center. E_D^1 for this modified donor is *reduced* below E_D by the appropriate donor-acceptor interaction energy $f(r)[=(e^2/\epsilon r)-(e/\epsilon)\cdot(a^5/r^6)$ in Eq. (1)]. If $h\nu=3.0$ eV in Eq. (1) then $f(r)\sim1.8$ eV, since $E_A=0.36$ eV. Thus $E_D^1=E_D-f(r)\sim2.1$ eV, and may account for the ~2.1-eV electron-trapping state observed in nonsemiconducting natural diamond.[35]

Platelet nitrogen in type-I diamond introduces donor levels with $E_D\gtrsim3.7$ eV.[9] The modified donor is therefore likely to be *ionized* in type-I diamond. The group-B infrared impurity-activated absorption bands are probably insensitive to the electronic state of the impurity center, since they are mainly determined by the mass defects of the substitutional atoms. The correlations reported by Holland can be understood if the $N9$ system is due to the creation of exciton states bound to ***neutral*** modified donor centers, provided that the ***majority*** of these donors are neutral in the absence of significant concentrations of deep platelet nitrogen donors.

If the large value of E_D' is attributed to a large electron effective mass m_e, then $m_h/m_e\sim0.2$. The binding energy E_B of the exciton to the neutral modified donor[55] is then $\sim0.07\times E_D^1$, i.e., ~0.15 eV, in very good agreement with the observed value [(5.41–5.26) eV].[4] Excitons can always form stable bound states at neutral donor centers, but cannot be formed by the successive capture of free electrons and holes if $m_h/m_e<1.4$. This may explain why the $N3$ system, unlike the other well-known Mössbauer-type systems in diamond, cannot be efficiently excited by band-gap radiation (Sec. II B), even for specimens in which it is very strongly excited in its 'mirror' absorption band. The part of the band-A spectrum between ~2.5 and ~3.4 eV, clearly resolved in emission spectra from type-II b diamonds (Figs. 5, 7, and 9), is probably due to the recombination of free holes at the neutral modified donor center.

The 'doublet' structure of the 5.26-eV $N9$ zero-phonon components[4] is similar in magnitude to that observed for a ④A bound exciton complex in diamond,[47] and derives from spin-orbit splitting of the valence band. Spin-orbit splittings appear to be characteristic of excitons bound to neutral but not to ionized donor[25] or acceptor centers. The previous tentative suggestion that the $N9$ system is connected with direct gap excitons[52] now appears to be incorrect.

E. Donor-Acceptor Pair Spectra in Synthetic Diamond

The characteristic charged-particle- or edge-photon-excited luminescence emission spectra from the samples of General Electric and other synthetic diamond which we have examined were discussed in Secs. IID1 and IIIB. The peak of the emission band lies at about 2.3 eV at 100°K and is at ~2.1 eV after correction for the energy-sensitivity of the photomultiplier, whereas under similar conditions of electron-beam excitation the peak lies at 2.8 eV for semiconducting natural specimens and at ~3.0 eV for intermediate and type-I natural speci-

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[48] W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. **133**, A1163 (1964).

[49] W. J. Choyke (private communication).

[50] F. A. Raal, Proc. Phys. Soc. (London) 74, 647 (1959).

[51] G. B. B. M. Sutherland, D. E. Blackwell, and W. G. Simeral, Nature **174**, 901 (1954).

[52] P. J. Dean and P. A. Crowther, *Proceedings of the Symposium on Radiative Recombination* (Dunod Cie., Paris, 1964).

[53] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[54] M. B. Holland (private communication).

[55] J. J. Hopfield, *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

mens. Visual examination shows that the emission from synthetic specimens is bright green, whereas natural unirradiated diamonds nearly always produce a distinct blue fluorescence. If the emission is due to recombinations at DA pairs, this implies that the donors and acceptors are more nearly randomly distributed in synthetic diamond, with relatively large DA spacings (see Sec. III B). It is unlikely that the difference arises from a different value of (E_A+E_D) in Eq. (1), since the value of E_D dominates this sum and both activation analysis[56] and electron-spin-resonance studies show that nitrogen is also likely to be the most important donor impurity in synthetic diamond. Support for the hypothesis that the DA pairs are predominantly unassociated in synthetic diamond comes from the relatively long mean decay time of the green luminescence (25 sec at 80°K; cf. 10 msec for the blue luminescence of natural diamond measured between 1.8 and 3.1 eV).[7]

The edge-excitation spectrum of synthetic diamond is also quite different from that of natural diamond[7] (Fig. 12). The $N9$ system is not observed, although curve C of Fig. 12 shows that excitation *minima* are sometimes observed close to, but not quite identical with, the positions of the main excitation *maxima* of the $N9$ system. Curves A and B, which have been corrected to constant source intensity, show that above 5.5 eV the excitation spectra simply follow the edge-absorption spectra,[38] with no oscillations. We have never observed an excitation spectrum of this kind for any type of natural diamond. The featureless excitation continuum starting at ~4.6 eV is a persistent property of synthetic diamond, but has been observed only once for natural diamond.

According to Fig. 10, $f(r)$ for a typical DA pair in synthetic diamond is $\lesssim 0.7$ eV, allowing for the shift to *higher* energy imposed by the transition probability in the pair luminescence spectrum. The extra electron at the ionized acceptor of a typical DA pair in the ground state may be at $E_A+f(r)$ above the valence band because of the presence of a neighboring ionized acceptor. Thus photons of energy

$$h\nu = E_g - [E_A + f(r)] \gtrsim 4.5 \text{ eV} \qquad (4)$$

are required to eject these electrons into the conduction band. Many of these electrons will be recaptured by the ①D members of the DA pairs thus resulting in the production of *excited* pair states. This weak *absorption* process will therefore be a very efficient band-A luminescence *excitation* process, thus accounting for the characteristic extrinsic excitation continuum of Fig. 12. The larger values of $f(r)$ in the DA pair distribution of natural diamond should provide an excitation spectrum tail extending to much lower energies, as is observed, particularly for type-I diamonds.[7,57]

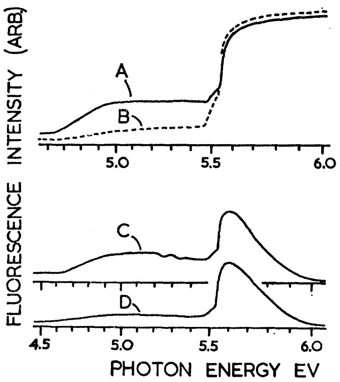

FIG. 12. Band-A luminescence excitation spectra of G. E. synthetic diamond. Curve A—specimen $C7$, 80°K, corrected for energy response of detection system. Curve B—specimen $C7$, 295°K, corrected for energy response of detection system. Curve C—specimen $E5a$, 80°K, uncorrected spectra. Curve D—specimen $E5a$, 295°K, uncorrected spectra. "C" and "E" designate crystals from two different batches obtained from G.E. Series C are pale green or straw-colored; E are more nearly water-white, but with dark inclusions (magnetic).

For nearest-neighbor pairs, $f(r)\sim 1.8$ eV and $E_A \sim 0.2$ eV, so that Eq. (4) predicts an absorption-luminescence excitation band at $h\nu \sim 3.5$ eV. It is very likely that the $N4$ system, which is strongly correlated in intensity with the $N3$ system,[9] represents this process. The observed energy of the zero-phonon absorption line is 3.60 eV. As expected the $N4$ center does not exhibit a 'mirror' luminescence spectrum.

According to the interpretation of the $N9$ system mentioned in Sec. III D, the excitation spectra of Fig. 12 provide further evidence for the absence of ②DA_1, and other close pairs, in synthetic diamond. This marked difference between the properties of DA pairs in natural and synthetic diamond probably arises from the large differences in growth conditions, the most obvious of which is the relatively rapid growth of the synthetic specimens.[58] Comparison of the spectra in Fig. 10 suggests that, under the growth conditions of synthetic diamond, the potential barrier in the donor-acceptor interaction discussed in Sec. III B 2 usually prevents the formation of very closely associated (non-effective-mass) donor-acceptor pairs. For typical concentrations of donors and acceptors in synthetic diamond ($\sim 10^{20}$ cm^{-3} for each type of center[22]), the mean D-A spacing is ~20 Å. At the emission peak (2.1 eV), r is ~5 Å. The difference between these two quantities could be mainly due to the predominence of radiative transitions at the close pairs for the high densities of excitation in cathodoluminescence. The marked spectral differences of Fig. 10 suggest a useful way by which natural and synthetic specimens may be distinguished (see Sec. II D 1).

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[56] E. C. Clark (private communication).

[57] J. Nahum and A. Halperin, J. Phys. Chem. Solids **23**, 345 (1962).

[58] F. P. Bundy, H. P. Bovenkerk, H. M. Strong, and R. H. Wentorf, Jr., J. Chem. Phys. **35**, 383 (1961).

F. Donor-Acceptor Pair Spectra in Electron-Irradiated Type-I Diamond

The band-*A* cathodoluminescence spectrum can sometimes be drastically altered by "room-temperature"[59] electron-bombardment damage sufficient to cause an appreciable green coloration (dose $\sim 5.10^{17}$ electrons cm^{-2}). The change apparently occurs only for those specimens which show the 2.14-eV emission system, often together with associated line at 3.15 eV and other weaker lines, before the irradiation.[19] The 3.15-eV line becomes enhanced by the irradiation and forms the upper energy limit of the emission spectrum (Ref. 19, Fig. 3), whereas before the irradiation it was merely superimposed on the high-energy tail of the normal band-*A* spectrum, if present at all. A system of sharp and broad lines of specimen-independent appearance is also produced on the low-energy side of the 3.15-eV line, and the low-energy limit of the spectrum is fairly clearly identifiable at just below 2.5 eV. Some of the broad lines are suggestive of phonon-assisted transitions, but their displacement from the zero-phonon lines suggests a phonon energy of ~ 0.07 eV, much lower than the value observed in the normal band-*A* spectrum (Sec. IIB2) or in the *N*9 spectrum,[4] but similar to the value observed in the *N*3 system (Fig. 11). We will call this modified band-*A* emission spectrum the "band-*R*" spectrum.

Dyer and du Preez have recently made a detailed study of the optical absorption properties of type-I diamonds resulting from irradiation by 0.78-MeV electrons.[18] Two distinct absorption systems were observed, each of which contains a well-developed Mössbauer-type system. One system is associated with a center (probably a vacancy) which acts as a donor (*GR*1 center), while the other center (apparently a combination defect involving nitrogen platelets and interstitials) acts as an electron acceptor (*ND*1 center). Electrons and holes can be exchanged between the two centers by suitable optical or thermal activations. The *ND*1 center is optically and paramagnetically active when ionized, while the *GR*1 center is optically active only when un-ionized. The binding energies of the centers are estimated from the spectra to be $E_A(ND1)=1.6$ eV,[60] $E_D(GR1)=2.8$ eV. The Mössbauer-type region of the *ND*1 absorption spectrum (zero-phonon line at 3.16 eV) appears to be the mirror image in the zero-phonon line of the band-*R* emission system, apart from the extra sharp lines (notably at 3.03 eV) observed only in the emission spectrum.[19]

The donor and acceptor centers introduced by electron irradiation might be expected to promote indirect pair recombinations. The value of E_A and E_D indicate that both the acceptor and the donor center are tightly bound, unlike the band-*A* *DA* centers, so that radiation would be expected to occur only for appreciably associated pairs.[30] Using Eq. (1), the predicted low-energy limit for the band-*R* pair spectrum is 1.1 eV, and the high-energy limit must be at least 1.6 eV above this [ignoring the polarization term of Eq. (1)]. If the line at 3.03 eV represents a transition at the most closely associated pair, then the simple theory and experiment are in unexpectedly good agreement, as is observed for the band-*A* spectrum (Sec. IIIC). The fact that the pair lines are not observed in absorption is consistent with the low transition probability expected for these associated centers.

The pair lines are superimposed upon the 3.16-eV system transition. By analogy with the *N*3 system (Sec. IIID2) it is reasonable to identify the 3.16-eV line with the creation of bound excitons at the isolated ionized *ND*1 acceptors. The predicted value of the transition energy $h\nu$ is $E_A+\Delta$ less than E_g. For *indirect* transitions

$$h\nu=5.48-(1.6+\Delta)=5.48-1.8=3.68\text{ eV}, \qquad (5)$$

using the value of Δ found for the 1.40-eV system.

Δ may be expected to be larger for the *ND*1 center than for the 1.40-eV center since the ionized *ND*1 center contains an unpaired electron, and there will be an appreciable correlation energy between the two electrons. The absorption structure at $h\nu\sim 3.7$ eV probably represents excitation of the unpaired electron into the conduction band, as proposed by Dyer and du Preez.[18]

The *GR*1 main zero-phonon line is probably due to excitation of the electron on the un-ionized donor to a higher excited state.[18] *Strong* luminescence might be expected from this system were it also associated with bound excitons, but only very weak luminescence is observed, even at He temperature.[61] A strong line is observed in luminescence at 2.14 eV, however, and is connected with the 3.16-eV emission line.[19] If the 2.14-eV line is associated with the production of bound *indirect* excitons at *ionized* *GR*1 centers, then the predicted transition energy is

$$h\nu=E_g-(E_D+\Delta)=5.48-(2.8+\Delta)\sim 2.5\text{ eV}, \qquad (6)$$

if the 1.40-eV system value of Δ is again used. The agreement with the observed value is similar to that in Eq. (5).

In terms of this identification the necessity for the 2.14-eV line to be present in the emission spectrum before the band-*R* system can quench the band-*A* system after radiation damage can be understood. The cathodoluminescence from specimens in which the 3.16- and 2.14-eV systems are prominent in the steady-state spectra often changes from a blue-dominant to a red-dominant emission over a period of ~ 1 min after the start of irradiation (~ 50-keV electrons and ~ 20 μA focused onto ~ 0.5-mm-diam spot at 100 →

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[59] Electron-beam densities >100 μA cm^{-2} were used by Ralph. Under these conditions the specimens, though mounted on a water-cooled plate, were probably heated to 200–300°C.

[60] Using the value of E_g given in Ref. 38.

[61] E. W. J. Mitchell (private communication).

150°K). The red-dominant steady-state spectrum is due to the very strong 2.14-eV emission system. It is probable that this change is due to the saturation of the normal band-*A* emission due to the compensation of the aluminum acceptors by electrons liberated from *GR*1 donors under the intense excitation. This process will only be possible if a large number of *GR*1 donors are present, and if the electrons from the *GR*1 donors are more likely to go to band-*A* acceptors rather than to the *ND*1 acceptors. This is likely since $E_A(ND1)$ is $\sim 4E_A$ (band-*A* acceptor). The whole effect was partially noticeable in an intermediate-type specimen which contained relatively few *ND*1 centers.[18]

IV. SUMMARY

Both natural and synthetic diamonds generally show strong visible and near-ultraviolet fluorescence under excitation conditions in which electronic transitions are produced of energy comparable to the indirect energy gap. This emission has been shown to be interpretable in terms of pair recombinations in which an electron bound on a nitrogen donor recombines with a hole bound to an aluminum acceptor. Transitions between donors and acceptors which are on near-neighbor and also at relatively remote lattice sites have both been observed. In common with recent investigations on

TABLE II. All the bands listed in this table have been observed in cathodoluminescence spectra, many in x-ray–excited luminescence and in photoluminescence also. The energies are quoted at 100°K. More tentative identifications are denoted "?."

Emission band (Peak energy eV)	Description and properties	Identification
(1) 2.8 eV (Band *A*)	Broad band extending from $\sim$1.4 to nearly 4.0 eV. Observed for type-I or type-IIa natural diamonds, particularly when excitons or free electrons and holes are produced.	Recombination of electrons and holes separately bound to donors and acceptors. The donors are isolated nitrogen atoms; acceptors are aluminum atoms. *D-D-A* and more complex centers probably also contribute to emission above 3 eV.
(2a) 2.8 eV (2b) 2.1 eV (Band *A*)	A pair of moderately broad bands emitted by natural type-IIb (semiconducting) diamond below 200°K.	Recombination of electrons and holes at donor-acceptor pairs as (1) above. Pairs of spacing $\sim$2.6 Å are rare for these specimens. *D-D-A* centers are also rare.
(3) 2.1 eV (Band *A*)	Band extending from $\sim$1.4 to $\lesssim$3.0 eV. Observed for synthetic diamond.	Recombination of electrons and holes at relatively diffuse *D-A* pairs [as (2b) above, $r \gtrsim 3.5$ Å].
(4) 3.03 eV (Band *R*)	Irregular system of sharp lines ($h\nu \lesssim 3.03$ eV) superimposed on *ND*1 [(5) below] emission spectrum.	Recombination of electrons and holes at *D-A* pairs made from *ND*1 acceptors and *GR*1 [(7) below] donors. Quenches band-*A* spectrum in suitable specimens.
(5) 3.15 or 3.16 eV (*ND*1)	Mössbauer-type emission spectrum. Observed in electron-irradiated type-I natural diamond.	Zero-phonon line due to annihilation of indirect excitons at ionized *ND*1 (platelet nitrogen+interstitial?) acceptor centers.
(6) 2.14 eV	Mössbauer-type emission spectrum. Observed in electron-irradiated natural diamond.	Zero-phonon line due to the annihilation of indirect excitons bound to ionized *GR*1 donors?
(7) 1.67 eV (*GR*1)	Mössbauer-type emission spectrum (very weak). Observed in electron-irradiated natural diamond.	Zero-phonon line due to an interbound state transition at the neutral vacant-site donor.
(8) 1.40 eV	Mössbauer-type emission spectrum. Strong in nitrogen-doped synthetic diamond.	Zero-phonon line due to the annihilation of indirect excitons bound to ionized isolated nitrogen donors.
(9) 3.00 eV (*N*3)	Mössbauer-type emission spectrum. Strong in coated diamonds, usually present only in type-I natural diamond. Efficiently excited only by optical absorption at the center itself. ⟨111⟩ symmetry axes.	Zero-phonon line due to the annihilation of indirect excitons bound to ionized modified nitrogen (②DA_1) donors.
(10a) 2.50 eV (*H*4) (10b) 2.46 eV (*H*3)	Mössbauer-type emission spectra. Produced by annealing electron-irradiated type-I diamonds at $\sim$600°C.	Transitions of unknown type at binary defect of unknown origin (⟨110⟩ axis).
(11) 5.25 eV 5.26 eV (*N*9)	Doublet observed in type-I intermediate-type natural diamond. Thermal-population factor when observed in emission. Splitting due to spin-orbit interaction.	Annihilation of indirect excitons bound to neutral modified nitrogen (③DA_1) donors.

silicon and germanium[62] individual pair lines have not been unambiguously identified, and few such lines have been seen. Approximate values of the energy parameters can still be obtained, however, and are in reasonable agreement with the known properties of the donor and acceptor. An absorption-emission system, commonly found in natural diamond, has been identified with transitions involving the creation or annihilation of the excited state of the nearest-neighbor *DA* pair center (*N*3 system). A newly detected Mössbauer-type emission spectrum, which is particularly prominent in the spectra from nitrogen-doped synthetic diamond, has been associated with the annihilation of *indirect* excitons bound to the ionized nitrogen donor.

Differences between the pair-luminescence excitation and emission spectrum of natural and synthetic diamond suggest that there is a significant spatial association of donors and acceptors in natural, but not in synthetic diamond. This suggests that there may be a barrier in the donor-acceptor association potential during crystal growth corresponding to a critical separation ($\gtrsim 3$ Å).

The absorption-emission properties of electron-irradiated natural diamond have been briefly discussed. The zero-phonon line of the *ND*1 system is tentatively identified with the creation or annihilation of *indirect-gap* excitons at an ionized acceptor center identified by Dyer and du Preez.[18] An emission line is also attributed to the annihilation of bound *indirect-gap* excitons at an ionized irradiation-induced donor center (*GR*1 center). Some possible pair spectrum lines involving *GR*1 donors and *ND*1 acceptors are also discussed. The discussed properties of these emission spectra and their probable interpretation are summarized in Table II.

Some of the identifications which have been made in this paper must be regarded as tentative at present. Nevertheless it is felt that the suggested models provide a consistent and reasonable interpretation of the large body of experimental evidence now available. The models should prove useful in suggesting further lines of investigation.

An absorption spectrum attributed to transitions at nitrogen ②*D* centers has been observed very recently in synthetic and in a few selected natural diamonds.[63] A steep rise of absorption is observed at photon energies $\gtrsim 4.0$ eV, probably due to the transition ②$D \rightarrow$ ①$D+e$ as predicted from Sec. III C.

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[62] C. Benoit a la Guillaume and J. Cernogora (Ge); A. Honig and R. Enck (Si), both in *Proceedings of the Symposium on Radiative Recombination* (Dunod et Cie., Paris, 1964).

[63] H. B. Dyer, F. A. Raal, L. du Preez, and J. H. N. Loubser, Phil. Mag. **11**, 763 (1965).