

## Ultraviolet Intrinsic and Extrinsic Photoconductivity of Natural Diamond

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A detailed investigation has been made of the photoconductivity response of several types of natural diamond in the spectral energy range from 3.0 to 5.9 eV. Oscillatory structure in the photoconductivity beyond the fundamental absorption edge at 5.49 eV has been shown to be closely related to similar oscillatory structure in the luminescence-excitation spectra, but does not appear in the absorption spectrum. The oscillations appear only together with the N9 absorption/luminescence system with no-phonon lines at 5.25 and 5.26 eV, which has recently been attributed to the creation and decay of indirect excitons bound to nearest-neighbor nitrogen-aluminum donor-acceptor pairs (5DA complex). The photoconductivity minima and the luminescence-excitation maxima are attributed to the enhanced probability of the creation of bound-exciton N9 states if the residual kinetic energy of free excitons is very low after the dissipation of the majority of their excess energy through the cascade emission of optical phonons. Photoconductivity quenching has also been observed in the region of the no-phonon lines of the N9 system, and the temperature dependence of this effect has been found to be consistent with one of the proposed decay modes of the 5DA complex. A photoconductivity threshold has been observed at 4.05 eV in all insulating diamonds, which is considered to be the photoionization limit for the isolated substitutional nitrogen donor. Photo-Hall-effect measurements have been made which support this explanation.

### I. INTRODUCTION

IN 1934 Robertson, Fox, and Martin<sup>1</sup> measured the photoconductivity spectra of a wide range of natural diamonds. On the basis of the optical absorption spectra and the photoconductivity response, they classified all diamonds into type I and type II. Type I diamonds are poor photoconductors and have an absorption edge beginning at  $\sim 3.7$  eV, whereas type-II diamonds are good photoconductors and transmit to 5.49 eV. More recent work has shown that type I diamonds contain large concentrations of nitrogen aggregated into platelets on {100}-type planes<sup>2</sup> and that type II diamonds are relatively pure and transmit as far as the indirect energy gap at 5.49 eV.<sup>3</sup> In addition, Robertson *et al.*<sup>1</sup> and subsequent workers,<sup>4,5</sup> observed a strong absorption system characterized by a sharp absorption doublet at 5.25 and 5.26 eV. This absorption system was termed N9 by Raal,<sup>6</sup> who showed that it was present in the majority of type I diamonds, although it is difficult to observe except in very thin samples because of the absorption associated with the platelet nitrogen. Diamonds in which the N9 absorption system could be clearly observed (i.e., samples with platelet-nitrogen absorption very small or absent) were called "intermediate-type" diamonds to distinguish them from type II diamonds.<sup>7</sup>

The N9 system was also observed even more clearly in luminescence excitation measurements by Nahum and Halperin<sup>8</sup> and by Dean and Male,<sup>9</sup> who also reported oscillatory structure beyond the absorption edge in diamonds containing the N9 system. The sharp doublet at 5.25 and 5.26 eV has also recently been observed in emission, under 60 kV electron excitation, together with associated phonon-assisted structure which is the approximate mirror image about the no-phonon lines of that seen in the luminescence-excitation spectrum.<sup>10</sup> It has been proposed that the N9 system in absorption and emission is due to the creation and decay of indirect excitons bound to nearest-neighbor nitrogen-aluminum donor-acceptor pairs.<sup>10-12</sup>

TABLE I. Comparison of the photoconductivity-threshold energies in Fig. 1 with those predicted from the intrinsic recombination radiation measurements.<sup>28</sup>  $E_g$  and  $E_{gz}$  are the indirect energy gap and the exciton-energy gap, and  $(\hbar\omega)_{TO}$  and  $(\hbar\omega)_{TA}$  represent the transverse-optical and transverse-acoustical phonon energies.

Photoconductivity threshold	Assignment	Energy from 90°K photoconductivity spectrum (eV)	Energy predicted from the recombination radiation spectrum at 100°K (eV)
W	$E_{gz} - (\hbar\omega)_{TO}$	$5.255 \pm 0.005$ (200°K)	5.268
X	$E_{gz} + (\hbar\omega)_{TA}$	$5.493 \pm 0.005$	5.496
Y	$E_{gz} + (\hbar\omega)_{TO}$	$5.542 \pm 0.005$	5.550
Z	$E_g + (\hbar\omega)_{TA}$	$5.583 \pm 0.010$	5.577

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<sup>1</sup> R. Robertson, J. J. Fox, and A. E. Martin, *Phil. Trans. Roy. Soc. London*, **A232**, 463 (1934).

<sup>2</sup> T. Evans and C. Phaal, *Proc. Roy. Soc. (London)* **A270**, 538 (1962).

<sup>3</sup> C. D. Clark, P. J. Dean, and P. V. Harris, *Proc. Roy. Soc. (London)* **A277**, 312 (1964).

<sup>4</sup> K. S. Bai, *Proc. Indian Acad. Sci.* **A19**, 253 (1944).

<sup>5</sup> K. G. Ramanathan, *Proc. Indian Acad. Sci.* **A24**, 137 (1946).

<sup>6</sup> F. A. Raal, *Proc. Phys. Soc. (London)* **24**, 649 (1959).

<sup>7</sup> C. D. Clark, R. W. Ditchburn, and H. B. Dyer, *Proc. Roy. Soc. (London)* **A234**, 363 (1956).

<sup>8</sup> J. Nahum and A. Halperin, *J. Phys. Chem. Solids* **23**, 345 (1962).

<sup>9</sup> P. J. Dean and J. C. Male, *Proc. Roy. Soc. (London)* **A277**, 330 (1964).

<sup>10</sup> D. R. Wight and P. J. Dean, *Phys. Rev.* **154**, 689 (1967).

<sup>11</sup> P. J. Dean, *Phys. Rev.* **139**, A588 (1965).

<sup>12</sup> P. A. Crowther and P. J. Dean, *J. Phys. Chem. Solids* **28**, 1115 (1967).

Nahum and Halperin<sup>8</sup> have described photoconductivity measurements on intermediate-type diamonds close to the absorption edge, finding structure associated with the N9 center. The present work is chiefly concerned with an extension of their photoconductivity measurements which support the interpretation of Dean *et al.*,<sup>10-12</sup> and the measurements have been extended beyond the absorption edge where oscillatory structure is observed, closely associated with the oscillatory luminescence-excitation, and similar in some respects to that recently reported in InSb,<sup>13-17</sup> GaSb,<sup>14</sup> CdS,<sup>18</sup> ZnTe,<sup>19</sup> and GaP.<sup>20</sup>

Although the nitrogen in type I diamonds occurs predominantly in aggregated platelet form, Smith *et al.*<sup>21</sup> detected electron-spin resonance in a small number of type I diamonds which was interpreted as arising from the presence of isolated substitutional nitrogen atoms in concentrations between  $10^{15}$  and  $10^{17}$  cm<sup>-3</sup>. Dyer *et al.*<sup>22</sup> have discovered a small number of natural diamonds in which the whole of the nitrogen, up to  $\sim 10^{17}$  cm<sup>-3</sup>, appears to be present at isolated substitutional sites, judged from the E.S.R. measurements and the absence of normal type I optical absorption. This new type of diamond has been classified as type Ib and the normal type I diamond has been reclassified as type Ia. The absorption edge of type Ib diamonds commences at  $\sim 2$  eV and rises very rapidly near 4.0 eV merging with the indirect absorption edge.<sup>22</sup> At 80°K, a series of absorption lines is observed at 4.07, 4.15, 4.24, 4.58, and 4.64 eV.<sup>22</sup> In the present work, thresholds corresponding to this series of lines have been found in the photoconductivity excitation spectra of a number of intermediate-type diamonds which would be expected to contain a small concentration of dispersed nitrogen.

## II. EXPERIMENTAL

Photocurrents were excited by light from a Hilger model E1 quartz prism spectrograph modified to a recording monochromator, using a 50-W deuterium arc as radiation source. The diamond specimens were mounted for electrical insulation on thin quartz plates

which were clamped to the copper nose-piece of a stainless-steel Dewar inside an evacuated chamber. Light from the monochromator was focused on the diamond by means of a quartz lens with an image reduction of  $\sim 5:1$ , ensuring that the whole of the radiation from the monochromator was utilized for a typical specimen size of  $\sim 2$  mm in linear dimensions. Electrical contacts to the diamonds were made with two 0.25-mm diameter tungsten wires  $\sim 1$  mm apart which were electron-beam welded with tantalum-doped gold<sup>23</sup> on the illuminated surface of the diamond. Contacts formed in this way were found to be rigid, mechanically strong, and electrically stable. The contact arrangement enabled photocurrents to be detected in regions of high absorption and where lifetimes are short.

All diamond samples were irradiated by light of energy  $\sim 5.5$  eV in the monochromator before photoconductivity measurements, to fill any deep traps which can cause transient effects especially in specimens which are marginally type I. In type I diamonds initial overshoot of photocurrent can occur, whilst in type II specimens initial undershoot may be observed. These trapping centers have been investigated by Nahum and Halperin.<sup>24</sup> Following the pretreatment, photocurrents in all spectral regions were observed to increase linearly with applied field up to  $\sim 800$  V cm<sup>-1</sup>. At higher fields saturation effects occurred and the signal to noise ratio decreased, these effects being specimen-dependent. Fields  $\sim 800$  V cm<sup>-1</sup> were, therefore, generally used for maximum sensitivity. Photocurrents were typically of the order of  $10^{-14}$  A with a monochromator spectral resolution of  $\sim 5$  meV, and were measured with E.I.L. 1086C and 62A vibrating reed electrometers.

Luminescence-excitation and optical-absorption measurements were made with an E.M.I. 6558 S-20 response photomultiplier mounted immediately behind the specimen. A Wratten 2B filter, transparent below  $\sim 3.1$  eV, was used to block the exciting light in luminescence excitation measurements. In absorption measurements an interference filter with peak transmission at 2250 Å and half-width 200 Å was used to eliminate the luminescence and any remaining visible scatter. The conventional method for the elimination of sample luminescence in optical-absorption measurements, with the specimen placed before the entrance slit of the monochromator, involved unacceptable loss of signal due to scatter by the small irregular crystals, some of which had coarse etched surfaces. Photo-Hall-effect measurements were made using a three-probe method similar to the one used by Klick and Maurer<sup>25</sup> and originally due to Evans.<sup>26</sup> The magnetic field was provided by a 2.4-kOe permanent magnet.

<sup>13</sup> H. J. Stocker, C. R. Stannard, H. Kaplan, and H. Levinstein, *Phys. Rev. Letters* **12**, 163 (1964).

<sup>14</sup> M. A. Habegger and H. Y. Fan, *Phys. Rev. Letters*, **12**, 99 (1964).

<sup>15</sup> D. N. Nasledov, Yu. G. Popov, and Yu. S. Smetannikova, *Fiz. Tverd. Tela*, **6**, 3728 (1964) [English transl.: *Soviet Phys.—Solid State* **6**, 2989 (1965)].

<sup>16</sup> H. J. Stocker, H. Levinstein, and C. R. Stannard, *Phys. Rev.* **150**, 613 (1966).

<sup>17</sup> V. J. Mazurczyk, G. V. Ilmenkov, and H. Y. Fan, *Phys. Rev. Letters* **21**, 250 (1966).

<sup>18</sup> Y. S. Park and D. W. Langer, *Phys. Rev. Letters* **13**, 392 (1964); D. W. Langer, Y. S. Park, and R. N. Euwema, *Phys. Rev.* **152**, 788 (1966).

<sup>19</sup> R. E. Nahory and H. Y. Fan, *Phys. Rev. Letters* **17**, 251 (1966).

<sup>20</sup> D. N. Nasledov, V. V. Negreskul, S. I. Radautsan, and S. V. Slobodchikov, *Fiz. Tverd. Tela*, **7**, 3671 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 2965 (1965)].

<sup>21</sup> W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.* **115**, 1546 (1959).

<sup>22</sup> H. B. Dyer, F. A. Raal, L. du Preez, and J. H. N. Loubser, *Phil. Mag.* **11**, 763 (1965).

<sup>23</sup> Supplied by Dr. W. F. Knippenberg, N. V. Philips's Gloeilampenfabrieken, Eindhoven.

<sup>24</sup> J. Nahum and A. Halperin, *J. Phys. Chem. Solids* **24**, 823 (1963).

<sup>25</sup> C. C. Klick and R. J. Maurer, *Phys. Rev.* **81**, 124 (1951).

<sup>26</sup> S. Evans, *Phys. Rev.* **57**, 47 (1940).

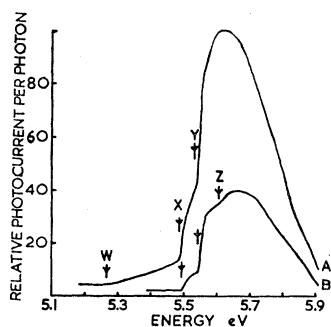


FIG. 1. Photoconductivity spectra of an almost perfectly compensated type IIb diamond. (A) photoconductivity at 200°K, (B) photoconductivity at 90°K.

All the spectra illustrated in Figs. 1-6 have been normalised point by point to the luminescence-excitation spectrum of a thin film of sodium salicylate which has an approximately uniform quantum efficiency over the energy range concerned.<sup>27</sup>

### III. RESULTS AND DISCUSSION

Figure 1 shows the photoconductivity spectrum of a specially selected type II diamond which is an almost perfectly compensated semiconductor with a dark conductivity of  $\sim 10^{-10} \Omega^{-1} \text{cm}^{-1}$  at 295°K. On cooling to  $\sim 200^\circ\text{K}$ , the resistivity increased sufficiently for dc photoconductivity measurements to be made. In the 200°K photoconductivity spectrum, there are three clearly defined thresholds *W*, *X*, and *Y* at 5.255, 5.487, and 5.536 eV ( $\pm 0.005$  eV). At 90°K, the thresholds *X* and *Y* can be observed at 5.493 and 5.542 eV ( $\pm 0.005$  eV), and a less clearly defined threshold *Z* is seen at  $5.583 \pm 0.010$  eV. These thresholds correspond closely with those seen in the intrinsic absorption edge spectrum at 100°K and 295°K,<sup>3</sup> and can be identified by comparison of the threshold energies with those predicted from the intrinsic recombination radiation spectrum.<sup>28</sup> The analysis in Table I suggests that the formation of free excitons and their subsequent ionization leads to photoconductivity.

Photoconductivity and luminescence-excitation spectra of three intermediate-type diamonds of weak,

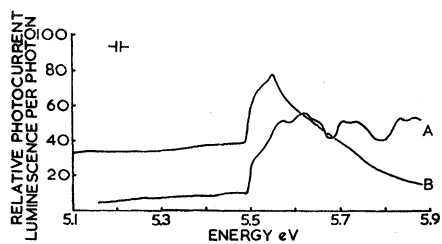


FIG. 2. Luminescence excitation and photoconductivity spectra of a very weak intermediate-type diamond at 90°K. (A) luminescence excitation, (B) photoconductivity.

<sup>27</sup> N. Kristianpoller and R. A. Knapp, *Appl. Opt.* **3**, 915 (1964).  
<sup>28</sup> P. J. Dean, E. C. Lightowers, and D. R. Wight, *Phys. Rev.* **140**, A352 (1965).

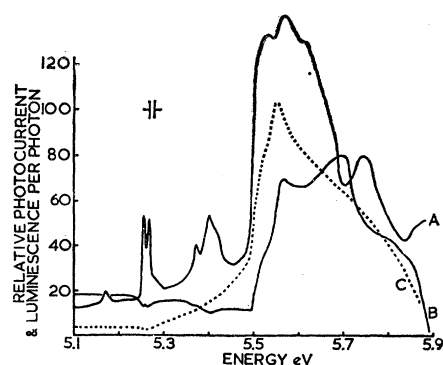


FIG. 3. Luminescence excitation and photoconductivity spectra of an intermediate-type diamond with a typical N9 center concentration. (A) luminescence excitation at 90°K, (B) photoconductivity at 90°K, (C) photoconductivity at 290°K.

normal, and very high N9 concentration are shown in Figs. 2, 3, and 4, respectively. The features present in the luminescence-excitation spectra have been fully described elsewhere.<sup>9</sup> The most prominent feature in the photoconductivity spectra is the structure on the high-energy side of the fundamental absorption edge. For a typical intermediate-type diamond (Fig. 3), the structure beyond the edge is oscillatory in form with the minima of the photoconductivity coinciding with the maxima of the luminescence excitation. The oscillations in the luminescence-excitation spectra can be followed to  $\sim 6.5$  eV using a concave-reflection-grating vacuum monochromator.<sup>9</sup> In the present work only the first two luminescence-excitation minima and photoconductivity-excitation maxima (neglecting the maxima in both spectra near 5.56 eV due to the penetration depth effects of the excitation<sup>29</sup>) were recorded because of absorption of the ultraviolet light by the quartz optics of the monochromator. When the N9 system is extremely strong, as shown in Fig. 4, the oscillations in the photoconductivity spectrum are generally less pronounced. Figure 2 shows the photoconductivity spectrum of a very weak intermediate-type diamond K80 in which there is no detectable trace of N9 or nitrogen-platelet absorption. Here the photoconductivity spectrum above  $\sim 5.5$  eV is of the form expected for an intrinsic photoconductor and is virtually identical with that shown in Fig. 1, although there is a very small trace of oscillatory structure. The photoconductive response of K80 is virtually unchanged at 290°K except that the phonon-assisted transitions corresponding to those of Fig. 1 can be detected for energies less than the indirect energy gap. These transitions can also be seen for the intermediate-type crystal in Fig. 3, where the 290°K photoconductivity spectrum also has the form expected for an intrinsic absorption process with the onset of anti-stokes phonon assisted transitions at  $\sim 5.26$  eV.<sup>3</sup> In spite of the very low concentration of N9 centers in K80, the oscillatory structure in the lumines-

<sup>29</sup> P. J. Dean and J. C. Male, *J. Phys. Chem. Solids* **25**, 1369 (1964).

cence-excitation spectrum, shown in Fig. 2, is still clearly observed and is a very sensitive indicator of the presence of N9 centers.

In the majority of diamonds, the photoconductivity response commences at  $\sim 4$  eV well before the absorption edge. In type Ia diamonds (Fig. 5), this region is dominant and structure is observed beyond the absorption edge only when the platlet-nitrogen concentration is very low. Similar results on type Ia diamonds were recently reported by Konorova *et al.*<sup>30</sup> All intermediate-type diamonds show weak structure in this continuum at energies  $\sim 5.25$  eV and above associated with the N9 structure seen in absorption and luminescence excitation. (Figs. 3-5).

The only type of diamond in which the continuum beginning at 4 eV is not observed in type IIb diamond, and a typical spectrum is also shown in Fig. 5. Type IIb diamonds are naturally occurring *p*-type semiconductors and are extremely pure with typical aluminum-acceptor and nitrogen-donor concentrations of  $\sim 5 \times 10^{16}$  cm<sup>-3</sup> and  $5 \times 10^{15}$  cm<sup>-3</sup>, respectively.<sup>28</sup>

#### A. Photoconductivity Near 5.25 eV Associated with the N9 Center

In Fig. 4 the behavior of the N9 no-phonon lines in the photoconductivity spectrum can be observed. At 90°K, the N9 center acts as a quenching center whilst at 290°K it behaves as an excitation center. In many intermediate-type diamonds it remains as a quenching center throughout the temperature range, and in other crystals the exact behavior is masked by the onset of phonon-assisted intrinsic transitions.

The N9 center has recently been attributed to a nearest-neighbor nitrogen-aluminum donor-acceptor pair, and because of the large ratio between the donor ionization energy  $\sim 4$  eV<sup>11</sup> and the acceptor ionization energy  $\sim 0.37$  eV,<sup>28</sup> this center can be treated as a modified donor with reduced ionization energy.<sup>10,11</sup>

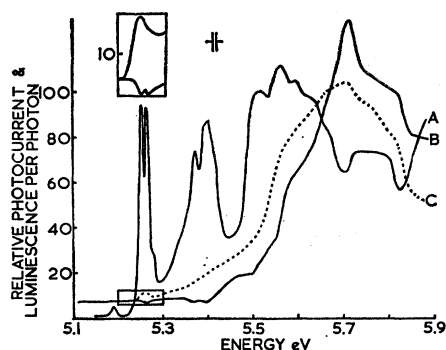


FIG. 4. Luminescence excitation and photoconductivity spectra of an intermediate-type diamond with an extremely high N9 center concentration. (A) luminescence excitation at 90°K, (B) photoconductivity at 90°K, (C) photoconductivity at 290°K.

<sup>30</sup> E. A. Konorova, L. A. Sorokina, and S. A. Shevchenko, *Fiz. Tver. Tela* 7, 1092 (1965) [English transl.: *Soviet Phys.—Solid State* 7, 876 (1965)].

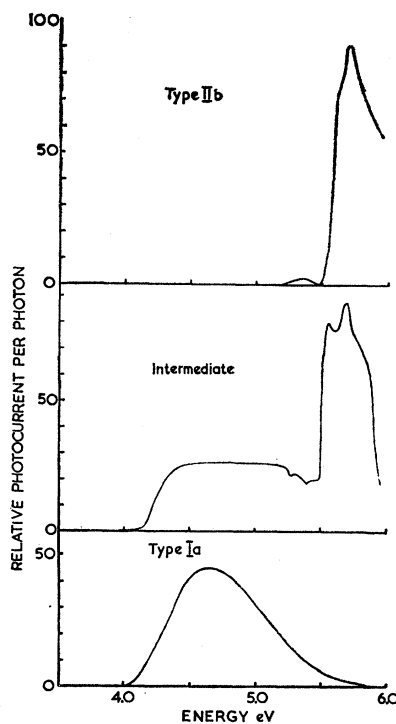


FIG. 5. Photoconductivity spectra at 90°K of a type IIb (*p*-type semiconducting) diamond, an intermediate-type diamond and a type Ia diamond.

When donors are in excess in the crystal as a whole, the modified donor will be neutral (a 3DA complex). The no-phonon lines at 5.25 and 5.26 eV in the absorption and luminescence-excitation spectra are due to the creation of an indirect exciton bound to the 3DA center, a 3DA to 5DA transition, and the splitting of the no-phonon line owes its origin to the spin-orbit splitting of the hole state of the exciton. In the photoconductivity spectrum of intermediate-type crystals, the continuum beginning at  $\sim 4$  eV is considered to be

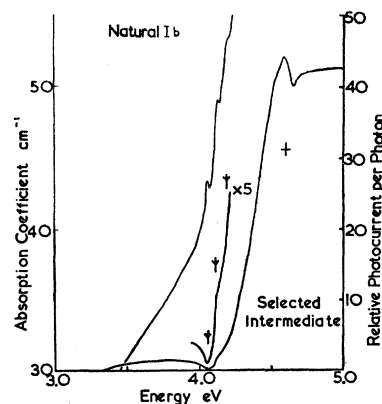
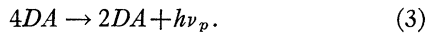
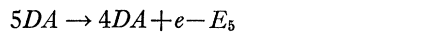
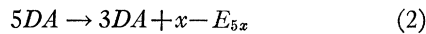
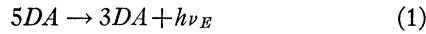


FIG. 6. Absorption spectrum of a natural type Ib diamond and the photoconductivity spectrum of a selected intermediate-type diamond showing the series of thresholds corresponding to the absorption maxima in the Ib spectrum. Both spectra were recorded at 90°K.

due to photo-ionization of the isolated nitrogen donor. (Section III C below.) The structure in the region of the N9 no-phonon lines is due to the competition between absorption at the nitrogen donor and N9 center. For a given excitation rate, the N9 bound-exciton absorption reduces the number of carriers photoexcited into the conduction band from the isolated nitrogen donors.

Crowther and Dean<sup>12</sup> have proposed several decay modes for the 5DA complex:



Process (1) represents resonance decay of the 5DA complex in which the hole and electron of the exciton recombine to produce emission in the N9 system. In process (2),  $x$  represents the free exciton and  $E_{5x}$  the binding energy of the exciton to the 3DA complex, which is  $\sim 160$  meV. The free exciton is thermally liberated from the 5DA center. In the third mode of decay, an electron is thermally liberated from the 5DA center and  $E_5$  represents the binding energy of the second electron. The resulting 4DA complex then decays to produce emission in the visible region.<sup>12</sup> At low temperatures only decay channels (1) and (3) are operative, since (2) is thermally quenched,<sup>10</sup> and of these two only process (3) gives rise to photoconductivity.

Assuming a uniform distribution of isolated donors and nearest-neighbor donor-acceptor pairs and that the electrodes collect the same proportion of carriers wherever these are generated in the crystal (which is reasonable since in regions of low absorption the electrode configuration does not appreciably affect the spectrum), it is then possible to derive an expression for the quenching current as a function of temperature in terms of  $E_5$  in Eq. (3) and the absorption coefficients due to isolated donors  $\alpha_1$  and to N9 centers  $\alpha_2$ .

$$\Delta I = K \left\{ [1 - \exp(-\alpha_1 t)] - \frac{[\alpha_1 + \alpha_2 \exp(-E_5/kT)]}{(\alpha_1 + \alpha_2)} \times [1 + \exp\{-(\alpha_1 + \alpha_2)t\}] \right\}, \quad (4)$$

$K$  is a constant containing the incident light intensity and photoconductivity gain, and  $t$  is the specimen thickness. This expression has been fitted by computer to a large range of values of  $\alpha_1$  and  $\alpha_2$ , reproducing the temperature dependence of the whole range of diamonds investigated. The temperature dependence of the quenching was carefully measured for a number of diamonds in which the transition from a quenching to an excitation center was clearly defined. The absorption coefficients  $\alpha_1$  and  $\alpha_2$  were measured in the region of 5.25 eV and using Eq. (4), values were determined for  $E_5$ . The mean value obtained was  $33 \pm 5$  meV in good

agreement with the value of 36 meV obtained by Wight and Dean.<sup>10</sup> Park and Reynolds<sup>31</sup> have shown that in some CdS crystals, the creation of bound-exciton states can lead to an enhancement of photoconductivity.

The Auger recombination mechanism, prominent in the decay of excitons at neutral donors,<sup>32</sup> is neglected in this discussion. This decay process may give rise to a photoconductivity maximum at the N9 no-phonon line even at low temperatures if the capture cross-section of ionized N9 centers is less than that for the centers responsible for the underlying photoconductivity-excitation process. The experimental results in Figs. 2-4 suggest that this condition is not met in intermediate-type crystals where the underlying photoconductivity-excitation process is due to photo-ionization of isolated nitrogen donors (Sec. III C). The Auger recombination process involving a bound-exciton complex is not expected to be very temperature sensitive, and is therefore unlikely to be primarily responsible for the quenching effects discussed in this section.

## B. Oscillations in the Intrinsic Region

Luminescence-excitation spectra in the region of the fundamental absorption edge have been measured for a large number of various types of diamond.<sup>9,12,29,33</sup> Although it has not been possible to establish a linear correlation between the strength of the oscillatory structure beyond the absorption edge and the strength of the N9 system because of surface-volume inhomogeneities and consequent penetration-depth spectral distortions, it has been well established that these two phenomena occur together. The present investigation has further established that oscillatory photoconductivity occurs only when the N9 system is also present in the luminescence excitation spectra; but the oscillations are most pronounced when the N9 system is relatively weak. The photoconductivity minima in the oscillatory structure coincide with the maxima in the luminescence-excitation spectra. If the high-energy photoconductivity minima are produced by the same mechanism as discussed in the previous section—that is, by direct creation of excitons bound to the N9 center—but in this case, with the emission of phonons into the lattice, then similar structure should be observed in the total optical absorption.

Male<sup>33</sup> measured the absorption coefficient of several thin samples of intermediate-type diamonds beyond the absorption edge and detected no structure due to the N9 center. Further careful measurements on cleavage fragments and a chemically etched sample have shown that there is no absorption related to the N9 system

<sup>31</sup> Y. S. Park and D. C. Reynolds, *Phys. Rev.* **132**, 2450 (1963).

<sup>32</sup> D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, *Phys. Rev. Letters* **17**, 1262 (1966).

<sup>33</sup> J. C. Male, Ph.D. thesis, University of London, 1962 (unpublished).

beyond the fundamental absorption edge. It is assumed, therefore, that the mechanism producing the oscillatory structure both in luminescence excitation and in photoconductivity involve an intrinsic absorption process.

Similar oscillatory structure in the photoconductivity beyond the absorption edge has been observed in InSb,<sup>13-17</sup> GaSb,<sup>14</sup> CdS,<sup>18</sup> ZnTe,<sup>19</sup> and GaP.<sup>20</sup> Stocker *et al.*<sup>13</sup> originally attributed the photoconductivity minima to a very much reduced lifetime of electrons in the conduction band due to transitions to ionized shallow donor states by cascade emission of longitudinal optical (LO) phonons whenever the electron energy is  $n(\hbar\omega)_{\text{LO}}$  greater than the conduction-band minimum. Habegger and Fan<sup>14</sup> also considered that the structure is due to the rapid reduction of energy of electrons injected into the conduction band by the cascade emission of optical phonons, but attributed the oscillatory nature of the photoconductivity response to the variation of the mobility of electrons with energy in the range between zero and  $(\hbar\omega)_{\text{LO}}$  when the major scattering mechanism is ionized impurity scattering. In CdS<sup>18</sup> it has been assumed that the free-exciton ground state fulfils the role of the shallow impurity state in Stocker's model.<sup>13</sup> Stocker *et al.*<sup>16</sup> have since shown, however, that oscillatory structure in the photoconductivity excitation spectrum may occur without the presence of a trapping center, at least for direct transitions where the electrons and holes photo-excited by monochromatic radiation are mono-energetic. Their mechanism is operative only at very low temperatures, where it may be assumed that the steady-state energy distribution of the photoexcited carriers is far from thermal equilibrium. Stocker *et al.* conclude that these photoconductivity oscillations are produced through the influence of the external electric field on this non-equilibrium energy distribution, which implies that the photocurrent is a nonlinear function of voltage when the oscillations occur.

These considerations have no relevance to the oscillatory structure discussed here, since these oscillations occur at zero external field (in the luminescence-excitation spectra) and can be observed at room temperature where the assumption of nonequilibrium energy distributions at zero applied field is unrealistic.

Oscillations in both the photoconductivity and the luminescence-excitation are only observed in diamond if the N9 system is also present. The current-voltage characteristic of the photoconductivity is linear and the structure is not affected by the value of the electric field up to  $\sim 800 \text{ Vcm}^{-1}$ . However, broadening of the oscillations in the luminescence-excitation spectra of diamond has been observed at the much larger electric field strengths necessary for the production of hot carriers,<sup>29</sup> and a similar effect has been reported recently in photoconductivity-excitation spectra of indium antimonide.<sup>16</sup>

The period of the oscillations in the excitation spectra of diamond suggests that, as for the other materials,

the cascade emission of zone-center optical phonons is involved. Enhancement of carrier mobility due to the reduced scattering cross section of hot carriers by ionized impurities proposed by Habegger and Fan has no relevance to the production of oscillatory structure in luminescence-excitation spectra. This fact considered together with the correlation between the presence of the N9 bound-exciton lines and the excitation oscillations in the intrinsic interband absorption region, although these pronounced oscillations do not appear in the absorption spectrum, strongly suggests that a mechanism similar to that originally proposed by Stocker *et al.*<sup>13</sup> is operative. Free excitons produced at energies given by

$$h\nu = E_{g\text{x}} + (\hbar\omega_c)_i + n\hbar\omega_{\text{opt}} \quad (5)$$

will rapidly lose energy by the cascade emission of zone-center optical phonons of energy  $\hbar\omega_{\text{opt}}$ . In Eq. (5),  $E_{g\text{x}}$  is the exciton-energy gap and  $(\hbar\omega_c)_i$  is a phonon which conserves momentum in the indirect transitions. In diamonds at low temperatures indirect transitions predominantly occur with the emission of either a transverse optical or a transverse acoustical phonon<sup>28</sup> and the energy separation between these two momentum-conserving phonons is approximately equal to the spacing between the two subcomponents observed within each peak in the luminescence-excitation oscillations.<sup>9</sup> The low-energy thresholds of the luminescence-excitation maxima and of the photoconductivity-excitation minima are described by Eq. (5) as nearly as can be determined. Just above these threshold energies, intrinsic absorption processes create excitons with low kinetic energy after optical-phonon emission.

We assume that low-energy excitons are preferentially trapped by the N9 centers and are lost to conduction processes at temperatures sufficiently low for thermal dissociation of the exciton complexes to be insignificant. If the capture cross section of the N9 centers is strongly velocity-dependent, excitons formed by radiation whose energy fails to match Eq. (5) will remain free during the relatively slow loss of their residual kinetic energy by interaction with acoustical phonons. The excitons are likely to dissociate during this latter process, releasing carriers for electrical conductivity. On the other hand, the excitons which are captured by N9 centers efficiently excite blue luminescence.<sup>11</sup> Thus Eq. (5) describes the threshold energies of *maxima* in the luminescence-excitation spectra, but *minima* in the photoconductivity-excitation spectra.

### C. Identification of the Donor Center

Figure 5 shows ultraviolet photoconductivity spectra of a range of natural diamonds, including all the detectable structure below the energy gap. Type Ib specimens have a similar spectrum to that shown for type Ia diamonds, except that the photosensitivity is

an order of magnitude lower. All diamonds except *p*-type semiconducting type IIb show a threshold at  $4.05 \pm 0.05$  eV. In some intermediate-type specimens a series of thresholds can be observed at 4.07, 4.15, and 4.24 eV corresponding to maxima in the absorption spectra of type Ib diamonds<sup>22</sup> which are known from ESR measurements to contain a high concentration of nitrogen donors at isolated substitutional sites. The photoconductivity response of a selected intermediate-type diamond and the absorption spectrum of a type Ib specimen are compared in Fig. 6.

Dean<sup>11</sup> has recently shown that the broad blue emission band which predominates in the luminescence-emission spectrum of natural diamonds can be interpreted in terms of recombination of electrons and holes separately trapped at nitrogen donors and aluminum acceptors of variable mutual separation. From this analysis it was shown that the donor ionization energy is  $\sim 4$  eV. Konorova *et al.*<sup>30</sup> also observed a threshold at  $\sim 4$  eV in the photoconductivity of type Ia diamonds, which was tentatively attributed to the presence of platelet nitrogen. This threshold in type Ia diamonds is, however, more probably associated with the presence of isolated substitutional nitrogen, since the onset of platelet absorption is at 3.7 eV and does not coincide with the photoconductivity threshold. Smith *et al.*<sup>21</sup> have observed isolated nitrogen donors in type Ia diamonds by ESR measurements.

In order to confirm that this photoconductivity threshold is due to the photo-ionization of donor centers, photo-Hall-effect measurements were made on a type IIa diamond with a strong photoconductivity threshold at 4.05 eV. The carriers were found to be electrons from the sign of the Hall coefficient, and the mobility was estimated to be  $\sim 2.8 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup> at 290°K. This is higher than the values given by Redfield<sup>34</sup> ( $1.8 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup> at 300°K) and by Klick and Maurer<sup>24</sup> ( $900$  cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup> at 300°K). It is difficult to estimate the reliability of the mobility measurement because of the likely inhomogeneity in the distribution of donors.

The diamond used in this measurement was a good type IIa, therefore the difference in the mobility between the present work and that of previous investigators may be due to enhanced scattering by ionized nitrogen donors in the earlier work. It should be noted that neither Redfield nor Klick and Maurer illuminated their diamonds with light of energy greater than the intrinsic energy gap ( $\sim 5.5$  eV), so that their measurements confirm the presence of a donor level.

#### IV. OTHER PHOTOCONDUCTIVITY EXCITATION FEATURES

A weak band has been observed between 3.3 and 4.1 eV which is not detectable in all samples and does not

appear to be associated in intensity with the 4.0 eV threshold. This has also been pointed out by Konorova *et al.*<sup>30</sup> This band is tentatively attributed to the photo-ionization of modified donors, i.e., neutral nearest-neighbor donor-acceptor pairs. In Fig. 6, in the photoconductivity spectrum presented, there is a minimum at  $\sim 4.6$  eV which is detectable in other samples. This is possibly due to quenching caused by the onset of absorption giving rise to luminescence.<sup>12</sup> In some type IIb samples there is a weak threshold near 5.15 eV. This is likely to be connected with the onset of electron transitions from compensated acceptors into the conduction band. This type of transition is not expected to exhibit a well-defined threshold because of the absence of a Coulomb interaction between the neutral acceptor and the conduction-band states. The value of the acceptor ionization energy estimated from this photoconductivity threshold is  $\sim 0.34$  eV, consistent with the value observed for aluminum acceptors from transport measurements.<sup>28</sup>

#### V. SUMMARY

Further evidence has been presented in support of the interpretation of the N9 absorption-emission system in terms of the creation and decay of indirect excitons bound to nearest neighbor donor-acceptor pairs. The thermal ionization energy of the second electron in the 5DA complex is found to be  $33 \pm 5$  meV in good agreement with the predictions of the above model and experimental evidence from luminescence measurements. Oscillations in photoconductivity response beyond the fundamental absorption edge which appear only in the presence of the N9 centers are attributed to a strongly velocity-dependent capture cross section of the N9 centers for free excitons. Excitons produced by intrinsic absorption processes well above the indirect energy gap rapidly lose excess energy by cascade emission of optical phonons, and it is assumed that they are preferentially trapped at the N9 centers if their residual energy is low after the optical phonon de-excitation process. The ionization energy of the isolated nitrogen donor (measured from the low-energy threshold of a broad photoconductivity-excitation continuum observed in all crystals other than the *p*-type IIb variety) is  $4.05 \pm 0.05$  eV.

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<sup>34</sup> A. G. Redfield, Phys. Rev. **94**, 526 (1954).